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Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic species

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Abstract—The standard partial molal properties of organic aqueous species at high pressures and temperatures can be predicted using an adaptation of a revised equation of state for inorganic aqueous ions and electrolytes (TANGER and HELGESON, 1988), together with correlations among equation of state parameters (SHOCK and HELGESON, 1988). These correlations include a charge-dependent relation between Born coefficients and the standard partial molal entropies of aqueous species at 25°C and 1 bar (SHOCK et al., 1989). Thermodynamic calculations indicate that in the liquid phase the standard partial molal volumes ($\bar{V}^0$), heat capacities ($\bar{C}_P^0$), and entropies ($\bar{S}^0$), as well as the apparent standard partial molal enthalpies of formation ($\Delta\bar{H}^0$) of aqueous electrolytes with organic anions maximize with increasing temperature at P_{SAT}* and approach $-\infty$ at the critical point of H_2O. In contrast, the corresponding properties of neutral organic aqueous species in the liquid phase minimize with increasing temperature P_{SAT} and approach ∞ at the critical point of H_2O. Predicted equilibrium constants for alkane solubilities and carboxylic acid dissociation reactions at elevated pressures and temperatures are in close agreement with experimental data reported in the literature, which supports the validity and generality of the equations of state as well as the predictive algorithms used in the calculations. As a consequence, high temperature/pressure standard partial molal properties, as well as equilibrium constants and other reaction properties, can be predicted for reactions involving a wide variety of organic aqueous species for which little or no experimental data are available at temperatures > 25°C. Present capabilities permit such predictions to be made for hydrothermal and magmatic conditions at pressures and temperatures as high as 5 kb and 1000°C.

INTRODUCTION

IF STABLE EQUILIBRIUM is achieved in the crust of the Earth, the predominant species in the system C-H-O should be methane, carbon dioxide, H_2O, and graphite or diamond (HOLLOWAY, 1984). However, in many crustal environments, kinetic inhibitions lead to metastable equilibrium states involving organic solids, liquids, gases, and/or aqueous species, which may persist over long periods of geologic time at both high and low pressures and temperatures (HELGESON and SHOCK, 1988; SHOCK, 1988). One such organic species is aqueous acetic acid (DRUMMOND and PALMER, 1986; PALMER and DRUMMOND, 1986). The important role played by metastable organic species in the rock-forming process is commonly obscured in the geologic record by processes such as regional metamorphism. Even in shallow environments where organic species can be readily identified, it is unclear how they interact with minerals. Despite evidence to the contrary (PRICE, 1982), degradation of organic material with increasing temperature is commonly considered complete at burial depths of the order of 5 km. Nevertheless, the effects of temperature and pressure on the rates of reaction of most organic species have not been documented (BOLES et al., 1988). In addition, the role of bacteria in diagenesis has not been quantified, especially at overburden pressures and temperatures > ~80°C.

Organic compounds are found in a wide variety of geochemical environments, ranging from soils and sedimentary basins to hydrothermal ore deposits, metamorphic rocks, and carbonaceous chondrites. In many instances, these compounds have a profound effect on the consequences of geochemical processes. For example, it has been suggested that organic matter in sedimentary rocks acts as a reducing agent for metals during ore deposition (JENNEY, 1903; GARRELS, 1955; HAUSEN and KERR, 1968; RADTKE and SCHEINER, 1970; HAJI-VASSILIOU and KERR, 1972; NASH et al., 1981; NAHASHIMA et al., 1984; IDIZ et al., 1986; JOHNSON et al., 1987). Similarly, organic acid anions in oilfield brines may to some extent form complexes with metal cations in ore-forming solutions derived from sedimentary basins (GERMANOV and MEL'KANOVITSKAGA, 1975; CAROTHERS and KHARAKA, 1978; GIORDANO and BARNES, 1981; GIORDANO, 1985; SVERJENSKY, 1986; DRUMMOND and PALMER, 1986). These ligands may also play an important role in the formation of secondary porosity in oil reservoir formations (CROSSEY et al., 1984; SURDHAM et al., 1984). The hydrothermal alteration of kerogens, as well as individual organic compounds, has been recognized as an integral part of the generation of several types of petroleum (PRICE, 1982; SIMONEIT and LONSDALE, 1982; SIMONEIT, 1983, 1984a,b, 1985; SIMONEIT et al., 1984; THORNTON and SEYFRIED, 1987; KAWKA and SIMONEIT, 1987; BRAULT et al., 1988). Other problems involving organic molecules include the formation of graphite in metamorphic processes, the generation, transport, and deposition of petroleum, the source of organic compounds found in meteorites, and the origin of life. A

* P_{SAT} represents pressures corresponding to liquid-vapor equilibrium for the system H_2O, except at temperature < 100°C where it refers to the reference pressure of 1 bar.

quantitative approach can be taken to all of these problems if a thermodynamic frame of reference can be established to characterize metastable equilibrium states involving organic species. To establish such a frame of reference requires values of the thermodynamic properties of a wide variety of organic molecules in various phases at high temperatures and pressures. Of these, the thermodynamic properties of aqueous organic species at high temperatures and pressures are among the least understood.

Experimentally determined thermodynamic properties are available for many organic aqueous species at low temperatures. These species include: **hydrocarbons** (CULBERSON and MCKETTA, 1951; CLAUSSEN and POLGLASE, 1952; MORRISON and BILLET, 1952; MASTERTON, 1954; MORRISON and JOHNSTONE, 1954; HIMMELBLAU, 1959; LANNUNG and GJALDBAEK, 1960; FRIEDMAN and SCHERAGA, 1965; MCAULIFFE, 1966, 1969; O'SULLIVAN and SMITH, 1970; WEN and HUNG, 1970; TIEPEL and GUBBINS, 1972; GILL et al., 1975; SADA et al., 1975; RICE et al., 1976; YAMAMOTO et al., 1976; MACKAY and SHIU, 1977; BLANCO and SMITH, 1978; PRICE, 1976, 1979; DELLA GATTA, et al., 1981; RETTICH et al., 1981; TEWARI et al., 1982; CROVETTO et al., 1982, 1984; HAYDUK, 1982, 1986; BACKLUND et al., 1984; OLOFSSON et al., 1985; NAGHIBI et al., 1986; CLEVER and YOUNG, 1987); **amino acids** (DALTON and SCHMIDT, 1933; COHN et al., 1934; DANIEL and COHN, 1936; COHN and EDSALL, 1943; ELLERTON et al., 1964; CABANI et al., 1977; SPINK and WADSÖ, 1975; KIRCHNEROVA et al., 1976; PRASAD and AHLUWALIA, 1976; AHLUWALIA et al., 1977; SHAHIDI and FARRELL, 1978, 1981; MILLERO et al., 1978; HUMPHREY et al., 1980; LEPORI and MOLLICA, 1980; SHAHIDI, 1980; SHAHIDI and FARRELL, 1981; MISHRA and AHLUWALIA, 1984; RAO, 1984a,b; BLACKBURN et al., 1985; JOLICOEUR et al., 1986); **carboxylic acids** (NOYES, 1907; NOYES et al., 1910; RICHARDS and GUCKER, 1925; HARNED and EHLERS, 1933a, 1933b; HARNED and EMBREE, 1935; WATSON and FELSING, 1941; HAMANN and STRAUSS, 1955; KING, 1969; LEUNG and GREENWALD, 1970; KONICEK and WADSÖ, 1971; HØILAND, 1974; TENG and LENZI, 1975; HØILAND and VIKINGSTAD, 1975, 1976; ALLRED and WOOLLEY, 1981; MANZUROLA and APPELBLAT, 1985); **alcohols, aldehydes,** and **ketones** (BUTLER et al., 1935; BUTLER and REID, 1935; BUTLER and RAMCHANDANI, 1935; KINOSHITA et al., 1958; ALEXANDER, 1959; KRESHECK et al., 1965; ALEXANDER and HILL, 1969; KRISHNAN and FRIEDMAN, 1969; ARNETT et al., 1969; FRIEDMAN and KRISHNAN, 1973; HERKOVITZ and KELLEY, 1973; JOLICOEUR and LACROIX, 1973, 1976; CABANI et al., 1974, 1975, 1976; SKÖLD et al., 1976; EDWARD et al., 1977; ROUX et al., 1978; SOKOLOWSKI et al., 1984; OTT et al., 1987); **ethers** and **esters** (CABANI et al., 1971, 1973; KUSANO et al., 1973; FRANKS et al., 1972; EDWARD et al., 1977; ROUX et al., 1978; SOKOLOWSKI et al., 1984; NILSSON and WADSÖ, 1986); **amides, ureas,** and **amines** (KONICEK and WADSÖ, 1971; CABANI et al., 1973, 1974; HERKOVITZ and KELLEY, 1973; KAULGUD and PATIL, 1974, 1976; SKÖLD et al., 1976; SHAHIDI et al., 1977; ROUX et al., 1978; LEPANJE et al., 1985); **carbohydrates** (HENDRICKS et al., 1934; FRANKS et al., 1972, 1973; SHAHIDI et al., 1976; SAVAGE and WOOD, 1976; BONNER and CERUTTI, 1976; HARADA et al., 1978; HØILAND and HOLVIK, 1978; KAWAIZUMI et al., 1981; JASRA and AHLUWALIA, 1982, 1984; TEWARI and GOLDBERG, 1984; BERNAL and VAN HOOK, 1986); and **tetraalkylammonium salts** and **other organic electrolytes** (WEN and SAITO, 1965; CONWAY et al., 1966; FRANKS and SMITH, 1967; RÜTEJANS et al., 1969; ARNETT and CAMPION, 1970; MASTROIANNI and CRISS, 1972; DESNOYERS et al., 1973; LEDUC and DESNOYERS, 1973; LEVINE and LINDENBAUM, 1973; LEDUC et al., 1974; JOLICOEUR et al., 1975; STOKES, 1975; PERRON et al., 1976; SHIN et al., 1976; BONNER and CERUTTI, 1976; DELISI et al., 1980; MAJEED and TIMIMI, 1981; FRENCH and CRISS, 1982; DANIL DE NAMOR et al., 1984; ALLEN et al., 1985; BASHFORD and WOOLLEY, 1985; WOOLLEY and BASHFORD, 1986). Of all of the studies of organic aqueous species reported in the literature, only ~30 are concerned with temperatures > 50°C (e.g., NOYES et al., 1910; ACKERMANN and SCHREINER, 1958; ELLIS, 1963; RÜTERJANS et al., 1969; SHOOR et al., 1969; LOWN et al., 1970; NEAL and GORING, 1970; FISHER and BARNES, 1972; PRICE, 1976, 1979; TSONOPOULOS et al., 1976; BERGSTRÖM and OLOFSSON, 1977, 1978; STRONG et al., 1979, 1980, 1981, 1982, 1985, 1987; READ, 1981; CROVETTO et al., 1982a, 1984; MAYRATH and WOOD, 1983; OLOFSSON, 1984; PRUETT and FELKER, 1985; BIGGERSTAFF, 1986; ARCHER, 1986a,b, 1987; PALMER and WESOLOWSKI, 1987). Although the various thermodynamic data for temperatures $\geq$ 25°C are extensive, in many cases they are contradictory, and for a large number of species there are no data at all. To overcome these problems, several methods have been proposed to estimate the standard partial molal properties of organic aqueous species at 25°C and 1 bar (HANSCH et al., 1968; HAMMETT, 1970; ALBERT and SERJEANT, 1971; TERASAWA et al., 1975; HINE and MOOKERJEE, 1975; NICHOLS et al., 1976; GUTHRIE, 1977; ABRAHAM, 1979, 1984; AKITT, 1980; CABANI et al., 1978, 1981; CABANI and GIANNI, 1979; PERRIN et al., 1981; GIANNI et al., 1982). With a few exceptions (e.g., SMITH et al., 1986), corresponding estimation of the thermodynamic properties of organic aqueous species at hydrothermal temperatures and pressures has received little attention. The purpose of the present communication is to remedy this situation by estimating equation of state parameters for organic aqueous species, which can then be used in the revised HKF (HELGESON et al., 1981) equations of state (TANGER and HELGESON, 1988) to predict the thermodynamic behavior of these species at high pressures and temperatures. The names, composition, and structural formulas of the organic aqueous species considered in the present study are tabulated in the Appendix.

Standard state conventions for organic aqueous species

The standard state for aqueous species adopted in the present communication is one of unit activity of the jth aqueous species in a hypothetical 1 molal solution referenced to infinite dilution at any temperature and pressure. The standard state for H_2O calls for unit activity of the pure liquid at all pressures and temperatures. Any standard partial molal property of the kth aqueous electrolyte ($\bar{\Xi}_k^0$) is related to the corresponding absolute standard partial molal property of its constituent ions ($\bar{\Xi}_j^{0\text{abs}}$) by

$$\bar{\Xi}_k^0 = \sum_j \nu_{j,k} \bar{\Xi}_j^{0\text{abs}} \qquad (1)$$

where the subscripts k and j refer to the electrolyte and ion, respectively, and $\nu_{j,k}$ stands for the stoichiometric number of moles of the jth ion in one mole of the kth single electrolyte. The conventional standard partial molal properties of the jth ion ($\bar{\Xi}_j^0$) are defined by

$$\bar{\Xi}_j^0 \equiv \bar{\Xi}_j^{0\text{abs}} - Z_j \bar{\Xi}_{H^+}^{0\text{abs}} \tag{2}$$

where $\bar{\Xi}_{H^+}^{0\text{abs}}$ refers to the absolute standard partial molal property of the hydrogen ion and Z_j stands for the charge on the jth ion. It follows from Eqns. (1) and (2) and the requirement for electrical neutrality of an aqueous electrolyte that

$$\bar{\Xi}_k^0 = \sum_j \nu_{j,k} \bar{\Xi}_j^0. \tag{3}$$

The gas standard state for the jth organic species corresponds to unit fugacity of the hypothetical pure ideal gas at 1 bar and any temperature.

Many compilations of the thermodynamic properties of reactions among organic gases, liquids, or solids and aqueous solutions are based on different standard states than those employed in the present study. For example, WILHELM et al. (1977) and ABRAHAM (1984) adopt a unit mole fraction standard state for the solute, as in Henry's law. HINE and MOOKERJEE (1975) and CABANI et al. (1981) use a standard state of unit molarity for the species in both the aqueous liquid and vapor phase. These differences in standard states affect the values of $\Delta\bar{G}_f^0$ and $\bar{S}^0$ calculated from the standard partial molal Gibbs free energies of solution ($\Delta\bar{G}_{\text{soln}}^0$) and standard partial molal entropies of solution ($\Delta\bar{S}_{\text{soln}}^0$) listed in these and other compilations, as well as those reported in various experimental studies. However, this is not the case with the standard partial molal heat capacities and volumes tabulated by CABANI et al. (1981), HØILAND (1986), and others.

TEMPERATURE/PRESSURE-DEPENDENCE OF THE STANDARD PARTIAL MOLAL PROPERTIES OF AQUEOUS ORGANIC SPECIES

The standard partial molal properties of aqueous electrolytes consisting of inorganic cations and organic anions exhibit similar behavior as functions of temperature and pressure to those of inorganic aqueous electrolytes. For example, the plot of $\bar{C}_P^0$ against temperature at P_{SAT} for sodium acetate in Fig. 1 is similar to that for NaCl given by HELGESON et al. (1981). The curve in Fig. 1 was generated by regression of the experimental data represented by the symbols (see below). It can be seen in this figure that the standard partial molal heat capacity of $NaCH_3COO$ in the liquid phase of the system H_2O maximizes as a function of temperature at P_{SAT}, which is characteristic of inorganic aqueous electrolytes (HELGESON et al., 1981). In contrast, $\bar{C}_P^0$ for most neutral inorganic aqueous species at P_{SAT} decreases to a minimum and then increases with increasing temperature (SHOCK et al., 1989). The standard partial molal volumes and heat capacities of neutral organic aqueous molecules in the liquid phase of the system H_2O exhibit the same behavior as a function of temperature as many of their inorganic counterparts. $\bar{V}^0$ and $\bar{C}_P^0$ of aqueous ethylene (BIGGERSTAFF, 1986; BIGGERSTAFF and WOOD, 1988a,b) are depicted as functions of temperature

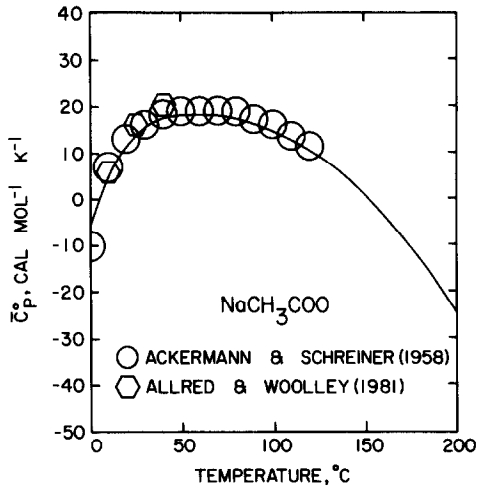


FIG. 1. Standard partial molal heat capacity ($\bar{C}_P^0$) of sodium acetate in water as a function of temperature at P_{SAT}. The symbols represent values taken from Table 2, which were calculated from the experimental data depicted in Fig. 3. The curve was generated from Eqn. (13) using parameters and thermodynamic data taken from Table 6 and SHOCK and HELGESON (1988).

at constant pressure in Fig. 2, where it can be seen that $\bar{C}_P^0$ of aqueous ethylene minimizes with increasing temperature, but the curve representing $\bar{V}^0$ of aqueous ethylene exhibits a reverse sigmoid configuration. The shapes of the curves in Fig. 2 are similar to those of other dissolved gases such as argon (BIGGERSTAFF et al., 1985; SHOCK et al., 1989). The curves in Fig. 2 were generated in the present study by regression of the experimental data represented by the symbols shown in the figures (see below). Note in Figs. 1 and 2 that the curves are closely consistent with the experimental standard partial molal properties of $NaCH_3COO$ and $C_2H_{4(aq)}$, and that they approach $-\infty$ and ∞, respectively, as temperature increases at P_{SAT} in the liquid phase region toward the critical point of H_2O. The examples shown in these figures of the behavior of charged and neutral organic aqueous species are consistent with the revised HKF equations of state (TANGER and HELGESON, 1988) and their extension to include neutral inorganic aqueous species (SHOCK et al., 1989).

