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Prediction of the thermodynamic properties of aqueous metal complexes to 1000°C and 5 kb

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Abstract—A large number of aqueous metal complexes contribute significantly to hydrothermal, metamorphic, and magmatic processes in the crust of the Earth. Nevertheless, relatively few thermodynamic data other than dissociation constants (K) for a few dozen of these complexes have been determined experimentally at elevated temperatures and pressures. The calculations summarized below are intended to supplement these experimental data by providing interim predictions of the thermodynamic properties of supercritical aqueous metal complexes using the revised HKF (Helgeson et al., 1981) equations of state for aqueous species (Tanger and Helgeson, 1988; Shock et al., 1992) and correlations among equations of state parameters and standard partial molal properties at 25°C and 1 bar (Shock and Helgeson, 1988, 1990; Shock et al., 1989). These equations and correlations permit retrieval of the conventional standard partial molal entropies ($\bar{S}^0$), volumes ($\bar{V}^0$), and heat capacities ($\bar{C}^0_P$) of aqueous metal complexes at 25°C and 1 bar from published values of log K in the supercritical region and the limited number of experimental dissociation constants available in the literature over relatively short ranges of elevated temperature at P_{SAT} (P_{SAT} and SAT are used in the present communication to refer to pressures corresponding to liquid-vapor equilibrium for the system H_2O, except at temperatures <100°C, where they refer to the reference pressure of 1 bar). The standard partial molal properties computed in this way can then be used to generate corresponding values of $\Delta\bar{S}^0$, $\Delta\bar{V}^0$, and $\Delta\bar{C}^0_P$ of association, which for similar complexes correlate linearly with $\bar{S}^0$, $\bar{V}^0$, and $\bar{C}^0_P$, respectively, of the constituent cations and ligands at 25°C and 1 bar. Generalizing these correlations and combining them with the equations of state permits prediction of the temperature and pressure dependence of log K and other thermodynamic properties of a large number of aqueous metal complexes. As a consequence, it is possible to retrieve values of log K at 25°C and 1 bar from the results of hydrothermal experiments at higher temperatures and pressures or to predict values of log K at hydrothermal conditions when no experimental data are available at temperatures and pressures above 25°C and 1 bar. Such predictions can be made for temperatures and pressures from 0°C and 1 bar to 1000°C and 5000 bars. *Copyright © 1997 Elsevier Science Ltd*

1. INTRODUCTION

Experimental, field, and theoretical studies indicate that a myriad of aqueous metal complexes contribute significantly to mineral solubilities in hydrothermal fluids in the Earth's crust (Hemley, 1959; Hemley and Jones, 1964; Hemley et al., 1992; Hemley and Hunt, 1992; Helgeson, 1964, 1969, 1970, 1979, 1985, 1992; Anderson and Burnham, 1967, 1983; Giordano and Barnes, 1979; Eugster, 1981, 1986; Seward, 1981; Wood and Crerar, 1985; Walther, 1986; Bourcier and Barnes, 1987; Walther and Schott, 1988; Sverjensky, 1986, 1987; Brimhall and Crerar, 1987; Eugster and Baumgartner, 1987; Mesmer et al., 1988; Gammons and Barnes, 1989; Oelkers and Helgeson, 1990, 1993; Saccocia and Seyfried, 1990; Palmer and Hyde, 1993; Chen et al., 1994; Gammons and Williams-Jones, 1995; Pokrovski et al., 1995; Pokrovskii and Helgeson, 1995; Rozelle and Baumgartner, 1995). Nevertheless, relatively few experimental data are available for these complexes and the prospect is dim for obtaining in the foreseeable future enough such data to provide a comprehensive thermodynamic frame of reference for calculating the relative stabilities of aqueous metal complexes in hydrothermal fluids. The purpose of the present communication is to address this problem by predicting the thermodynamic properties of these complexes at high pressures and temperatures from equations of state and correlation algorithms. Predictions of this kind should considerably facilitate interpretation of experimental mineral solubilities and calculation of chemical mass transfer among minerals and supercritical electrolyte solutions in geochemical processes.

Numerous methods have been proposed to calculate the logarithms of dissociation constants for aqueous complexes at temperatures and pressures greater than 25°C and 1 bar. The more successful of these are summarized in Table 1. Predictions of log K as a function of temperature at P_{SAT} commonly rely on estimated or measured standard partial molal enthalpies or entropies of dissociation, together with assumptions about the temperature dependence of the standard partial molal heat capacities of reaction which are generally unreliable at temperatures above ~150–250°C, depending on the assumption (Gurney, 1936, 1938, 1953; Cobble, 1964; Criss and Cobble, 1964a,b; Helgeson, 1967, 1969; Lindsay, 1980; Murray and Cobble, 1980; Arnórsson et al., 1982, 1983;

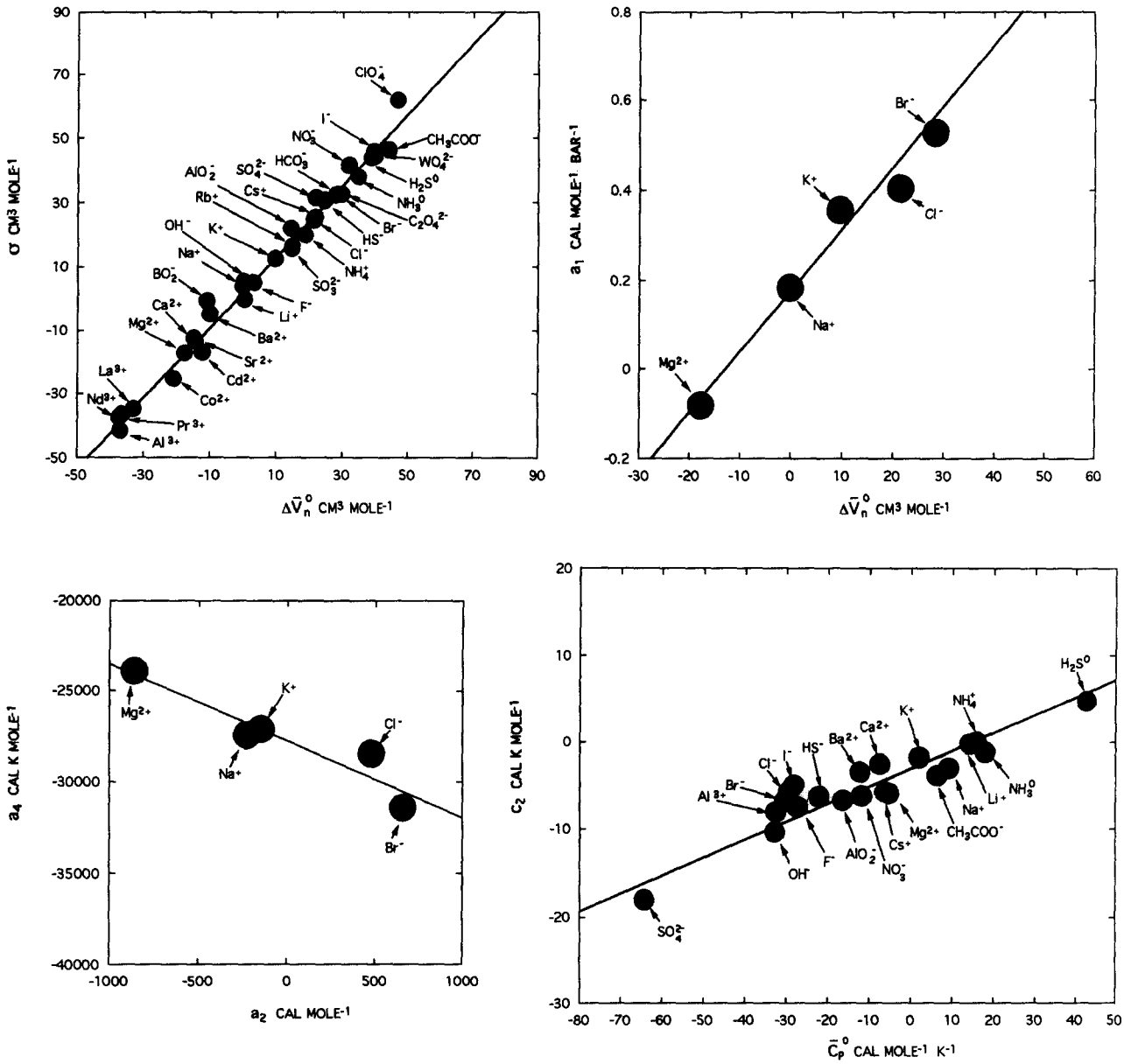

Fig. 1. Correlation plots of equations of state parameters as a function of the standard partial molal properties of aqueous ions, neutral species, and complexes at 25°C and 1 bar taken from Shock and Helgeson (1988). The lines are consistent with Eqns. 27–30.

Smith et al., 1986; Ruaya, 1988). Logarithmic correlations of dissociation constants with solvent density have also been used to estimate dissociation constants, particularly at supercritical temperatures and pressures (Franck, 1956, 1981; Marshall, 1968, 1969, 1970, 1972a,b; Eugster and Baumgartner, 1987; Mesmer et al., 1988; Anderson et al., 1991). Other approaches include application of statistical theories of ion association (Bjerrum, 1926; Fuoss, 1958; Gilkerson, 1956, 1970) to prediction of dissociation constants at high temperatures and pressures (Pearson et al., 1963; Gilkerson, 1970; Wright et al., 1961; Oelkers and Helgeson, 1990; Walther and Schott, 1988; Brady and Walther, 1990). In addition, strictly electrostatic models have been used for this purpose with varying degrees of success over restricted ranges of pressure and temperature by Ryzhenko (1974), Bryzgalin and Rafal'skiy (1981), Bryzgalin (1986), Ryzhenko and Bryzgalin (1987), Walther and Schott (1988), Brady and Walther (1990), and others. Dissociation constants at supercritical temperatures and pressures have also been generated recently from solubility data (Hemley et al., 1977a,b, 1980; Eugster and Baumgartner, 1987; Woodland and Walther, 1987; Sverjensky et al., 1991; Fein et al., 1992; Hemley et al., 1992; Zhu and Sverjensky, 1991, 1992; Pokrovskii and Helgeson, 1992, 1995; Xie and Walther, 1993a,b; Cygan et al., 1994; Gao, 1994; Pokrovski et al., 1995) and Monte Carlo calculations (Oelkers and Helgeson, 1993).

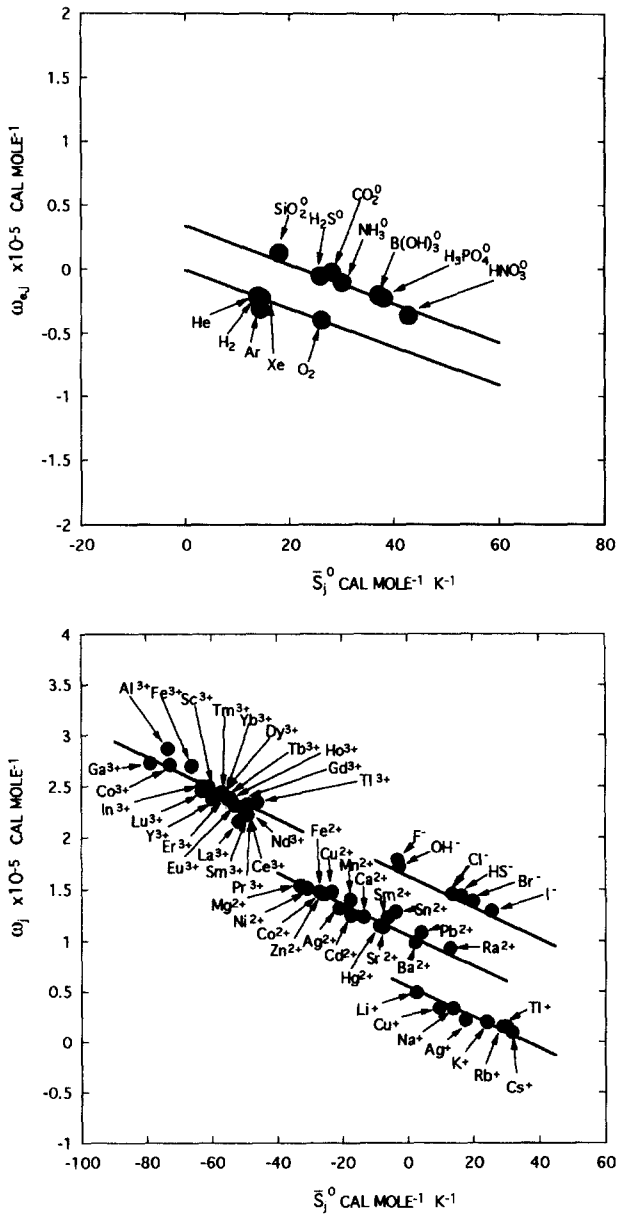

Fig. 2. Correlation of the Born coefficients of aqueous species with their standard partial molal entropies at 25°C and 1 bar taken from Shock et al. (1989).

None of the predictive approaches adduced above can be used with confidence to predict dissociation constants for a wide variety of aqueous species over extensive ranges of temperature and pressure without experimental calibration. In contrast, algorithms adopted in the present study require experimental dissociation constants for aqueous complexes at only one temperature and pressure in order to predict values of the dissociation constants to 5 kb and 1000°C (see below). The approach is based on recent advances in high temperature solution chemistry, which have led to general equations of state and correlation algorithms that can be used to calculate the standard partial molal thermodynamic properties of aqueous ions, inorganic acids, dissolved gases, and organic molecules at both high and low temperatures and pressures (Sverjensky, 1987; Tanger and Helgeson, 1988; Shock and Helgeson, 1988, 1990; Oelkers and Helgeson, 1988; Shock et al., 1989, 1992, 1997a,b; Shock and Koretsky, 1993, 1995; Sassani and Shock, 1995; Amend and Helgeson, 1997). These equations of state and correlations have been extended and supplemented in the present study to describe the temperature and pressure dependence of the standard partial molal thermodynamic properties of aqueous metal complexes at high temperatures and pressures.

2. SUMMARY OF THERMODYNAMIC RELATIONS

The standard state adopted in the present study for H_2O is one of unit activity of the pure liquid at any temperature and pressure. The standard state for aqueous species other than H_2O calls for unit activity of the species in a hypothetical one molal solution referenced to infinite dilution at any temperature and pressure. The standard state for gases is characterized by unit fugacity of the hypothetical perfect gas at 1 bar and any temperature.

The standard Gibbs free energies of formation of aqueous species at elevated temperatures and pressures computed below are apparent standard partial molal Gibbs free energies of formation ($\Delta\bar{G}^0$) defined by (Benson, 1968; Helgeson et al., 1981)

$$\Delta\bar{G}^0 = \Delta\bar{G}_f^0 + (\bar{G}_{P,T}^0 - \bar{G}_{P_r,T_r}^0) \quad (1)$$

where $\Delta\bar{G}_f^0$ refers to the standard partial molal Gibbs free energy of formation of the species from its elements in their stable state at the reference temperature (T_r) and pressure (P_r), and ($\bar{G}_{P,T}^0 - \bar{G}_{P_r,T_r}^0$) refers to the difference in the standard partial molal Gibbs free energy of the species at the

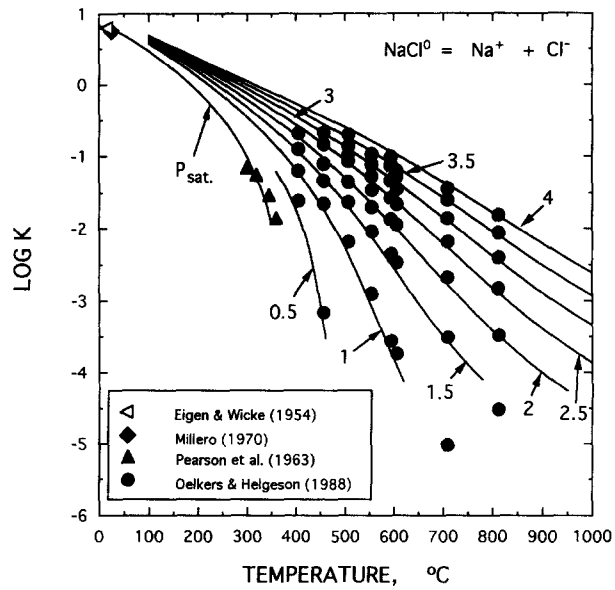

Fig. 3. Logarithm of the dissociation constant of $NaCl^0$ as a function of temperature and pressure (labelled in kb). The curves were generated by regression of the experimental data represented by the symbols (see text and Table 2).

pressure and temperature of interest (P and T) and that at the reference pressure and temperature (P_r and T_r), which is given by

$$\bar{G}^0_{P,T} - \bar{G}^0_{P_r,T_r} = -\bar{S}^0_{P_r,T_r}(T - T_r) + \int_{T_r}^{T} \bar{C}^0_{P_r} dT - T\int_{T_r}^{T} \bar{C}^0_{P_r} d\ln T + \int_{P_r}^{P} \bar{V}^0_T dP \quad (2)$$

The integrals in Eqn. 2 can be evaluated with the aid of the revised HKF equations of state for the standard partial molal volumes and heat capacities of aqueous species summarized below.

2.1. Equations of State for Aqueous Species

The standard partial molal volumes ($\bar{V}^0$) and heat capacities ($\bar{C}^0_P$) of both charged and neutral aqueous species can be expressed as (Tanger and Helgeson, 1988; Shock et al., 1989)

$$\bar{V}^0 = a_1 + \frac{a_2}{\psi + P} + \left(a_3 + \frac{a_4}{(\psi + P)}\right)\left(\frac{1}{T - \theta}\right) - \omega Q + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial \omega}{\partial P}\right)_T \quad (3)$$

$$\bar{C}^0_P = c_1 + \frac{c_2}{(T - \theta)^2} - \frac{2T}{(T - \theta)^3}\left[a_3(P - P_r) + a_4 \ln\left(\frac{\psi + P}{\psi + P_r}\right)\right] + \omega TX + 2TY\left(\frac{\partial \omega}{\partial T}\right)_P - T\left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial^2 \omega}{\partial T^2}\right)_P \quad (4)$$

where c_1, c_2, a_1, a_2, a_3, and a_4 represent temperature/pressure-independent coefficients characteristic of the aqueous species, ω stands for the conventional Born coefficient of the species (see below), θ and ψ refer to solvent parameters equal to 228 K and 2600 bars, respectively, and Q, Y, and X denote partial derivatives of the reciprocal of the dielectric constant of H_2O (ϵ), which can be written as

$$Q = \frac{1}{\epsilon}\left(\frac{\partial \ln \epsilon}{\partial P}\right)_T \quad (5)$$

$$Y = \frac{1}{\epsilon}\left(\frac{\partial \ln \epsilon}{\partial T}\right)_P \quad (6)$$

$$X = \frac{1}{\epsilon}\left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_P - \left(\frac{\partial \ln \epsilon}{\partial T}\right)^2_P\right] \quad (7)$$

Values of ϵ and its partial derivatives with respect to temperature and pressure to 1000°C and 5 kb are given by Shock et al. (1992).

The conventional Born coefficient of the jth aqueous ion (ω_j) can be expressed as

$$\omega_j = \omega_j^{\text{abs.}} - Z_j \omega_{H^+}^{\text{abs.}} \quad (8)$$

where ω_j^{abs} and $\omega_{H^+}^{\text{abs.}}$ refer to the absolute Born coefficients of the jth ion and H^+, respectively, and Z_j refers to the charge on the jth ion. The absolute Born coefficient of the jth aqueous species is defined by

$$\omega_j^{\text{abs.}} = \frac{\eta Z_j^2}{r_{e,j}} \quad (9)$$

where $\eta = 1.66027 \times 10^5$ Å cal mol^{-1} and $r_{e,j}$ denotes the effective electrostatic radius of the species, which for monatomic ions can be calculated from (Tanger and Helgeson, 1988; Shock et al., 1992)

$$r_{e,j} = r_{e,j,P_r,T_r} + |Z_j| g \quad (10)$$

where g (in Ångstroms) designates a solvent function of temperature and density given by Shock et al. (1992) and r_{e,j,P_r,T_r} for monatomic aqueous ions is given by (Helgeson and Kirkham, 1976; Helgeson et al., 1981)

$$r_{e,j,P_r,T_r} = r_{x,j} + |Z_j| k_Z \quad (11)$$

where $r_{x,j}$ stands for the crystallographic radius of the jth ion (Shock and Helgeson, 1988) and k_z represents a charge-dependent constant equal to 0.0 for anions and 0.94 for cations. The effective electrostatic radii at 1 bar and 298.15 K of either monatomic or polyatomic aqueous ions can be calculated from (Shock and Helgeson, 1988)

$$r_{e,j,P_r,T_r} = \frac{Z_j^2(\eta Y_{P_r,T_r} - 100)}{\bar{S}^0_{P_r,T_r} - \alpha_Z} \quad (12)$$

where Y_{P_r,T_r} refers to the Y Born function (Eqn. 6) at the reference pressure and temperature, which is equal to -5.802×10^{-5} K^{-1}, $\bar{S}^0_{P_r,T_r}$ denotes the standard partial molal entropy of the subscripted ion at 1 bar and 298.15 K, and α_Z designates a charge-dependent correlation parameter. Combining Eqns. 9 and 10 leads to

$$\omega_j^{\text{abs.}} = \frac{\eta Z_j^2}{r_{e,j,P_r,T_r} + |Z_j| g} \quad (13)$$

The analog of Eqn. 13 for the hydrogen ion can be expressed as

$$\omega_{H^+}^{\text{abs.}} = \frac{\eta}{3.08 + g} \quad (14)$$

where 3.08 (Å) corresponds to the effective electrostatic radius of the hydrogen ion at 1 bar and 298.15 K (Helgeson and Kirkham, 1976). Combining Eqns. 8, 13, and 14 results in

$$\omega_j = \eta Z_j\left[\frac{Z_j}{r_{e,j,P_r,T_r} + |Z_j| g} - \frac{1}{3.08 + g}\right] \quad (15)$$

Because $g = 0$ at 1 bar and 298.15 K (Tanger and Helgeson, 1988; Shock et al., 1992), the conventional Born coefficient

of the jth ion at the reference pressure and temperature (ω_{j,P_r,T_r}) can be expressed as

$$\omega_{j,P_r,T_r} = \eta Z_j \left[\frac{Z_j}{r_{e,j,P_r,T_r}} - \frac{1}{3.08} \right] \quad (16)$$

It follows from Eqns. 12 and 16 that ω_{j,P_r,T_r} for ionic species with the same charge is a linear function of $\bar{S}^0_{j,P_r,T_r}$. Similarly, ω_{j,P_r,T_r} for neutral aqueous species with similar characteristics correlates linearly with $\bar{S}^0_{j,P_r,T_r}$ (Shock et al., 1989; Shock and Helgeson, 1990). The Born coefficient for the jth neutral aqueous species is given by

$$\omega_j = \omega_{j,P_r,T_r} = \omega_j^{\text{abs.}} = \frac{\eta Z^2_{e,j}}{r_{e,j,P_r,T_r}} \quad (17)$$

where $Z_{e,j}$ stands for the effective charge of the jth species (Helgeson et al., 1981; Shock et al., 1989; Shock et al., 1992).