Summary of the revised HKF equations of state for aqueous ions and electrolytes

The conventional standard partial molal properties of aqueous species are expressed in the revised HKF equations of state as the sum of structural and solvation contributions, which can be expressed as

$$\bar{\Xi}^0 = \Delta\bar{\Xi}_n^0 + \Delta\bar{\Xi}_s^0 \tag{4}$$

where $\bar{\Xi}^0$ stands for a given conventional standard partial molal property of an aqueous species or electrolyte, and $\bar{\Xi}_n^0$ and $\bar{\Xi}_s^0$ refer to the conventional nonsolvation (structural) and solvation contributions to that property, respectively. The nonsolvation contribution is taken to be the sum of an intrinsic term and a term arising from local disruption of the solvent structure caused by the presence of the species in solution. In the case of ionic species, this term reflects local solvent collapse, but for neutral aqueous species it represents cavity formation. The solvation contributions to the standard

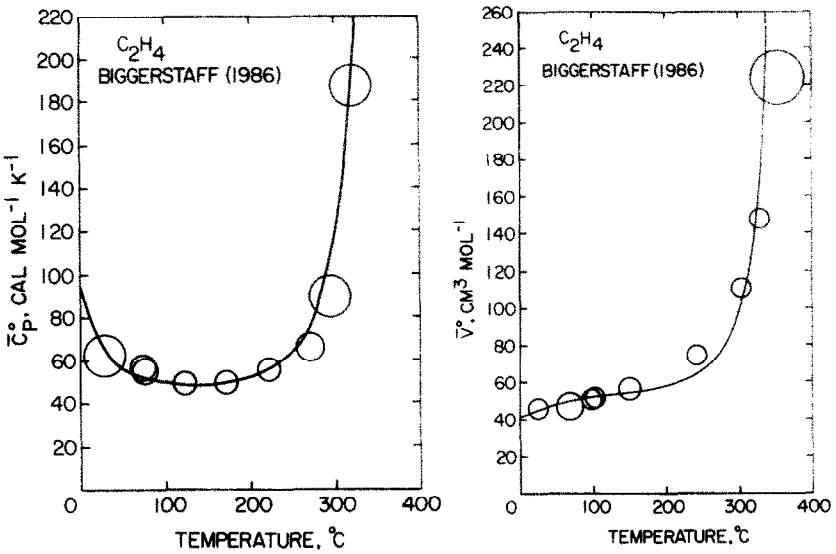


FIG. 2. Standard partial molal heat capacity ($\bar{C}^0_P$) and volume ($\bar{V}^0$) of ethylene in water as a function of temperature at constant pressure (~180 bars for $\bar{C}^0_P$ and ~210 bars for $\bar{V}^0$). The symbols represent data taken from BIGGERSTAFF (1986), but the curves were generated from Eqns. (27) and (28) using parameters and thermodynamic data taken from Table 6 (see text).

partial molal volume, heat capacity, and entropy of an aqueous species can be expressed in terms of Born transfer theory as

$$\Delta\bar{V}^0_s = -\omega Q + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial P}\right)_T, \tag{5}$$

$$\Delta\bar{C}^0_{P,s} = \omega TX + 2TY\left(\frac{\partial\omega}{\partial T}\right)_P - T\left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_P, \tag{6}$$

and

$$\Delta\bar{S}^0_s = \omega Y - \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial T}\right)_P, \tag{7}$$

where $\Delta\bar{V}^0_s$, $\Delta\bar{C}^0_{P,s}$, and $\Delta\bar{S}^0_s$ refer to the standard partial molal volume, heat capacity, and entropy of solvation, ϵ stands for the dielectric constant of H_2O, ω designates the conventional Born coefficient (see below), and Q, X, and Y denote Born functions defined by

$$Q \equiv \frac{1}{\epsilon}\left(\frac{\partial \ln\epsilon}{\partial P}\right)_T, \tag{8}$$

$$X \equiv \frac{1}{\epsilon}\left(\left(\frac{\partial^2 \ln\epsilon}{\partial T^2}\right)_P - \left(\frac{\partial \ln\epsilon}{\partial T}\right)^2_P\right), \tag{9}$$

and

$$Y \equiv \frac{1}{\epsilon}\left(\frac{\partial \ln\epsilon}{\partial T}\right)_P. \tag{10}$$

The nonsolvation counterparts of Eqns. (5) and (6) are given by

$$\Delta\bar{V}^0_n = \sigma + \frac{\xi}{T-\Theta} = a_1 + \frac{a_2}{\Psi+P} + \left(a_3 + \frac{a_4}{\Psi+P}\right)\left(\frac{1}{T-\Theta}\right) \tag{11}$$

where

$$\sigma = a_1 + \frac{a_2}{\Psi+P} \tag{11A}$$

and

$$\xi = a_3 + \frac{a_4}{\Psi+P}, \tag{11B}$$

and

$$\Delta\bar{C}_{P,n} = c_1 + \frac{c_2}{(T-\Theta)^2} - \left(\frac{2T}{(T-\Theta)^3}\right)\left(a_3(P-P_r) + a_4 \ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right), \tag{12}$$

where $\Delta\bar{V}^0_n$ and $\Delta\bar{C}^0_{P,n}$ stand for the nonsolvation or structural analogs of $\Delta\bar{V}^0_s$ and $\Delta\bar{C}^0_{P,s}$, respectively, σ, ξ, a_1, a_2, a_3, a_4, c_1, and c_2 represent species-dependent nonsolvation parameters, T_r, P_r, T, and P designate the reference temperature and pressure of 298.15 K and 1 bar, and the temperature and pressure of interest, and Ψ and Θ denote solvent parameters equal to 2600 bars and 228 K, respectively.

The revised HKF equations for the standard partial molal volume ($\bar{V}^0$), heat capacity ($\bar{C}^0_P$), entropy ($\bar{S}^0$) and the apparent standard partial molal enthalpy ($\Delta\bar{H}^0$) and Gibbs free energy of formation ($\Delta\bar{G}^0$) of ionic aqueous species and electrolytes are given by (TANGER and HELGESON, 1988)

$$\bar{V}^0 = \Delta\bar{V}^0_n + \Delta\bar{V}^0_s = \sigma + \frac{\xi}{T-\Theta} - \omega Q + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial P}\right)_T = a_1 + \frac{a_2}{\Psi+P} + \left(a_3 + \frac{a_4}{\Psi+P}\right)\left(\frac{1}{T-\Theta}\right) - \omega Q + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial P}\right)_T, \tag{13}$$

$$\bar{C}^0_P = \Delta\bar{C}^0_{P,n} + \Delta\bar{C}^0_{P,s}$$
$$= c_1 + \frac{c_2}{(T-\Theta)^2} - \left(\frac{2T}{(T-\Theta)^3}\right)\left(a_3(P-P_r) + a_4 \ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right) + \omega TX + 2TY\left(\frac{\partial\omega}{\partial T}\right)_P - T\left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_P, \quad (14)$$

$$\bar{S}^0 = \bar{S}^0_{P_r,T_r} + c_1 \ln\left(\frac{T}{T_r}\right) - \frac{c_2}{\Theta}\left[\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right) + \frac{1}{\Theta}\ln\left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right)\right] + \left(\frac{1}{T-\Theta}\right)^2\left(a_3(P-P_r) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right) + \omega Y - \left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_P - \omega_{P_r,T_r}Y_{P_r,T_r}, \quad (15)$$

$$\Delta\bar{H}^0 \equiv \Delta\bar{H}^0_f + (\bar{H}^0_{P,T} - \bar{H}^0_{P_r,T_r})$$
$$= \Delta\bar{H}^0_f + c_1(T-T_r) - c_2\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right)\right) + a_1(P-P_r) + a_2\ln\left(\frac{\Psi+P}{\Psi+P_r}\right) + \left(\frac{2T-\Theta}{(T-\Theta)^2}\right)\left(a_3(P-P_r) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right) + \omega\left(\frac{1}{\epsilon}-1\right) + \omega TY - T\left(\frac{1}{\epsilon}-1\right)\left(\frac{\partial\omega}{\partial T}\right)_P - \omega_{P_r,T_r}\left(\frac{1}{\epsilon_{P_r,T_r}}-1\right) - \omega_{P_r,T_r}T_rY_{P_r,T_r}, \quad (16)$$

and

$$\Delta\bar{G}^0_{P,T} \equiv \Delta\bar{G}^0_f + (\bar{G}^0_{P,T} - \bar{G}^0_{P_r,T_r})$$
$$= \Delta\bar{G}^0_f - \bar{S}^0_{P_r,T_r}(T-T_r) - c_1\left(T\ln\left(\frac{T}{T_r}\right) - T + T_r\right) + a_1(P-P_r) + a_2\ln\left(\frac{\Psi+P}{\Psi+P_r}\right) - c_2\left(\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right)\right)\left(\frac{\Theta-T}{\Theta}\right) - \frac{T}{\Theta^2}\ln\left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right)\right) + \left(\frac{1}{T-\Theta}\right)\left(a_3(P-P_r) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right) + \omega\left(\frac{1}{\epsilon}-1\right) - \omega_{P_r,T_r}\left(\frac{1}{\epsilon_{P_r,T_r}}-1\right) + \omega_{P_r,T_r}Y_{P_r,T_r}(T-T_r), \quad (17)$$

where $\Delta\bar{G}^0_f$ and $\Delta\bar{H}^0_f$, respectively, represent the standard partial molal Gibbs free energy and enthalpy of formation from the elements in their stable form at P_r and T_r, ($\bar{H}^0_{P,T} - \bar{H}^0_{P_r,T_r}$) and ($\bar{G}^0_{P,T} - \bar{G}^0_{P_r,T_r}$) correspond to the difference in the conventional standard partial molal enthalpy and Gibbs free energy of formation of an aqueous species at P and T and those at the reference pressure and temperature, and ω stands for the conventional Born coefficient, which is defined for the jth ionic species by

$$\omega_j = \omega^{\text{abs}}_j - Z_j\omega^{\text{abs}}_{H^+} \quad (18)$$

where Z_j again stands for the charge on the jth aqueous species, $\omega^{\text{abs}}_{H^+}$ refers to the absolute Born coefficient of the hydrogen ion, which is taken to be 0.5387×10^5 cal mol^{-1} (HELGESON and KIRKHAM, 1976), and ω^{abs}_j designates the absolute Born coefficient of the jth species defined by

$$\omega^{\text{abs}}_j \equiv \frac{N^0e^2Z_j^2}{2r_{e,j}} = \frac{\eta Z_j^2}{r_{e,j}} \quad (19)$$

where $\eta = N^0e^2/2 = 1.66027 \times 10^5$ Å cal mol^{-1}, N^0 designates Avogadro's number (6.02252×10^{23} mol^{-1}), e stands for the absolute electronic charge (4.80298×10^{-10} *esu*), and $r_{e,j}$ denotes the effective electrostatic radius of the jth species, which is given in terms of its crystallographic counterpart by

$$r_{e,j} = r_{x,j} + Z_j\Gamma_\pm \quad (20)$$

where

$$\Gamma_\pm \equiv k_z + g \quad (21)$$

where k_z represents a charge-dependent constant equivalent to 0.0 for anions and 0.94 for cations, and g stands for a solvent function of temperature and density. The g function has been characterized at temperatures $\leq$ 450°C by fitting orthogonal temperature-density polynomials to values of the Born coefficient (ω_k) and its partial derivatives that were generated from standard partial molal heat capacities and volumes of NaCl (TANGER and HELGESON, 1988). Values of the g function at higher temperatures were obtained by first assuming $r_{e,j}$ for neutral aqueous species to be independent of temperature and pressure, and then fitting orthogonal polynomials to values of g derived from experimental dissociation constants of $NaCl^0$ in the supercritical region, which were smoothed before fitting to be consistent with those at lower temperatures (SHOCK et al., 1990). These explicit functions for ω_k or g permit calculation of the partial derivatives of ω in Eqns. (5)–(7) and (13)–(16). At low temperatures and pressures, the g function and its derivative approach 0. As a consequence, $\Gamma_\pm$, and therefore $r_{e,j}$ are essentially constant at temperatures below 170°C and pressures corresponding to the vapor-liquid saturation curve for H_2O (P_{SAT}). $\Gamma_\pm$ and $r_{e,j}$ are also essentially constant at (SHOCK et al., 1990)

$$T < 175°C \quad \text{if} \quad P \leq 2450 \text{ bars} \quad (22a)$$

and

$$\rho > 1.0 \text{ gm cm}^{-3} \text{ if } 2450 \text{ bars} < P < 5000 \text{ bars}. \quad (22b)$$

Summary of the revised HKF equations of state for neutral aqueous species

In the case of neutral aqueous species, the solvation terms in the revised HKF equations of state can be expressed in terms of effective Born coefficients (ω_e). The effective Born

coefficient of the jth neutral aqueous species is given by (HELGESON et al., 1981)

$$\omega_{e,j} = \frac{Z_{e,j}^2 \eta}{r_{e,j}}, \quad (23)$$

where $Z_{e,j}$ refers to the effective charge of the jth neutral aqueous species (see below). Values of $\omega_{e,j}$ can be obtained by regression of experimental data with the revised HKF equations of state. As in the case of neutral inorganic aqueous species (SHOCK et al., 1989), the effective Born coefficients of neutral organic aqueous species are taken to be independent of temperature and pressure. Under these circumstances, the solvation contributions to the standard partial molal properties of neutral organic aqueous species can be expressed as

$$\Delta \bar{V}_s^0 = -\omega_e Q \quad (24)$$

$$\Delta \bar{C}_{P,s}^0 = \omega_e TX \quad (25)$$

$$\Delta \bar{S}_s^0 = \omega_e Y \quad (26)$$

where Q, X, and Y stand for the Born functions given by Eqns. (8)–(10). It follows that Eqns. (13)–(17) reduce to

$$\bar{V}^0 = a_1 + a_2\left(\frac{1}{\Psi + P}\right) + \left(a_3 + a_4\left(\frac{1}{\Psi + P}\right)\right)\left(\frac{1}{T - \Theta}\right) - \omega_e Q \quad (27)$$

$$\bar{C}_P^0 = c_1 + c_2\left(\frac{1}{T - \Theta}\right)^2 - 2T\left(\frac{1}{T - \Theta}\right)^3\left(a_3(P - P_r) + a_4 \ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right) + \omega_e TX, \quad (28)$$

$$\bar{S}^0 = \bar{S}_{P_r,T_r}^0 + c_1 \ln\left(\frac{T}{T_r}\right) - \frac{c_2}{\Theta}\left[\left(\frac{1}{T - \Theta}\right) - \left(\frac{1}{T_r - \Theta}\right) + \frac{1}{\Theta}\ln\left(\frac{T_r(T - \Theta)}{T(T_r - \Theta)}\right)\right] + \left(\frac{1}{T - \Theta}\right)^2\left[a_3(P - P_r) + a_4 \ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right] + \omega_e(Y_{P,T} - Y_{P_r,T_r}). \quad (29)$$

$$\Delta \bar{H}_{P,T}^0 \equiv \Delta \bar{H}_f^0 + (\bar{H}_{P,T}^0 - \bar{H}_{P_r,T_r}^0)$$
$$= \Delta \bar{H}_f^0 + c_1(T - T_r) - c_2\left(\left(\frac{1}{T - \Theta}\right) - \left(\frac{1}{T_r - \Theta}\right)\right) + a_1(P - P_r) + a_2 \ln\left(\frac{\Psi + P}{\Psi + P_r}\right) + \left(\frac{2T - \Theta}{(T - \Theta)^2}\right)\left(a_3(P - P_r) + a_4 \ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right) + \omega_e\left(TY_{P,T} - T_r Y_{P_r,T_r} - \left(\frac{1}{\epsilon_{P_r,T_r}} - 1\right) + \left(\frac{1}{\epsilon_{P,T}} - 1\right)\right). \quad (30)$$

and

$$\Delta \bar{G}_{P,T}^0 \equiv \Delta \bar{G}_f^0 + (\bar{G}_{P,T}^0 - \bar{G}_{P_r,T_r}^0)$$
$$= \Delta \bar{G}_f^0 + -\bar{S}_{P_r,T_r}^0(T - T_r) - c_1\left(T \ln\left(\frac{T}{T_r}\right) - T + T_r\right) + a_1(P - P_r) + a_2 \ln\left(\frac{\Psi + P}{\Psi + P_r}\right) - c_2\left(\left(\left(\frac{1}{T - \Theta}\right) - \left(\frac{1}{T_r - \Theta}\right)\right)\left(\frac{\Theta - T}{\Theta}\right) - \frac{T}{\Theta^2}\ln\left(\frac{T_r(T - \Theta)}{T(T_r - \Theta)}\right)\right) + \left(\frac{1}{T - \Theta}\right)\left(a_3(P - P_r) + a_4 \ln\left(\frac{\Psi + P}{\Psi + P_r}\right)\right) + \omega_e\left(Y_{P_r,T_r}(T - T_r) + \left(\frac{1}{\epsilon_{P,T}} - 1\right) - \left(\frac{1}{\epsilon_{P_r,T_r}} - 1\right)\right). \quad (31)$$

Values of ω_e for neutral organic aqueous species obtained by regression of experimental data or generated from correlation algorithms (see below) are negative and consistent with non-zero effective charges (Z_e). The effective charge is a manifestation of the disruptive effect of these neutral molecules on the electrostatic forces of attraction among the solvent dipoles at high temperatures and pressures. The presence of volatile neutral molecules causes repulsion of the H_2O dipoles, which results in negative values of $r_{e,j}$ and $\omega_{e,j}$ (SHOCK et al., 1989). Dissolved noble gases are among the most volatile inorganic aqueous species. Among organic aqueous species, the hydrocarbon gases are among the most volatile. In both cases, ω_e is negative for each of the dissolved gases. Repulsion and disruption of the electrostatic forces of attraction among the solvent dipoles by neutral organic aqueous species at high temperatures and pressures increases (and hence ω_e becomes more negative) with increasing length of the carbon chain and/or addition of functional groups (see below).

REGRESSION OF EXPERIMENTAL PARTIAL MOLAL PROPERTIES

In accord with extrapolations of the partial molal properties of inorganic electrolytes to infinite dilution by HELGESON et al. (1981), TANGER and HELGESON (1988), and SHOCK and HELGESON (1988), the Hückel equation was used in the present study to extrapolate to infinite dilution the apparent molal heat capacities and volumes of aqueous electrolytes consisting of inorganic cations and organic ligands. The Hückel equation for a completely dissociated electrolyte is given by

$$\log \bar{\gamma}_{\pm,k} = -\frac{|Z_+ Z_-| A_\gamma I^{1/2}}{1 + \mathring{a}_k B_\gamma I^{1/2}} + \Gamma_\gamma + b_{\gamma,k} I \quad (32)$$

where $\bar{\gamma}_{\pm,k}$ stands for the mean ionic activity coefficient of the kth electrolyte, A_γ and B_γ represent the Debye-Hückel coefficients (see below), $\mathring{a}_k$ refers to the ion size parameter, $b_{\gamma,k}$ denotes an electrolyte-dependent extended term coeffi-

cient, Γ_γ designates the mole fraction to molality conversion factor given by

$$\Gamma_\gamma \equiv -\log(1 + 0.0180153\, m_k), \tag{33}$$

and $\bar{I}$ stands for the effective ionic strength defined by

$$\bar{I} \equiv \frac{1}{2}\sum_j Z_j^2 m_j, \tag{34}$$

where m_k and m_j represent the molalities of the subscripted electrolyte and ion, respectively. A_γ and B_γ in Eqn. (32) can be expressed as

$$A_\gamma \equiv \frac{(2\pi N^0)^{1/2}e^3\rho^{1/2}}{2.302585(1000)^{1/2}(\epsilon kT)^{3/2}} = \frac{1.824829238 \times 10^6\rho^{1/2}}{(\epsilon T)^{3/2}} \tag{35}$$

and

$$B_\gamma \equiv \left(\frac{8\pi N^0\rho e^2}{1000\epsilon kT}\right)^{1/2} = \frac{50.29158649 \times 10^8\rho^{1/2}}{(\epsilon T)^{1/2}} \tag{36}$$

where $\pi = 3.14159265$, k denotes Boltzman's constant (1.38054×10^{-16} erg K^{-1}), and ρ and ϵ stand for the density and dielectric constant of H_2O, respectively.

Regression equations

Taking account of Eqns. (32) and (33), together with the relation between the apparent molal property of a single electrolyte solution (ϕ_Ξ) and the corresponding partial molal property of the solute given by

$$\phi_\Xi = \frac{1}{m_k}\int_0^{m_k} \bar{\Xi}_k \mathrm{d}m_k, \tag{37}$$

permits us to write

$$\phi_V = \bar{V}_k^0 + \psi_k A_V \bar{I}^{1/2}\alpha^* + 2\psi_k A_\gamma B_V \beta^* + \frac{\nu_k b_{V,k}\bar{I}}{4} \tag{38}$$

and

$$\phi_{C_P} = \bar{C}_{P,k}^0 + \psi_k A_J \bar{I}^{1/2}\alpha^* - \frac{\psi_k(2A_HB_H - A_GB_JT)\beta^*}{2.303RT^2} + \frac{2\psi_k A_\gamma (B_H)^2\zeta^*}{2.303RT^2} - \frac{\nu_k b_{J,k}\bar{I}}{4}, \tag{39}$$

where

$$\psi_k = \sum_j \frac{\nu_{j,k}Z_j^2}{2}, \tag{40}$$

where $\nu_{j,k}$ again denotes the stoichiometric number of moles of the jth ion in one mole of the kth single electrolyte, $\nu_k \equiv \sum_j \nu_{j,k}$, $\bar{\Xi}_k$ represents a partial molal property of the aqueous electrolyte defined by

$$\bar{\Xi}_k \equiv \left(\frac{\partial \Xi}{\partial m_k}\right)_{P,T}, \tag{41}$$

and

$$A_G = -2(2.303)RTA_\gamma, \tag{42}$$

$$A_H \equiv -\left(\frac{\partial(A_G/T)}{\partial T}\right)_P, \tag{43}$$

$$A_J \equiv \left(\frac{\partial A_H}{\partial T}\right)_P, \tag{44}$$

$$A_V \equiv \left(\frac{\partial A_G}{\partial P}\right)_T, \tag{45}$$

$$B_H \equiv 2(2.303)RT\left(\frac{\partial B_\gamma}{\partial T}\right)_P, \tag{46}$$

$$B_V \equiv 2(2.303)RT\left(\frac{\partial B_\gamma}{\partial P}\right)_T, \tag{47}$$

$$B_J \equiv \left(\frac{\partial B_H}{\partial T}\right)_P, \tag{48}$$

$$b_{V,k} \equiv 2(2.303)RT\left(\frac{\partial b_\gamma}{\partial P}\right)_T, \tag{49}$$

$$b_{J,k} \equiv 2(2.303)R\left[2T\left(\frac{\partial b_\gamma}{\partial T}\right)_P + T^2\left(\frac{\partial^2 b_\gamma}{\partial T^2}\right)_P\right], \tag{50}$$

and

$$\alpha^* \equiv \frac{1}{\Lambda} - \frac{\sigma^*}{3}, \tag{51}$$

$$\beta^* \equiv \frac{1}{\mathring{a}_k^3 B_\gamma^4 \bar{I}}\left[\frac{\Lambda^2}{2} - 3\Lambda + \frac{1}{\Lambda} + 3\ln\Lambda + 1.5\right], \tag{52}$$

$$\zeta^* \equiv \frac{1}{\mathring{a}_k^3 B_\gamma^5 \bar{I}}\left[\frac{\Lambda^2}{2} - 4\Lambda + 6\ln\Lambda + \frac{4}{\Lambda} - \frac{1}{2\Lambda^2}\right], \tag{53}$$

where

$$\sigma^* \equiv \frac{3}{\mathring{a}_k^3 B_\gamma^3 \bar{I}^{3/2}}\left[\Lambda - \frac{1}{\Lambda} - 2\ln\Lambda\right], \tag{54}$$

and

$$\Lambda \equiv 1 + \mathring{a}_k B_\gamma \bar{I}^{1/2}. \tag{55}$$

Rearrangement of Eqns. (38) and (39) yields the following difference functions ($\rho_{\Xi,k}$) for the kth electrolyte (HELGESON et al., 1981)

$$\rho_{V,k} \equiv \phi_V - \psi_k A_V \bar{I}^{1/2}\alpha^* - 2\psi_k A_\gamma B_V \beta^* = \bar{V}_k^0 + \frac{\nu_k b_{V,k}\bar{I}}{4} \tag{56}$$

and

$$\rho_{J,k} \equiv \phi_{C_P} - \psi_k A_J \bar{I}^{1/2}\alpha^* + \frac{\psi_k(2A_HB_H - A_GB_JT)\beta^*}{2.303RT^2} - \frac{2\psi_k A_\gamma (B_H)^2\zeta^*}{2.303RT^2} = \bar{C}_{P,k}^0 - \frac{\nu_k b_{J,k}\bar{I}}{4}, \tag{57}$$

which can be used to extrapolate experimental values of ϕ_V and ϕ_{C_P} to infinite dilution. Values of ρ_V and ρ_J calculated from Eqns. (56) and (57) using experimental data for aqueous electrolytes consisting of inorganic cations and organic anions are plotted against ionic strength in Fig. 3. Corresponding plots of ϕ_{C_P} against molality are shown for neutral organic aqueous species in Fig. 4. The latter plots were generated from Eqns. (56) and (57) after replacing I with m and setting the Debye-Hückel terms to zero for the neutral species. The resulting expressions are consistent with $\rho_V = \phi_V$, $\rho_J = \phi_{C_P}$, and modified regular solution theory (HELGESON et al., 1981) for the short-range interaction of neutral organic species with solvent dipoles. It can be seen in Figs. 3 and 4 that for the most part the distribution of the experimental data represented by the symbols is closely consistent with the linear curves drawn through the data. The intercepts of the curves shown in Figs. 3 and 4 correspond to the standard partial molal volumes and heat capacities of the electrolytes and neutral species given in Tables 1 and 2. Values of $\bar{V}^0$ and $\bar{C}_P^0$ reported in the literature for other organic aqueous species over a range of temperature are also shown in these tables. It should perhaps be noted that the slopes of the curves for each electrolyte in Figs. 3 and 4 exhibit a smooth distribution with temperature.

Organic aqueous electrolytes

Values of ω_j for the organic anions in the electrolytes shown in Fig. 3 were calculated in the present study from values of $\bar{S}_j^0$ by taking account of the charge-dependent correlations among these variables described by SHOCK et al. (1989), which are reproduced in Fig. 5. The curves in Fig. 5 are consistent with

$$\omega_j = -1514.4\bar{S}_j^0 + \beta_Z \tag{58}$$

where

$$\beta_Z = \frac{-\alpha_Z \eta}{Y\eta - 100} - Z_j \omega_{H^+}^{abs} \tag{59}$$

where α_Z is equal to 72, 141, 211, and 286 for monovalent, divalent, trivalent, and tetravalent ions, respectively. Values of ω_j for anions calculated from Eqn. (58) were used together with values of ω_j for cations (SHOCK and HELGESON, 1988) to calculate values of ω_k from $\omega_k = \sum_j \nu_{j,k}\omega_j$ for electrolytes.

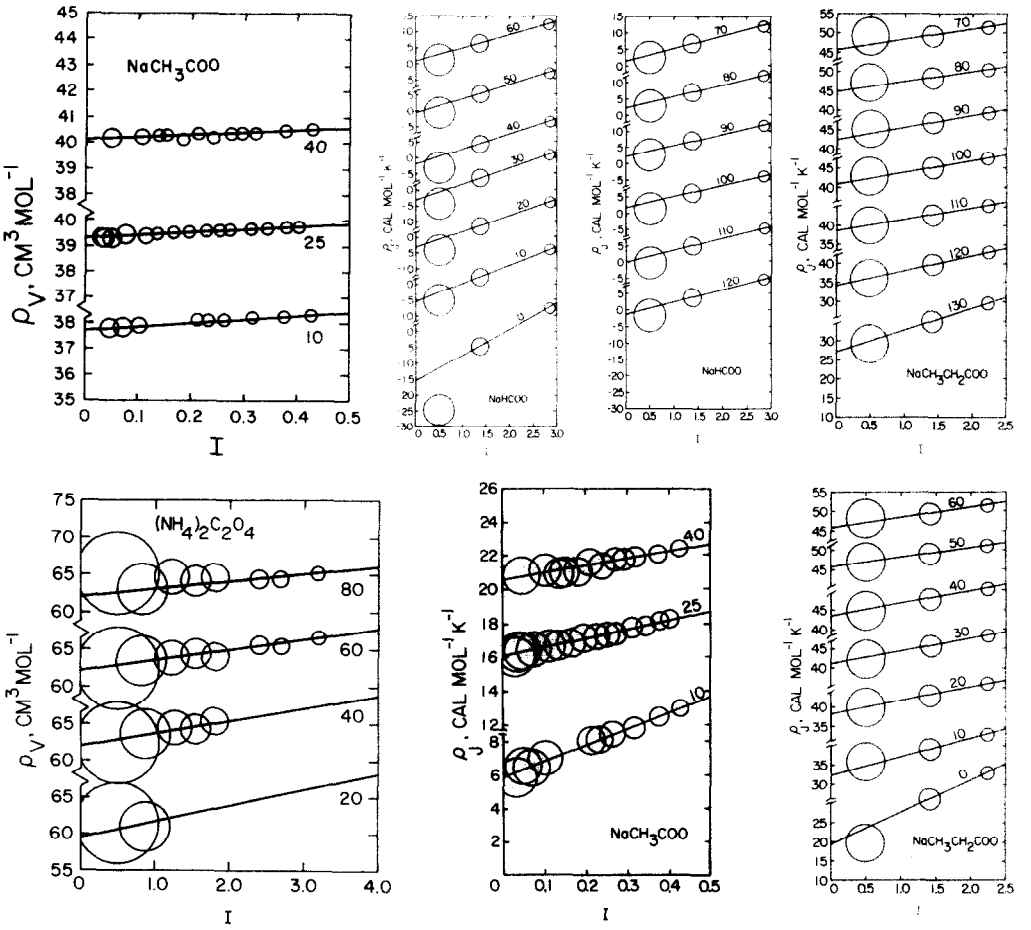


FIG. 3. ρ_V and ρ_J (Eqns. 56 and 57) as functions of stoichiometric ionic strength at various temperatures and 1 bar for the aqueous electrolytes with organic anions identified in the Appendix. The symbols represent data taken from ACKERMANN and SCHREINER (1958), ALLRED and WOOLLEY (1981), and SÖHNEL et al. (1984).

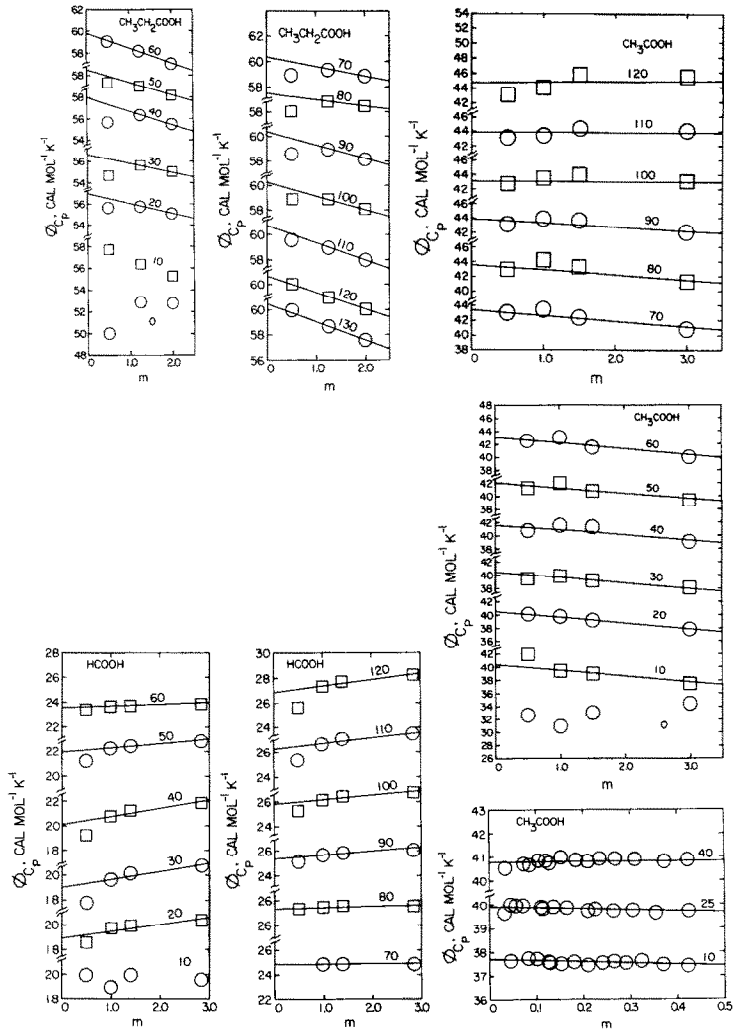


FIG. 4. ϕ_V and ϕ_{C_P} as functions of molality at various temperatures and 1 bar for aqueous formic, acetic, and propanoic acids (see Appendix). The symbols represent experimental data taken from ACKERMANN and SCHREINER (1958) and ALLRED and WOOLLEY (1981).

These Born coefficients were used in turn to calculate values of $\Delta\bar{V}^0_s$ and $\Delta\bar{C}^0_{P,s}$ for the electrolytes from Eqns. (5) and (6). Values of the standard partial molal volumes and heat capacities of solvation were then used to evaluate the first identity in Eqns. (13) and (14) using the values of $\bar{V}^0$ and $\bar{C}^0_P$ taken from Tables 1 and 2 to calculate the values of $\Delta\bar{V}^0_n$ and $\Delta\bar{C}^0_{P,n}$ shown as symbols in the regression plots in Fig. 6. The regression curves in these plots are discussed below.

Neutral organic aqueous species

Of the values of $\bar{C}^0_P$ for neutral organic aqueous species shown in Table 2, only those for $C_2H_{4(aq)}$, $HCOOH_{(aq)}$, and $CH_3COOH_{(aq)}$ exhibit sufficient character in their temperature distribution to permit definitive retrieval of c_1, c_2 and ω_e for the species by regression of the values of $\bar{C}^0_P$ in the table with Eqns. (25), (28), and the first identity in Eqn. (14). The values of $\omega_{e,j}$ generated in the regression calculations for these three species are plotted against $\bar{S}^0_j$ in Fig. 7, together with values for neutral inorganic aqueous species taken from SHOCK et al. (1989). It can be seen in Fig. 7 that the symbol representing aqueous ethylene falls on the lower curve, which is consistent with its high volatility. The equation of the lower curve in Fig. 7 can be expressed as

$$\omega_{e,j} = -1514.4\bar{S}^0_j. \qquad (60)$$

In contrast to $C_2H_{4(aq)}$, the two organic species with functional groups in Fig. 7 fall along the upper curve, which corresponds to the correlation of $\omega_{e,j}$ and $\bar{S}^0_j$ for less volatile neutral inorganic aqueous species given by (SHOCK et al., 1989)

$$\omega_{e,j} = -1514.4\bar{S}^0_j + 0.34 \times 10^5. \qquad (61)$$

The latter correlation curve was used in the absence of experimental standard partial molal heat capacity data at high temperatures to predict values of $\omega_{e,j}$ for alkylbenzenes and neutral organic aqueous species with functional groups. Estimates of $\omega_{e,j}$ for the highly volatile hydrocarbons were made with the aid of the lower curve in Fig. 7. The values of $\omega_{e,j}$

Table 1. Experimental standard partial molal volumes ($\bar{V}°$) of neutral organic aqueous species and aqueous electrolytes with organic anions at 1 bar and various temperatures. The various organic species shown below are identified in the Appendix.

$NaCH_3COO$		$(NH_4)_2C_2O_4$		methanol		ethanol	
T	$\bar{V}°$[a]	T	$\bar{V}°$[a]	T	$\bar{V}°$[a]	T	$\bar{V}°$[a]
10	37.81[b]	20	59.5[d]	1	38.02[e]	1	54.66[e]
25	39.34[b]	40	61.9[d]	20	38.05[e]	20	54.97[e]
25	39.41[c]	60	62.2[d]	25	38.17[f]	25	58.05[f]
40	40.17[b]	80	62.0[d]	40	38.37[e]	40	55.36[e]
				50	38.58[e]	50	55.71[e]
1-propanol		1-butanol		2-butanol		1-pentanol	
T	$\bar{V}°$[a]	T	$\bar{V}°$[a]	T	$\bar{V}°$[a]	T	$\bar{V}°$[a]
1	70.00[e]	0.5	85.9[g]	0.5	86.15[g]	1	101.15[e]
20	70.20[e]	1	85.54[e]	1	85.86[e]	20	101.92[e]
25	70.70[f]	5	86.0[g]	5	86.2[g]	25	102.68[f]
40	70.80[e]	20	85.77[e]	20	86.42[e]	40	102.91[e]
50	70.29[e]	25	86.65[g]	25	86.75[g]	50	103.52[e]
2-propanol		25	86.6[f]	25	86.62[f]	CH_3COOH	
T	$\bar{V}°$[a]	40	86.37[e]	40	87.63[e]	T	$\bar{V}°$[a]
1	71.39[e]	40	87.6[g]	40	87.6[g]	10	50.60[b]
20	71.73[e]	50	86.72[e]	50	88.44[e]	25	52.01[b]
25	71.90[f]					40	53.11[b]
40	72.55[e]						
50	73.18[e]						

a. $Cm^3\ mol^{-1}$. b. Allred and Woolley (1981). c. King (1969). d. Söhnel et al. (1984). e. Friedman and Scheraga (1965). f. Høiland (1986). g. Franks and Smith (1968a).

estimated in this manner are consistent with high-temperature/pressure experimental equilibrium constants reported in the literature for reactions involving these species (see below).

Values of $\Delta\bar{V}^0_s$ and $\Delta\bar{C}^0_{P,s}$ for neutral organic aqueous species were computed in the present study from Eqns. (24) and (25) using the values of $\omega_{e,j}$ generated in the manner described above. These solvation properties, together with

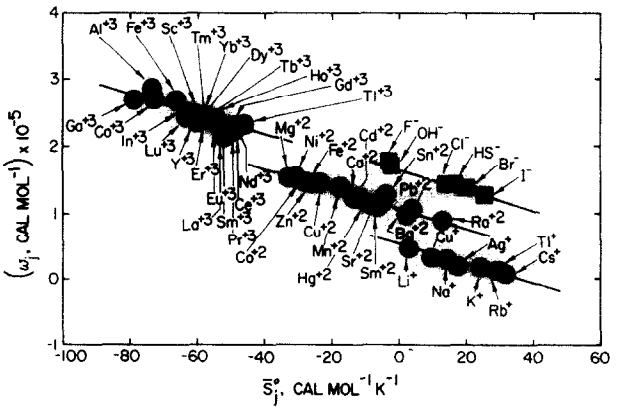


FIG. 5. Correlation of the conventional Born coefficients (ω_j) of aqueous ions with their standard partial molal entropies ($\bar{S}^0_j$) at 25°C and 1 bar. The symbols represent values taken from SHOCK and HELGESON (1988). The curves are consistent with Eqn. (58).

the values of $\bar{V}^0$ and $\bar{C}^0_P$ in Tables 1 and 2 were used to calculate the values of $\Delta\bar{V}^0_n$ and $\Delta\bar{C}^0_{P,n}$ represented by the symbols in the regression plots shown in Fig. 8. Taking account of Eqns. (11) and (12), the slopes and intercepts of $\Delta\bar{V}^0_n$ as a function of $1/(T-\Theta)$ and $\Delta\bar{C}^0_{P,n}$ as a function of $1/(T-\Theta)^2$ in the regression plots shown in Figs. 6 and 8 correspond to σ and ξ, and for $P \approx P_r$, c_1 and c_2, respectively. These equation of state parameters are listed in Table 3 for both neutral organic aqueous species and organic aqueous anions.