Taking account of Eqns. 1–10, the apparent standard partial molal Gibbs free energy of formation for both charged and neutral aqueous species at a given pressure and temperature ($\Delta\bar{G}^0$) can be expressed as

$$\begin{aligned} \Delta\bar{G}^0 = \Delta\bar{G}^0_f - \bar{S}^0_{P_r,T_r}(T - T_r) - c_1 f_1(T) - c_2 f_2(T) \\ + a_1 f_1(P) + a_2 f_2(P) + a_3 f_1(P, T) \\ + a_4 f_2(P, T) + \omega_{P_r,T_r} f_3(P, T) + f_4(P, T) \end{aligned} \quad (18)$$

where

$$f_1(T) = T \ln \left(\frac{T}{T_r} \right) - T + T_r \quad (19)$$

$$f_2(T) = \left[\left(\frac{1}{T - \theta} \right) - \left(\frac{1}{T_r - \theta} \right) \right] \times \left(\frac{\theta - T}{\theta} \right) - \frac{T}{\theta^2} \ln \left[\frac{T_r(T - \theta)}{T(T_r - \theta)} \right] \quad (20)$$

$$f_1(P) = P - P_r \quad (21)$$

$$f_2(P) = \ln \left(\frac{\psi + P}{\psi + P_r} \right) \quad (22)$$

$$f_1(P, T) = \ln \left(\frac{P - P_r}{T - \theta} \right) \quad (23)$$

$$f_2(P, T) = \left(\frac{1}{T - \theta} \right) \ln \left(\frac{\psi + P}{\psi + P_r} \right) \quad (24)$$

$$f_3(P, T) = \left[\frac{1}{\epsilon} - \frac{1}{\epsilon_{P_r,T_r}} + Y_{P_r,T_r}(T - T_r) \right] \quad (25)$$

and

$$f_4(P, T) = k[\omega - \omega_{P_r,T_r}] \left(\frac{1}{\epsilon} - 1 \right) \quad (26)$$

where k stands for a switch constant which is equal to unity for ionic aqueous species and zero for neutral aqueous species. The conventional Born coefficients in Eqns. 18 and 26 (ω and ω_{P_r,T_r}) for charged aqueous species are given by appropriate statements of Eqns. 15 and 16, which can be combined with Eqns. 11 or 12 for monatomic and polyatomic aqueous ions, respectively. As indicated above, values of ω for neutral aqueous species can be computed from an appropriate statement of the first identity in Eqn. 17 using linear correlations of ω_{j,P_r,T_r} with $\bar{S}^0_{j,P_r,T_r}$ (see below).

Equation 18 permits calculation of the apparent standard partial molal Gibbs free energies of formation of aqueous species to 1000°C and 5 kb (Tanger and Helgeson, 1988; Shock et al., 1989). Values of the equation of state coefficients in Eqn. (18) for numerous aqueous ions have been generated by regression of experimentally determined standard partial molal volumes and heat capacities of a wide array of electrolytes (Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock et al., 1989). Although in principle the same approach could be taken for aqueous complexes, relatively few experimentally determined standard partial molal volumes and heat capacities are available for aqueous complexes (Archer and Wood, 1985; Nguyen-Trung and Hovey, 1990; Majer and Wood, 1994). In contrast, experimentally derived dissociation constants have been reported for many such complexes at both low and high temperatures and pressures. Regression of these dissociation constants as functions of temperature and pressure can be carried out with statements of Eqn. 18 for each of the complexes and its dissociated ions. By incorporating in the regression equations correlation algorithms linking the equation of state coefficients of the complexes with the standard partial molal entropies, volumes, and heat capacities of the species at 25°C and 1.0 bar, values of the latter properties can be retrieved directly from the regression calculations.

3. REGRESSION EQUATIONS FOR AQUEOUS COMPLEXES

It has been demonstrated (Shock and Helgeson, 1988, 1990; Shock et al., 1989) that equations of state parameters for aqueous species obtained by regression of experimental standard partial molal volumes and heat capacities of electrolytes, neutral molecules, and charged complexes with Eqns. 3 and 4 correlate linearly with one another and/or with the standard partial molal entropies, volumes, or heat capacities of the species at 25°C and 1 bar. A number of these correlations are depicted in Fig. 1. The correlations for ionic species depicted in this figure are consistent with

$$\sigma = (1.11)\Delta\bar{V}^0_{n,P_r,T_r} + 1.8 \quad (27)$$

$$a_1 = (0.013684)\Delta\bar{V}^0_{n,P_r,T_r} + 0.1765 \quad (28)$$

$$a_4 = -(4.134)a_2 - 27790 \quad (29)$$

$$c_2 = (2037)\bar{C}^0_{P_r,T_r} - 30460 \quad (30)$$

where $\Delta\bar{V}^0_{n,P_r,T_r}$, a_2 and $\bar{C}^0_{P_r,T_r}$ are in cm^3 mole^{-1}, cal mole^{-1}, and cal mole^{-1} K^{-1}, respectively,

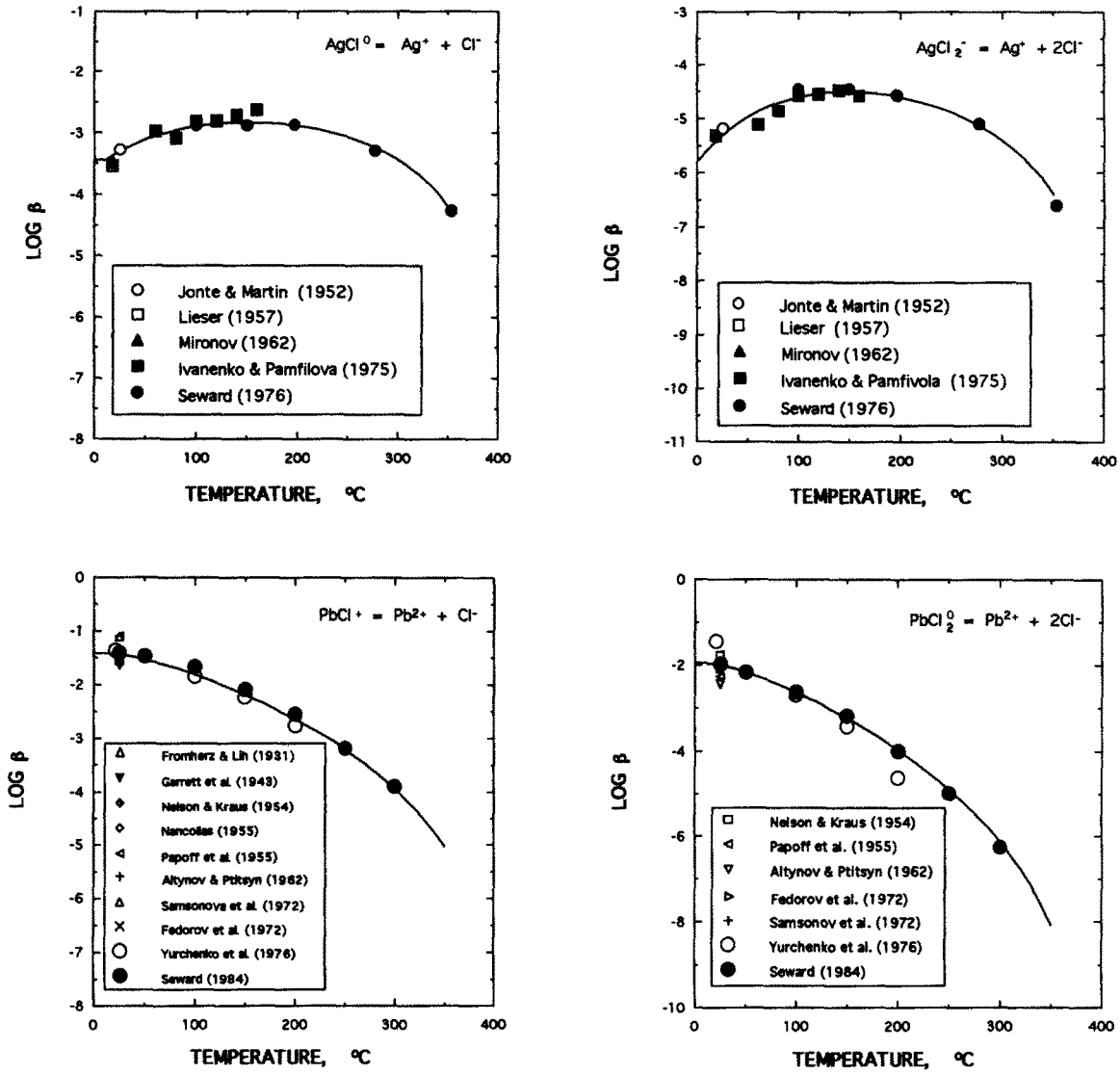

Fig. 4. Logarithms of the overall dissociation constants (β) of chloride complexes as functions of temperature at P_{SAT}. The curves were generated by regression of the experimental data represented by the symbols (see text and Table 2).

$$\Delta\bar{V}^0_{n,P_r,T_r} = \bar{V}^0_{P_r,T_r} + \omega_{P_r,T_r}Q_{P_r,T_r} \quad (31)$$

$$\sigma = a_1 + \frac{a_2}{\psi + P_r} \quad (32)$$

Combining Eqns. 3 and 27 through 32 leads to the following equations for a_1, a_2, a_3, a_4, and c_1 in terms of $\bar{V}^0_{P_r,T_r}$, $\bar{C}^0_{P_r,T_r}$, and ω_{P_r,T_r}:

$$a_1 = (0.013684)(\bar{V}^0_{P_r,T_r} + (41.84)\omega_{P_r,T_r}Q_{P_r,T_r}) + 0.1765 \quad (33)$$

$$a_2 = (33.423)(\bar{V}^0_{P_r,T_r} + (41.84)\omega_{P_r,T_r}Q_{P_r,T_r}) - 347.23 \quad (34)$$

$$a_3 = -(0.1435)(\bar{V}^0_{P_r,T_r} + (41.84)\omega_{P_r,T_r}Q_{P_r,T_r}) + 7.0274 \quad (35)$$

$$a_4 = -(138.17)(\bar{V}^0_{P_r,T_r} + (41.84)\omega_{P_r,T_r}Q_{P_r,T_r}) - 26355 \quad (36)$$

$$c_1 = (0.6087)\bar{C}^0_{P_r,T_r} + \omega_{P_r,T_r}T_rX_{P_r,T_r} + 5.85 \quad (37)$$

where $\bar{V}^0_{P_r,T_r}$ is in cm^3 mole^{-1} and ω_{P_r,T_r} is in cal mole^{-1}. The values of Q_{P_r,T_r} and X_{P_r,T_r} are 5.903×10^{-7} (bar^{-1}) and -3.09×10^{-7} (K^{-2}), respectively. Substituting Eqns. 30 and 33–37 in Eqn. 18 results in a regression equation for the standard Gibbs free energy of formation of an aqueous species as a function of temperature and pressure in which the only

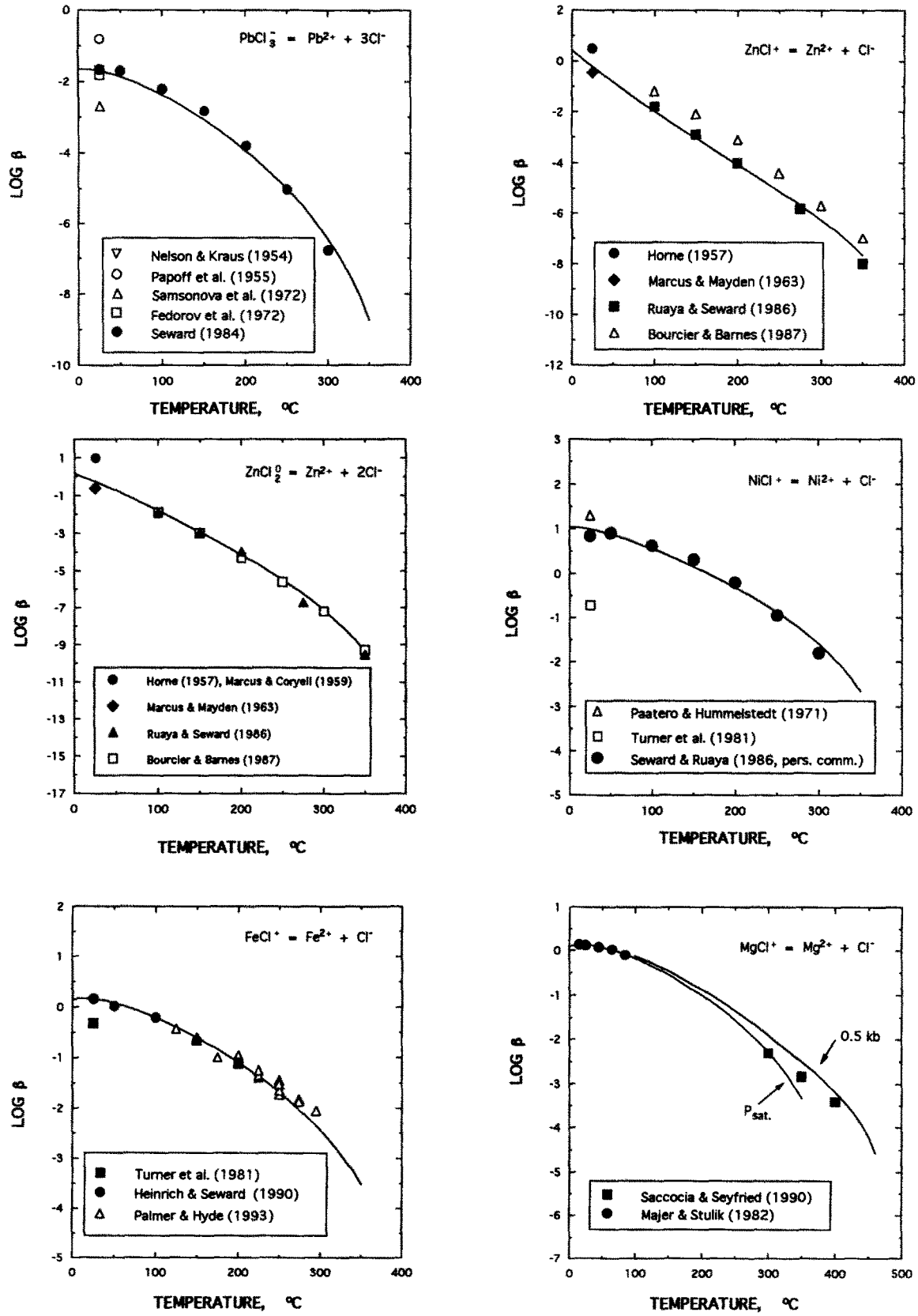

Fig. 4. (continued)

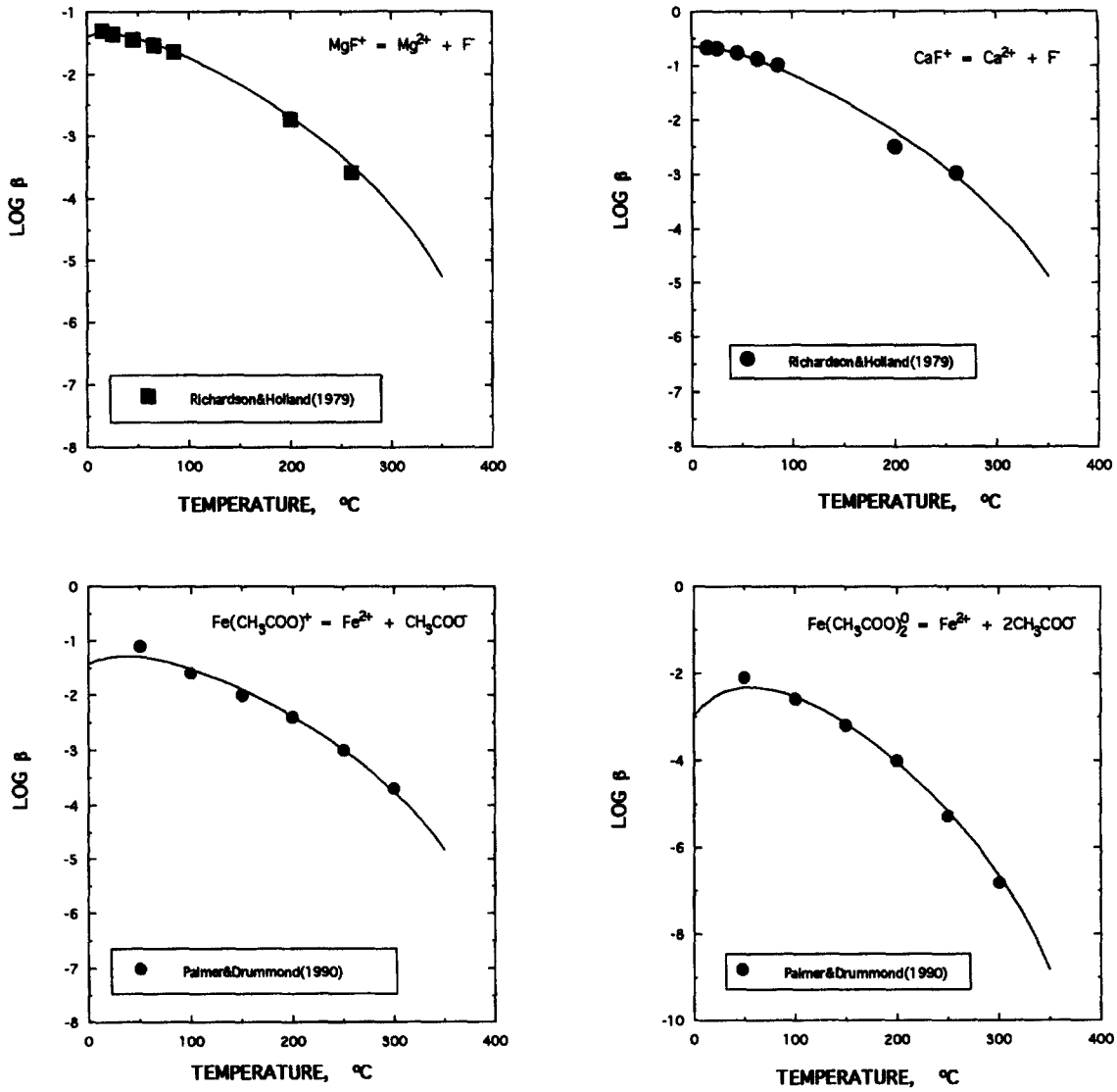

Fig. 5. Logarithms of the overall dissociation constants (β) of fluoride, acetate, sulfate, and silica complexes as functions of temperature at P_{SAT}. The curves were generated by regression of the experimental data represented by the symbols (see text and Table 2).

regression parameters are $\bar{V}^0_{P_r,T_r}$, $\bar{S}^0_{P_r,T_r}$, $\bar{C}^0_{P_r,T_r}$, and/or ω_{P_r,T_r}. This expression can be written as

$$\Delta\bar{G}^0 = \Delta\bar{G}^0_f - \bar{S}^0_{P_r,T_r}(T - T_r) - f_1(T)$$
$$[(0.6087)\bar{C}^0_{P_r,T_r} + \omega_{P_r,T_r}T_rX_{P_r,T_r} + 5.85]$$
$$- f_2(T)[(2037)\bar{C}^0_{P_r,T_r} - 30460] + f_1(P)$$
$$\times [(0.013684)(\bar{V}^0_{P_r,T_r} + (41.84)\omega_{P_r,T_r}Q_{P_r,T_r}) + 0.1765]$$
$$+ f_2(P)[(33.423)(\bar{V}^0_{P_r,T_r} + (41.84)\omega_{P_r,T_r}Q_{P_r,T_r}) - 347.23]$$
$$+ f_1(P, T)[-(0.1435)(\bar{V}^0_{P_r,T_r}$$
$$+ (41.84)\omega_{P_r,T_r}Q_{P_r,T_r}) + 7.0274] + f_2(P, T)$$
$$\times [-(138.17)(\bar{V}^0_{P_r,T_r} + (41.84)\omega_{P_r,T_r}Q_{P_r,T_r})$$
$$- 26355] + \omega_{P_r,T_r}f_3(P, T) + f_4(P, T) \quad (38)$$

Many of the experimental data considered in the present study were obtained at pressures below 200 bars, where the pressure terms in Eqn. 31 contribute negligibly to $\Delta\bar{G}^0$. Under these circumstances, Eqn. 38 reduces to

$$\Delta\bar{G}^0 = \Delta\bar{G}^0_f - \bar{S}^0_{P_r,T_r}(T - T_r) - f_1(T)$$
$$[(0.6087)\bar{C}^0_{P_r,T_r} + \omega_{P_r,T_r}T_rX_{P_r,T_r} + 5.85] - f_2(T)$$
$$[(2037)\bar{C}^0_{P_r,T_r} - 30460] + \omega_{P_r,T_r}f_3(P, T) + f_4(P, T) \quad (39)$$

Note that it follows from Eqn. 26 that $f_4(P, T)$ in Eqns. 38 and 39 is equal to zero for neutral aqueous species.

In cases where insufficient experimental data are available to warrant retrieval of ω_{P_r,T_r} by regression of the data with Eqns. 38 or 39, ω_{P_r,T_r} can be eliminated from the regression equations by combining them with the equation representing the linear curves shown in Fig. 2. The curves in this figure

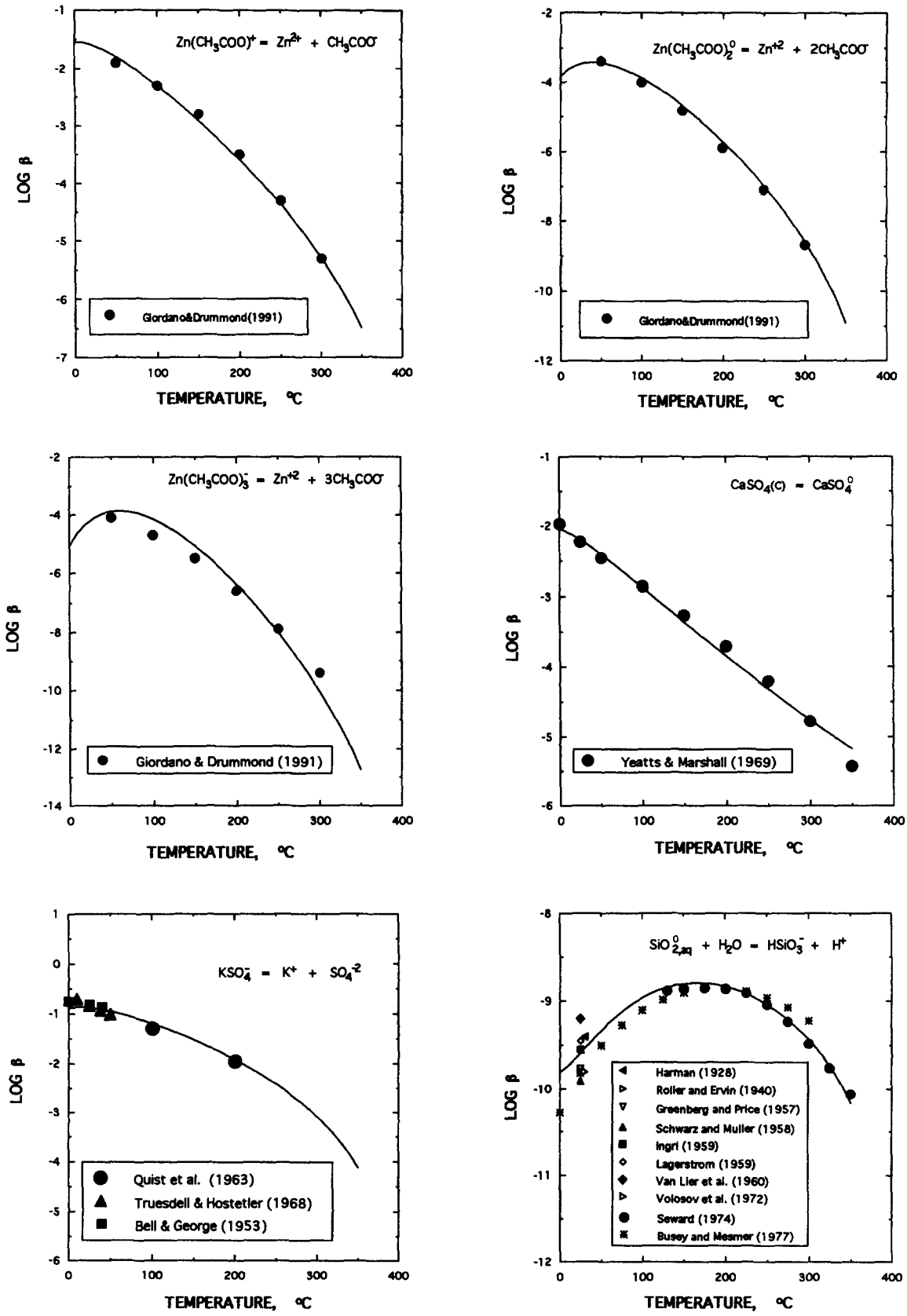

Fig. 5. (continued)

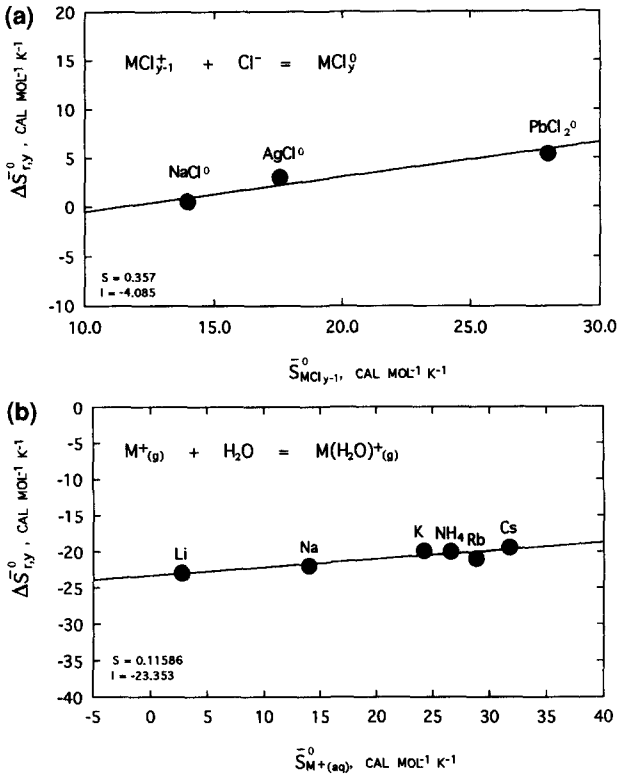

Fig. 6. a. Correlation of the stepwise standard partial molal entropies of association of chloride complexes ($\Delta\bar{S}^0_{r,y}$) with the standard partial molal entropy of the aqueous cationic species ($\bar{S}^0_{MCl_{y-1}^{z+1}}$) at 25°C and 1 bar (Eqns. 43–47). The symbols represent values computed from thermodynamic data taken from Table 2. b. Correlation of the standard partial molal entropy of association corresponding to addition of a single water molecule to a gaseous cation ($\Delta\bar{S}^0_{r,y}$) with the standard partial molal entropy of the cation ($\bar{S}^0_{M^+_{(aq)}}$). The solid line (Eqn. 48) represents regression of the experimental data (Kebarle, 1974) represented by the symbols.

are consistent with Eqns. 12 and 16, which can be combined after dropping the subscript j to give

$$\omega_{P_r,T_r} = -1514.4\bar{S}^0_{P_r,T_r} + \beta_Z \qquad (40)$$

where $\bar{S}^0_{P_r,T_r}$ is in cal mole^{-1} K^{-1} and β_Z ($\times 10^{-5}$) = 0.5512, 1.0586, 1.5795, −1.6295, and 3.2120 for Z = 1, 2, 3, −1, and −2, respectively (Shock and Helgeson, 1988). In the case of the curves for the neutral aqueous species shown in Fig. 2, β_Z = 0.0 for the lower curve (which represents the more volatile species) and β_Z = 34,000 cal mol^{-1} for the upper curve (Shock et al., 1989).