CORRELATIONS AMONG NONSOLVATION EQUATION OF STATE PARAMETERS FOR AQUEOUS ORGANIC MOLECULES

It can be seen in Fig. 9 that the σ and $\Delta\bar{V}^0_n$ parameters generated above (which are listed in Table 3) for the organic anions CH_3COO^- and $C_2O_4^{-2}$ are consistent with those for

Table 2. Experimental standard partial molal heat capacities ($\bar{C}°_P$) of neutral organic aqueous species and aqueous electrolytes with organic anions (see Appendix) at 1 bar and various temperatures.[a]

$NaCH_3COO$		$NaHCOO$		$NaCH_3CH_2COO$	
T	$\bar{C}°_P$[b]	T	$\bar{C}°_P$[b]	T	$\bar{C}°_P$[b]
0	−10.0	0	−15.7	0	19.3
10	7.3	10	−5.2	10	32.3
10	6.05[c]	20	−3.2	20	38.0
20	13.2	30	−3.2	30	41.1
25	16.1[c]	40	−1.9	40	43.6
30	16.2	50	−0.5	50	45.7
40	18.7	60	0.9	60	45.7
40	20.4[c]	70	1.6	70	45.6
50	19.3	80	2.3	80	45.0
60	19.2	90	2.0	90	42.5
70	19.3	100	1.8	100	40.9
80	19.5	110	0.0	110	38.6
90	17.4	120	−2.5	120	34.2
100	16.3			130	27.0
110	13.7				
120	11.4				
CH_3COOH		$HCOOH$		CH_3CH_2COOH	
T	$\bar{C}°_P$[b]	T	$\bar{C}°_P$[b]	T	$\bar{C}°_P$[b]
10	40.3	20	18.9	20	57.0
10	38.29[c]	30	19.1	30	56.7
20	40.7	40	20.2	40	58.0
25	40.56[c]	50	21.9	50	58.5
30	40.3	60	23.6	60	59.8
40	41.7	70	24.9	70	60.4
40	41.28[c]	80	25.3	80	60.6
50	42.2	90	25.4	90	60.7
60	43.2	100	25.8	100	60.2
70	43.3	110	26.3	110	60.4
80	43.7	120	26.8	120	59.5
90	43.9			130	60.3
100	43.1				
110	44.0				
120	44.7				

a. Unless indicated otherwise, the values of $\bar{C}°_P$ given in this table were taken from Ackermann and Schreiner (1958). b. Cal mol^{-1} K^{-1}. c. Allred and Woolley (1981).

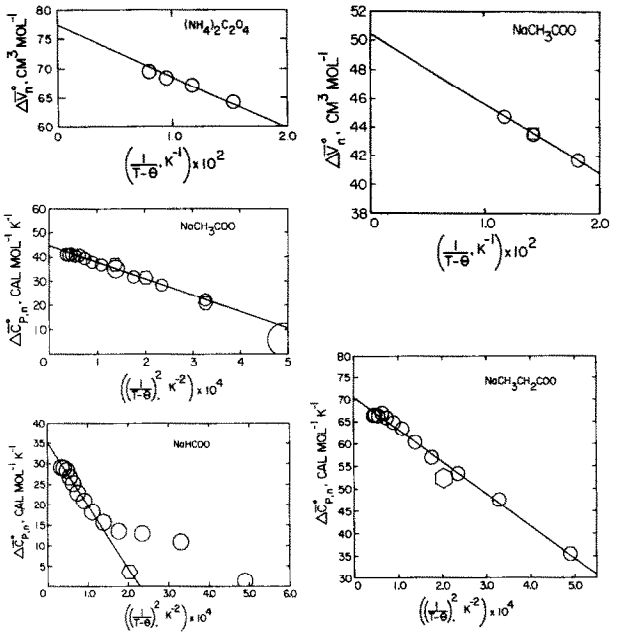


FIG. 6. Graphic representation of Eqns. (11) and (12) for the nonsolvation contributions to the standard partial molal volumes ($\Delta\bar{V}_n^0$) and heat capacities ($\Delta\bar{C}_{P,n}^0$) of the aqueous electrolytes with organic anions identified in the Appendix at various temperatures and P_{SAT}. The symbols represent values calculated from experimental data taken from the references given in the caption of Fig. 3, but the linear curves correspond to regression values representing fits of Eqns. (11) and (12) to the data.

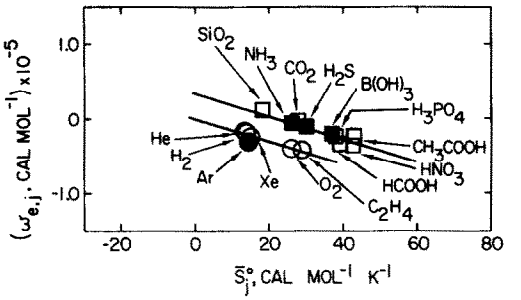


FIG. 7. Correlation of the effective Born coefficients ($\omega_{e,j}$) of neutral organic (see Appendix) and inorganic aqueous species with their standard partial molal entropies ($\bar{S}_j^0$) at 25°C and 1 bar. The curves drawn through the symbols were generated by SHOCK et al. (1989). They are based solely on regression of the data represented by the symbols for the inorganic species (see text).

the inorganic ions in the figure and the correlation curve represented by (SHOCK and HELGESON, 1988)

$$\sigma = 1.11\Delta\bar{V}_n^0 + 1.8. \quad (62)$$

Equation (62) applies also to the upper linear curve in Fig. 10, which represents neutral inorganic aqueous species as well as C_2H_4. In contrast, the values of σ and $\Delta\bar{V}_n^0$ in Table 3 for neutral organic aqueous alcohols are consistent with the lower linear curve in Fig. 10. The equation of the lower correlation curve in this figure can be expressed as

$$\sigma = 1.0125\Delta\bar{V}_n^0, \quad (63)$$

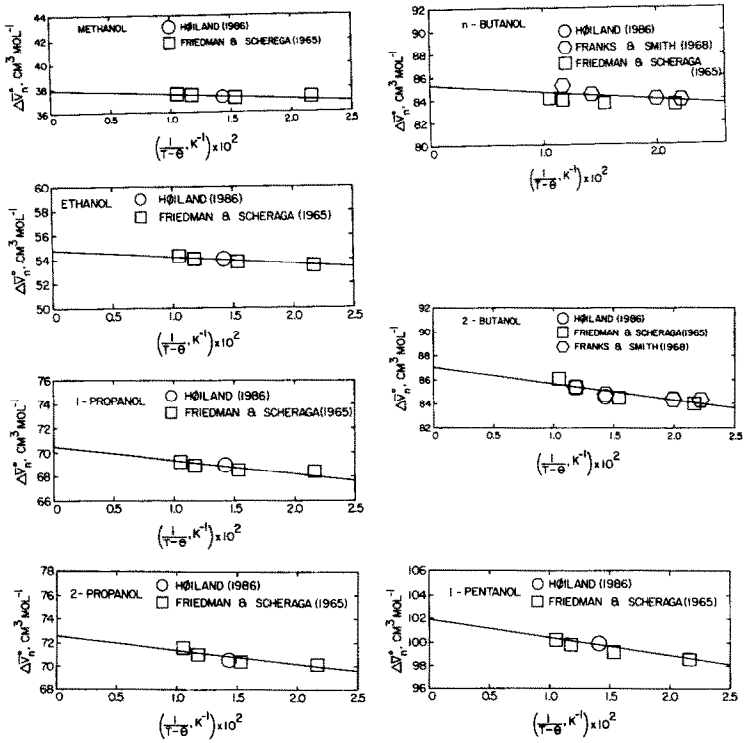


FIG. 8. Graphic representation of Eqn. (11) for the nonsolvation contribution to the standard partial molal volumes ($\Delta\bar{V}_n^0$) of neutral organic aqueous species (see Appendix) at various temperatures and 1 bar. The symbols represent experimental data reported in the literature, but the curves correspond to fits of Eqn. (11) to the data.

Table 3. Summary of estimated and regression values of ω_e together with equation of state parameters generated by regression of nonsolvation contributions to the standard partial molal volumes and heat capacities of charged and neutral organic aqueous species identified in the Appendix as a function of temperature at 1 bar (see text).

Aqueous Species	$\bar{V}^\circ$	$\Delta\bar{V}^\circ_n$	σ	$\xi\times10^{-2}$
CH_3COO^-	40.5	44.0	46.43	-1.83
$C_2O_4^{-2}$	24.04	29.67	32.6	-2.526
C_2H_4	45.5	44.5	53.2	-6.09
CH_3COOH	52.01	51.43	56.87	-3.79
methanol	38.17	37.30	37.9	-0.4
ethanol	55.08	54.06	54.65	-0.535
1-propanol	70.70	69.01	70.5	-1.15
2-propanol	71.90	70.58	72.55	-1.18
1-butanol	86.6	84.4	85.3	-0.68
2-butanol	86.62	84.65	87.05	-1.375
1-pentanol	102.68	99.91	101.9	-1.5

Aqueous Species	$\bar{C}^\circ_P$	c_1	$c_2\times10^{-4}$	$\omega_e\times10^{-5}$
$HCOO^-$	-22.0	17.0	-12.4	1.3003[b]
CH_3COO^-	6.2	26.3	-3.86	1.3182[b]
$CH_3CH_2COO^-$	30.9	52.3	-4.2	1.2276[b]
C_2H_4	62.5	39.1	9.7	-0.4[a]
HCOOH	19.0	22.1924	-3.1196	-0.3442[a]
CH_3COOH	40.56	40.8037	-0.9218	-0.2337[a]
CH_3CH_2COOH	56.0	54.313	-0.246	-0.4[a]

[a]Regression values (see text). [b]Estimated from Eqn. (58) using the values of $\bar{S}^\circ$ given in Table 6.

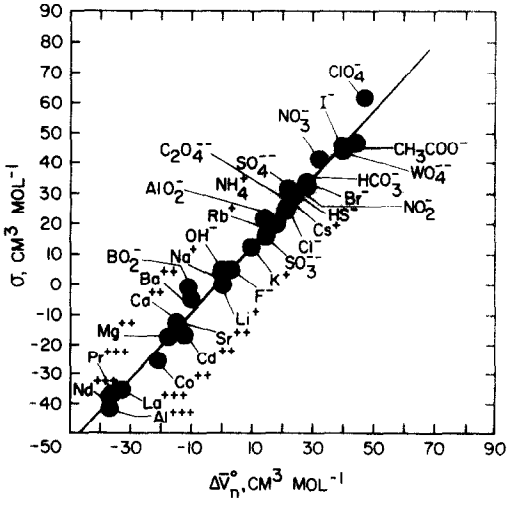


FIG. 9. Correlation of σ for organic (see Appendix) and inorganic aqueous ions with their nonsolvation standard partial molal volumes ($\Delta\bar{V}^0_n$) at 25°C and 1 bar. The symbols represent data taken from Table 3 and SHOCK and HELGESON (1988). The curve is consistent with Eqn. (62).

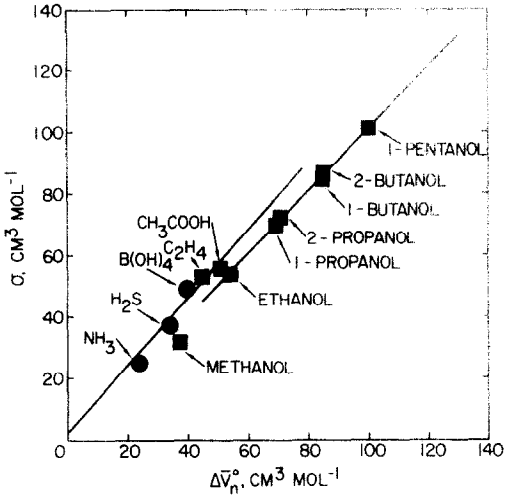


FIG. 10. Correlation of σ for neutral organic (see Appendix) and inorganic aqueous species with their nonsolvation standard partial molal volumes ($\Delta\bar{V}^0_n$) at 25°C and 1 bar. The symbols represent data taken from Table 3 and SHOCK et al. (1989). The upper curve corresponds to the correlation curve shown in Fig. 9 for aqueous ions. The correlation curve for the neutral organic aqueous species containing functional groups is consistent with Eqn. (63).

which can be used to estimate values of σ for neutral organic aqueous species that have functional groups for which no experimental data are available at temperatures other than 25°C. Similarly, in the absence of experimental density data at elevated temperatures, values of σ for organic aqueous ions and aqueous hydrocarbons can be estimated from Eqn. (62).

Values of the c_2 parameter for n-amino acids, 1-alcohols, 2-ketones, and other organic aqueous molecules with functional groups were estimated in the present study with the aid of the correlation shown for the n-carboxylic acids in Fig. 11. The curve in this figure is consistent with

$$c_2 \times 10^{-4} = 0.0676\bar{C}^0_P - 4.054. \qquad (64)$$

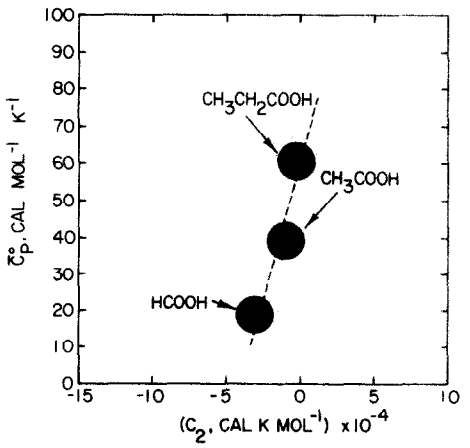


FIG. 11. Correlation of c_2 for neutral organic aqueous species (see Appendix) with their standard partial molal heat capacities ($\bar{C}^0_P$) at 25°C and 1 bar. The symbols represent data taken from Table 3. The curve is consistent with Eqn. (64).

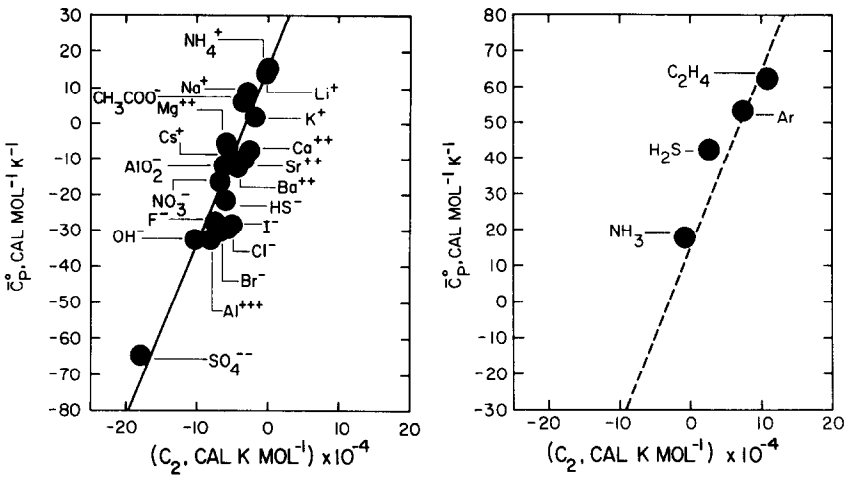


FIG. 12. Correlation of c_2 for organic (see Appendix) and inorganic aqueous ions and neutral species with their standard partial molal heat capacities ($\bar{C}_P^0$) at 25°C and 1 bar. The symbols represent data taken from SHOCK and HELGESON (1988) and SHOCK et al. (1989). The curves are consistent with Eqn. (65).

In contrast, the equation of the two curves in Fig. 12 is

$$c_2 \times 10^{-4} = 0.2037\bar{C}_P^0 - 3.0346. \quad (65)$$

Note in Fig. 12 that the values of c_2 and $\bar{C}_P^0$ for C_2H_4 are consistent with Eqn. (65) and the correlation curves for ions and neutral inorganic aqueous species. Consequently, Eqn. (65) was used to estimate values of c_2 for organic anions, as well as those for neutral organic species that are devoid of functional groups.

The values of $\bar{V}^0$ and $\bar{C}_P^0$ for the neutral organic aqueous species listed in Tables 1 and 2 are plotted as symbols in Figs. 13 and 14. The curves in these plots were generated in the present study from Eqns. (27) and (28) using equation of state parameters taken from Table 3. It can be seen in Figs. 13 and 14 that the curves represent closely almost all of the experimental data, some of which exhibit considerable scatter at low temperatures. Although it can be seen in Figs. 1, 2, 13, and 14 that only the experimental data for aqueous C_2H_4 extend to temperatures high enough to exhibit an increase toward ∞ at the critical point of H_2O, the calculations indicate that all the other neutral organic aqueous species behave in a similar fashion, which is consistent with the temperature dependence of experimental equilibrium constants for reactions involving these species at high temperatures and P_{SAT}.