The apparent standard partial molal Gibbs free energy of formation of an aqueous complex ($\Delta\bar{G}^0_c$) can be expressed in terms of the logarithm of its overall dissociation constant (log β) by writing

$$\Delta\bar{G}^0_c = 2.303\,RT\log\beta + \sum_i \hat{n}_{i,c}\Delta\bar{G}^0_i \qquad (41)$$

where $\hat{n}_{i,c}$ stands for the stoichiometric reaction coefficient of the ith cation or anion in the reaction representing overall dissociation of the cth complex (which is positive for products and negative for reactants), $\Delta\bar{G}^0_i$ refers to the apparent standard partial molal Gibbs free energy of formation of the ith ion, and $\log\beta = \sum_c \log K_c$, where K_c stands for the stepwise dissociation constant of the cth complex. Eqn. 41 was used together with Eqns. 38–40 to regress experimental dissociation constant data reported in the literature as a function of temperature and pressure.

4. RETRIEVAL OF THERMODYNAMIC PROPERTIES OF AQUEOUS SPECIES FROM EXPERIMENTAL DISSOCIATION CONSTANT DATA

Experimental dissociation constants reported in the literature for fifty-seven aqueous complexes were regressed in the present study with Eqns. 38 or 39 and 41 to retrieve equations of state parameters and the standard partial molal properties of the species at 25°C and 1 bar given in Tables 2 and 3. The apparent standard partial molal Gibbs free energies of formation of the cations and ligands in the dissociational reactions required to evaluate Eqn. 41 were computed from Eqn. 18 using parameters and thermodynamic properties taken from Shock and Helgeson (1988). In each case, the amount of experimental data available and the pressure-temperature distribution of the data were taken into account in determining the number of parameters that could be retrieved with confidence from the regression calculations. The types of parameters retrieved in the calculations are shown in Table 4. The dissociation constants are represented below by symbols in the figures depicting log K or log β as a function of temperature. The solid curves in these figures correspond to dissociation constants computed from the standard partial molal Gibbs free energies of formation of the complexes, which were generated from Eqns. 18–26 and 41 using the equation of state parameters and thermodynamic properties at 25°C and 1 bar for the complexes retrieved from the regression calculations (Tables 2 and 3) and those for the cations and ligands given by Shock and Helgeson (1988). The retrieval calculations used to generate the parameters in Table 2 are described below in terms of four groups of dissociational reactions.

4.1. $NaCl^0$*

Dissociation constants of $NaCl^0$ have been determined experimentally from 10 to 800°C and P_{SAT} (see note *) to 4 kb, which is a wider range of pressure and temperature than that for any other aqueous complex for which experimental data are available (Eigen and Wicke, 1954; Pearson et al., 1963; Quist and Marshall, 1968a; Dunn and Marshall, 1969; Millero, 1970; Oelkers and Helgeson, 1988; Zimmerman et al., 1995). Over a substantial part of this range of temperatures and pressures, the g function in Eqns. 10 and 13–15 established by Tanger and Helgeson (1988) permits calculation of $\Delta\bar{G}^0_i$ in Eqn. 41 for Na^+ and Cl^-, which in turn makes it possible to use Eqn. 41 to calculate values of $\Delta\bar{G}^0_c$ for $NaCl^0$ from those of log K. The experimental

* The neutral ion pair is distinguished in the present communication from its dissociated counterpart by superscripting the species with a zero, as in $NaCl^0$, to distinguish it from its dissociated counterpart NaCl.

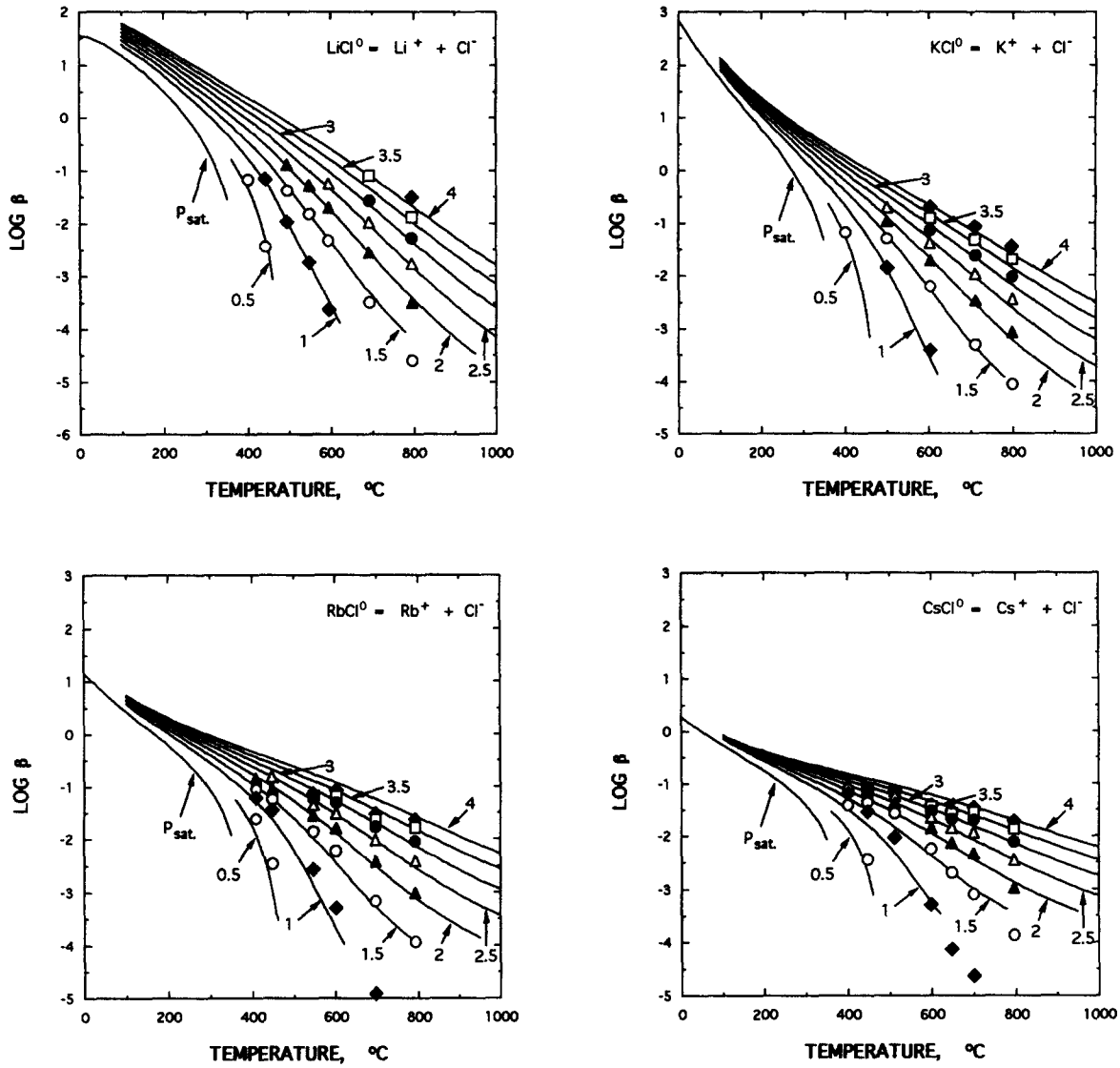

Fig. 7. Logarithms of the dissociation constants of $LiCl^0$, KCl^0, $RbCl^0$, and $CsCl^0$ as functions of temperature at constant pressure (labelled in kb). The curves were generated by regression of the experimental data (Oelkers and Helgeson, 1988) represented by the symbols (see text and Table 4).

values of log K used in these calculations are depicted in Fig. 3.

Values of $\Delta\bar{G}^0_{NaCl}$ derived from the experimental dissociation constants for $NaCl^0$ represented by the symbols shown in Fig. 3 were regressed in the present study using Eqn. 38 to retrieve values of $\Delta\bar{G}^0_{f,P_r,T_r}$, $\bar{S}^0_{P_r,T_r}$, $\bar{C}^0_{P_r,T_r}$ and $\bar{V}^0_{P_r,T_r}$ and the equations of state parameters for $NaCl^0$ listed in Table 2. These values have been used to extend the range of temperatures and pressures for the g function in Eqns. 10 and 13–15 using the complete set of experimental values of log K for $NaCl^0$ (Shock et al., 1992). It can be seen in Fig. 3 that the regression curves are closely consistent with all of the experimental data shown in the figure. Combining the equation of state parameters for $NaCl^0$ in Table 2 with Eqn. 18 and the values of the g function computed by Shock et al. (1992) permits calculation of $\Delta\bar{G}^0_{NaCl^0}$ at pressures and temperatures from 1 to 5 kb and 25 to 1000°C.

The values of $\bar{S}^0_{P_r,T_r}$, $\bar{C}^0_{P_r,T_r}$, and $\bar{V}^0_{P_r,T_r}$, and ω for $NaCl^0$ retrieved in the regression calculations described above are similar to those for numerous other alkali halide and monovalent chloride complexes (see below). The standard partial molal properties of all these species vary smoothly and systematically as functions of the corresponding properties of the cations and anions. However, for many of the neutral aqueous complexes considered in the following pages, the experimental equilibrium constants reported in the literature do not extend over sufficient ranges of low pressure and high temperature to retrieve reliable values of ω. Under these circumstances, the hypothesis was adopted as a first approximation that the Born coefficients for all neutral metal complexes are approximately the same as that derived above for $NaCl^0$, which leads to

$$\omega_{P_r,T_r} = -0.038 \times 10^5 \quad (42)$$

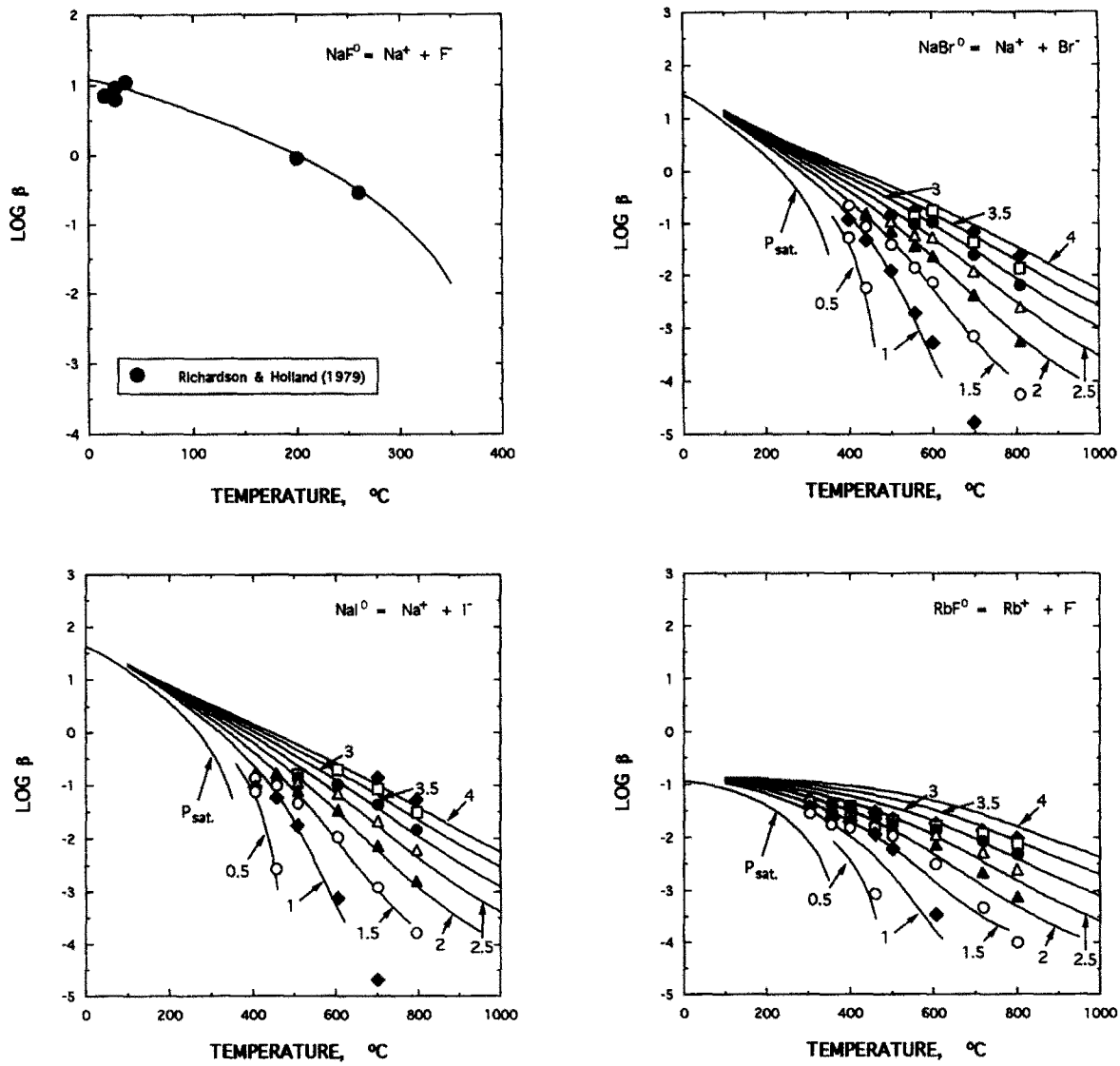

Fig. 8. Logarithms of the dissociation constants of NaF^0, $NaBr^0$, NaI^0, RbF^0, $RbBr^0$, RbI^0, KBr^0, KI^0, $CsBr^0$, and CsI^0 as functions of temperature and pressure (labelled in kb). The curves were generated by regression of the experimental data reported by Richardson and Holland (1979) and Oelkers and Helgeson (1988) represented by the symbols (see text and Table 4).

This hypothesis is strongly supported by the fact that values of ω retrieved by regression of log K for neutral metal complexes for which sufficient experimental data are available to justify such retrieval are remarkably close to that of $NaCl^0$ (see below).

4.2. $AgCl^0$, $AgCl_2^-$, $PbCl^+$, $PbCl_2^0$, $PbCl_3^-$, $ZnCl^+$, $ZnCl_2^0$, $NiCl^+$, $FeCl^+$, $MgCl^+$, MgF^+, CaF^+, $Fe(CH_3COO)^+$, $Fe(CH_3COO)_2^0$, $Zn(CH_3COO)^+$, $Zn(CH_3COO)_2^0$, $Zn(CH_3COO)_3^-$, $CaSO_4^0$, KSO_4^-, and $HSiO_3^-$

Regression of the experimental values of the logarithms of the stepwise and overall dissociation constants (log K and log β, respectively) represented by the symbols in Figs. 4 and 5 resulted in the curves shown in the figures and the equations of state parameters given for these species in Table 2. It can be seen in Figs. 4 and 5 that the regression curves closely represent the bulk of the experimental data, some of which (e.g., those for the dissociation of $ZnCl^+$) contradict one another. A distinctive feature of the experimental dissociation constants shown in Figs. 4 and 5 is that they represent a wide range of temperature at low pressures. Under these circumstances, reliable values of $\Delta\bar{G}^0_{f,P_r,T_r}$, $\bar{S}^0_{P_r,T_r}$, and $\bar{C}^0_{P_r,T_r}$ can be obtained by regression of the experimental data with Eqns. 39 and 41 using Eqns. 40 or 42.

The experimentally derived dissociation constants for the two silver chloride complexes in Fig. 4 cover a wide range of temperature from 18° to 353°C, which permits retrieval of $\Delta\bar{G}^0_{f,P_r,T_r}$, $\bar{S}^0_{P_r,T_r}$, $\bar{C}^0_{P_r,T_r}$, and ω_{P_r,T_r} from regression of the data with Eqn. 39. It can be seen in Fig. 4 that the regression

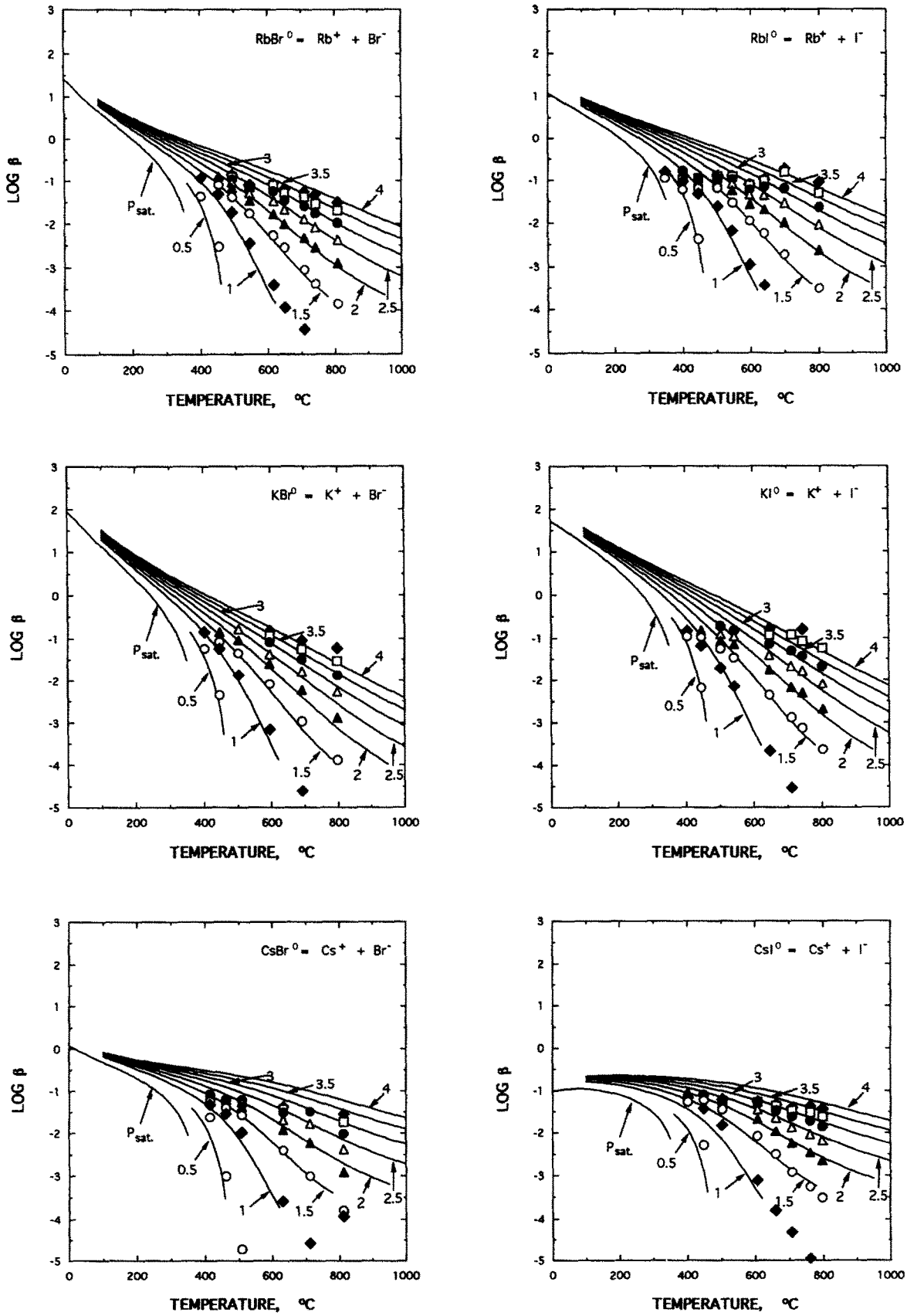

Fig. 8. (continued)

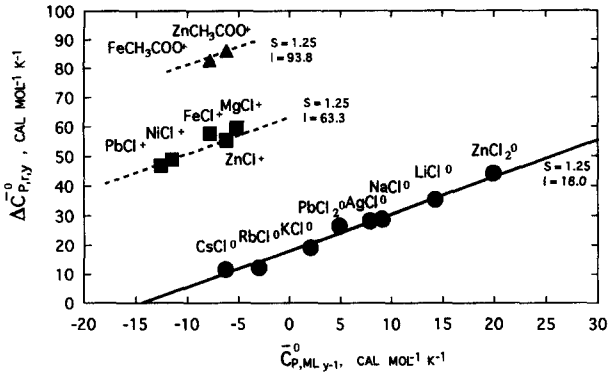

Fig. 9. Correlation of the standard partial molal heat capacity of association ($\Delta\bar{C}^0_{P,r,y}$) for addition of a monovalent ligand to a mono valent or divalent cationic species (ML^{z+1}_{y-1}) with the standard partial molal heat capacity of the monovalent or divalent cationic species ($\bar{C}^0_{P,ML^{z+1}_{y-1}}$) at 25°C and 1 bar (Eqn. 51). The symbols represent values computed from thermodynamic data taken from Table 2.

curves for these species are consistent with the data near 25°C and the high temperature values of log K and log β reported by Seward (1976), but not with those determined by Ivanenko and Pamfilova (1975). It is apparent in Fig. 4 that the trend of the values of log β for $AgCl_2^-$ given by Ivanenko and Pamfilova (1975) is not consistent with the results of other experimental studies at or near 25°C. Values of log β reported by Zotov et al. (1986a,b) were not included in Fig. 4 because they are based on assumptions for the heat capacities of reaction inconsistent with the equations of state used in the present study. Experimental data reported in the literature for $AgCl_3^{2-}$ and $AgCl_4^{3-}$ are considered in later pages.