COMPARISON OF PREDICTED AND EXPERIMENTAL EQUILIBRIUM CONSTANTS AT HIGH TEMPERATURES AND PRESSURES

Equilibrium constants (K) can be calculated from predicted apparent standard partial molal Gibbs free energies of formation ($\Delta\bar{G}^0$) by taking account of the relation

$$\log K = \frac{-\Delta\bar{G}_r^0}{2.303RT} \quad (66)$$

where $\Delta\bar{G}_r^0$ represents the standard partial molal Gibbs free energy of reaction defined by

$$\Delta\bar{G}_r^0 \equiv \sum_r \hat{n}_{i,r}\Delta\bar{G}^0 \quad (67)$$

where $\hat{n}_{i,r}$ corresponds to the reaction coefficient of the ith species in the reaction, which is positive for products and negative for reactants. Both experimental and independently predicted values of log K at high temperatures and P_{SAT} are shown in Fig. 15 for

$$C_2H_{4(g)} \rightleftarrows C_2H_{4(aq)} \quad (68)$$

$$HCOOH_{(aq)} \rightleftarrows HCOO^- + H^+ \quad (69)$$

$$CH_3COOH_{(aq)} \rightleftarrows CH_3COO^- + H^+ \quad (70)$$

and

$$CH_3CH_2COOH_{(aq)} \rightleftarrows CH_3CH_2COO^- + H^+. \quad (71)$$

The symbols in Fig. 15 represent experimental measurements, but the curves above and below 25°C correspond to values of log K computed independently in the present study from Eqns. (17), (31), (66), and (67) using equation of state parameters and thermodynamic data taken from Tables 3 and 6. It can be seen in Fig. 15 that in every case except one data point, the predicted curves fall within the uncertainty of the experimental measurements indicated by the sizes of the symbols. In contrast to the other curves and symbols for reactions (68), (69), and (71) in Fig. 15, those for the dissociation of acetic acid (reaction 70) include experimental and independently predicted values of log K at pressures higher than P_{SAT}. The close agreement of the predicted curves and experimental values of log K for this reaction at 1, 2, and 3 kb validates the relative accuracy of the estimated values of a_1, a_2, a_3, and a_4 for both CH_3COO^- and $CH_3COOH_{(aq)}$ in Table 6. These parameters were generated with the aid of the correlations of $\Delta\bar{V}_n^0$ with a_1, and a_2 with a_4 shown in Fig. 16, which are apparently charge-independent. The curves in Fig. 16, which were used to estimate volumetric equation of state parameters for inorganic neutral aqueous species by SHOCK et al. (1989) are consistent with

$$a_1 = 1.3684 \times 10^{-2}\Delta\bar{V}_n^0 + 0.1765, \quad (72)$$

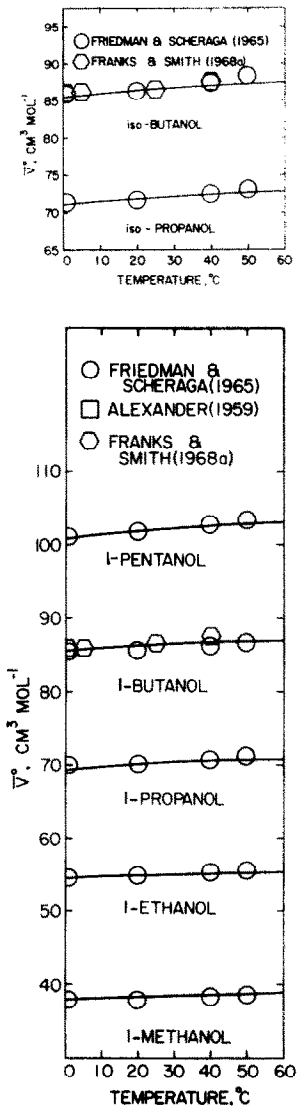


FIG. 13. Standard partial molal volumes ($\bar{V}^0$) of aqueous iso- and 1-alcohols (see Appendix) as a function of temperature at P_{SAT}. The symbols represent data taken from Table 1, but the curves were generated from Eqn. (27) using parameters taken from Table 6.

and

$$a_4 = -4.134a_2 - 27790. \quad (73)$$

The fact that the high-pressure/temperature predictions of log K for reaction (70) closely represent all of the experimental data represented by the symbols in Fig. 15, together with the fact that the curves were not generated by regression of the data strongly supports the validity and generality of the equations of state and the correlations shown in Figs. 9–12 and 16. The strategy used to estimate equation of state parameters for neutral organic aqueous species from values of $\bar{S}^0$, $\bar{V}^0$, and $\bar{C}_P^0$ at 25°C and 1 bar is summarized in Table 4, and that for charged aqueous species is given in Table 8 of Shock and Helgeson (1988). Procedures for calculating conventional and effective Born coefficients, as well as standard partial molal solvation and nonsolvation properties are summarized at the top of Table 4. These procedures are followed in the table by those for estimating equation of state parameters. Uncertainties attending such estimates can be minimized (SHOCK and HELGESON, 1988) if the estimates are made in the manner described in Table 4. In cases where values of $\bar{S}^0$, $\bar{C}_P^0$, and $\bar{V}^0$ at 25°C and 1 bar are not available, they can be estimated along with values of ΔG_f^0 and ΔH_f^0 if the aqueous organic species is a straight-chain polymer. The standard partial molal properties of these species at 25°C and 1 bar correlate closely with the number of moles of carbon atoms in the alkyl chain (see below).

CORRELATION OF $\bar{V}^0$, $\bar{C}_P^0$, $\bar{S}^0$, $\Delta\bar{H}_f^0$, AND ΔG_f^0 AT 25°C AND 1 BAR WITH THE ALKYL CHAIN LENGTH OF *n*-POLYMERS

Various correlations have been proposed between the length of the alkyl chain in straight-chain polymers and their standard partial molal volumes, heat capacities, entropies, enthalpies, and Gibbs free energies of solution, hydration, and solubility, as well as pairwise interaction parameters, specific viscosity, and other properties at 25°C and 1 bar (DANIEL and COHN, 1936; KINOSHITA et al., 1958; ARNETT

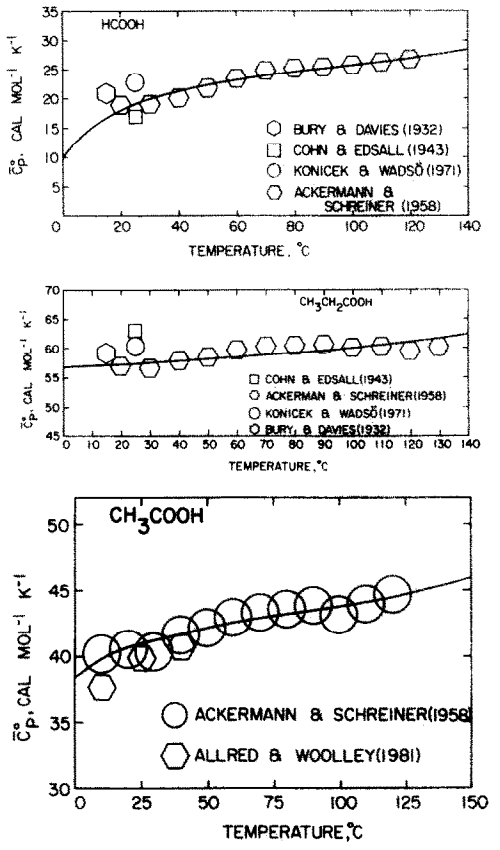


FIG. 14. Standard partial molal heat capacities ($\bar{C}_P^0$) of aqueous carboxylic acids (see Appendix) as a function of temperature at P_{SAT}. The symbols represent data taken from Table 2, but the curves were generated from Eqn. (28) using parameters taken from Table 6.

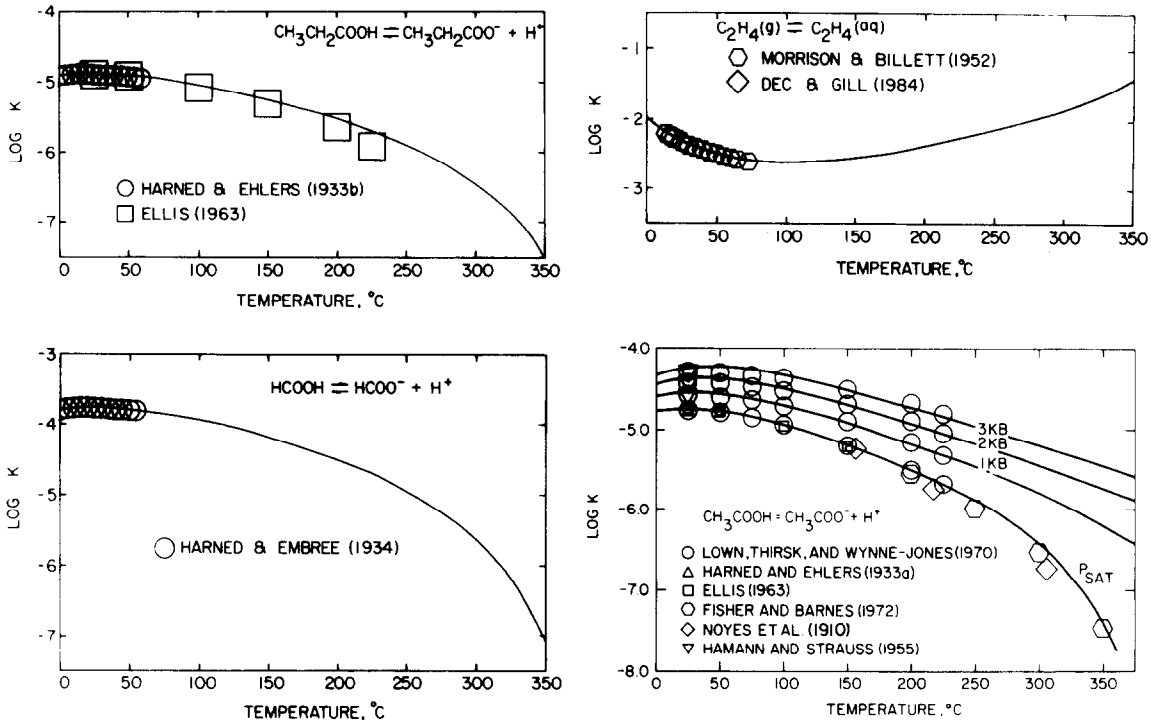


FIG. 15. Logarithm of the equilibrium constant for the dissociation of aqueous formic, acetic, and propanoic acids, together with that for the solubility of ethylene gas (see Appendix) as a function of temperature at P_{SAT} and, in the case of the dissociation of acetic acid, also at 1, 2, and 3 kb. The symbols represent experimental data reported in the literature, but the curves correspond to independent predictions made from Eqns. (17), (31), (66), and (67) using parameters and thermodynamic data taken from Table 6.

et al., 1969; MCAULIFFE, 1969; CABANI et al., 1971, 1975; KONICEK and WADSÖ, 1971; KUSANO et al., 1973; KIRCHNEROVA et al., 1976; SPINK and WADSÖ, 1975; TERASAWA et al., 1975; PRASAD and AHLUWALIA, 1976; SKÖLD et al., 1976; JOLICOEUR and LACROIX, 1976; HARADA et al., 1978; AKITT, 1980; DELLA GATTA et al., 1981; ABRAHAM, 1984; BACKLUND et al., 1984; SOKOLOWSKI et al., 1984; RICHON and VIALLARD, 1985; BLACKBURN et al., 1985; NILSSON and WADSÖ, 1986). The standard partial molal volumes, heat capacities, and entropies, together with the standard partial molal enthalpies and Gibbs free energies of formation from the elements of aqueous n-polymers (see Appendix) at 25°C

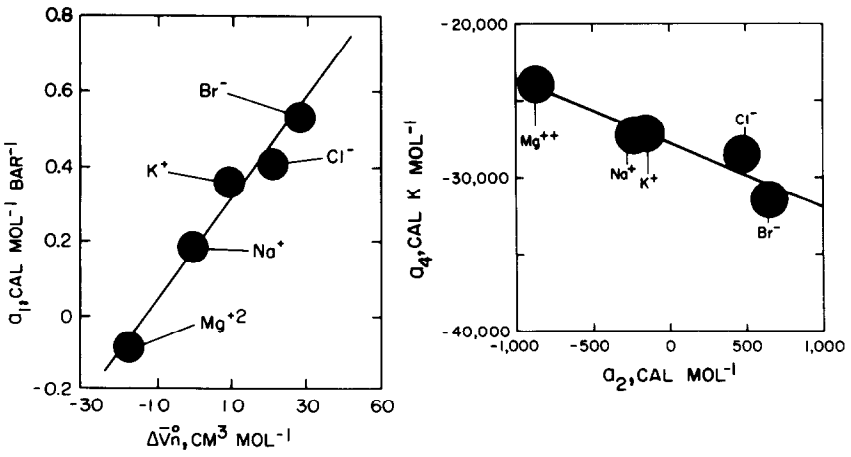


FIG. 16. Correlation of a_1 with $\Delta\bar{V}_n^0$ and a_4 with a_2 for aqueous ions (SHOCK and HELGESON, 1988). The symbols represent values taken from TANGER and HELGESON (1988). The curves are consistent with Eqns. (72) and (73).

Table 4. Outline of the strategy used in the present study to minimize uncertainty in estimated equation of state parameters for neutral organic aqueous species (see text).[a] Neutral organic aqueous species with functional groups are designated by the column heading A, and those without functional groups are designated B.

Estimation Strategy			
Parameter or Property to be Estimated	Known Property	Equation to be Used	Parameter or Property to be Calculated
ω_e	$\bar{S}^\circ$	A B 61 60	
	ω_e	24	$\Delta\bar{V}^\circ_s$[b]
		25	$\Delta\bar{C}^\circ_{P,s}$
	$\bar{V}^\circ$, $\Delta\bar{V}^\circ_s$	13	$\Delta\bar{V}^\circ_n$
	$\bar{C}^\circ_P$, $\Delta\bar{C}^\circ_{P,s}$	14	$\Delta\bar{C}^\circ_{P,n}$
a_1	$\Delta\bar{V}^\circ_n$, σ	72	
	(Case 1)	11A	a_2[c]
a_1	$\Delta\bar{V}^\circ_n$	72	
σ	(Case 2)	A B 63 62	
		11A	a_2[c]
a_4	a_2	73	
	$\Delta\bar{V}^\circ_n$, a_1 a_2, a_4	11	a_3[c]
c_2	$\bar{C}^\circ_P$	A B 64 65	
	$\Delta\bar{C}^\circ_{P,n}$, c_2	12	c_1

a. Corresponding estimates for charged aqueous species can be made using the strategy given in Table 8 of Shock and Helgeson (1988). b. Calculation of $\Delta\bar{V}^\circ_s$ in cm^3 mol^{-1} from Eqn. (24) using values of ω_e computed in the present study requires multiplication of the right side of Eqn. (24) by 41.8393 cm^3 bar cal^{-1}. c. Calculation of a_2 in cal mol^{-1} and a_3 in cal K mol^{-1} bar^{-1} from Eqns. (11) and (11A) using values of σ and $\Delta\bar{V}^\circ_n$ expressed in cm^3 mol^{-1} requires multiplication of the latter properties by 0.0239 cal cm^{-3} bar^{-1}.

and 1 bar are plotted in Figs. 17–21 as functions of the number of moles of carbon atoms in the alkyl chain. It can be seen in these figures that for polymers in which the alkyl chain contains 2 or more (or in the case of ΔG^0_f of the alkynes and alkenes, and both ΔG^0_f and ΔH^0_f of the amino acids, 3 or more) moles of carbon atoms, the linear curves shown in the figures are in close agreement with the experimental data represented by the symbols. The disagreement of the curves and symbols for carbon numbers ≤ 2 or ≤ 3 in Figs. 17–21 is discussed below. Note that the slopes of the curves in these figures are characteristic of the standard partial molal property, but independent of the type of functional group that

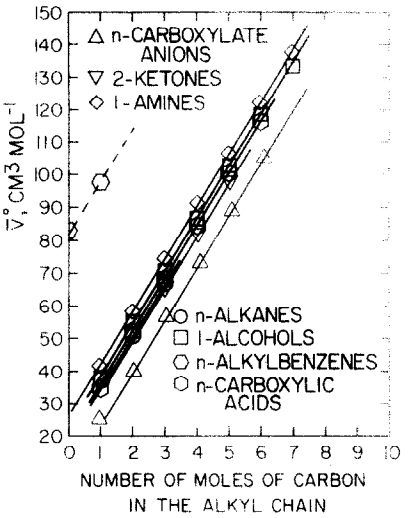


FIG. 17. Correlation of the standard partial molal volumes ($\bar{V}^0$) at 25°C and 1 bar of aqueous *n*-polymers (see Appendix) with the number of moles of carbon in the alkyl chain. The symbols represent experimental data taken from Table 6. The curves are consistent with Eqn. (76) and the slopes and intercepts given in Table 5. The dashed curve represents a tentative estimate for *n*-alkylbenzenes which is based solely on the value of $\bar{V}^0$ shown for toluene (see text).

distinguishes the various polymers. These slopes are given in Table 5, together with the intercepts of the curves for each property and type of polymer.

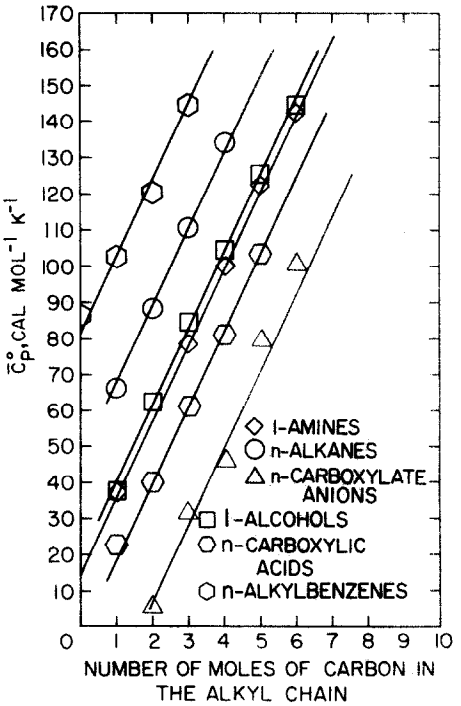


FIG. 18. Correlation of the standard partial molal heat capacities ($\bar{C}^0_P$) at 25°C and 1 bar of aqueous *n*-polymers (see Appendix) with the number of moles of carbon in the alkyl chain. The symbols represent experimental data taken from Table 6. The correlation curves are consistent with Eqn. (76) and the slopes and intercepts given in Table 5.

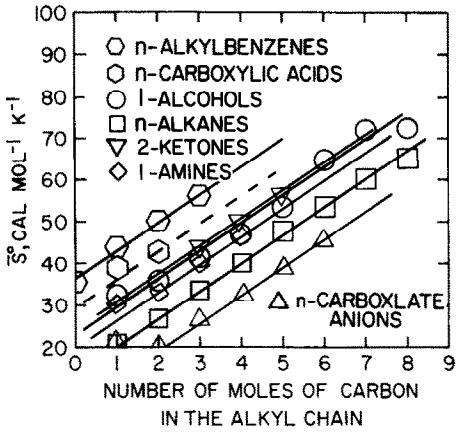


FIG. 19. Correlation of the standard partial molal entropies ($\bar{S}^0$) at 25°C and 1 bar of aqueous *n*-polymers (see Appendix) with the number of moles of carbon in the alkyl chain. The symbols represent experimental data taken from Table 6. The correlation curves are consistent with Eqn. (76) and the slopes and intercepts given in Table 5. The dashed curve represents a tentative estimate for carboxylic acids which is based solely on the value of $\bar{S}^0$ shown for acetic acid (see text).

It can be seen in Figs. 17–21 that in many cases the symbols representing the standard partial molal properties of species containing only one, or in certain cases two moles of carbon

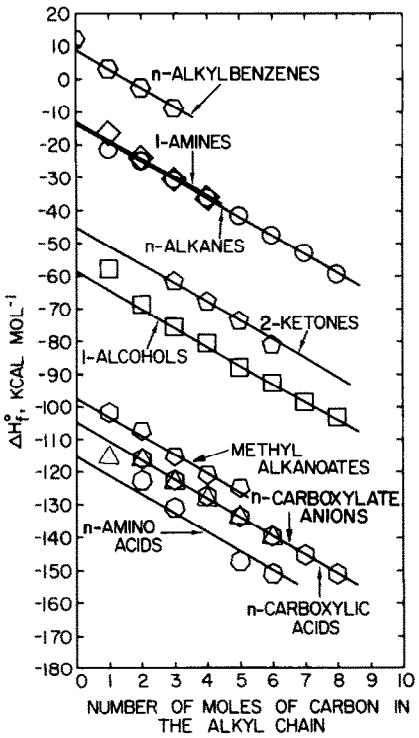


FIG. 20. Correlation of the standard partial molal enthalpy of formation from the elements (ΔH_f^0) at 25°C and 1 bar of aqueous *n*-polymers (see Appendix) with the number of moles of carbon in the alkyl chain. The symbols represent either experimental data shown in Table 6 or values taken from compilations by ABRAHAM (1984) and STULL et al. (1969). The curves are consistent with Eqn. (76) and the slopes and intercepts given in Table 5.