In contrast to the dissociation constants for the silver chloride complexes shown in Fig. 4, none of the experimental dissociation constants for the three lead chloride complexes represented by the symbols for these species in the figure extend to temperatures high enough to retrieve values of ω_{P_r,T_r}. Consequently, Eqns. 39 and 40 or 42 were used to retrieve the values of $\Delta\bar{G}^0_{f,P_r,T_r}$, $\bar{S}^0_{P_r,T_r}$, and $\bar{C}^0_{P_r,T_r}$ for $PbCl^+$, $PbCl_2^0$, and $PbCl_3^-$ in Table 2. It can be seen in Fig. 4 that the regression curves for all three lead chloride complexes agree closely with the experimental data of Seward (1984). The experimental data for the fourth lead chloride complex reported by Seward (1984) are the subject of subsequent discussion.

Although the experimental dissociation constants of the silver and lead chloride complexes discussed above were obtained from direct measurements of the solubility of crystalline silver chloride ($AgCl_{(c)}$) and spectrophotometric studies of Pb-chloride solutions, the experimental dissociation constants represented by reported by Ruaya and Seward (1986) for the zinc chloride complexes in Fig. 4 were derived indirectly by measuring $AgCl_{(c)}$ solubilities in HCl solutions containing zinc chloride. Consequently, the dissociation constants for $ZnCl^+$ and $ZnCl_2^0$ derived by Ruaya and Seward (1986) depend on their earlier measurements of log K and log β for the silver chloride complexes. Substantial disagreement between the experimental data reported by Ruaya and Seward (1986) and Bourcier and Barnes (1987) is evident in Fig. 4. The dissociation constants reported by Bourcier and Barnes (1987) were derived from measured solubilities of $ZnO_{(c)}$ and $ZnCO_{3(c)}$ in $NaCl—CO_2—H_2O$ solutions using independently estimated equilibrium constants for the hydrolysis of these minerals which are incon-

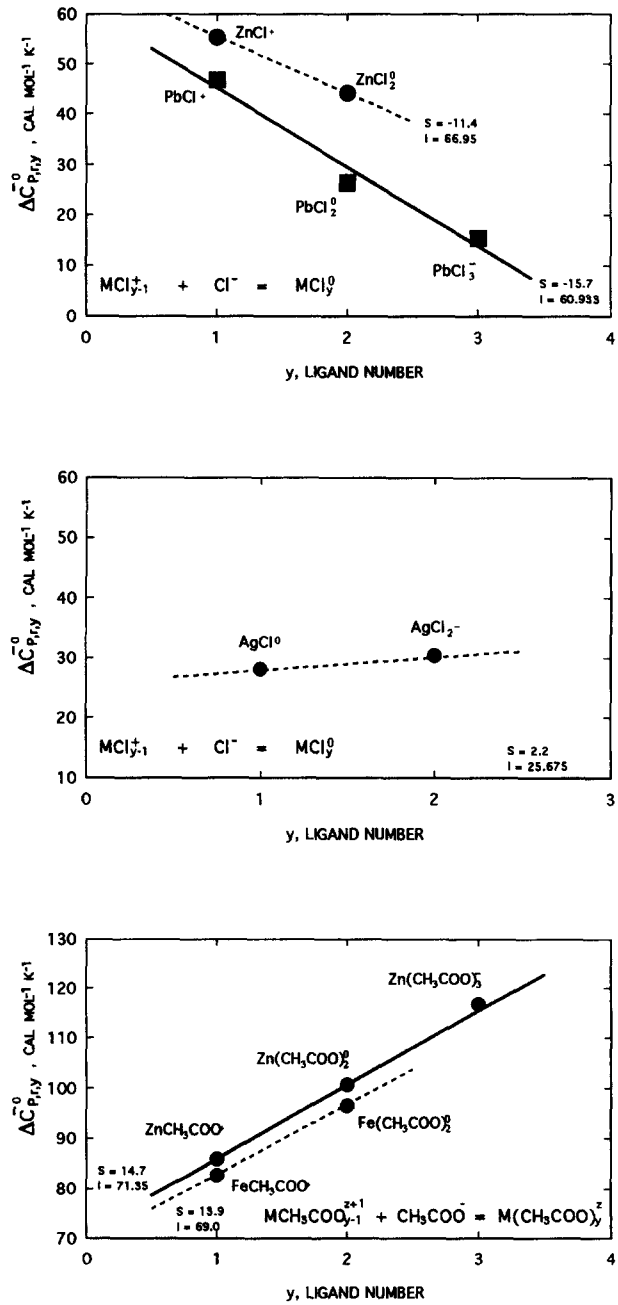

Fig. 10. Correlation of the stepwise standard partial molal heat capacities of association ($\Delta\bar{C}^0_{P,r,y}$) corresponding to addition of a monovalent ligand to a monovalent or divalent cation with the ligand number y at 25°C and 1 bar (Eqn. 55). The symbols represent values computed using thermodynamic data taken from Table 2.

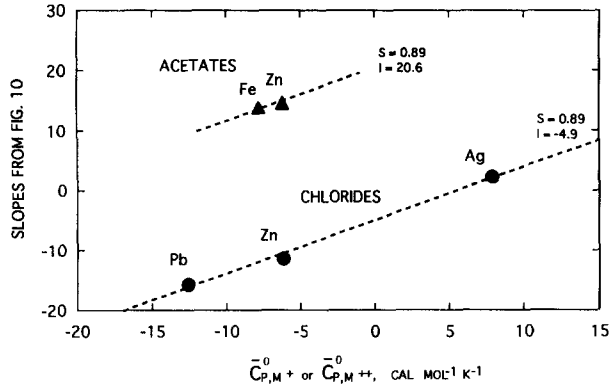

Fig. 11. Slopes ($\hat{a}$) of the lines in Fig. 10 as a function of the standard molal heat capacities of the cations ($\bar{C}^0_{P,M^{Z+y}}$) at 25°C and 1 bar. The lines are consistent with Eqns. 56–57.

sistent with thermodynamic data given by Shock and Helgeson (1988). Attempts were made in the present study to resolve these discrepancies without success. Because the dissociation constants for $ZnCl^+$ and $ZnCl_2^0$ in Fig. 4 reported by Ruaya and Seward (1986) are consistent with those determined at 25°C and 1 bar by Marcus and Mayden (1963), they were used in the present study to retrieve the equations of state parameters for these species in Table 2. Equations 39 and 40 or 42 were used in the regression calculations to retrieve values of $\Delta\bar{G}^0_{f,P_r,T_r}$, $\bar{S}^0_{P_r,T_r}$, and $\bar{C}^0_{P_r,T_r}$ for both $ZnCl^+$ and $ZnCl_2^0$. Predicted values of log β for these complexes can be compared with the independently derived experimental values of log β (Plyasunov and Ivanov, 1991; Cygan et al., 1994; see below). The experimental values of log K and log β for the remaining complexes shown in Figs. 4 and 5 were regressed with Eqns. 39 and 40 for the charged complexes and Eqns. 39 and 42 for the neutral complexes. Because the data for $CaSO_4^0$ extend to 350°C, $\Delta\bar{G}^0_{f,P_r,T_r}$,

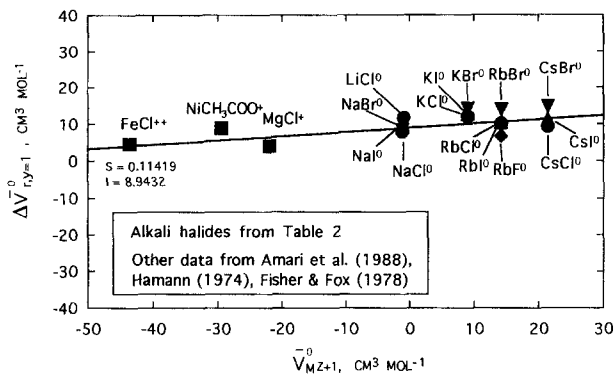

Fig. 12. Correlation of the standard partial molal volume of association for addition of a monovalent ligand to a monovalent cation ($\Delta\bar{V}^0_{r,y=1}$) with the standard partial molal volume of the cation ($\bar{V}^0_{M^{Z+1}}$) at 25°C and 1 bar (Eqn. 61). The solid squares represent values computed from thermodynamic data taken from Amari et al. (1988), Hamann (1974), and Fisher and Fox (1978). The symbols for the volumes of the alkali halides correspond to values taken from Table 2.

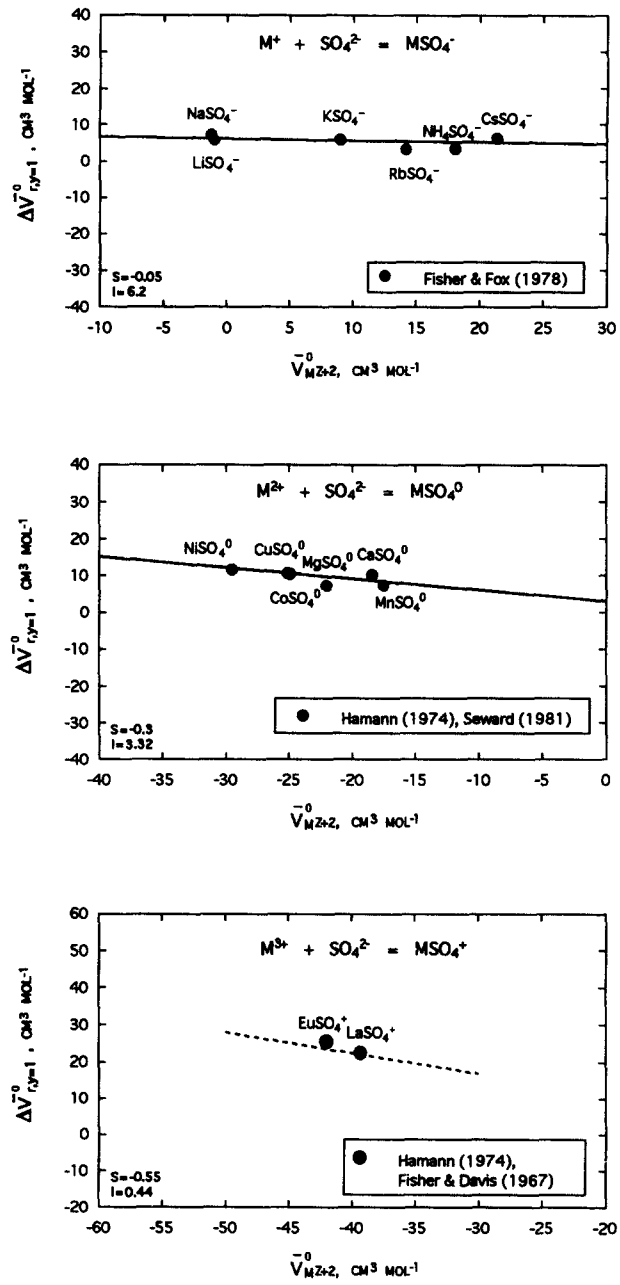

Fig. 13. Correlation of the standard partial molal volumes of association of sulfate ion pairs involving monovalent, divalent or trivalent cations ($\Delta\bar{V}^0_{r,y=1}$) with the standard partial molal volumes of the cations ($\bar{V}^0_{M^{Z+2}}$) at 25°C and 1 bar (Eqn. 63). The symbols represent experimental values reported in the literature. The dashed line was generated from the slopes and intercepts of the solid lines consistent with Eqns. 63–65.

$\bar{S}^0_{P_r,T_r}$, $\bar{C}^0_{P_r,T_r}$, and ω_{P_r,T_r} were retrieved for $CaSO_4^0$ using only Eqn. 39. The results of the regression calculations are shown in Table 2.

4.3. $LiCl^0$, KCl^0, $RbCl^0$, and $CsCl^0$

Log K values for $LiCl^0$, KCl^0, $RbCl^0$, and $CsCl^0$ have been computed from conductance measurements reported in the literature for temperatures from 300 to 800°C at

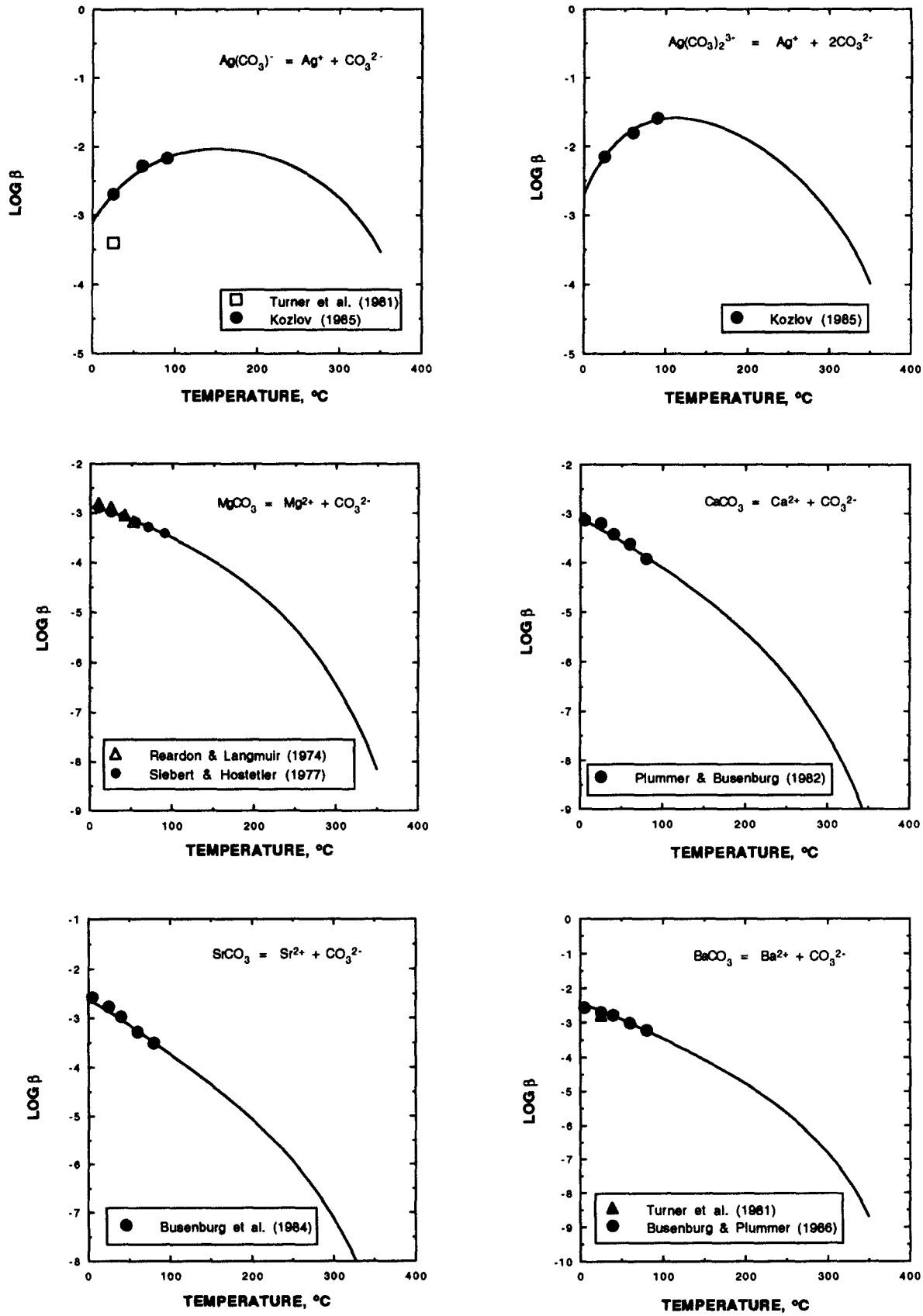

Fig. 14. Logarithms of the dissociation constants of carbonate complexes as functions of temperature at P_{SAT}. The curves were generated by regression of the experimental data represented by the symbols using equations and estimates cited in Table 4 (see text).

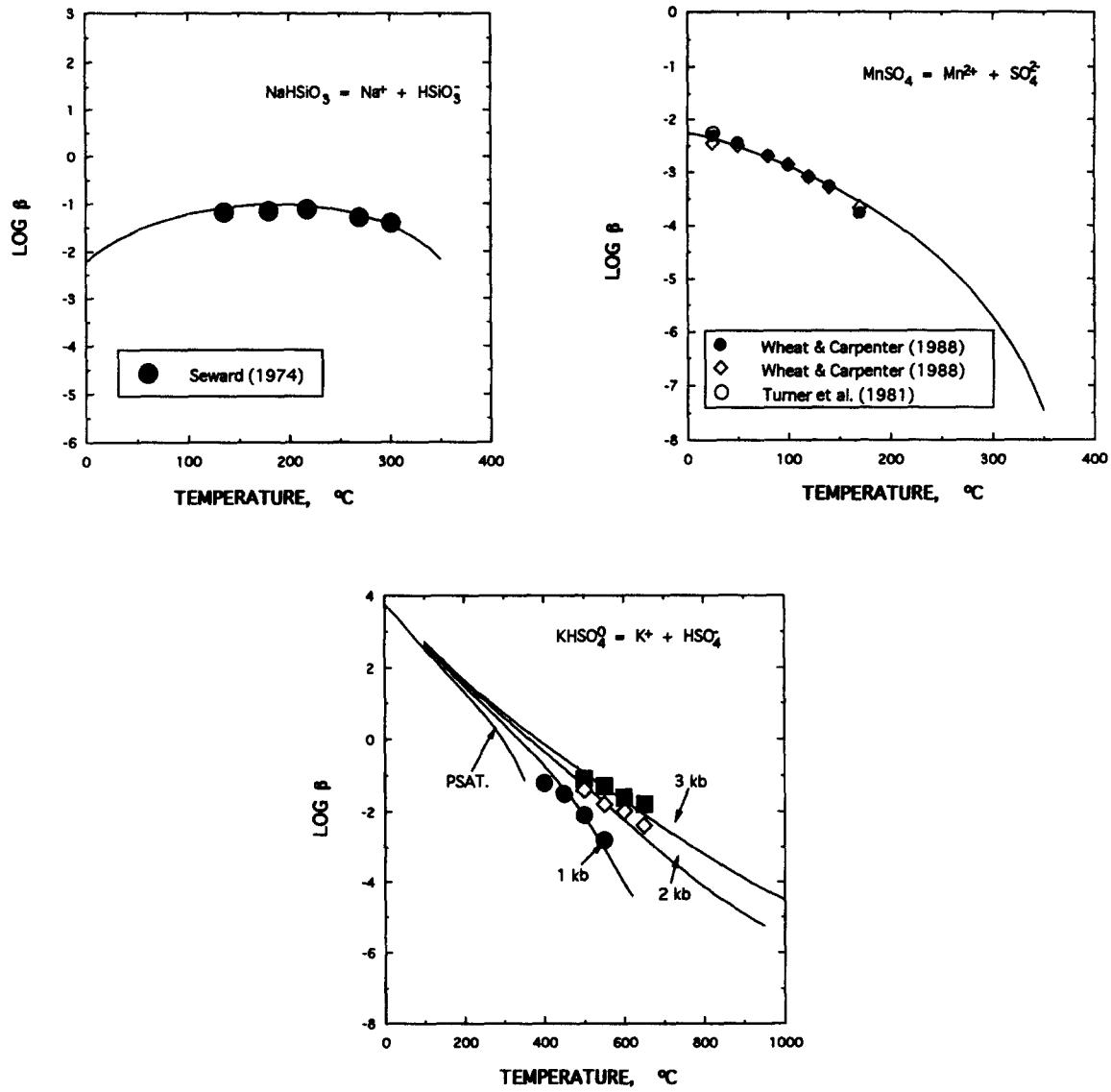

Fig. 15. Logarithms of the dissociation constants of $NaHSiO_3^0$, $MnSO_4^0$, and $KHSO_4^0$ as functions of temperature at constant pressure (labelled in kb) and/or at P_{SAT}. The curves were generated by regression of the experimental data represented by the symbols using equations and estimates cited in Table 4 (see text). The experimental dissociation constants for $KHSO_4^0$ were taken from Helgeson and Kirkham (1976).

pressures from 500 bars to 4 kb by Oelkers and Helgeson (1988). Nevertheless, because no experimental conductance data are available for temperatures below 300°C, reliable values of $\Delta\bar{G}^0_{f,P_r,T_r}$, $\bar{S}^0_{P_r,T_r}$, $\bar{C}^0_{P_r,T_r}$, $\bar{V}^0_{P_r,T_r}$ and ω_{P_r,T_r} cannot be retrieved simultaneously by regression of the supercritical values of log K with Eqn. 38. This problem can be overcome in a first approximation by using the values of $\bar{S}^0_{P_r,T_r}$ in Table 2 for $NaCl^0$, $AgCl^0$, and $PbCl_2^0$ and the approach described below to generate estimates of $\bar{S}^0_{P_r,T_r}$ for $LiCl^0$, KCl^0, $RbCl^0$, and $CsCl^0$, which can then be used in regression calculations to obtain values of $\Delta\bar{G}^0_{f,P_r,T_r}$, $\bar{C}^0_{P_r,T_r}$, $\bar{V}^0_{P_r,T_r}$, and ω_{P_r,T_r} from the supercritical dissociation constants for $LiCl^0$, KCl^0, $RbCl^0$, and $CsCl^0$ reported by Oelkers and Helgeson (1988).

The standard partial molal entropies shown in Table 2 can be used to calculate standard partial molal entropies for stepwise association ($\Delta\bar{S}^0_{r,y}$) reactions to form chloride complexes represented by MCl_y^Z where M designates a metal cation, and y and Z stand for the number of ligands and the charge on the yth complex, respectively. The stepwise association reaction for this complex can be written as

$$MCl_{y-1}^{Z+1} + Cl^- = MCl_y^Z \qquad (43)$$

for which the standard partial molal entropy of reaction is given by

$$\Delta\bar{S}^0_{r,y} = \bar{S}^0_{MCl_y^Z} - \bar{S}^0_{MCl_{y-1}^{Z+1}} - \bar{S}^0_{Cl^-} \qquad (44)$$

Following earlier observations of the systematic variation of $\Delta\bar{S}^0_{r,y}$ with ligand number (George, 1959; Nancollas,

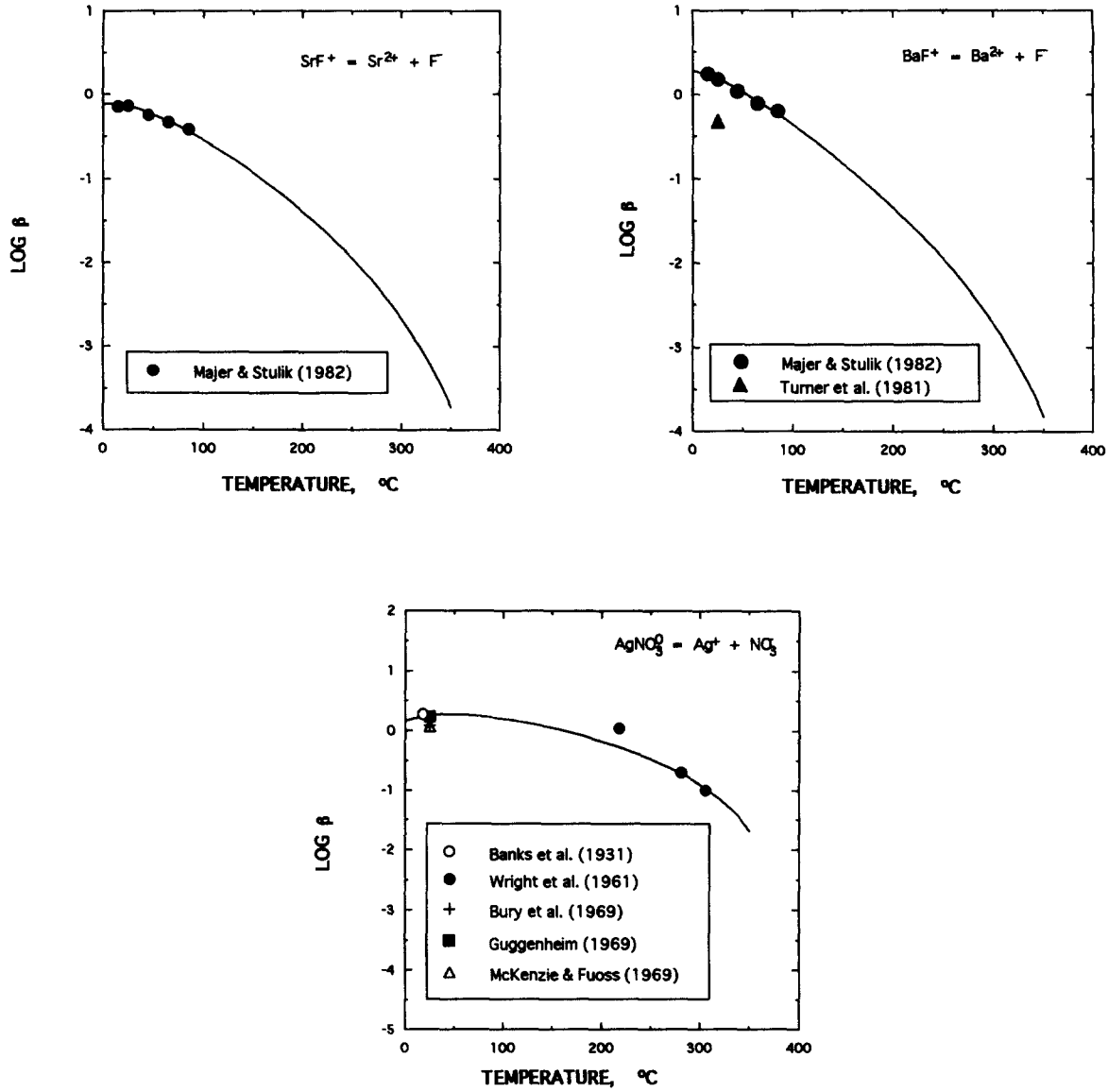

Fig. 16. Logarithms of the dissociation constants of fluoride and nitrate complexes as a function of temperature at P_{SAT}. The curves were generated by regression of the experimental data represented by the symbols using equations and estimates cited in Table 4 (see text).

1960; Davies, 1962), it might be expected that $\Delta\bar{S}^0_{r,y}$ would correlate with $\bar{S}^0_{MCl_{y-1}^{Z+1}}$ for a given ligand. It can be seen in Fig. 6a that this indeed appears to be the case at 25°C and 1 bar for $Z = 0$ and $y = 1$ or 2. The stepwise standard partial molal entropies of association for the three chloride complexes shown in this figure are approximately consistent with

$$\Delta\bar{S}^0_{r,y} = \alpha_{Z=0,Cl^-}\bar{S}^0_{MCl_{y-1}^{Z+1}} + \beta_{Z=0,Cl^-} \quad (45)$$

where

$$\alpha_{Z=0,Cl^-} = 0.357 \quad (46)$$

$$\beta_{Z=0,Cl^-} = -4.085 \quad (47)$$

For $Z = 0$ and $y = 1$ or 2, the correlation of $\Delta\bar{S}^0_{r,y}$ with $\bar{S}^0_{MCl_{y-1}^{Z+1}}$ in Fig. 6a at 25°C and 1 bar is analogous to the correlation shown in Fig. 6b for the standard partial molal entropies of hydration of gaseous ions at 25°C and 1 bar with $\bar{S}^0_{M^+_{(aq)}}$, which is consistent with

$$\Delta\bar{S}^0_{r,y} = 0.1159\bar{S}^0_{M^+_{(aq)}} - 23.353 \quad (48)$$

Correlations such as those shown in Figs. 6a,b are similar to other correlations between various functions of the standard partial molal entropies of aqueous complexes and the inverse radii of the ions in the complexes (Cobble, 1953a,b; Helgeson, 1969; Helgeson et al., 1981).

Regression of the experimental values of log K for $LiCl^0$, KCl^0, $RbCl^0$, and $CsCl^0$ represented by the symbols in Fig. 7 with Eqns. 38 and 45 through 47 generated the values

of $\Delta\bar{G}^0_{f,P_r,T_r}$, $\bar{C}^0_{P_r,T_r}$, $\bar{V}^0_{P_r,T_r}$, and ω_{P_r,T_r} shown for these species in Table 2. It can be seen in Fig. 7 that the regression curves are clearly consistent with the bulk of the experimental data represented by the symbols.

4.4. RbF^0 and MX^0 (Where M Represents Na^+, K^+, Rb^+, or Cs^+, and X Stands for Br^- or I^-)

Experimental values of log K for these fluoride, bromide, and iodide species are available only for temperatures above 300°C. Accordingly, simultaneous retrieval of reliable values of $\Delta\bar{G}^0_{f,P_r,T_r}$, $\bar{V}^0_{P_r,T_r}$, ω_{P_r,T_r}, and either $\bar{S}^0_{P_r,T_r}$ or $\bar{C}^0_{P_r,T_r}$ by regression of the high temperature/pressure dissociation constant data again requires independent values of one or the other of the latter two properties. Owing to the wide range of values represented by the standard molal entropies of Cl^-, Br^-, I^-, or F^- at 25°C and 1 bar, values of $\bar{S}^0_{P_r,T_r}$ for fluoride, bromide, and iodide complexes cannot be estimated with confidence using Eqns. 45–47, which are strictly valid only for chloride complexes. Consequently, regression of log K data arrays for RbF^0 and the alkali bromide and iodide complexes requires independently estimated values of $\bar{C}^0_{P_r,T_r}$.

The curves in Fig. 8 were generated by regression of the experimental data represented by the symbols with Eqn. 38 to retrieve values of $\Delta\bar{G}^0_{f,P_r,T_r}$, $\bar{S}^0_{P_r,T_r}$, $\bar{V}^0_{P_r,T_r}$, and ω for each of the complexes using estimated values of the standard partial molal heat capacities of association at 25°C and 1 bar (see below). It can be seen in these figures that the regression curves are clearly consistent with the bulk of the experimental data represented by the symbols.

5. STANDARD MOLAL HEAT CAPACITY CORRELATIONS AT 25°C AND 1 BAR

Reaction 43 can be generalized for addition of the yth monovalent ligand (L^-) to the complex represented by $y-1$ (ML^{Z+1}_{y-1}) to form the yth complex with charge Z (ML^Z_y) by writing

$$ML^{Z+1}_{y-1} + L^- = ML^Z_y \qquad (49)$$

for which the standard partial molal heat capacity of reaction ($\Delta\bar{C}^0_{P_r,y}$) is given by

$$\Delta\bar{C}^0_{P_r,y} = \bar{C}^0_{P,ML^Z_y} - \bar{C}^0_{P,ML^{Z+1}_{y-1}} - \bar{C}^0_{P,L^-} \qquad (50)$$

Various correlations among the terms in this equation have been developed for different groups of complexes, a number of which are discussed below.

5.1. Standard Partial Molal Heat Capacities of Complexes Containing Mono- and Divalent Cations and Monovalent Ligands

By analogy with Fig. 6a and Eqn. 45, it might be expected that the values of $\Delta\bar{C}^0_{P_r,y}$ for the association of neutral chloride complexes would exhibit a linear correlation with $\bar{C}^0_{P,MCl^{Z+1}_{y-1}}$. Values of $\bar{C}^0_{P_r,T_r}$ for the aqueous metal complexes containing monovalent ligands in Table 2 were used together with values of $\bar{C}^0_{P_r,T_r}$ for the metal cations and ligands at 25°C and 1 bar (Shock and Helgeson, 1988) and Eqn. 50 to calculate the values of $\Delta\bar{C}^0_{P_r,y}$ represented by the symbols shown in Fig. 9. Although a number of the symbols shown in this figure are scattered and only two data points are available for the acetate complexes, it can be seen that the symbols fall into three groups which are approximately consistent with the three parallel lines shown in the figure. The equations of these lines are given by

$$\Delta\bar{C}^0_{P_r,y=1\text{ or }2} = 1.25\bar{C}^0_{P,M^{Z+1}} + d_{Z+1} \qquad (51)$$

where d_{Z+1} equals 18.0 cal mol^{-1} K^{-1} for chloride complexes of monovalent cations, 63.3 cal mol^{-1} K^{-1} for chloride complexes of divalent cations, and 93.8 cal mol^{-1} K^{-1} for acetate complexes of divalent cations. Adopting the hypothesis that in a first approximation d_{Z+1} for the chloride complexes in Fig. 9 can be regarded as a linear function of cation charge, it follows from the intercepts of the two lower lines in this figure that

$$d_{Z+1} = 45.3(Z+1) - 27.3 \qquad (52)$$

which can be combined with Eqn. 51 to give

$$\Delta\bar{C}^0_{P_r,y=1\text{ or }2} = 1.25\bar{C}^0_{P,M^{Z+1}} + 45.3(Z+1) - 27.3 \qquad (53)$$

For acetate complexes of divalent metals we can write an explicit statement of Eqn. 51 as

$$\Delta\bar{C}^0_{P_r,y=1} = 1.25\bar{C}^0_{P,M^{2+}} + 93.8 \qquad (54)$$

Equations 53 and 54 can be used to calculate provisional estimates of $\Delta\bar{C}^0_{P_r}$ at 25°C and 1 bar from which values of $\bar{C}^0_{P_r,T_r}$ can be computed for aqueous metal complexes with monovalent ligands for which insufficient experimental data are available to permit retrieval of accurate values of $\bar{C}^0_{P_r,T_r}$ by regression of the data. Although Eqns. 53 and 54 were generated for chloride and acetate complexes, respectively, they can also be used for other complexes of monovalent ligands with heat capacities ($\bar{C}^0_{P,L^-}$) that are within a few cal mol^{-1} deg^{-1} of the values for Cl^- or CH_3COO^-. For example, Eqn. 53 can be used to estimate heat capacities of association for fluoride, bromide, iodide, and cyanide complexes. Unlike the values of $\bar{S}^0_{P_r,T_r}$, those of $\bar{C}^0_{P_r,T_r}$ for F^-, Cl^-, Br^-, I^-, and CN^- at 25°C and 1 bar fall in a narrow range (from −27.1 to −30.4 cal mol^{-1} K^{-1}). Hence, the values of the parameters in Eqn. 51 for all these ligands should be essentially the same as those for Cl^- in Eqn. 53. Adopting this hypothesis in a first approximation, Eqn. 53 can be used to generate provisional estimates of the standard partial molal heat capacity of reaction at 25°C and 1 bar for stepwise association of complexes involving F^-, Br^-, I^-, and CN^- that have the stoichiometry represented by ML^0, ML^+, or ML^0_2. A number of such estimates are shown in Tables 3 and 12.

Estimates of $\bar{C}^0_{P_r,y}$ at 25°C and 1 bar for aqueous metal

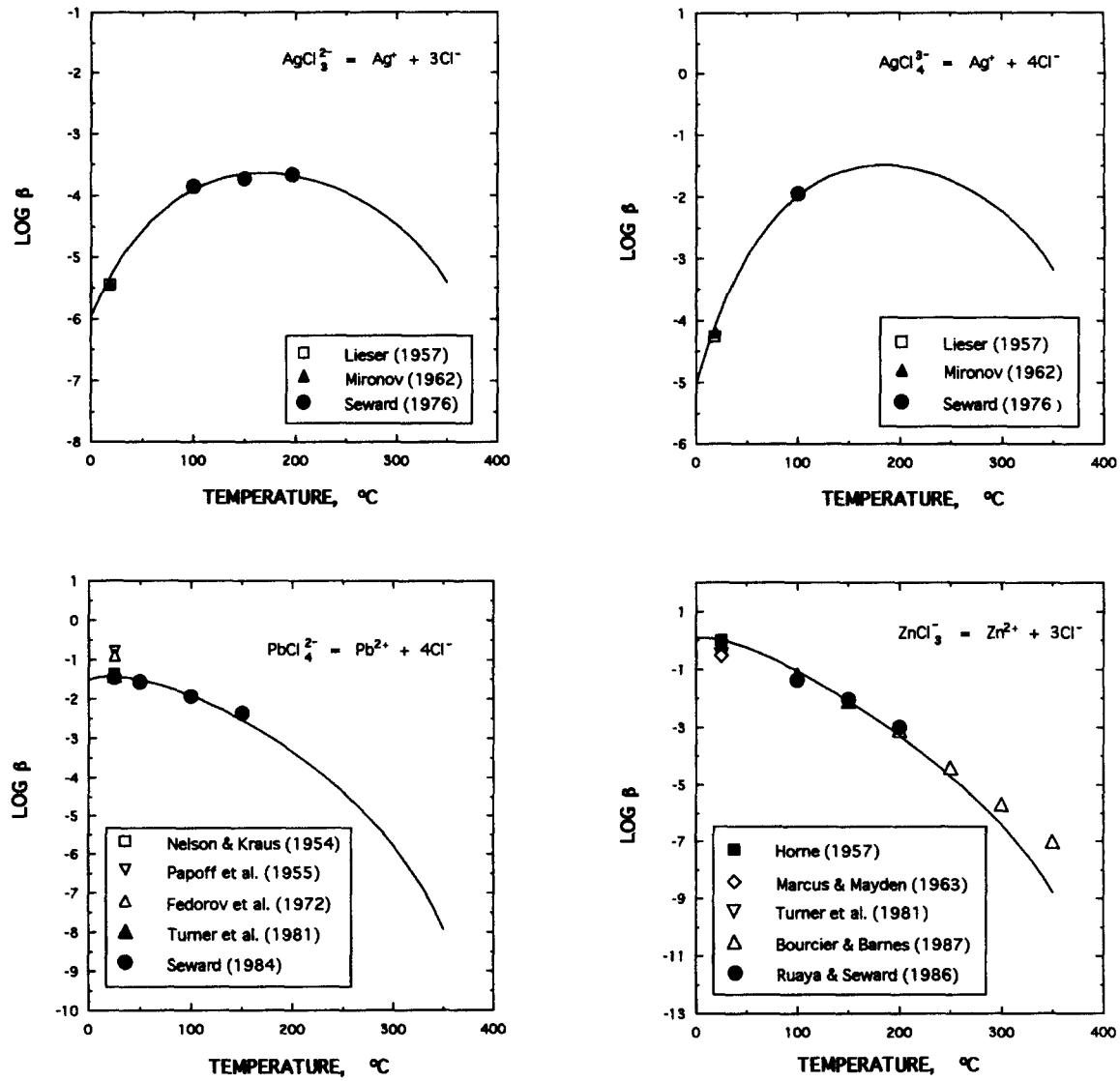

Fig. 17. Logarithms of the dissociation constants of chloride complexes as functions of temperature at P_{SAT}. The curves were generated by regression of the experimental data represented by the symbols using equations and estimates cited in Table 4 (see text).

complexes containing monovalent ligands for which $y > 1$ can be calculated by taking account of the provisional correlations are shown in Fig. 10, where the values of $\bar{C}^0_{P,y}$ in Table 2 for chloride complexes of Zn^{2+}, Pb^{2+}, and Ag^+, and those for acetate complexes of Fe^{2+} and Zn^{2+}, are plotted against y. The solid and dashed lines in Fig. 10 are consistent with

$$\Delta\bar{C}^0_{P,y>1} = \hat{a}y + \Delta\bar{C}^0_{P,y=1} \quad (55)$$

where $\Delta\bar{C}^0_{P,y=1}$ is given by Eqns. 53 or 54 and $\hat{a}$ is equal to 2.2, −11.4, −15.7, 13.9, and 14.7 cal mol^{-1} K^{-1} for silver, zinc, and lead chloride complexes, and iron and zinc acetate complexes, respectively. These values of $\hat{a}$ are plotted as symbols in Fig. 11 against the standard partial molal heat capacities at 25°C and 1 bar of the cations in the complexes ($\bar{C}^0_{P,M^{z+y}}$). The lines in this figure for the chloride and acetate complexes are consistent with

$$\hat{a} = 0.89\bar{C}^0_{P,M^{z+y}} - 4.9 \quad (56)$$

$$\hat{a} = 0.89\bar{C}^0_{P,M^{z+y}} + 20.6 \quad (57)$$

respectively.

Combining Eqns. 55 and 56 for chloride complexes leads to

$$\Delta\bar{C}^0_{P,y>1} = (0.89\bar{C}^0_{P,M^{z+y}} - 4.9)y + \Delta\bar{C}^0_{P,y=1} \quad (58)$$

Similarly, combining Eqns. 55 and 57 for acetate complexes results in

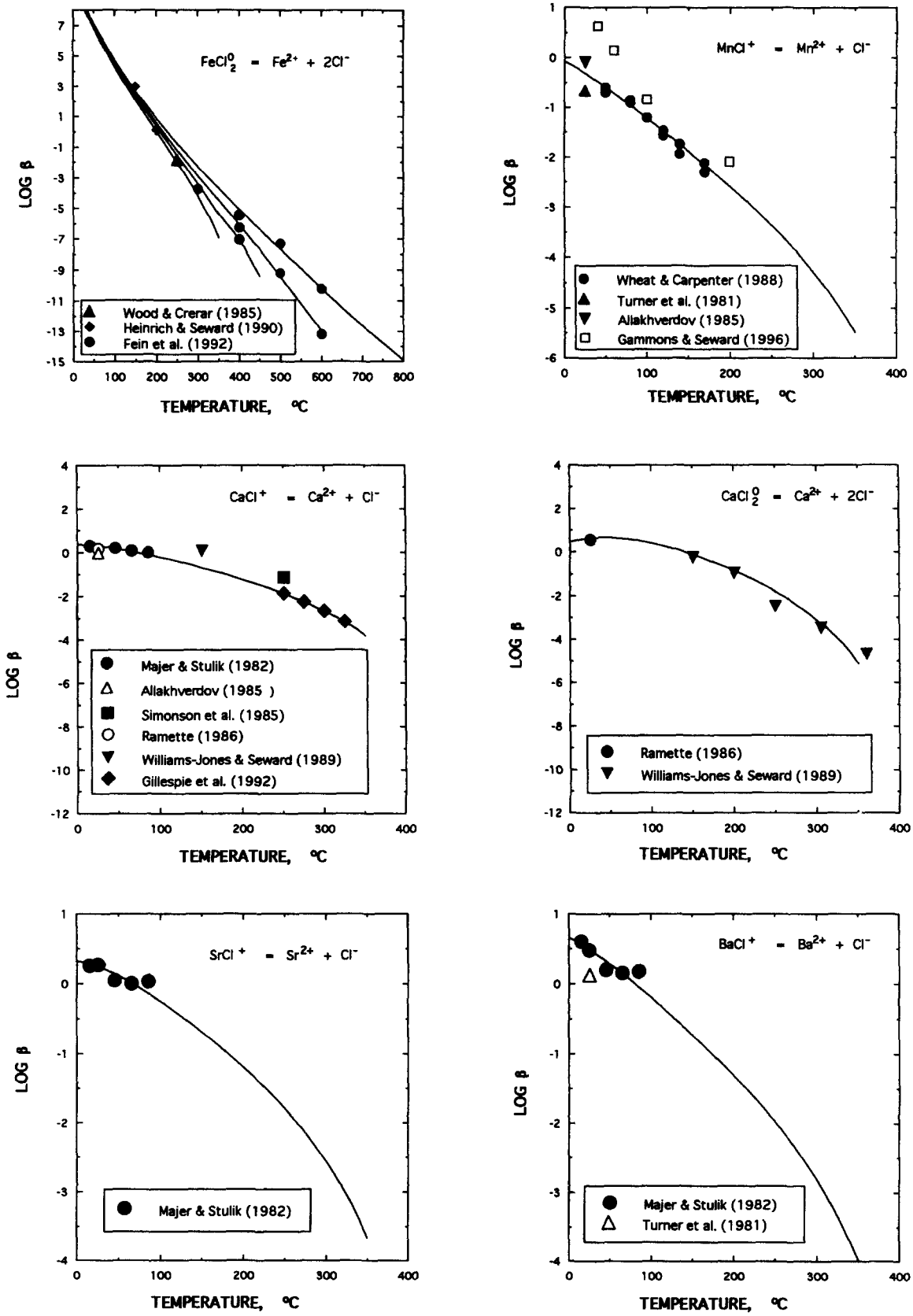

Fig. 17. (continued)

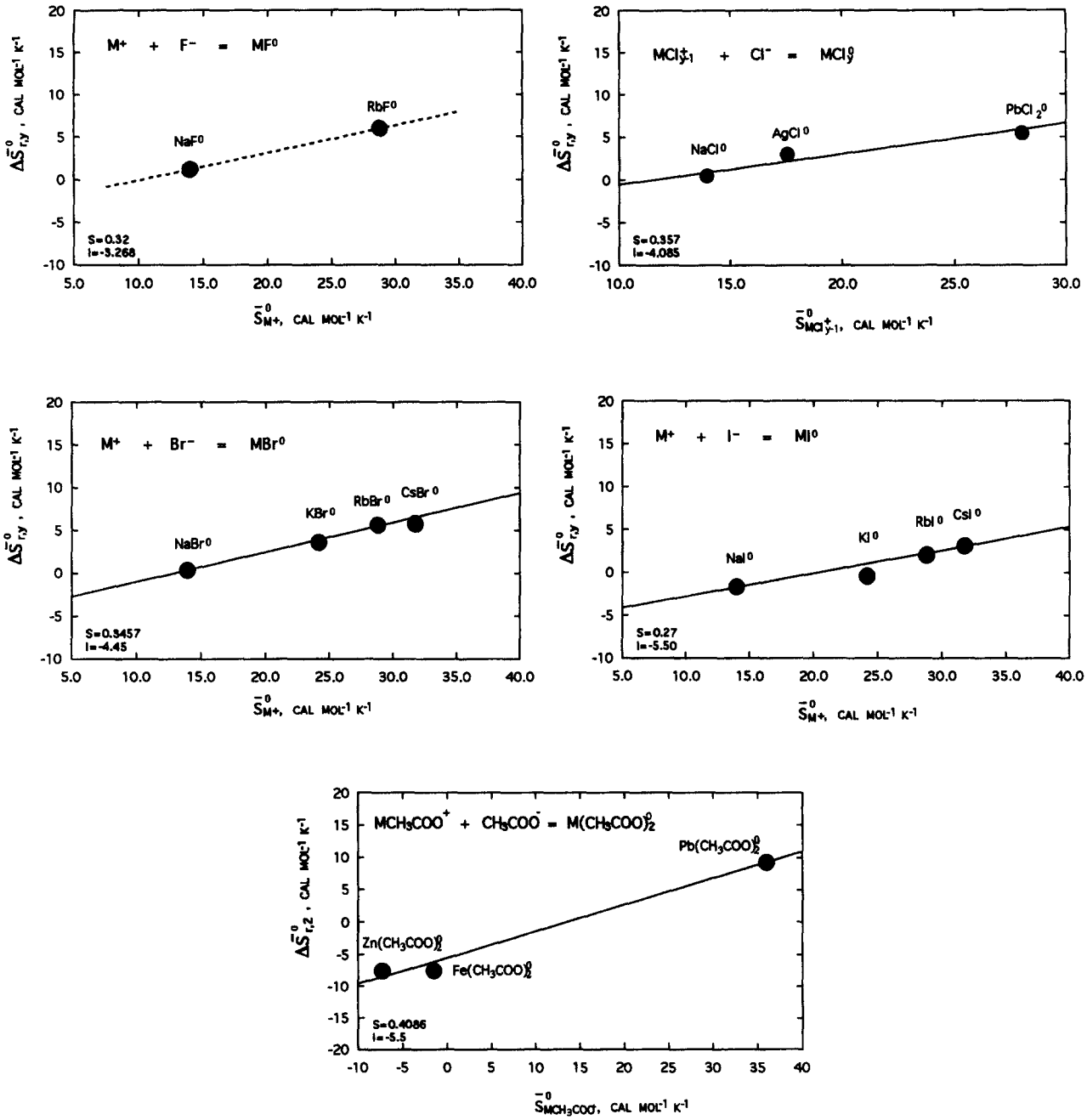

Fig. 18. Correlation of the standard partial molal entropy of association ($\Delta\bar{S}^0_{r,y}$, y = 1, or 2) for addition of a monovalent ligand to a cationic species (ML^+_{y-1}) with the standard partial molal entropy of the cationic species ($\bar{S}^0_{M^+}$ or $\bar{S}^0_{ML^+_{y-1}}$) at 25°C and 1 bar. The symbols represent values computed using thermodynamic data taken from Tables 2 and 3. The lines shown are consistent with Eqn. 66.

$$\Delta\bar{C}^0_{P_{r,y>1}} = (0.89\bar{C}^0_{P,M^{Z+y}} + 20.6)y + \Delta\bar{C}^0_{P_{r,y=1}} \quad (59)$$

Equations 53 and 58 for chloride complexes and 54 and 59 for divalent metal acetate complexes can be used to calculate provisional estimates of $\Delta\bar{C}^0_{P_{r,y}}$ for metal ion complexes containing these and similar ligands (for application of these equations to acetate complexes, see Shock and Koretsky, 1993).