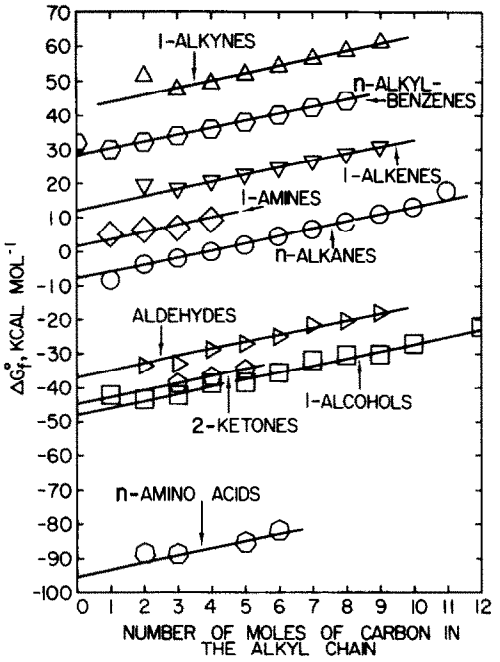
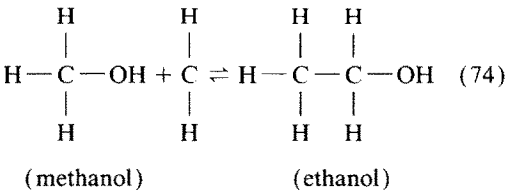


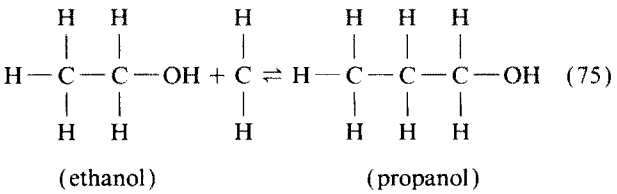
FIG. 21. Correlation of the standard partial molal Gibbs free energy of formation from the elements (ΔG_f^0) at 25°C and 1 bar of aqueous *n*-polymers (see Appendix) with the number of moles of carbon in the alkyl chain. The symbols represent either experimental data shown in Table 6 or values taken from compilations by ABRAHAM (1984) and STULL et al. (1969). The curves are consistent with Eqn. (76) and the slopes and intercepts given in Table 5.

atoms are not consistent with the linear curves shown in the figures. These discrepancies are an expected consequence of structural differences in the positions of the methylene (CH_2) groups in the chain. For example, in a normal alkane, only the first and last CH_2 groups are linked between a hydrogen and a carbon atom. All the rest occur between carbon atoms. Similarly, the first CH_2 group in alcohols with more than one such group is linked between a hydrogen and a carbon atom, but the last one occurs between a carbon and a hydroxyl. The first step along the series of alcohols to form ethanol from methanol can be represented by



(74)

and the second from ethanol to propanol as



(75)

which can be extended by successively adding more and more

Table 5. Summary of the slopes and intercepts of the correlations in Figs. 17–21 between the standard partial molal properties of aqueous n-polymers identified in the Appendix and the number of moles of carbon in the alkyl chain at 25°C and 1 bar (Eqn. 76).

Property	$\bar{S}^\circ$	$\bar{C}^\circ_P$	$\bar{V}^\circ$
Slope	6.7 cal mol^{-1} K^{-1}	21.2 cal mol^{-1} K^{-1}	15.8 cm^3 mol^{-1}
Group	Intercepts		
n-Alkanes	12.8	47.0	19.6
n-Alkylbenzenes	31.3	81.3	81.6
1-Alcohols	23.2	19.0	22.6
2-Ketones	23.2		18.9
1-Amines	20.0	14.4	26.8
n-Carboxylic Acids	29.3	−2.4	20.0
n-Carboxylate Anions	5.1	−36.2	8.0

Property	$\Delta\bar{G}^\circ_f$	$\Delta\bar{H}^\circ_f$
Slope	2050 cal mol^{-1}	−5670 cal mol^{-1}
Group	Intercepts	
n-Alkanes	−7600	−13500
1-Alkenes	11900	
1-Alkynes	42200	
n-Alkylbenzenes	28200	8600
1-Alcohols	−47800	−58400
Aldehydes	−36700	
2-Ketones	−44800	−45200
1-Amines	1800	−12300
n-Carboxylic Acids		−105000
n-Carboxylate Anions		−105870
n-Amino Acids	−95400	−115500
Methyl Alkanoates		−97800

CH_2 groups between carbon atoms. These steps are more similar to one another than any of them are to the first step, which is manifested in Figs. 17–21 by the fact that the symbols representing methanol are not consistent with the linear trends of the other alcohols. Similar observations apply to the other polymer groups shown in these figures.

Experimental data at 25°C and 1 bar are not available for many aqueous organic species of geochemical interest. Accordingly, estimates of $\bar{V}^0$, $\bar{C}^0_P$, $\bar{S}^0$, $\Delta\bar{H}^0_f$, and ΔG^0_f for straight-chain polymers for which no experimental data are available were made in the present study from the correlations shown in Figs. 17 through 21, which are consistent with

$$\hat{\Xi}^0_j = \hat{m}\mathbf{n} + \hat{p} \qquad (76)$$

in which $\mathbf{n}$ represents the number of moles of carbon atoms in the alkyl chain, and $\hat{m}$ and $\hat{p}$ correspond to the slopes and intercepts of the curves given in Table 5. The estimates are listed in Table 6, together with many of the experimental values depicted in Figs. 17 through 21. Corresponding equation of state parameters for the species generated either by regression of experimental data or estimation from the algorithms summarized in Table 4 are also given in Table 6, which permits prediction of the thermodynamic properties of the species at temperatures from 0 to 1000°C and pressures from P_{SAT} to 5 kb. Because the algorithms cited in Table 4 are consistent with the correlations shown in Figs. 17–19, the respective equation of state coefficients for the species in each of the n-polymer groups in Table 6 also exhibit linear correlations with the number of moles of carbon atoms in the alkyl chain.

PREDICTIONS OF EQUILIBRIUM CONSTANTS AND THE STANDARD PARTIAL MOLAL PROPERTIES OF ORGANIC AQUEOUS SPECIES AT HIGH TEMPERATURES AND PRESSURES

The logarithms of equilibrium constants for hydrocarbon gas solubility reactions in aqueous solutions are shown in Fig. 22 as a function of temperature at P_{SAT}. The symbols in this figure represent experimental data, but the curves were generated independently using Eqns. (31), (66), and (67), together with thermodynamic data and equation of state parameters taken from Table 6. Note that the independently predicted values of log K for

$$CH_{4(g)} \rightleftarrows CH_{4(aq)} \qquad (77)$$

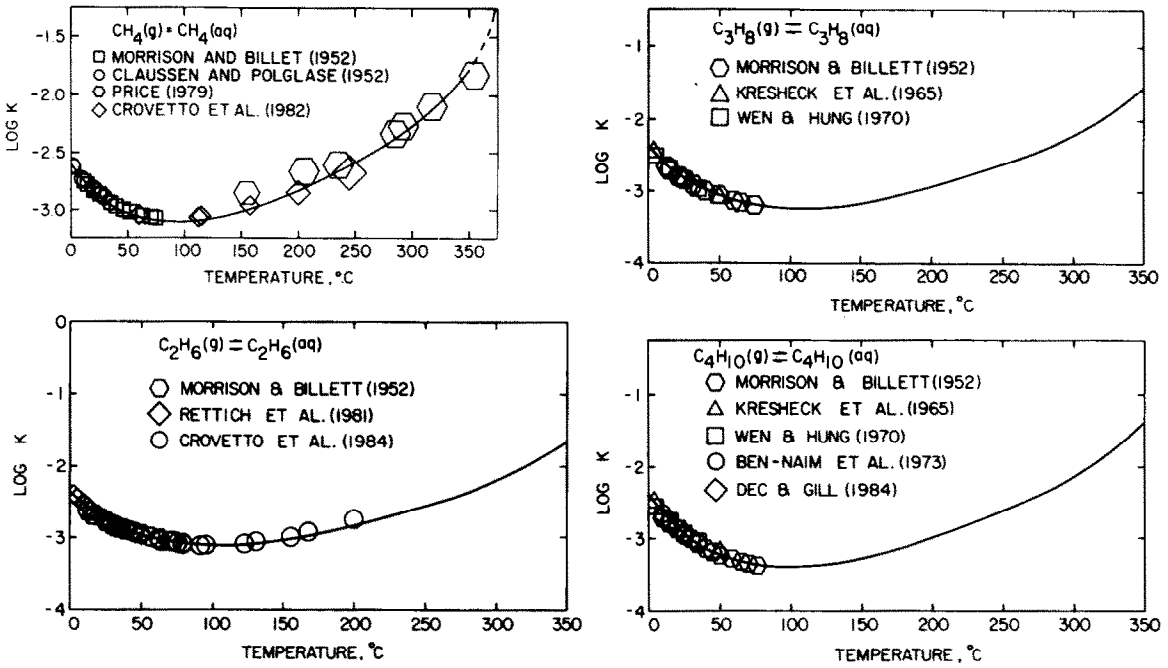


FIG. 22. Logarithms of the equilibrium constants for hydrocarbon (see Appendix) gas solubilities in water as a function of temperature at P_{SAT}. The symbols represent experimental data reported in the literature, but the curves correspond to independent predictions generated from Eqns. (31), (66), and (67) using equation of state parameters and thermodynamic data taken from Table 6.

are in close agreement with their experimental counterparts at all temperatures, including those in excess of 300°C. The curves shown for log K as a function of temperature for the dissolution of ethane (C_2H_4), propane (C_3H_8), and butane (C_4H_{10}) are also in close agreement with the more limited range of experimental data shown in the figure. The validity of the predictions for these gases at temperatures higher than those for which experimental data are available is not only supported by the agreement in Fig. 22 between the corresponding predictions of equilibrium constants for methane solubility and those measured experimentally, but also by similar agreement between independent predictions and experimental equilibrium constants at high temperatures for reactions involving other dissolved gases (SHOCK et al., 1989).

The close agreement between the predicted equilibrium constants and their experimental counterparts in Figs. 15 and 22 suggests that reliable predictions of the standard partial molal properties of organic aqueous species can also be made for higher temperatures and pressures. Accordingly, Eqns. (13)–(17) and (27)–(31) were used in the present study together with parameters and data taken from Table 6 to predict the standard partial molal properties of both charged and neutral organic aqueous species at supercritical pressures and temperatures. As examples, calculated standard partial molal volumes, heat capacities, and entropies, as well as the apparent standard partial molal enthalpies and Gibbs free energies of formation of aqueous methane ($CH_{4(aq)}$), octane ($C_8H_{18(aq)}$), acetic acid ($CH_3COOH_{(aq)}$), acetate (CH_3COO^-), toluene ($C_6H_5CH_3$), and glycine (CH_2NH_2COOH) are shown in Figs. 23–27 as functions of temperature to 1000°C at pressures to 5 kb.

It can be seen in Figs. 23–26 that $\bar{V}^0$, $\bar{C}^0_P$, $\bar{S}^0$, and $\Delta\bar{H}^0$ at P_{SAT} for the neutral organic aqueous species shown in the figures increase dramatically at high temperatures in the liquid phase region and approach ∞ at the critical point of H_2O. In contrast, the corresponding properties of CH_3COO^- at P_{SAT} in these figures decrease with increasing temperature in the liquid phase region at high temperatures and approach $-\infty$ at the critical point of H_2O. Curves representing $\Delta\bar{G}^0$ are depicted in Fig. 27 for the species shown in Figs. 23–26. It can be seen in Fig. 27 that the $\Delta\bar{G}^0$ values for all of the neutral organic aqueous species decrease monotonically with increasing temperature at all of the pressures shown in the figure. In contrast, the curves for CH_3COO^- and P_{SAT} and 1 kb in Fig. 27 exhibit minima at ~200 and ~500°C, respectively. The configurations of the curves for the neutral and charged organic aqueous species shown in Figs. 23–27 are typical of those exhibited by corresponding curves for other organic aqueous species.

Predictive uncertainties

Uncertainties in predicted values of $\bar{V}^0$, $\bar{C}^0_P$, $\bar{S}^0$, $\Delta\bar{H}^0$, and $\Delta\bar{G}^0$ at P_{SAT} for aqueous species at high temperatures and pressures have been assessed and discussed in detail elsewhere (SHOCK and HELGESON, 1988; SHOCK et al., 1989). Although considered in the context of inorganic aqueous species, these uncertainties apply also to their organic counterparts.

As indicated in Table 4, values of the a_3 and c_1 parameters can be estimated from expressions of the revised HKF equations of state for $\bar{V}^0$ and $\bar{C}^0_P$, together with values of a_1, a_2, a_4, and c_2. As a consequence, the uncertainties in these pa-

Table 6. Summary of experimental, retrieved, and estimated standard partial molal thermodynamic properties of organic aqueous species identified in the Appendix at 25°C and 1 bar and the parameters required to calculate the corresponding properties at higher pressures and temperatures from Eqns.

Species	$\Delta\bar{G}^{\circ}_f$[a]	$\Delta\bar{H}^{\circ}_f$[a]	$\bar{S}^{\circ}$[b]	$\bar{C}^{\circ}_P$[b]	$\bar{V}^{\circ}$[c]	$a_1^d\times10$	$a_2^g\times10^{-2}$	a_3^g	$a_4^f\times10^{-4}$	c_1^b	$c_2^g\times10^{-4}$	$\omega_e^g\times10^{-5}$
methane	−8234.[g]	−21010.[h]	20.99[h]	66.3[h]	37.3[i]	6.7617	8.7279	2.3212	−3.1397	42.0941	10.4707	0.3179
ethane	−3886.[g]	−24650.[h]	26.81[h]	88.3[h]	51.2[i]	8.6340	13.3011	0.5205	−3.3288	54.1755	14.9521	0.4060
propane	−1963.[g]	−30490.[h]	33.37[h]	110.6[h]	67.0[i]	10.7625	18.4948	−1.5133	−3.5435	66.3294	19.4946	0.5053
n-butane	36.[g]	−36230.[h]	40.02[h]	133.9[h]	82.8[i]	12.8905	23.6960	−3.5683	−3.7585	79.0569	24.2408	0.6061
n-pentane	2130.[k]	−41560.[k]	47.5[k]	153.[j]	98.6[j]	15.0143	28.8771	−5.5949	−3.9727	89.2070	28.1315	0.7193
n-hexane	4420.[k]	−47400.[k]	52.9[k]	175.2[j]	114.4[j]	17.1487	34.0927	−7.6530	−4.1883	101.4642	32.6536	0.8011
n-heptane	6470.[k]	−52950.[k]	60.0[k]	196.4[j]	130.2[j]	19.2745	39.2810	−9.6879	−4.4028	112.8980	36.9721	0.9086
n-octane	8580.[k]	−59410.[k]	63.8[k]	217.6[j]	146.0[j]	21.4171	44.5126	−11.7437	−4.6191	124.7924	41.2905	0.9662
ethylene	19450.[l]	8570.[l]	28.7[k]	62.5[m]	45.5[m]	7.8560	12.6391	−1.8737	−3.3014	39.1[ff]	9.7[ff]	0.4[ff]
1-propene	17910.[l]	−290.[l]	36.7[j]	83.7[n]	61.3[n]	9.9655	16.5518	−0.7564	−3.4632	50.0997	14.0151	0.5558
1-butene	20310.[q]	−5635.[p]	43.4[r]	104.9[n]	77.1[n]	12.0932	21.7476	−2.7991	−3.6779	61.5894	18.3335	0.6572
1-pentene	22470.[q]	−11200.[p]	50.1[r]	126.1[n]	92.9[n]	14.2210	26.9431	−4.8413	−3.8927	73.0791	22.6520	0.7587
1-hexene	24370.[q]	−17025.[p]	56.8[r]	147.3[n]	108.7[n]	16.3488	32.1387	−6.8838	−4.1075	84.5689	26.9704	0.8602
1-heptene	26450.[q]	−22670.[p]	63.5[r]	168.5[n]	124.5[n]	18.4766	37.3342	−8.9260	−4.3223	96.0586	31.2889	0.9616
1-octene	28720.[q]	−28120.[p]	70.2[r]	189.7[n]	140.3[n]	20.6044	42.5297	−10.9682	−4.5371	107.5483	35.6073	1.0631
ethyne	51890.[s]	50700.[s]	30.0[t]	53.0[u]	49.3[v]	8.3577	12.6272	0.7833	−3.3009	33.0423	7.7615	0.4543
1-propyne	47880.[q]	38970.[p]	36.7[w]	74.2[w]	65.1[w]	10.4855	17.8227	−1.2588	−3.5157	44.5321	12.0799	0.5558
1-butyne	50030.[q]	33400.[p]	43.4[w]	95.4[w]	80.9[w]	12.6132	23.0185	−3.3011	−3.7305	56.0218	16.3984	0.6572
1-pentyne	52160.[q]	27800.[p]	50.1[w]	116.6[w]	96.7[w]	14.7410	28.2140	−5.3433	−3.9453	67.5117	20.7168	0.7587
1-hexyne	54420.[q]	22340.[p]	56.8[w]	137.8[w]	112.5[w]	16.8688	33.4096	−7.3857	−4.1601	79.0012	25.0353	0.8602
1-heptyne	56730.[q]	16980.[p]	63.7[w]	159.0[w]	128.3[w]	18.9956	38.6015	−9.4245	−4.3747	90.4632	29.3537	0.9647
1-octyne	58860.[q]	11330.[p]	70.2[w]	180.2[w]	144.1[w]	21.1244	43.8006	−11.4705	−4.5896	101.9808	33.6721	1.0631
benzene	32000.[q]	12230.[q]	35.5[q]	86.3[y]	83.5[x]	13.1244	18.1143	11.8225	−3.5277	80.8626	1.7799	0.1976
toluene	30260.[q]	3280.[q]	43.9[q]	102.8[y]	97.71[u]	15.0259	21.9153	12.1349	−3.6849	93.9240	2.8953	0.3248
ethylbenzene	32440.[q]	−2500.[q]	49.8[q]	120.5[y]	113.8[j]	17.1974	26.2574	12.4885	−3.8644	108.3695	4.0918	0.4142
n-propylbenzene	34170.[q]	−8630.[q]	56.1[q]	144.8[y]	129.6[j]	19.3272	30.5152	12.8372	−4.0404	128.4523	5.7345	0.5096
n-butylbenzene	36110.[q]	−14430.[p]	62.8[j]	166.0[j]	145.4[j]	21.4550	34.7658	13.1931	−4.2162	145.8054	7.1676	0.6110
n-pentylbenzene	38210.[q]	−19750.[p]	69.5[j]	187.2[j]	161.2[j]	23.5828	39.0164	13.5490	−4.3918	163.1584	8.6007	0.7125
n-hexylbenzene	40390.[q]	−25590.[p]	76.2[j]	208.4[j]	177[j]	25.7106	43.2732	13.8894	−4.5678	180.5115	10.0338	0.8140
n-heptylbenzene	42640.[g]	−31090.[j]	82.9[j]	229.6[j]	192.8[j]	27.8384	47.5238	14.2453	−4.7435	197.8642	11.4670	0.9154
n-octylbenzene	44690.[g]	−36760.[j]	89.6[j]	250.8[j]	208.6[j]	29.9662	51.7744	14.6016	−4.9193	215.2173	12.9001	1.0169
methanol	−42050.[q]	−58870.[q]	32.2[q]	37.8[z]	38.17[aa]	6.9383	5.5146	11.4018	−3.0069	39.4852	−1.4986	−0.1476
ethanol	−43330.[q]	−68650.[q]	35.9[q]	62.2[z]	55.08[aa]	9.2333	9.9581	12.1445	−3.1906	60.0175	0.1507	−0.2037
1-propanol	−41910.[q]	−75320.[q]	41.4[q]	84.3[z]	70.70[aa]	11.3426	14.3252	12.1079	−3.3711	78.3142	1.6447	−0.2869
1-butanol	−38840.[q]	−80320.[q]	46.9[q]	104.4[z]	86.60[aa]	13.4902	17.9400	14.1816	−3.5205	94.8858	3.0034	−0.3702
1-pentanol	−38470.[q]	−87730.[q]	53.4[q]	125.2[z]	102.68[aa]	15.6573	22.6230	13.6464	−3.7141	111.9216	4.4095	−0.4687
1-hexanol	−35490.[q]	−92690.[q]	64.8[q]	144.4[bb]	118.65[aa]	17.7843	27.4289	12.5890	−3.9128	126.8936	5.7074	−0.6413
1-heptanol	−32000.[q]	−97270.[q]	72.1[q]	174.2[bb]	133.43[aa]	19.7695	31.3977	12.9129	−4.0769	151.5815	7.7219	−0.7519
1-octanol	−30250.[q]	−103060.[q]	72.3[q]	195.[j]	149.2[j]	21.9264	35.7093	13.2670	−4.2551	169.4962	9.1280	−0.7549
phenol	−12585.[s]	−36640.[s]	45.8[t]	75.3[u]	86.17[aa]	13.4370	18.7373	11.8793	−3.5535	69.9366	1.0363	−0.3536
acetone	−38500.[q]	−61720.[q]	44.4[q]	57.7[u]	66.92[aa]	10.8100	13.4912	11.4350	−3.3366	54.9496	−0.1534	−0.3324
2-butanone	−36730.[q]	−67880.[q]	50.3[q]	80.4[u]	82.52[aa]	12.9145	17.6967	11.7839	−3.5105	73.7083	1.3810	−0.4217
2-pentanone	−34390.[q]	−73460.[q]	56.3[q]	101.6[cc]	98.0[aa]	15.0021	21.8653	12.1372	−3.6828	91.1588	2.8142	−0.5126
2-hexanone	−32480.[g]	−79220.[j]	63.4[j]	122.8[cc]	113.7[j]	17.1141	26.0886	12.4806	−3.8574	108.4560	4.2473	−0.6201
2-heptanone	−30430.[g]	−84890.[j]	70.1[j]	144.0[cc]	129.5[j]	19.2419	30.3392	12.8366	−4.0331	125.8091	5.6804	−0.7216
2-octanone	−28380.[g]	−90560.[j]	76.8[j]	165.2[cc]	145.3[j]	21.3697	34.5960	13.1769	−4.2091	143.1620	7.1135	−0.8231