The experimental dissociation constants and regression curves depicted in Figs. 3–5, 7, and 8 for the metal ion complexes shown in Table 2 represent wide ranges of pressure and temperature. Experimental values of log K are also available for many other complexes, but only over relatively restricted ranges of temperature at low or at high pressures. Regression of the latter values of log K to retrieve reliable equations of state parameters and values of $\Delta\bar{G}^0_{f,P_r,T_r}$ and $\bar{S}^0_{P_r,T_r}$ for the complexes at 25°C and 1 bar requires independent values of $\bar{C}^0_{P_r,T_r}$ and $\bar{V}^0_{P_r,T_r}$ for these species, which, in

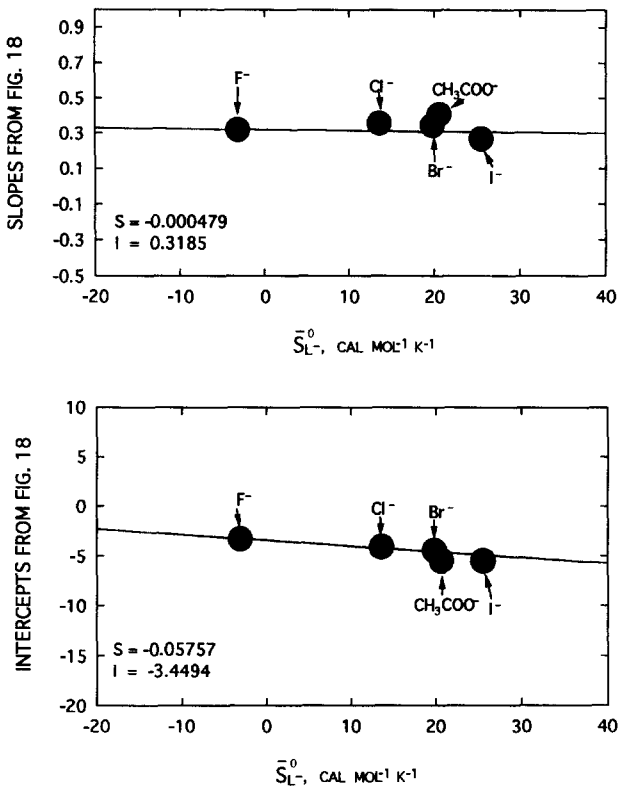

Fig. 19. Slopes ($\alpha_{Z=0,L^-}$) and intercepts ($\beta_{Z=0,L^-}$) of the lines in Fig. 18 (symbols) as functions of the standard partial molal entropies of the ligands ($\bar{S}^0_{L^-}$) at 25°C and 1 bar. The lines shown are consistent with Eqns. 67–68.

the latter case, can be estimated from correlation algorithms like those summarized below.

6. STANDARD MOLAL VOLUME CORRELATIONS AT 25°C AND 1 BAR

6.1. Complexes Containing Monovalent Ligands

The values of $\bar{V}^0_{P_r,T_r}$ for metal complexes of monovalent ligands given in Table 2 can be used together with values of $\bar{V}^0_{P_r,T_r}$ for metal cations and ligands (Shock and Helgeson, 1988) to calculate the standard partial molal volume of association ($\Delta\bar{V}^0_{r,y}$) from

$$\Delta\bar{V}^0_{r,y} = \bar{V}^0_{ML_y^Z} - \bar{V}^0_{ML_{y-1}^{Z+1}} - \bar{V}^0_{L^-} \qquad (60)$$

Values of $\Delta\bar{V}^0_{r,y=1}$ at 25°C and 1 bar computed from Eqn. 60 for monovalent, divalent, and trivalent halide complexes, and one divalent acetate complex are plotted as symbols in Fig. 12. Although the standard partial molal volumes at 25°C and 1 bar of aqueous F^-, Cl^-, Br^-, I^-, and CH_3COO^- differ substantially from one another (Shock and Helgeson, 1988), it can be seen in this figure that $\Delta\bar{V}^0_{r,y=1}$ for metal ion complexes involving these ligands are not much different from one another. Although the symbols in Fig. 12 exhibit considerable scatter and overlap, it can be deduced by inspection of the figure that they are within ~5 cm^{-1} of the values represented by the straight line, which is consistent with

$$\Delta\bar{V}^0_{r,y} = 0.11419\bar{V}^0_{M^{Z+1}} + 8.9432 \qquad (61)$$

Estimating stepwise standard partial molal volumes of association at 25°C and 1 bar for $y > 1$ is hampered by the paucity of pertinent experimental data. However, the fact

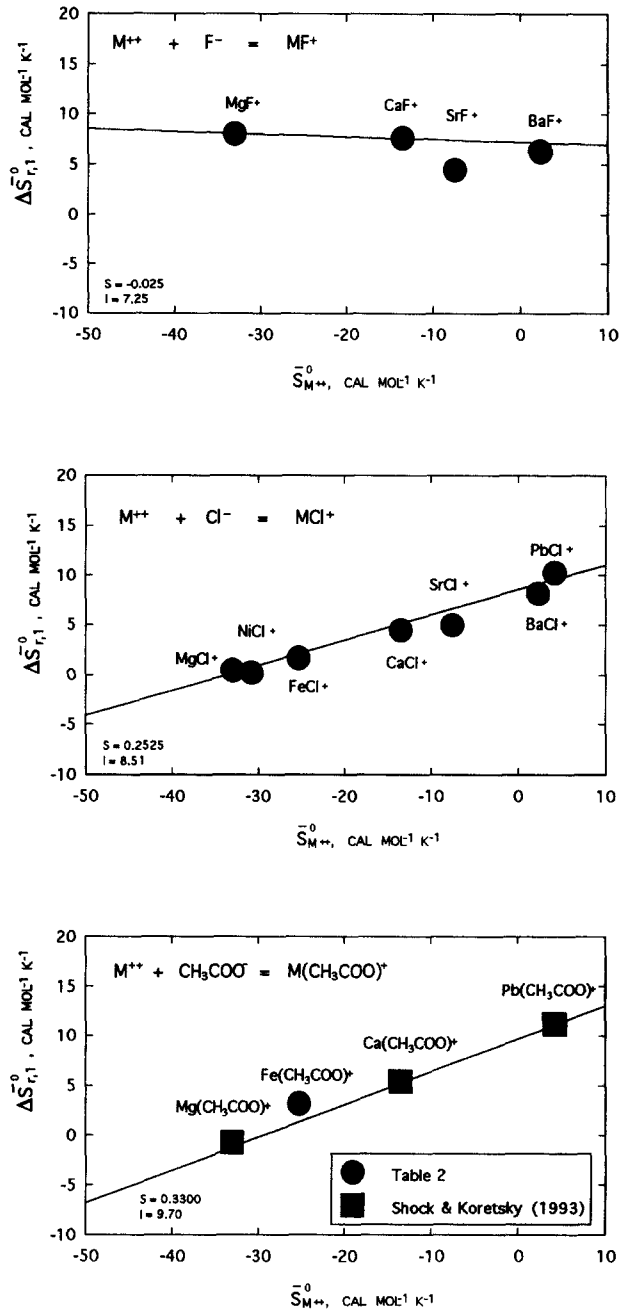

Fig. 20. Correlation of the standard partial molal entropy of association ($\Delta\bar{S}^0_{r,y}$, $y = 1$) corresponding to addition of a monovalent ligand to a divalent cation with the standard partial molal entropy of the cation ($\bar{S}^0_{M^{2+}}$) at 25°C and 1 bar. The symbols represent values computed using thermodynamic data taken from Shock and Koretsky (1993) or Tables 2 and 3.

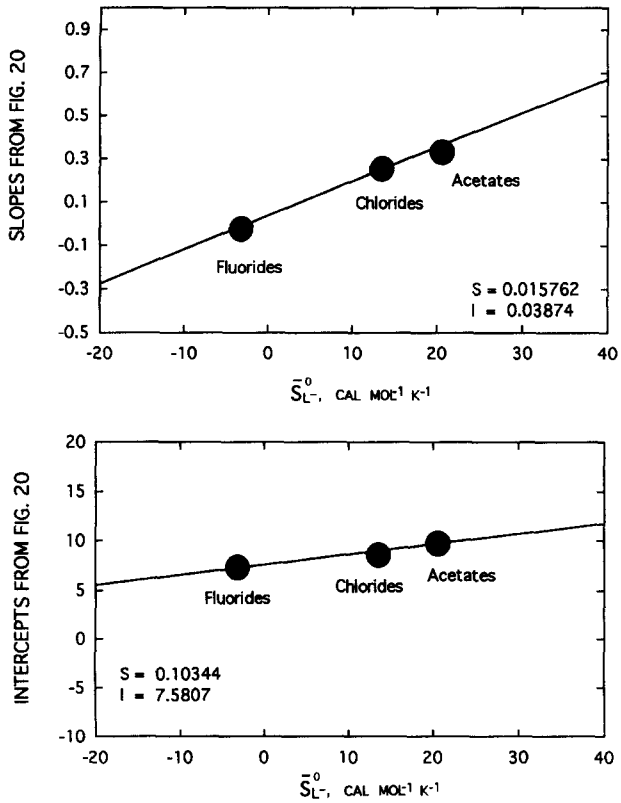

Fig. 21. Slopes ($\alpha_{Z=1,L}$) and intercepts ($\beta_{Z=1,L^-}$) of the lines in Fig. 20 (symbols) as functions of the standard partial molal entropies of the ligands ($\bar{S}^0_{L^-}$) at 25°C and 1 bar. The lines shown are consistent with Eqns. 69–70.

that Eqn. 61 represents adequately $\Delta\bar{V}^0_{r,y=1}$ in Fig. 12 for both charged and neutral aqueous complexes involving cations of different charge and a variety of ligands suggests that Eqn. 61 can be generalized in a first approximation to

$$\Delta\bar{V}^0_{r,y} = 0.11419\bar{V}^0_{M^{Z+1}_{y-1}} + 8.9432 \qquad (62)$$

Prediction of the standard partial molal volumes of $Zn(CN)_4^{2-}$ and $Cd(CN)_4^{2-}$ from Eqn. 62 yields values of 119.6 and 133.0 cm^3 mol^{-1}, respectively. As provisional estimates, these values compare favorably with 110.6 and 125.8 cm^3 mol^{-1}, respectively, given by Akitt (1980).

6.2. Standard Partial Molal Volumes of Complexes Containing Divalent Ligands

Standard partial molal volumes of association of metal sulfate complexes ($\Delta\bar{V}^0_{r,y}$) are plotted in Fig. 13 as symbols against the standard partial molal volumes of the cations in the complexes ($\bar{V}^0_{M^{Z+2}}$) given by Shock and Helgeson (1988). It can be seen in this figure that the solid lines are consistent with the bulk of the experimental data represented by the symbols. The equations of these two solid lines can be expressed as

$$\Delta\bar{V}^0_{r,y=1} = \gamma_Z\bar{V}^0_{M^{2+}} + \delta_Z \qquad (63)$$

where γ_Z and δ_Z represent the slopes and intercepts of the solid lines, which are given by

$$\gamma_Z = -0.25Z - 0.3 \qquad (64)$$
$$\delta_Z = -2.88Z + 3.32 \qquad (65)$$

where Z represents the charge on the complex. Although Eqns. 64 and 65 are each constrained only by data for sulfate

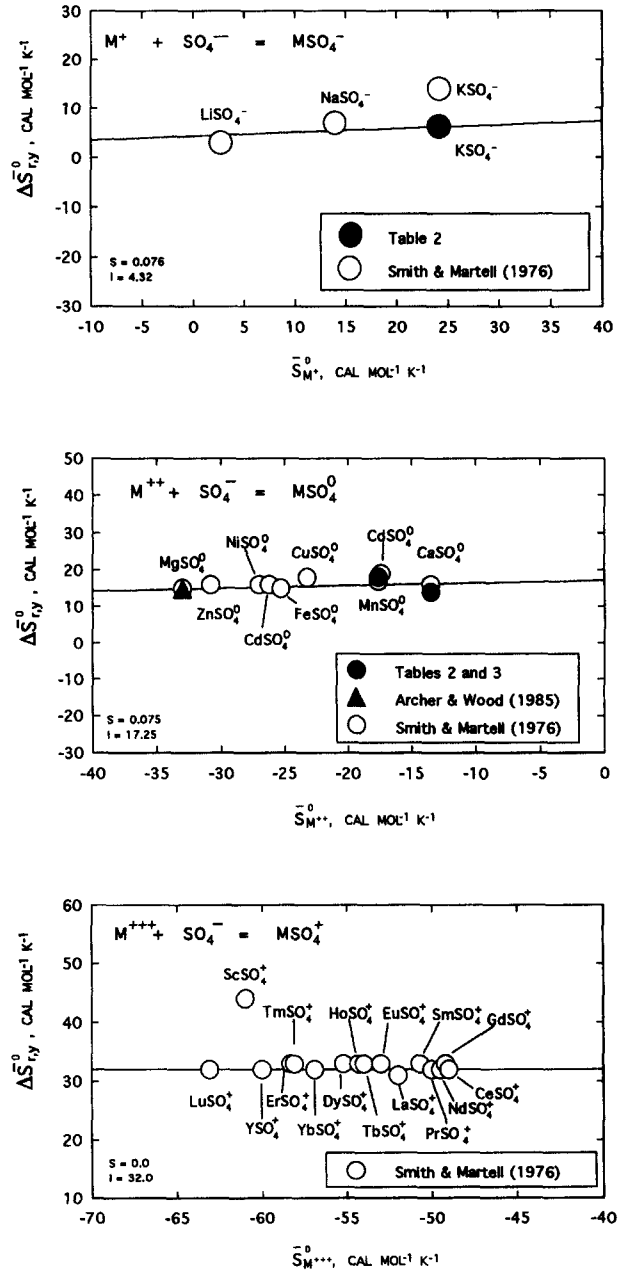

Fig. 22. Correlation of the standard partial molal entropies of association ($\Delta\bar{S}^0_{r,y}$, $y = 1$) of sulfate complexes involving monovalent, divalent, and trivalent cations with the standard partial molal entropies of the cations ($\bar{S}^0_{M^{Z+2}}$) at 25°C and 1 bar (Eqn. 79). The symbols represent experimental values reported in the literature with the exception of those for KSO_4^-, $CaSO_4^0$, and $MnSO_4^0$ which were computed from thermodynamic data taken from Tables 2 and 3.

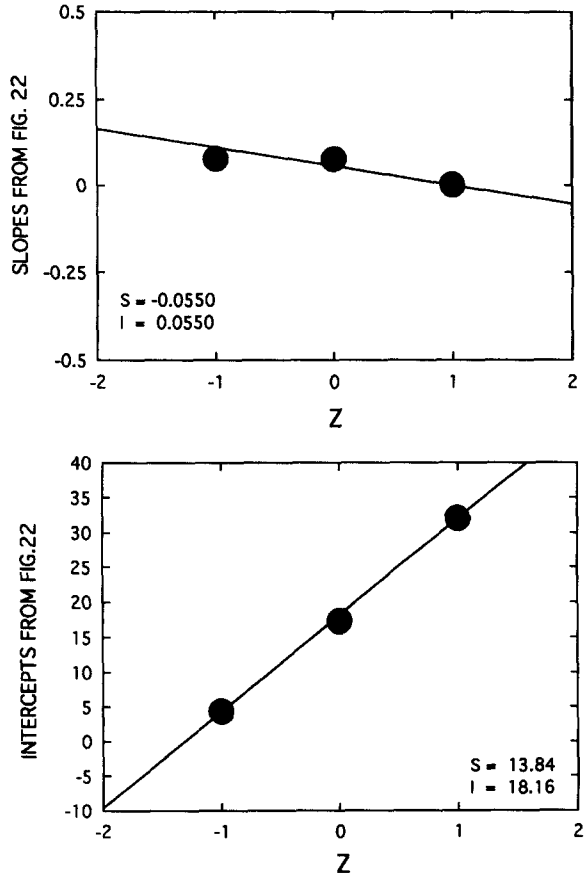

Fig. 23. Slopes ($\alpha_{Z,SO_4^{2-}}$) and intercepts ($\beta_{Z,SO_4^{2-}}$) of the lines in Fig. 22 (symbols) as functions of the charge on the complex (Z). The lines shown are consistent with Eqns. 80–81.

complexes of monovalent and divalent metals, their validity is strongly supported by the fact that they were used to generate the dashed curve in Fig. 13, which is (independently) consistent with the distribution of the two symbols shown in the figure for $EuSO_4^-$ and $LaSO_4^-$. It thus appears that Eqns. 63–65 can be used to calculate provisional estimates of the standard partial molal volumes of association of a wide variety of metal ion sulfate complexes for which $y = 1$. Because only a few standard partial molal volumes of association are available for complexes containing other divalent ligands (Seward, 1981), corresponding estimates of $\Delta\bar{V}^0_{r,y=1}$ cannot be made for these species unless Eqns. 63–65 are deemed to be applicable also to complexes such as metal carbonates. Although it seems likely in a first approximation, this assumption cannot be substantiated at the present time.

7. REGRESSION OF DISSOCIATION CONSTANTS OVER LIMITED RANGES OF TEMPERATURE

It can be seen in Figs. 14–17 that experimental dissociation constants are available for a number of aqueous metal complexes over relatively small ranges of temperature at P_{SAT} and, in a couple of instances, at elevated pressures. By taking account of the standard partial molal heat capacity and volume correlations summarized above, these various data can be regressed with Eqn. 39 and either Eqn. 40 or 42 to compute equation of state parameters and to retrieve values of $\Delta\bar{G}^0_{f,P_r,T_r}$ and $\bar{S}^0_{P_r,T_r}$ for the metal ion complexes shown in these figures. The results of such regression calculations are listed in Table 3 and the equations used in the regression analysis are summarized in Table 4. Although the parameters and properties in Table 3 are much more uncertain than those in Table 2, they can be used to calculate provisional estimates of log K for reactions at temperatures and pressures well beyond those for which experimental data are available. The regression calculations are discussed in detail below.

7.1. Carbonate Complexes

Experimentally derived dissociation constants for carbonate complexes of Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} reported in the literature are represented by the symbols shown in Fig. 14. The regression curves shown in the figure were generated from the equations of state parameters and standard partial molal properties at 25°C and 1 bar for these species given in Table 3. Estimated standard partial molal

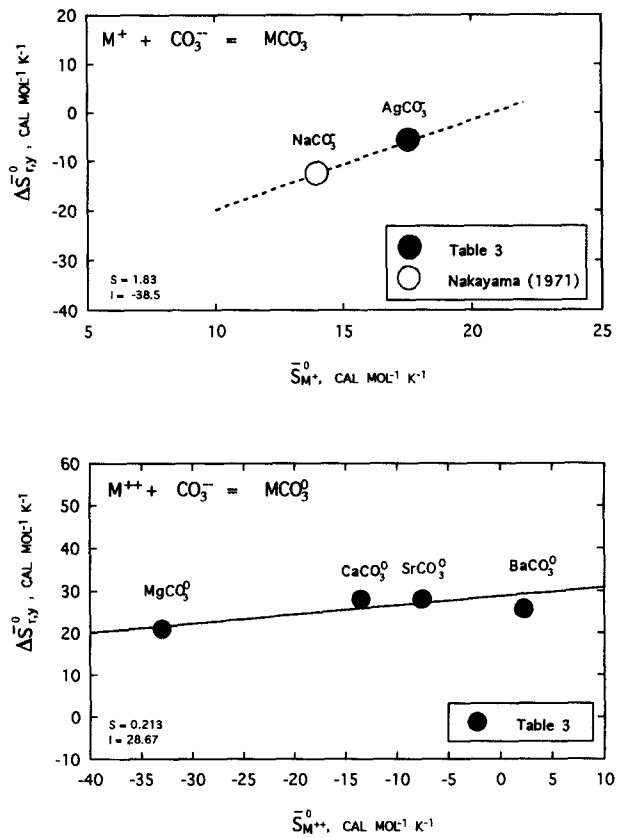

Fig. 24. Correlation of the standard partial molal entropies of association ($\Delta\bar{S}^0_{r,y}$, $y = 1$) of carbonate complexes involving monovalent and divalent cations with the standard partial molal entropies of the cations ($\bar{S}^0_{M^{z+}}$) at 25°C and 1 bar (Eqn. 83). The symbols represent values computed from thermodynamic data taken from Table 3, or in the case of $NaCO_3^-$, those given by Nakayama (1971). The lines shown are consistent with Eqns. 84–85.

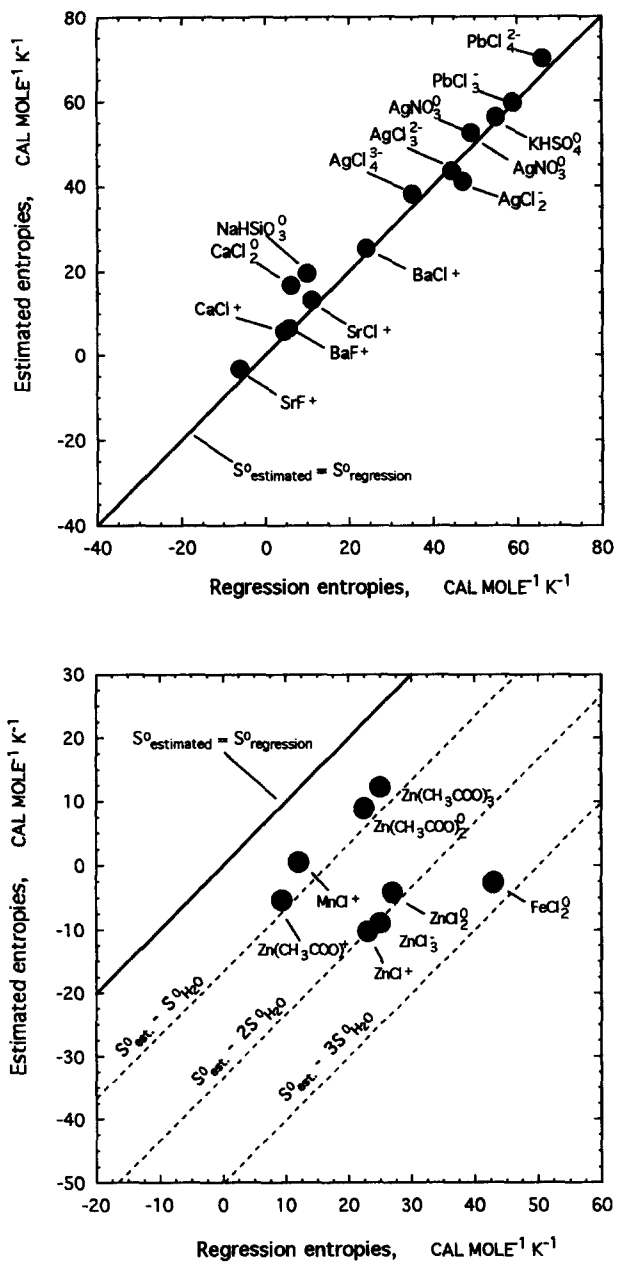

Fig. 25. Estimated values of $\bar{S}^0_{P_r,T_r}$ for metal complexes, Eqns. 66–85 as a function of their regression counterparts in Tables 2 and 3. The symbols represent standard molal entropies taken from Tables 2 and 3 which were *not* used in generating Eqns. 66–85. The solid line represents perfect agreement between estimated and regression entropies. The dashed lines represent offsets of this line (see text).

heat capacities of the complexes were used in the regression calculations. It was assumed that the standard partial molal heat capacities of association of metal carbonate complexes can be taken to be equal to their sulfate counterparts, which probably introduces minimal uncertainties because the experimental dissociation constants represent temperatures below 100°C and the values of $\bar{C}^0_{P_r,T_r}$ for the CO_3^{2-} and SO_4^{2-} ions differ by only 5.1 cal mol^{-1} deg^{-1} (Shock and Helgeson, 1988). Nevertheless, these assumptions and the limited regression data array restrict the curves above 100°C in Fig. 14 to the status of provisional estimates.

7.2. Hydroxysilicate and Sulfate Complexes

Experimental equilibrium constants reported in the literature for the dissociation of $NaHSiO_3^0$, $MnSO_4^0$, and $KHSO_4^0$ are represented by the symbols in Fig. 15. It can be seen in this figure that the regression curves are in close agreement with all but a few of these symbols. Because the dissociation constants for $KHSO_4^0$ in Fig. 15 extend over less than 200°C at any given pressure, they cannot be regressed to obtain reliable values of both $\bar{S}^0_{P_r,T_r}$ and $\bar{C}^0_{P_r,T_r}$ for $KHSO_4^0$. Consequently, these data were regressed with Eqn. 38 using an estimated value of $\bar{C}^0_{P_r,T_r}$ for $KHSO_4^0$ computed from Eqn. 53, which permitted retrieval of the values of $\Delta\bar{G}^0_{f,P_r,T_r}$, $\bar{S}^0_{P_r,T_r}$, $\bar{V}^0_{P_r,T_r}$, and ω for $KHSO_4^0$ given in Table 3.

7.3. Fluoride and Nitrate Complexes

Experimentally derived logarithms of dissociation constants reported in the literature for SrF^+ and BaF^+ correspond to the symbols in Fig. 16. The regression curves in this figure were generated from Eqns. 39 and 40 using estimated standard partial molal heat capacities and volumes computed from Eqns. 53 and 61, respectively. The standard partial molal entropies of SrF^+ and BaF^+ were retrieved from the trends with temperature of the log K values from Majer and Stulik (1982). These entropies, together with the estimated heat capacities, result in large decreases in the calculated values of log K at elevated temperatures (Fig. 16). Dissociation constants reported in the literature for $AgNO_3^0$ are represented by the symbols in Fig. 16. The regression curve shown in this figure was generated from Eqns. 39 and 42 using values of $\bar{C}^0_{P_r,T_r}$ and $\bar{V}^0_{P_r,T_r}$ calculated from Eqns. 53 and 61, respectively. It can be seen in Fig. 16 that the regression curves are closely consistent with all but one of the experimental data points.

7.4. Chloride Complexes

Experimental dissociation constants reported in the literature for $AgCl_3^{2-}$, $AgCl_4^{3-}$, $PbCl_4^{2-}$, $ZnCl_3^-$, $FeCl_2^0$, $MnCl^+$, $CaCl^+$, $CaCl_2^0$, $SrCl^+$, and $BaCl^+$ are represented by the symbols in Fig. 17. Unlike the experimental data depicted in Figs. 14–16, most of the sets of dissociation constants represented by the symbols in Fig. 17 consist of experimental data taken from a variety of sources, not all of which are in agreement with one another. For example, the trend with temperature of the dissociation constants for $ZnCl_3^-$ reported by Bourcier and Barnes (1987) shown in Fig. 17 is not consistent with that defined by the dissociation constants reported by Ruaya and Seward (1986). Discrepancies between the results of Bourcier and Barnes (1987) and Ruaya and Seward (1986) were already discussed for $ZnCl^+$ (see above and Fig. 4). Based on this discussion, the data from Ruaya and Seward (1986) were used to constrain the regres-

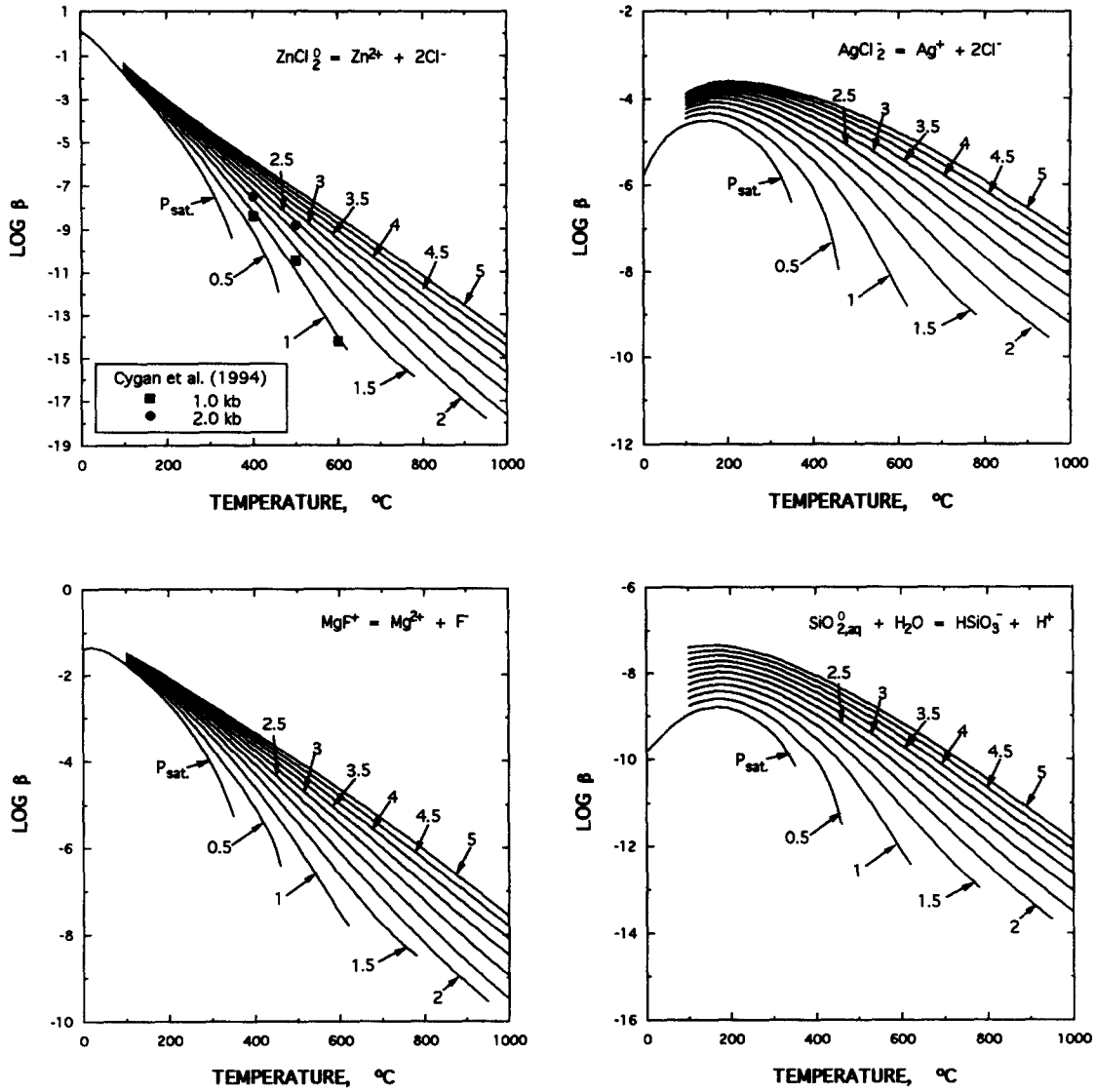

Fig. 26. Curves representing the logarithims of predicted dissociation constants for selected complexes as a function of temperature at constant pressure (labelled in kb) generated from the equations of state using parameters and properties taken from Table 2 (see text). The symbols represent experimental data reported in the literature. Note that the curves representing dissociation of $ZnCl_2^0$ were generated independently from the experimental data depicted in the figure.

sion curves depicted in Fig. 17. Values of log β for $ZnCl_4^{2-}$ have been omitted from Fig. 17. Discrepancies exist between the trends with temperature of the log β values for $ZnCl_4^{2-}$ reported by Bourcier and Barnes (1987) and Ruaya and Seward (1986). In addition, the values of log β for $ZnCl_4^{2-}$ at 300°C from either study are inconsistent with the sphalerite solubility measurements given by Cygan et al. (1994) who suggested that $ZnCl_2^0$ predominated under the experimental conditions investigated. The values of log β for $ZnCl_2^0$ obtained by Cygan et al. (1994) are closely consistent with those calculated in the present study (see below). Consequently, because of the uncertainties surrounding the experimental measurement of $ZnCl_4^{2-}$ at elevated temperatures, an equation of state representation of $ZnCl_4^{2-}$ is not included in the present study.

Discrepancies between the calculated curves and some of the symbols representing experimental dissociation constants for $CaCl_2^0$, $SrCl^+$, and $BaCl^+$ in Fig. 17 are probably attributable to experimental uncertainties. Although the calculated curve for the dissociation constant of $CaCl_2^0$ is consistent with the data from 25 to 200°C from Ramette (1986) and Williams-Jones and Seward (1989), it is not consistent with all of the data at temperatures greater than 200°C from Williams-Jones and Seward (1989), nor with the results in Frantz and Marshall (1982). In the former study, the uncertainties associated with obtaining dissociation constants probably increase sig-

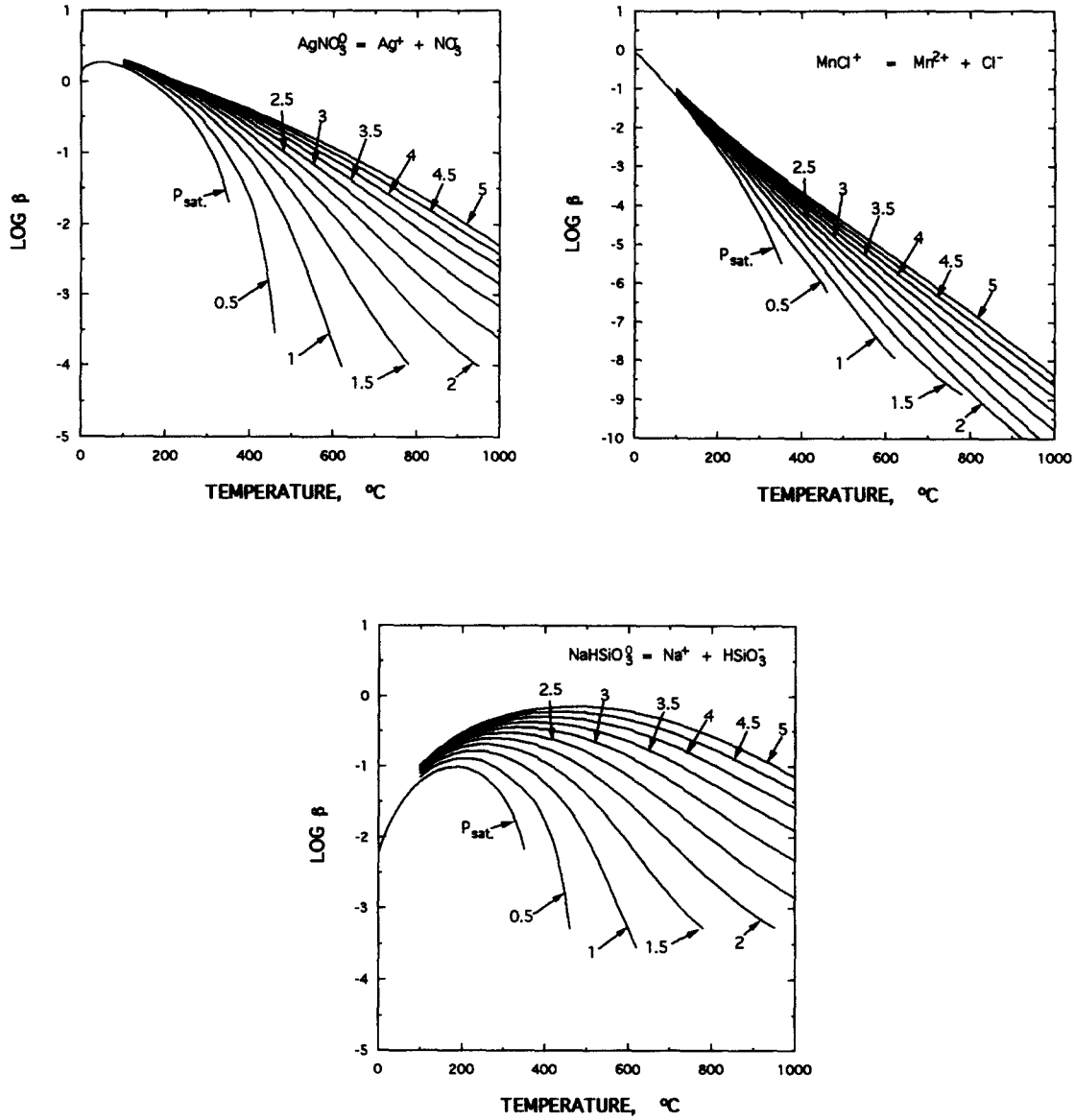

Fig. 27. Curves representing the logarithms of predicted dissociation constants for selected complexes as a function of temperature at constant pressure (labelled in kb) generated from the equations of state using parameters and properties taken from Table 3 (see text).

nificantly with increasing temperature because the dissociation constants were obtained from a speciation model of the solubility of AgCl in HCl-$CaCl_2$ solutions. In the latter study, uncertainty exists as to the species present in the solutions in the conductance experiments. The experimental dissociation constants of $SrCl^+$ and $BaCl^+$ depicted in Fig. 17 scatter somewhat about the calculated curves for these complexes, probably because of the substantial uncertainties associated with deriving experimental log K values when the latter are range from about 0 to +1.0. Nevertheless, it can be seen in Fig. 17 that the regression curves are closely consistent with the bulk of the experimental values of log K represented by the symbols, which strongly supports the validity of the estimated standard partial molal heat capacities given in Table 3. The regression values of $\bar{S}^0_{P_r,T_r}$ shown in this table can be used together with those in Table 2 to generate standard partial molal entropy correlations for $\Delta\bar{S}^0_r$ similar to those adduced above for $\Delta\bar{C}^0_{P,r}$ and $\Delta\bar{V}^0_r$ at 25°C and 1 bar. These correlations are summarized below.

8. STANDARD MOLAL ENTROPY CORRELATIONS AT 25°C AND 1 BAR

8.1. Complexes Containing Monovalent Ligands

Figure 6a and Eqns. 45 through 47 describe the dependence of the standard partial molal entropy of association at

25°C and 1 bar for neutral metal chloride complexes of the form ML_y^Z for $Z = 0$ on $\bar{S}^0_{MCl_{y-1}^{Z+1}}$. Let us now explore the extent to which similar relations hold for the standard partial molal entropies of charged metal complexes containing a variety of monovalent ligands.

Standard partial molal entropies of association of M^+ or ML^+ with F^-, Cl^-, Br^-, I^-, or CH_3COO^- ($\Delta\bar{S}^0_{r,y}$, where $y = 1$ or 2) at 25°C and 1 bar computed from values of $\bar{S}^0_{ML_y^Z}$, taken from Tables 2 and 3 using values of $\bar{S}^0_{P_r,T_r}$ for ions taken from Shock and Helgeson (1988), are plotted as symbols against $\bar{S}^0_{ML_{y-1}^+}$ in Fig. 18. For the fluoride complexes, a dashed line has been drawn because there are only two data points. However, it can be seen in the other diagrams in Fig. 18 that in most cases the solid straight lines are in close agreement with the experimental data represented by the symbols. All the lines in Fig. 18 are consistent with those shown in Fig. 19 and the relation,

$$\Delta\bar{S}^0_{r,y} = \alpha_{Z,L^-}\bar{S}^0_{ML_{y-1}^{Z+1}} + \beta_{Z,L^-} \tag{66}$$

where

$$\alpha_{Z=0,L^-} = -0.000479\bar{S}^0_{L^-} + 0.3185 \tag{67}$$

$$\beta_{Z=0,L^-} = -0.05757\bar{S}^0_{L^-} - 3.4494 \tag{68}$$

The points representing $\Delta\bar{S}^0_{r,y=1\text{ or }2}$ for the three chloride complexes $NaCl^0$, $AgCl^0$, and $PbCl_2^0$ in Fig. 18 and the line drawn through them are identical to those in Fig. 6a. Analogous relations for complexes involving divalent cations and monovalent ligands are depicted in Figs. 20 and 21. The solid symbols in Fig. 20 refer to standard partial molal entropies of association computed from values of $\bar{S}^0_{M^{+2}}$ taken from Shock and Koretsky (1993) and Tables 2 and 3 using values of $\bar{S}^0_{P_r,T_r}$ for ions given by Shock and Helgeson (1988). The equations of the lines in Fig. 21 are given by

$$\alpha_{Z=1,L^-} = 0.015762\bar{S}^0_{L^-} + 0.03874 \tag{69}$$

$$\beta_{Z=1,L^-} = 0.10344\bar{S}^0_{L^-} + 7.5807 \tag{70}$$

which can be combined with Eqn. 66 to compute values of $\Delta\bar{S}^0_{r,y=1}$ at 25°C and 1 bar for complexes containing divalent cations.

Because the lines in Figs. 19 and 21 are for the most part constrained by only a few data points, they should be considered as first approximations. Nevertheless, the lines in Figs. 6a and 18–21 are consistent with one another and with generalization of α_{Z,L^-} and β_{Z,L^-} in Eqn. 66 to

$$\alpha_{Z,L^-} = a_Z\bar{S}^0_{L^-} + a'_Z \tag{71}$$

$$\beta_{Z,L^-} = b_Z\bar{S}^0_{L^-} + b'_Z \tag{72}$$

which can be combined with Eqn. 66 to give

$$\Delta\bar{S}^0_{r,y} = (a_Z\bar{S}^0_{L^-} + a'_Z)\bar{S}^0_{ML_{y-1}^{Z+1}} + b_Z\bar{S}^0_{L^-} + b'_Z \tag{73}$$

where

$$a_Z = 0.016241Z - 0.000479 \tag{74}$$

$$a'_Z = -0.36097Z + 0.3209 \tag{75}$$

$$b_Z = 0.32102Z - 0.05996 \tag{76}$$

$$b'_Z = 8.2198Z - 1.557 \tag{77}$$

where Z again stands for the charge on the complex. Equations 73–77 are consistent with all of the lines in Figs. 6a and 18–21. Note that it follows from these equations that the standard partial molal entropy change accompanying addition of a monovalent ligand to the species ML_{y-1}^{Z+1} for $y \geq 1$ at 25°C and 1 bar can be calculated directly from the standard molal entropies of the cation (M^{Z+y}) and ligand (L^-) at 25°C and 1 bar. Because Eqns. 73–77 are consistent with the bulk of the experimental data represented by the symbols in Figs. 6a and 18–21, it appears that these equations can be used to generate close estimates of the standard molal entropies of association of aqueous complexes with monovalent ligands at 25°C and 1 bar. Let us now consider complexes with divalent ligands.

8.2. Standard Partial Molal Entropies of Sulfate Complexes

Standard partial molal entropies of association of sulfate complexes ($\Delta\bar{S}^0_{r,y=1}$) involving monovalent, divalent, and trivalent cations consistent with

$$M^{Z+2} + SO_4^{2-} = MSO_4^Z \tag{78}$$

are represented by the symbols in Fig. 22. The slopes and intercepts of the straight lines in this figure are plotted as symbols in Fig. 23. The equations of the lines in Fig. 22 are given by

$$\Delta\bar{S}^0_{r,y=1} = \alpha_{Z,SO_4^{2-}}\bar{S}^0_{M^{Z+2}} + \beta_{Z,SO_4^{2-}} \tag{79}$$

where

$$\alpha_{Z,SO_4^{2-}} = -0.055Z + 0.055 \tag{80}$$

$$\beta_{Z,SO_4^{2-}} = 13.84Z + 18.16 \tag{81}$$

It can be deduced from Figs. 22 and 23 that Eqns. 79 through 81 represent the bulk of the experimental data represented by the symbols.

8.3. Standard Partial Molal Entropies of Carbonate Complexes

The standard partial molal entropies of association of $MgCO_3^0$, $CaCO_3^0$, $SrCO_3^0$, $BaCO_3^0$, and $AgCO_3^-$ computed from those of the carbonate complexes in Table 3 and values of the standard molal entropies of the cation (M^{Z+y}) and ligand (L^-) at 25°C and 1 bar for the constituent ions taken from Shock and Helgeson (1988) for

$$M^{Z+2} + CO_3^{2-} = MCO_3^Z \tag{82}$$

are plotted as symbols Fig. 24. Although the dashed line shown in this figure is constrained by only two data points, it appears by analogy with the sulfate complexes represented by the symbols and lines in Fig. 22 that the lines in Fig. 24

can be used in a first approximation to generate provisional estimates of $\Delta\bar{S}^0_{r,y}$ at 25°C and 1 bar for carbonate complexes containing variously charged cations. The requisite equation of the lines in Fig. 24 is given by

$$\Delta\bar{S}^0_{r,y=1} = \gamma_{Z,CO_3^{2-}}\bar{S}^0_{M^{Z+2}} + \delta_{Z,CO_3^{2-}} \quad (83)$$

where

$$\gamma_{Z,CO_3^{2-}} = -1.617Z + 0.213 \quad (84)$$

$$\delta_{Z,CO_3^{2-}} = 66.82Z + 28.67 \quad (85)$$

Equations 83 and 85 represent combinations of the slopes and intercepts of the lines shown in Fig. 24, which is consistent with the hypothesis that they are linear functions of cation charge (Z) like those for the sulfate complexes in Fig. 23.