a. Cal mol^{-1}. b. Cal mol^{-1} K^{-1}. c. Cm^3 mol^{-1}. d. Cal mol^{-1} bar^{-1}. e. Cal K mol^{-1} bar^{-1}. f. Cal K mol^{-1}. g. Calculated from the values of $\Delta\bar{H}^{\circ}_f$ and $\bar{S}^{\circ}$ given in the table using values of $\bar{S}^{\circ}$ of the elements taken from Wagman et al. (1982). h. Calculated from standard partial molal reaction properties given by Olofsson et al. (1985) using standard partial molal properties of gases taken from the Thermo. Res. Cent. Hydrocar. Proj. (1982). i. Masterton (1954). j. Calculated from Eqn. (76) using parameters taken from Table 5. k. Calculated from standard partial molal reaction properties given by Abraham (1984) using standard partial molal properties of gases taken from the Thermo. Res. Cent. Hydrocar. Pro. (1982). l. Calculated from standard partial molal reaction properties given by Dec and Gill (1984) using standard partial molal properties of gases taken from Stull et al. (1969). m. Biggerstaff (1986). n. Calculated from Eqn. (76) using slopes taken from Table 5 and the experimental values of $\bar{C}^{\circ}_P$ and $\bar{V}^{\circ}$ of ethylene to constrain the intercepts (20.1 cal mol^{-1}K^{-1} and 13.9 cm^{3}mol^{-1}, respectively). p. Calculated from the values of $\Delta\bar{G}^{\circ}_f$ and $\bar{S}^{\circ}$ given in the table using values of $\bar{S}^{\circ}$ of the elements taken from Wagman et al. (1982). q. Calculated from standard partial molal reaction properties given by Abraham (1984) using standard partial molal properties of gases taken from Stull et al. (1969). r. Calculated from Eqn. (76) using the slope given in Table 5 and the experimental value of $\bar{S}^{\circ}$ of propene to constrain the intercept (16.6 cal mol^{-1}K^{-1}). s. Calculated from standard partial molal reaction properties given by Cabani et al. (1981) using standard partial molal properties of gases taken from Stull et al. (1969). t. Calculated from the values of $\Delta\bar{G}^{\circ}_f$ and $\Delta\bar{H}^{\circ}_f$ given in the table using values of $\bar{S}^{\circ}$ of the elements taken from Wagman et

rameters reflect directly the uncertainties in $\bar{V}^0$ and $\bar{C}^0_P$ at 25° and 1 bar, which are estimated to be $\sim \pm 2$ cm^3 mol^{-1} and of the order of ± 2 cal mol^{-1} K^{-1}, respectively (SHOCK and HELGESON, 1988). In general, uncertainties in calculated values of $\bar{V}^0$ and $\bar{C}^0_P$ arising from uncertainties in values of a_4 and c_2 that were estimated from the correlations shown in Figs. 9–12 and 16 decrease with increasing temperature and pressure (SHOCK and HELGESON, 1988). Those for $\bar{V}^0$ decrease from ± 0.05 cm^3 mol^{-1} at 25°C and 1 bar to $\pm 1 \times 10^{-3}$ cm^3 mol^{-1} at 1000°C and 5 kb. The corresponding uncertainties in calculated values of $\bar{C}^0_P$ decrease from ± 0.5 cal mol^{-1} K^{-1} at 25°C and 5 kb to $\pm 6 \times 10^{-4}$ cal mol^{-1} K^{-1} at 1000°C and 5 kb. Uncertainties in calculated values of $\bar{C}^0_P$ arising from uncertainties in estimated values of c_2 are independent of pressure, but decrease with increasing temperature from ± 4 cal mol^{-1} K^{-1} at 25°C to ± 0.2 cal mol^{-1}

(13)-17) and (29)-(33). Except where noted otherwise, the values of a_1, a_2, a_3, a_4, c_1, c_2, and ω_e shown below were estimated using the strategy shown in Table 4 (see text)[ww].

Species	$\Delta\bar{G}°_f$	$\Delta\bar{H}°_f$	$\bar{S}°$	$\bar{C}°_P$	$\bar{V}°$	$a_1 \times 10$	$a_2 \times 10^{-2}$	a_3	$a_4 \times 10^{-4}$	c_1	$c_2 \times 10^{-4}$	$\omega_e \times 10^{-5}$
formic acid	-88982.[gg]	-101680.[gg]	38.9[gg]	19.0[u]	34.69[aa]	6.3957	4.6630	10.7209	-2.9717	22.1924[ff]	-3.1196[ff]	-0.3442[ff]
acetic acid	-94760.[gg]	-116100.[gg]	42.7[gg]	40.56[ii]	52.01[aa]	8.8031	12.4572	3.5477	-3.2939	40.8037[ff]	-0.9218[ff]	-0.2337[ff]
propanoic acid	-93430.[g]	-122470.[q]	49.4[j]	56.0[u]	67.9[aa]	10.9213	13.7115	11.4582	-3.3457	54.313[ff]	-0.246[ff]	-0.4[ff]
butanoic acid	-91190.[g]	-127950.[q]	56.1[j]	80.5[u]	84.61[aa]	13.1708	18.2050	11.8362	-3.5315	72.9853	1.3878	-0.5096
pentanoic acid	-89210.[g]	-133690.[q]	62.8[j]	103.3[u]	100.5[aa]	15.3109	22.4858	12.1803	-3.7085	91.7185	2.9291	-0.6110
hexanoic acid	-87080.[g]	-139290.[q]	69.5[j]	125.2[j]	116.55[aa]	17.4729	26.8090	12.5312	-3.8872	109.6753	4.4095	-0.7125
heptanoic acid	-85150.[g]	-145080.[q]	76.2[j]	146.4[j]	132.3[j]	19.5938	31.0465	12.8851	-4.0624	127.0284	5.8426	-0.8140
octanoic acid	-83400.[g]	-151050.[q]	82.9[j]	167.6[j]	148.1[j]	21.7216	35.2971	13.2410	-4.2381	144.3812	7.2758	-0.9154
formate	-83862.[jj]	-101680.[jj]	21.7[jj]	-22.0[ff]	26.16[kk]	5.7842[vv]	6.3405[vv]	3.2606[vv]	-3.0410[vv]	17.0[ff]	-12.4[ff]	1.3003[ff]
acetate	-88270.[gg]	-116180.[p]	20.6[hh]	6.2[ff]	40.5[ff]	7.7525[vv]	8.6996[vv]	7.5825[vv]	-3.1385[vv]	26.3[ff]	-3.86[ff]	1.3182[ff]
propanoate	-86770.[jj]	-122630.[jj]	26.5[jj]	30.9[ff]	54.95[kk]	9.6992[vv]	15.9017[vv]	-0.5003[vv]	-3.4363[vv]	52.3[ff]	-4.2[ff]	1.2276[ff]
butanoate	-84610.[jj]	-127930.[jj]	31.8[jj]	44.5[jj]	70.3[kk]	11.7724[vv]	20.9657[vv]	-2.4947[vv]	-3.6456[vv]	42.8123	6.0300	1.1469
pentanoate	-82600.[jj]	-134410.[jj]	38.3[jj]	78.8[jj]	86.31[kk]	13.9304[vv]	26.2319[vv]	-4.5589[vv]	-3.8633[vv]	62.0175	13.0170	1.0496
hexanoate	-80450.[jj]	-139890.[jj]	45.3[jj]	100.[jj]	102.21[kk]	16.0700[vv]	31.4589[vv]	-6.6186[vv]	-4.0794[vv]	73.4573	17.3354	0.9427
heptanoate	-78390.[s]	-145560.[j]	52.0[j]	112.2[j]	118.6[j]	18.2787[vv]	36.8480[vv]	-8.7285[vv]	-4.3022[vv]	79.6770	19.8205	0.8417
octanoate	-76340.[s]	-151230.[j]	58.7[j]	133.4[j]	134.4[j]	20.4065[vv]	42.0436[vv]	-10.7711[vv]	-4.5170[vv]	91.1664	24.1390	0.7402
methanamine	5040.[q]	-16320.[q]	30.5[q]	37.0[u]	41.88[aa]	7.4547	6.7824	10.8884	-3.0593	39.0324	-1.5527	-0.1219
ethanamine	6300.[q]	-23830.[q]	33.6[q]	56.8[j]	58.61[aa]	9.7281	11.3257	11.2651	-3.2471	55.6799	-0.2142	-0.1688
1-propanamine	7010.[q]	-30680.[q]	40.8[q]	78.[u]	74.15[u]	11.8178	15.5013	11.6113	-3.4197	72.9633	1.2188	-0.2779
1-butanamine	9410.[q]	-36110.[q]	47.2[q]	101.[u]	89.80[aa]	13.9266	19.7205	11.9476	-3.5941	91.9109	2.7736	-0.3748
1-pentanamine	12800.[g]	-40650.[j]	53.5[j]	123.[u]	105.7[aa]	16.0701	24.0048	12.3010	-3.7713	110.0099	4.2608	-0.4702
1-hexanamine	14860.[g]	-46320.[j]	60.2[j]	144.[u]	121.6[aa]	18.2115	28.2822	12.6611	-3.9481	127.1903	5.6804	-0.5717
1-heptanamine	16910.[g]	-51990.[j]	66.9[j]	162.8[j]	137.6[aa]	20.3667	32.5921	13.0098	-4.1263	142.4729	6.9513	-0.6731
1-octanamine	18960.[g]	-57660.[j]	73.6[j]	184.0[j]	153.2[j]	22.4671	36.7896	13.3574	-4.2998	159.8259	8.3844	-0.7746
glycine	-88618.[gg]	-122846.[gg]	37.84[gg]	9.4[rr]	43.25[rr]	7.6046	7.0825	10.9119	-3.0717	14.1998	-3.4185	-0.2330
alanine	-88800.[ss]	-132130.[tt]	40.0[t]	33.8[rr]	60.45[rr]	9.9472	11.7629	11.3023	-3.2652	34.9465	-1.7690	-0.2658
ABA[qq]	-87120.[g]	-138180.[j]	46.7[dd]	53.1[ll]	76.5[mm]	12.1092	16.0862	11.6529	-3.4439	50.6605	-0.4643	-0.3672
valine	-85300.[ss]	-147300.[tt]	42.6[t]	72.2[rr]	90.79[rr]	14.0856	20.0343	11.9842	-3.6071	67.7090	0.8267	-0.3051
leucine	-82000.[ss]	-151070.[tt]	51.5[t]	95.1[rr]	107.57[rr]	16.3362	24.5312	12.3587	-3.7930	86.2214	2.3748	-0.4399
isoleucine	-82200.[ss]	-150900.[tt]	52.8[t]	91.6[rr]	105.45[rr]	16.0395	23.9414	12.3010	-3.7686	83.0208	2.1382	-0.4596
serine	-122100.[ss]	-170800.[tt]	46.5[t]	28.1[rr]	60.62[rr]	9.9372	11.7454	11.2943	-3.2645	29.1225	-2.1543	-0.3642
threonine	-120000.[g]	-179100.[nn]	53.2[uu]	50.2[rr]	76.86[rr]	12.1251	16.1194	11.6532	-3.4453	47.2520	-0.6604	-0.4657
aspartic acid	-172400.[ss]	-226370.[tt]	54.8[t]	30.4[rr]	71.79[rr]	11.4232	14.7124	11.5470	-3.3871	29.9488	-1.9989	-0.4899
glutamic acid	-173000.[ss]	-232000.[ee]	70.5[t]	42.3[rr]	89.36[rr]	13.7471	19.3606	11.9216	-3.5793	38.0235	-1.1944	-0.7276
asparagine	-128650.[g]	-186660.[pp]	55.2[pp]	29.9[rr]	77.18[rr]	12.1587	16.1812	11.6715	-3.4478	29.4616	-2.0327	-0.4959
glutamine	-126600.[ss]	-192330.[nn]	61.9[t]	44.7[rr]	94.36[rr]	14.4753	20.8173	12.0386	-3.6395	41.2938	-1.0322	-0.5974
phenylalanine	-49500.[ss]	-110080.[nn]	52.9[t]	91.8[rr]	121.92[rr]	18.2927	28.4440	12.6752	-3.9548	83.1794	2.1517	-0.4611
tryptophan	-26900.[ss]	-97800.[ss]	36.6[t]	100.4[rr]	144.0[rr]	21.3975	34.6481	13.1912	-4.2113	92.8723	2.7330	-0.2143
tyrosine	-87300.[ss]	-157400.[ss]	45.5[t]	71.5[rr]	123.[rr]	18.4784	28.8127	12.7114	-3.9700	66.7005	0.7794	-0.3490
methionine	-120200.[ss]	-177600.[ss]	65.7[t]	70.[rr]	105.3[rr]	15.9529	23.7688	12.2862	-3.7615	62.5883	0.6780	-0.6550

al. (1982). u. Cabani et al. (1981). v. Theoretical value taken from Pierotti (1965). w. Calculated from Eqn. (76) using slopes given in Table 5 and the experimental values of $\bar{S}°$, $\bar{C}°_P$, and $\bar{V}°$ of ethyne to constrain the intercepts (16.6 cal $mol^{-1}K^{-1}$, 10.6 cal $mol^{-1}K^{-1}$, and 17.7 $cm^3 mol^{-1}$, respectively). x. Makhatadze and Privalov (1988). y. Gill et al. (1976). z. Jolicoeur and Lacroix (1976). aa. Høiland (1986). bb. Hill and White (1974). cc. Calculated from Eqn. (76) using the slope given in Table 5 and the experimental value of $\bar{C}°_P$ of 2-butanone to constrain the intercept (-4.4 cal $mol^{-1}K^{-1}$). dd. Calculated from Eqn. (76) using the slope given in Table 5 and the experimental value of $\bar{S}°$ of alanine to constrain the intercept (19.9 cal $mol^{-1}K^{-1}$). ee. Calculated from Eqn. (76) using the slope given in Table 5 and the experimental value of $\Delta\bar{H}°_f$ of aspartic acid to constrain the intercept (-203690 cal mol^{-1}). ff. Regression values taken from Table 3. gg. Wagman et al. (1982). hh. Retrieved by fitting log K data as a function of temperature (see text) using the value of $\bar{S}°$ of the acetic acid molecule given above. ii. Allred and Woolley (1981). jj. Calculated from the standard partial molal dissociation properties reported by Larson and Hepler (1969) using the standard partial molal properties of the neutral acid molecules given above. kk. Calculated from the values of $\bar{V}°$ for sodium salts given by Høiland (1986) using the value of $\bar{V}°$ for Na^+ adopted by Shock and Helgeson (1988). ll. Calorimetric value taken from Spink and Wadso (1975). mm. Cohn et al. (1934). nn. Calculated from the standard partial molal reaction properties reported by Prasad and Ahluwalia (1976) using standard partial molal properties of pure amino acids taken from Domalski (1972). pp. Calculated from Eqn. (76) using the slope given in Table 5 and an intercept (-163980 cal mol^{-1}) constrained by the value given in the table for glutamine. qq. α-aminobutyric acid. rr. Jolicoeur et al. (1986). ss. Hutchens (1976). tt. Calculated from standard partial molal reaction properties given by Hutchens (1976) using values of the corresponding properties of the pure amino acids taken from Domalski (1972). uu. Calculated from Eqn. (76) using the slope given in Table 5 and the experimental value of $\bar{S}°$ of serine to constrain the intercept (26.4 cal $mol^{-1}K^{-1}$). vv. Estimated using the strategy shown in Table 8 of Shock and Helgeson (1988). ww. If values of σ are given for the species in Table 3, the strategy used to estimate a_1 corresponds to Case 1 in Table 4. Otherwise, a_1 was estimated using Case 2 in Table 4.

K^{-1} at 1000°C. Uncertainties in calculated values of $\bar{V}^0$ caused by uncertainties in the a_2 parameter are independent of temperature and decrease from ±0.78 cm^3 mol^{-1} at 1 bar to ±0.27 cm^3 mol^{-1} at 5 kb, but the uncertainty introduced by estimated values of a_1 is ±2.1 cm^3 mol^{-1} regardless of temperature and pressure.

Uncertainties in calculated values of $\bar{S}^0$, $\Delta\bar{H}^0$, and $\Delta\bar{G}^0$ arising from uncertainties in estimated values of the a_4 parameter also decrease with increasing temperature and pressure. Over the range 25°C and 1 kb to 1000°C and 5 kb these uncertainties decrease from ±0.01 to ±2 × 10^{-4} cal mol^{-1} K^{-1} for $\bar{S}^0$, ±5 to ±0.5 cal mol^{-1} for $\Delta\bar{H}^0$, and ~ ±10 to ±2 cal mol^{-1} for $\Delta\bar{G}^0$. In contrast, uncertainties in the c_2 parameter cause increasing uncertainties in calculated values of $\bar{S}^0$, $\Delta\bar{H}^0$, and $\Delta\bar{G}^0$ at elevated temperatures, reaching ±0.45 cal mol^{-1} K^{-1} at 100°C and ±0.7 cal mol^{-1} K^{-1} at 1000°C for $\bar{S}^0$, ±150 cal mol^{-1} at 100°C and ±226 cal mol^{-1} at 1000°C for $\Delta\bar{H}^0$, and ~ ±50 cal mol^{-1} at 100°C and ±940

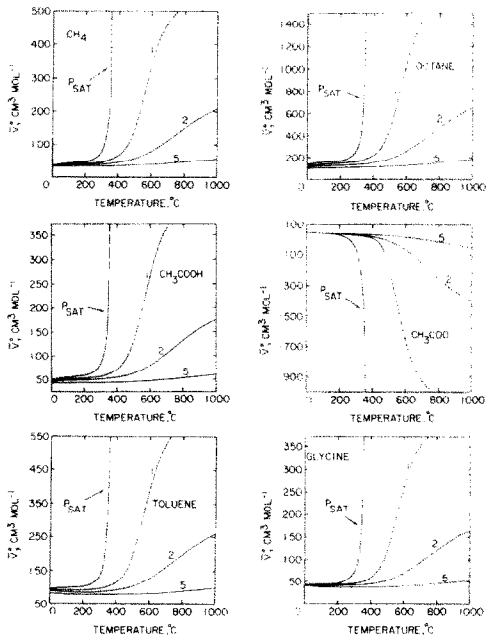


FIG. 23. Standard partial molal volumes ($\bar{V}^0$) of aqueous methane, octane, acetic acid, acetate, toluene, and glycine (see Appendix) in H_2O as functions of temperature in the liquid phase region at P_{SAT} and constant pressure (labeled in kb) calculated from Eqn. (27) using equation of state parameters taken from Table 6.

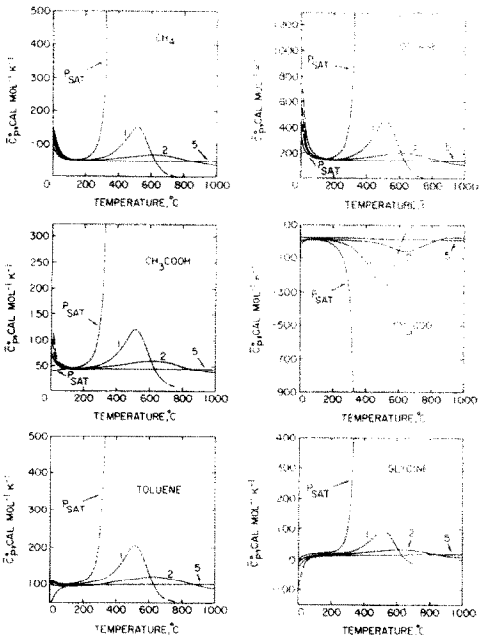


FIG. 24. Standard partial molal heat capacities ($\bar{C}_P^0$) of aqueous methane, octane, acetic acid, acetate, toluene, and glycine (see Appendix) in H_2O as functions of temperature in the liquid phase region at P_{SAT} and constant pressure (labeled in kb) calculated from Eqn. (28) using equation of state parameters taken from Table 6.

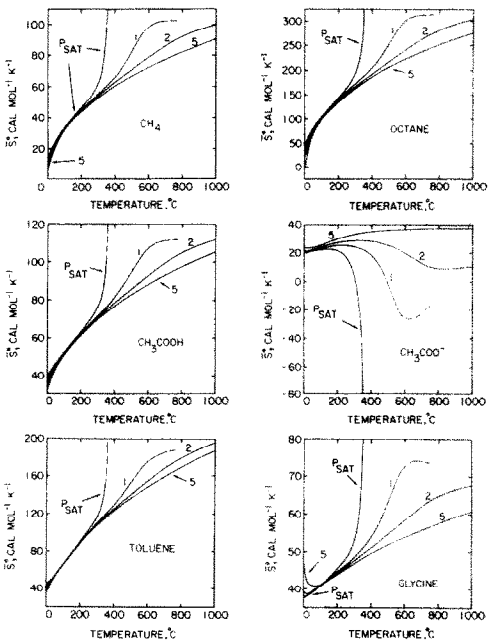


FIG. 25. Standard partial molal entropies ($\bar{S}^0$) of aqueous methane, octane, acetic acid, acetate, toluene, and glycine (see Appendix) in H_2O as functions of temperature in the liquid phase region at P_{SAT} and constant pressure (labeled in kb) calculated from Eqn. (29) using equation of state parameters and thermodynamic data taken from Table 6.

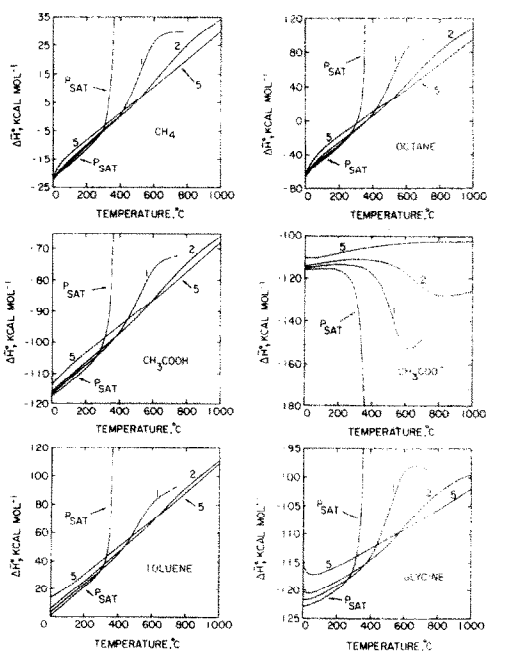


FIG. 26. Apparent standard partial molal enthalpies of formation ($\Delta\bar{H}^0$) of aqueous methane, octane, acetic acid, acetate, toluene, and glycine (see Appendix) in H_2O as functions of temperature in the liquid phase region at P_{SAT} and constant pressure (labeled in kb) calculated from Eqn. (30) using equation of state parameters and thermodynamic data taken from Table 6.

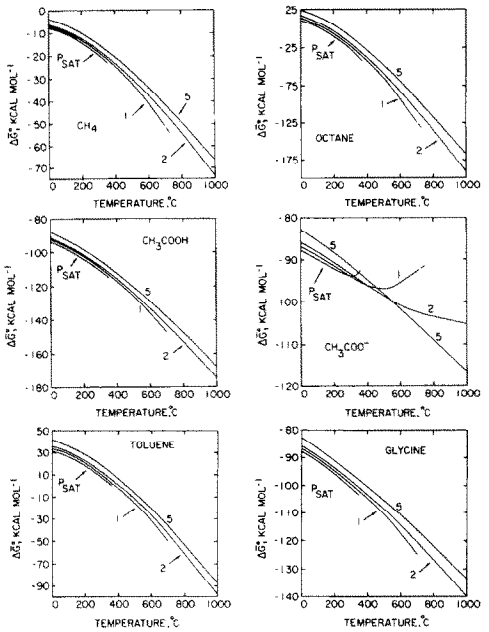


FIG. 27. Apparent standard partial molal Gibbs free energies of formation ($\Delta\bar{G}^0$) of aqueous methane, octane, acetic acid, acetate, toluene, and glycine (see Appendix) in H_2O as functions of temperature in the liquid phase region at P_{SAT} and constant pressure (labeled in kb) calculated from Eqn. (31) using equation of state parameters and thermodynamic data taken from Table 6.

cal mol^{-1} at 1000°C for $\Delta\bar{G}^0$. Uncertainties in the a_1 and a_2 parameters cause increasing uncertainties in calculated values of $\Delta\bar{H}^0$ and $\Delta\bar{G}^0$ with increasing pressure. Those in $\Delta\bar{H}^0$ resulting from uncertainties in a_1 vary from ±25 cal mol^{-1} at 500 bars to ±250 cal mol^{-1} at 5 kb and those arising from uncertainties in a_2 vary from ±16 cal mol^{-1} at 1 kb to ±52 cal mol^{-1} at 5 kb. Uncertainties in estimated a_1 and a_2 values cause maximum uncertainties in calculated values of $\Delta\bar{G}^0$ at 5 kb, which correspond to ±250 and ±18 cal mol^{-1}, respectively. A more extensive discussion of uncertainties arising from the correlation algorithms for the nonsolvation equation of state parameters can be found in SHOCK and HELGESON (1988).

Estimated values of $\omega_{e,j}$ for neutral species generally have an associated uncertainty of ~5000 cal mol^{-1}, which causes increasing uncertainties in calculated standard partial molal properties with increasing temperature in the vicinity of the critical point of H_2O. At other pressures and temperatures, uncertainties arising from estimates of $\omega_{e,j}$ are generally less than those caused by the nonsolvation equation of state parameters (SHOCK et al., 1989). As an example, uncertainties in $\omega_{e,j}$ result in corresponding uncertainties in $\Delta\bar{G}^0$ of ±2.6 cal mol^{-1} at 25°C and 1 kb and ±328 cal mol^{-1} at 500°C and 1 kb.

CONCLUDING REMARKS

Calculation of high-temperature/pressure equilibrium constants and other thermodynamic properties of reactions involving organic aqueous species of geochemical interest can be carried out for a large number of equilibria using the thermodynamic data and equation of state parameters given in Table 6. These reactions include the solubilities of hydrocarbon gases, liquids, and solids, as well as those for solubility reactions of amino acids and the dissociation of metal-organic complexes and carboxylic acids in hydrothermal solutions. Other applications of the equations, parameters, and data discussed above include oxidation and reduction of organic and inorganic aqueous species and their influence on mineral stabilities and the hydrothermal transport of petroleum (HELGESON and SHOCK, 1988), calculation of speciation among organic aqueous species related to metastable states of chemical equilibrium in diagenetic processes (SHOCK, 1988, 1989a) and during aqueous alteration on meteorite parent bodies (SHOCK and SCHULTE, 1990), and identification of geochemical constraints on the abiotic synthesis of organic compounds in hydrothermal systems (SHOCK, 1989b). The revised HKF equations of state and their extension to 5 kb and 1000°C have been incorporated in a revised version of the computer program SUPCRT, which is available together with a new data file including thermodynamic data and equation of state parameters for all of the organic species listed in Table 6, as well as those for the inorganic species considered previously (SHOCK and HELGESON, 1988; SHOCK et al., 1989). The revised program can be obtained from the Laboratory of Theoretical Geochemistry (otherwise known as Prediction Central) at the University of California, Berkeley.

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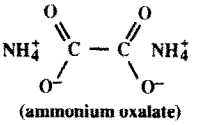
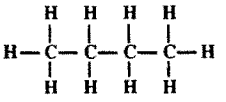
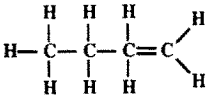
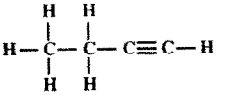
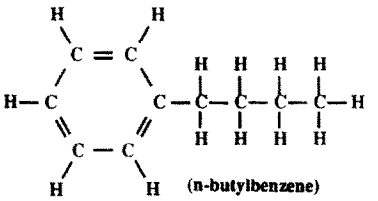
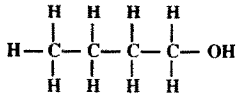
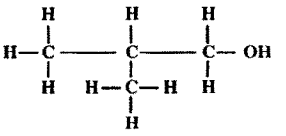
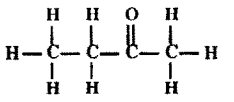
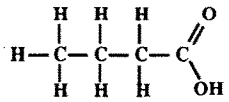
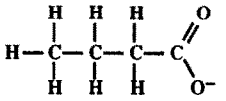
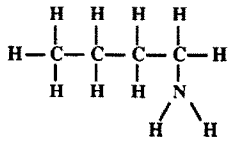
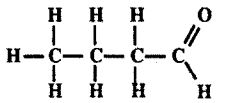
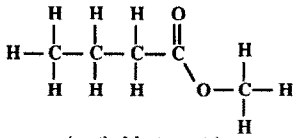
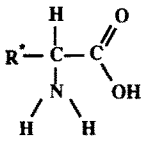
APPENDIX

Nomenclature, Composition, and Structures of the Organic Aqueous Species Considered in the Present Study

Group	Name	Chemical Formula	Sample Structural Formula
Electrolytes	sodium formate	$NaHCOO$	
	sodium acetate	$NaCH_3COO$	
	sodium propanoate	$NaCH_3CH_2COO$	
	ammonium oxalate	$(NH_4)_2C_2O_4$	 (ammonium oxalate)
n-Alkanes		C_nH_{2n+2}	
	methane	CH_4	
	ethane	C_2H_6	
	propane	C_3H_8	
	n-butane	C_4H_{10}	 (n-butane)
	n-pentane	C_5H_{12}	
	n-hexane	C_6H_{14}	
	n-heptane	C_7H_{16}	
	n-octane	C_8H_{18}	
1-Alkenes		C_nH_{2n}	
	ethylene	C_2H_4	
	1-propene	C_3H_6	
	1-butene	C_4H_8	 (1-butene)
	1-pentene	C_5H_{10}	
	1-hexene	C_6H_{12}	
	1-heptene	C_7H_{14}	
	1-octene	C_8H_{16}	
1-Alkynes		C_nH_{2n-2}	
	ethyne	C_2H_2	
	1-propyne	C_3H_4	
	1-butyne	C_4H_6	 (1-butyne)
	1-pentyne	C_5H_8	
	1-hexyne	C_6H_{10}	
	1-heptyne	C_7H_{12}	
	1-octyne	C_8H_{14}	
n-Alkylbenezenes		$C_6H_5C_nH_{2n+1}$	
	benzene	C_6H_6	
	toluene	$C_6H_5CH_3$	
	ethylbenzene	$C_6H_5C_2H_5$	
	n-propylbenzene	$C_6H_5C_3H_7$	
	n-butylbenzene	$C_6H_5C_4H_9$	 (n-butylbenzene)
	n-pentylbenzene	$C_6H_5C_5H_{11}$	
	n-hexylbenzene	$C_6H_5C_6H_{13}$	
	n-heptylbenzene	$C_6H_5C_7H_{15}$	
	n-octylbenzene	$C_6H_5C_8H_{17}$	
1-Alcohols		$C_nH_{2n+2}O$	
	methanol	CH_3OH	
	ethanol	C_2H_5OH	
	1-propanol	C_3H_7OH	
	1-butanol	C_4H_9OH	 (1-butanol)
	1-pentanol	$C_5H_{11}OH$	
	1-hexanol	$C_6H_{13}OH$	
	1-heptanol	$C_7H_{15}OH$	
	1-octanol	$C_8H_{17}OH$	
iso-Alcohols		$(CH_3)_2CH(CH_2)_nOH$	
	iso-propanol	$(CH_3)_2CHOH$	
	iso-butanol	$(CH_3)_2CHCH_2OH$	 (iso-butanol)
2-Ketones		$C_nH_{2n}O$	
	acetone	C_3H_6O	
	2-butanone	C_4H_8O	
	2-pentanone	$C_5H_{10}O$	 (2-butanone)
	2-hexanone	$C_6H_{12}O$	
	2-heptanone	$C_7H_{14}O$	
	2-octanone	$C_8H_{16}O$	

APPENDIX

Nomenclature, Composition, and Structures of the Organic Aqueous Species Considered in the Present Study (Cont'd.)

Group	Name	Chemical Formula	Sample Structural Formula
n-Carboxylic Acids		$C_nH_{2n}O_2$	
	formic	$HCOOH$	
	acetic	CH_3COOH	
	propanoic	C_2H_5COOH	
	butanoic	C_3H_7COOH	
	pentanoic	C_4H_9COOH	
	hexanoic	$C_5H_{11}COOH$	
	heptanoic	$C_6H_{13}COOH$	
	octanoic	$C_7H_{15}COOH$	 (butanoic acid)
n-Carboxylate Anions		$C_nH_{2n-1}O_2^-$	
	formate	$HCOO^-$	
	acetate	CH_3COO^-	
	propanoate	$C_2H_5COO^-$	
	butanoate	$C_3H_7COO^-$	
	pentanoate	$C_4H_9COO^-$	
	hexanoate	$C_5H_{11}COO^-$	
	heptanoate	$C_6H_{13}COO^-$	
	octanoate	$C_7H_{15}COO^-$	 (butanoate anion)
1-Amines		$C_nH_{2n+3}N$	
	methanamine	CH_3NH_2	
	ethanamine	$C_2H_5NH_2$	
	1-propanamine	$C_3H_7NH_2$	
	1-butanamine	$C_4H_9NH_2$	
	1-pentanamine	$C_5H_{11}NH_2$	
	1-hexanamine	$C_6H_{13}NH_2$	
	1-heptanamine	$C_7H_{15}NH_2$	
	1-octanamine	$C_8H_{17}NH_2$	 (1-butanamine)
Aldehydes		$C_nH_{2n}O$	
	formaldehyde	CH_2O	
	acetaldehyde	C_2H_4O	
	propanal	C_3H_6O	
	butanal	C_4H_8O	
	pentanal	$C_5H_{10}O$	
	hexanal	$C_6H_{12}O$	
	heptanal	$C_7H_{14}O$	
	octanal	$C_8H_{16}O$	 (butanal)
Methyl Alkanoates (Esters)		$C_nH_{2n-1}O_2CH_3$	
	methyl formate	CHO_2CH_3	
	methyl acetate	$C_2H_3O_2CH_3$	
	methyl propanoate	$C_3H_5O_2CH_3$	
	methyl butanoate	$C_4H_7O_2CH_3$	
	methyl pentanoate	$C_5H_9O_2CH_3$	
	methyl hexanoate	$C_6H_{11}O_2CH_3$	
	methyl heptanoate	$C_7H_{13}O_2CH_3$	
	methyl octanoate	$C_8H_{15}O_2CH_3$	 (methyl-butanoate)
n-Amino Acids			
	glycine	$C_2H_5NO_2$	
	alanine	$C_3H_7NO_2$	
	a-aminobutyric acid	$C_4H_9NO_2$	
	valine	$C_5H_{11}NO_2$	
	leucine	$C_6H_{13}NO_2$	
	isoleucine	$C_6H_{13}NO_2$	
	serine	$C_3H_7NO_3$	
	threonine	$C_4H_9NO_3$	
	aspartic acid	$C_4H_7NO_4$	
	glutamic acid	$C_5H_9NO_4$	
	asparagine	$C_4H_8N_2O_3$	
	glutamine	$C_5H_{10}N_2O_3$	
	phenylalanine	$C_9H_{11}NO_2$	
	tryptophan	$C_{11}H_{12}N_2O_2$	
	tyrosine	$C_9H_{11}NO_3$	
	methionine	$C_5H_{11}NO_2S$	 (glycine)

*R represents an amino acid side-chain which consists of a normal or branched alkyl group or an aromatic group with associated –COOH, $-NH_2$,=O, or other functional groups.