8.4. Uncertainties Associated with the Estimation of the Standard Partial Molal Entropies of Aqueous Complexes at 25°C and 1 bar

The algorithms summarized above permit calculation of provisional estimates of the standard molal entropies of association for a large number of complexes at 25°C and 1 bar, from which values of $\bar{S}^0_{P_r,T_r}$ for the complexes can be computed using values of $\bar{S}^0_{P_r,T_r}$ for the constituent ions taken from Shock and Helgeson (1988). The uncertainties associated with values of $\bar{S}^0_{P_r,T_r}$ for complexes computed in this way can be assessed in Fig. 25, where values of $\bar{S}^0_{P_r,T_r}$ for complexes computed from estimates of the standard molal entropies of association at 25°C and 1 bar generated from Eqns. 66–85 can be compared with those taken from Tables 2 and 3, which were derived by regression. It can be deduced from Fig. 25 that the differences between the symbols which represent complexes which were not considered in deriving Eqns. 66–85 and the solid correlation line representing $\bar{S}^0_{estimated} = \bar{S}^0_{regression}$ in the figure are for the most part less than about 5 cal mol^{-1} K^{-1}. However, this is not true in the case of the zinc, iron, and manganese complexes shown in Fig. 25, where it can be seen that the symbols tend to cluster systematically along lines with offsets from $\bar{S}^0_{estimated} = \bar{S}^0_{regression}$ of $1x\bar{S}^0_{H_2O}$, $2x\bar{S}^0_{H_2O}$, and $3x\bar{S}^0_{H_2O}$, where $\bar{S}^0_{H_2O}$ is equal to 16.71 cal mol^{-1} K^{-1} at 25°C and 1 bar. This observation is consistent with extensive evidence indicating release of one or more water molecules from the inner coordination sphere of the central cations in these complexes during outer/inner sphere transitions and coordination changes (e.g., Ahrland, 1972; Libus and Tialowska, 1975; Irish and Jarv, 1983; Apted et al., 1985; Susak and Crerar, 1985; Ruaya and Seward, 1986; Farges et al., 1993; Sharps et al., 1993; Shurvell and Durham, 1978).

The uncertainty analysis summarized above indicates that values of $\bar{S}^0_{P_r,T_r}$ for complexes other than those involving zinc, iron, and manganese can be estimated at 25°C and 1 bar with reasonable confidence from Eqns. 66 to 85. Such estimates permit estimation of dissociation constants for a wide variety of complexes at high temperatures and pressures.

9. PREDICTION OF DISSOCIATION CONSTANTS AT ELEVATED TEMPERATURES AND PRESSURES

The thermodynamic properties of the metal-ion complexes in Tables 2 and 3 together with those given by Shock and Helgeson (1988) can be used to calculate dissociation constants from the equations of state over broad ranges of elevated temperatures and pressures. Values of log K or log β computed in this manner are listed in Tables 5–11 and depicted as curves in Figs. 26 and 27, which extend to much higher temperatures and pressures than the corresponding curves in Figs. 4–17.

Although few in number, the symbols shown for the dissociation of $ZnCl_2^0$ in Fig. 26 correspond to data that were *not* used to constrain the regression calculations described above. It can be seen in this figure that the curves generated independently from the experimental data are in close agreement with these symbols. Calculated values of equations of state parameters and the standard molal thermodynamic properties at 25°C and 1 bar are given in Table 12 for various metal-ion complexes of geologic interest for which relatively few experimental data are available in the literature. These include complexes consisting of Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^+, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Tl^+, Tl^{3+}, Au^+, Au^{3+}, Hg^{2+}, or Pb^{2+} with F^-, Cl^-, HS^-, or $HSiO_3^-$. Calculated values of log β for dissociation of these complexes at high temperatures and pressures are given in Tables 13–19. These values of log β can be used to help characterize aqueous speciation and mineral solubilities in experimental or natural hydrothermal fluids such as those investigated by Hemley et al. (1992), who concluded that neutral species predominate in the supercritical region. To illustrate the behavior of log β for these various complexes as a function of temperature and pressure, the values of log β given in these tables for 6 of the complexes as a function of temperature and pressure are depicted as curves in Fig. 28, where it can be seen that in 2 of the cases it is possible to compare the predicted curves with experimental data reported in the literature. For example, the curve generated independently from the experimental value of the solubility of gold as $AuCl_2^-$ at 300°C and P_{SAT} in Fig. 28 is in close agreement with the experimental data reported by Gammons and Williams-Jones (1995). Similarly, the predicted curve representing the solubility of gold as $Au(HS)_2^-$, which is based in part on the experimental value at 250°C and P_{SAT} given by Shenberger and Barnes (1989), is closely consistent with the experimental data they report at both higher and lower temperatures. In addition, the pressure dependence of the predicted curves for $Au(HS)_2^-$ in Fig. 28 is based on estimated equation of state coefficients and an estimated value of the standard partial molal volume of $Au(HS)_2^-$ (Table 12) close to that reported by Zotov and Baranova (1995). It can be seen in Fig. 28 that the data reported for this reaction by Seward (1973) and Benning and Seward (1996) are not in agreement with the other experimental data represented by the symbols for the solubility of gold as $Au(HS)_2^-$. However, the equilibrium constants reported by Seward (1973) and Benning and Seward (1996) are based on values of the dissociation constant of H_2S which

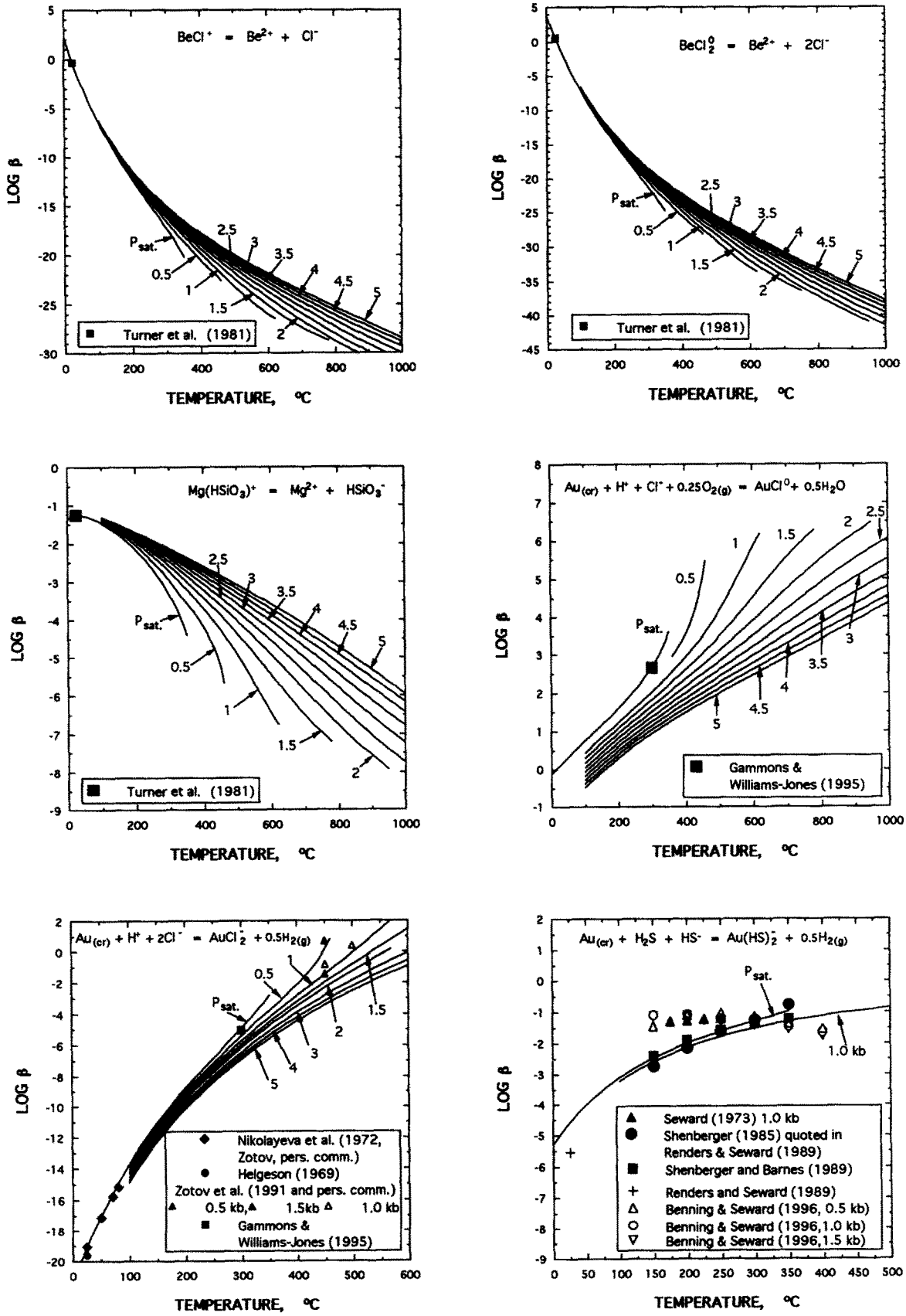

Fig. 28. Curves representing the logarithms of predicted dissociation and solubility constants for selected complexes as a function of temperature at constant pressure (labelled in kb) generated from the equations of state using parameters and properties taken from Table 12 (see text). The symbols represent experimental data reported in the literature.

TABLE 1. Summary of the characteristics of predictive algorithms other than those adopted in the present study for calculating dissociation constants at elevated temperatures and pressures.

Pressure and Temperature Range	Assumption	Reference
P_{SAT} at 0° to 350°C	$\Delta\bar{C}^0_{P,r} = 0$ for isocoulombic reactions.[1]	Gurney, 1936, 1938, 1953; Lindsay, 1980; Murray and Cobble, 1980; Ruaya, 1988; Phillips and Silvester, 1983.
P_{SAT} to 1000 bars and 0° to 250°C	Ratio of the nonelectrostatic to the electrostatic heat capacities of reaction is a constant.	Helgeson, 1967, 1969; Arnórsson et al., 1982, 1983; Smith et al., 1986.
1000–4000 bars and 400° to 850°C	The logarithms of dissociation constants are linear functions of the logarithms of the specific volume of water at constant temperature.	Franck, 1956, 1981; Marshall, 1968, 1969, 1970, 1972a, 1972b; Eugster and Baumgartner, 1987; Mesmer et al., 1988; Anderson et al., 1991.
P_{SAT} to 4000 bars and 0° to 800°C	Statistical theories.	Bjerrum, 1926; Fuoss, 1958; Gilkerson, 1956, 1970; Oelkers and Helgeson, 1990, 1991; Pearson et al., 1963; Wright et al., 1961; Walther and Schott, 1988; Brady and Walther, 1990.
P_{SAT} to 4000 bars and 0° to 550°C	Electrostatic forces control the behavior of dissociation constants.	Ryzhenko, 1974; Bryzgalin and Rafal'skiy, 1981; Bryzgalin and Ryzhenko, 1981; Bryzgalin, 1986.

[1]Although the assumption that the standard partial molal heat capacity of reaction ($\Delta\bar{C}^0_{P,r}$) for the dissociation of aqueous species is zero or constant has been made repeatedly in the literature, experimental data indicate that this assumption is approximately valid only for isocoulombic reactions, and then only to ~ 200° – 300°C, depending on the species involved.

TABLE 2. Summary of equations of state parameters and standard partial molal properties at 25°C and 1 bar of complexes obtained by regression of the logarithms of the dissociation constants reported in the literature for broad ranges of temperature and pressure (see text).

Species	ΔG^o_f [a,g]	ΔH^o_f [a,h]	S^o [b,g]	C^o_{pr} [b,g]	V^o [c,g]	a_1 [d,i] x 10	a_2 [a,i] x 10^{-2}	a_3 [e,i]	a_4 [f,i] x 10^{-4}	c_1 [b,i]	c_2 [f,i] x 10^{-4}	ω [a,g] x 10^{-5}
$NaCl^0$	-92910	-96160	28	8.5	24	5.0364	4.5189	3.9669	-2.9658	10.798	-1.3031	-0.038
$AgCl^0$	-17450	-18270	34.1	6.7	25.24[l]	5.2088	4.9399	3.8015	-2.9832	9.8168	-1.6698	-0.03
$AgCl_2^-$	-51560	-61130	47	7.8	54.37[l]	9.5149	15.4544	-0.3312	-3.4178	19.185	-1.4457	0.9169[p]
$ZnCl^+$	-66850	-66240	23	19.9	-1.28[l]	1.6583	-3.7293	7.2088	-2.6248	19.6947	1.0191	0.2025[p]
$ZnCl_2^0$	-98300	-109080	27.03	34.7	24.82[l]	5.1486	4.7929	3.8592	-2.9771	26.1528	4.0338	-0.038[q]
$PbCl^+$	-39050	-38630	28	4.9	8.53[l]	2.9756	-0.513	5.9446	-2.7577	10.2182	-2.0364	0.1281[p]
$PbCl_2^0$	-71200	-77700	47	2	35.74[l]	6.6429	8.4416	2.4251	-3.1279	6.9886	-2.6272	-0.038[q]
$PbCl_3^-$	-102150	-117700	59	-11.9	66.07[l]	11.0547	19.2141	-1.8089	-3.5733	5.9698	-5.4586	0.7356[p]
$NiCl^+$	-40920	-51400	-17	8.1	-6.63[l]	1.1319	-5.0147	7.714	-2.5716	18.3863	-1.3846	0.8111[p]
$FeCl^+$	-53030	-61260	-10.06	20.6	1.06[l]	2.1468	-2.5367	6.7401	-2.6741	24.6912	1.1617	0.7003[p]
$MgCl^+$	-139700	-150933	-19	25	1.26[m]	2.223	-2.3505	6.6669	-2.6818	28.6016	2.058	0.8449[p]
MgF^+	-177690	-190950	-28.07	39.1	-17.47[l]	-0.2975	-8.5049	9.0858	-2.4274	38.0239	4.9301	0.9706[p]
CaF^+	-200390	-208600	-9	30.1	-13.46[l]	0.1568	-7.3958	8.6499	-2.4732	30.1743	3.0968	0.6911[p]
$Fe(CH_3COO)^+$	-111900	-139060	-1.5	81.3	23.86[l]	5.2246	4.9785	3.7863	-2.9848	59.116	13.5263	0.5756[p]
$Fe(CH_3COO)_2^0$	-201800	-259100	11.53	184.2	76.13[l]	12.1698	21.937	-2.8791	-3.6858	113.7691	34.487	-0.038[q]
$Zn(CH_3COO)^+$	-125660	-155120	9.4	86.2	21.52[l]	4.8484	4.06	4.1473	-2.9468	60.4626	14.5244	0.41[p]
$Zn(CH_3COO)_2^0$	-216450	-271500	22.47	193.3	73.02[l]	11.7443	20.8978	-2.4707	-3.6429	119.1022	36.3407	-0.038[q]
$Zn(CH_3COO)_3^-$	-305740	-394090	25	316.5	130.41[l]	20.0332	41.1373	-10.4257	-4.4796	203.1827	61.4365	1.2513[p]
KSO_4^-	-246640	-276980	35	-10.9	27.8[n]	5.9408	6.7274	3.0989	-3.0571	9.9089	-5.2549	1.0996[p]
$CaSO_4^0$	-312930	-345900	5	-25	4.7[n]	2.4079	-1.8992	6.4895	-2.7004	-8.4942	-8.1271	-0.001
$HSiO_3^-$	-242801	-273872	5	-21	5[o]	2.9735	-0.5181	5.9467	-2.7575	8.1489	-7.3123	1.5511[p]
$LiCl^0$	-99250	-105680	13.14[j]	20.3	28	5.5837	5.8554	3.4416	-3.021	17.7136	1.1006	-0.038
KCl^0	-95430	-95390	42.25[j]	-8.3	38.3	6.9932	9.297	2.0889	-3.1633	0.9522	-4.7253	-0.038
$RbCl^0$	-97870	-96800	48.56[j]	-20	41.6	7.4542	10.4227	1.6465	-3.2098	-5.6468	-7.1086	-0.01
$CsCl^0$	-100900	-100950	52.58[j]	-24	48	8.401	12.7344	0.7379	-3.3054	-6.0563	-7.9234	0.2
NaF^0	-128570	-135860	12	11.2[k]	5.71[l]	2.5336	-1.5922	6.3689	-2.7131	12.3804	-0.7531	-0.038
RbF^0	-136450	-139710	31.6	-16[k]	19	4.3647	2.8788	4.6115	-2.898	-3.2196	-6.2938	-0.001
$NaBr^0$	-85610	-84830	34.1	7.97[k]	32.04	6.1257	7.1789	2.9214	-3.0757	10.1926	-1.4111	-0.07
KBr^0	-90010	-86320	47.5	-7.97[k]	46	8.058	11.897	1.067	-3.2708	1.4496	-4.658	-0.005
$RbBr^0$	-91010	-85730	54.2	-19.19[k]	49	8.4668	12.8952	0.6747	-3.312	-5.172	-6.9436	-0.01
$CsBr^0$	-94610	-88490	57.3	-26.57[k]	57	9.5646	15.5757	-0.3789	-3.4228	-9.4143	-8.4469	-0.001
NaI^0	-72900	-69101	37.7	10.14[k]	43	7.6488	10.8979	1.4597	-3.2295	12.1001	-0.969	-0.001
KI^0	-77740	-71829	49.2	-5.8[k]	59	9.8369	16.2406	-0.6402	-3.4503	2.7214	-4.216	-0.005
RbI^0	-78900	-71720	56.3	-17.02[k]	64	10.5225	17.9145	-1.2982	-3.5195	-3.8174	-6.5015	-0.001
CsI^0	-83460	-77820	60.3	-24.4[k]	72	11.6513	20.6709	-2.3815	-3.6335	-7.212	-8.0048	0.1

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. Retrieved from regression calculations using equations cited in Table 4, unless otherwise indicated. h. Calculated from the values of ΔG^0_f and S^0 shown above, using standard molal entropies of the elements consistent with Shock and Helgeson (1988). i. Calculated from the values of S^0, $C_P{}^0$ and V^0 shown above using Eqns. (33)-(37). j. Calculated from Eqns. (45)-(47) and S^0 values taken from Shock and Helgeson (1988). k. Calculated from Eqns. (50)-(52) using $C_P{}^0$ values from Shock and Helgeson (1988). l. Calculated from Eqn. (61) using V^0 values taken from Shock and Helgeson (1988). m. Calculated from the volume of dissociation reported by Fisher and Fox (1978) using standard molal volumes of aqueous ions taken from Shock and Helgeson (1988). n. Calculated from the volume of association reported by Hamann (1974) using standard molal volumes of aqueous ions taken from Shock and Helgeson (1988). o. Calculated from Eqn. (92) given by Shock and Helgeson (1988). p. Calculated from Eqn. (40) using values of S^0 shown above. q. Calculated from Eqn. (42).

TABLE 3. Summary of estimated and regression-generated equations of state parameters and the standard partial molal thermodynamic properties at 25°C and 1 bar of complexes for which relatively few experimental association data are available at elevated temperatures and pressures (see text).

Species	ΔG^0_f [a,g]	ΔH^0_f [a,h]	S^0 [b,g]	C^0_{pr} [b,i]	V^0 [c,i]	a_1 [d,j] x 10	a_2 [a,j] x 10^{-2}	a_3 [e,j]	a_4 [f,j] x 10^{-4}	c_1 [b,j]	c_2 [f,j] x 10^{-4}	ω [a,j] x 10^{-5}
$Ag(CO_3)^-$	-111430	-142490	0	-10.2	-0.42	2.2588	-2.2632	6.6326	-2.6854	15.2147	-5.1123	1.631
$Ag(CO_3)_2^{3-}$	-236890	-304200	-19	-28.3	1.64	3.7128	1.2872	5.2371	-2.8322	36.5589	-8.7993	5.0992
$MgCO_3^0$	-238760	-270570	-24	-27.4	-18.18	-0.7355	-9.5745	9.5062	-2.3831	-10.2416	-8.6159	-0.038
$CaCO_3^0$	-262850	-287390	2.5	-29.6	-15.66	-0.3907	-8.7325	9.1753	-2.4179	-11.5309	-9.0641	-0.038
$SrCO_3^0$	-264860	-288620	8.5	-32.1	-15.24	-0.3332	-8.5922	9.1201	-2.4237	-12.9961	-9.5733	-0.038
$BaCO_3^0$	-263830	-285850	16	-34.4	-11.81	0.1361	-7.4461	8.6697	-2.4711	-14.344	-10.0418	-0.038
$NaHSiO_3^0$	-307890	-333894	10	24.61	12.72	3.4928	0.75	5.4483	-2.81	20.2395	1.9785	-0.038
$KHSO_4^0$	-243400	-267400	55	57.72	53.77	9.1226	14.4964	0.0453	-3.3782	39.9849	8.723	-0.001
SrF^+	-202290	-210670	-6.2	16.11	-12.79	0.2336	-7.2081	8.5761	-2.481	21.5706	0.2471	0.6472
BaF^+	-201120	-206510	5.5	10.71	-7	0.9652	-5.4218	7.874	-2.5548	16.7505	-0.8529	0.4675
$CaCl^+$	-163100	-168607	4.5	17.47	5.74	2.7148	-1.1497	6.1949	-2.7314	20.8839	0.5241	0.4862
$CaCl_2^0$	-194000	-211060	6	30.96	32.64	6.2187	7.4058	2.8322	-3.0851	23.961	3.272	-0.038
$SrCl^+$	-165800	-169790	11	11.84	6.41	2.7719	-1.0104	6.1402	-2.7372	16.6402	-0.6227	0.3837
$BaCl^+$	-164730	-165323	24	6.67	11.87	3.4534	0.6537	5.4861	-2.806	11.8213	-1.6759	0.1895
$FeCl_2^0$	-73480	-78490	43	29.2	27.43	5.5057	5.665	3.5164	-3.0131	22.9295	2.9135	-0.038
$MnCl^+$	-86290	-88280	12	25.12	6.74	2.8119	-0.9126	6.1017	-2.7412	24.2838	2.0824	0.3686
$ZnCl_3^-$	-129310	-151060	25	41.97	53.9	9.5636	15.5732	-0.3779	-3.4227	42.2912	5.5147	1.2513
$PbCl_4^{--}$	-133177	-159209	66	-35.18	99.86	16.1777	31.723	-6.7255	-4.0904	5.9335	-10.2007	2.2126
$AgCl_3^{--}$	-82710	-105613	44.5	10.69	86.82	14.504	27.6363	-5.1192	-3.9214	35.8339	-0.857	2.5402
$AgCl_4^{---}$	-112280	-150616	35	16.09	122.97	20.0386	41.1504	-10.4309	-4.4801	55.0238	0.243	4.2796
$AgNO_3^0$	-7738	-23320	49	31.28	36.64	6.766	8.7423	2.3069	-3.1404	24.1485	3.3372	-0.038
$MnSO_4^0$	-235640	-266750	5	-20.6	2.8	2.1354	-2.5645	6.751	-2.6729	-6.2564	-7.2308	-0.038

[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] Retrieved from regression calculations using equations cited in Table 4, unless otherwise indicated. [h] Calculated from the values of ΔG^0_f and $S°$ shown above using standard molal entropies of the elements consistent with Shock and Helgeson (1988). [i] Predicted from Eqns. (53)–(59) and (60)–(65) unless otherwise noted. [j] Calculated from the values of $S°$, C^0_P and $V°$ shown above using Eqns. (33)–(37).

TABLE 4. Identities of estimated and regression-generated standard partial molal properties at 25°C and 1 bar of complexes together with the numbers of the equations used in the calculations (see text)[1].

Complex	Estimated Properties	Regression-generated Properties	Equations Used
NaCl°		$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$, $\overline{V}^0_{P_r,T_r}$, ω	38
$AgCl°$, $AgCl_2^-$		$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$, ω	39
$AgCl_3^{2-}$, $AgCl_4^{3-}$, $PbCl_4^{2-}$	$\overline{C}^0_{P_r,T_r}$, ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$	39, 40, 53-59
$PbCl^+$, $PbCl_3^-$, $ZnCl^+$, $NiCl^+$, $MgCl^+$, $FeCl^+$,	ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$	39, 40
$PbCl_2^0$, $ZnCl_2^0$, NaF°	ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$	39, 40, 42
KSO_4^-, $HSiO_3^-$	ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$	39, 40
$CaSO_4^0$		$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$, ω	39, 40
LiCl°, KCl°, RbCl°, CsCl°	$\overline{S}^0_{P_r,T_r}$	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$, ω	38, 45-47
NaBr°, NaI°, RbF°, RbBr°, RbI°, KBr°, KI°, CsBr°, CsI°	$\overline{C}^0_{P_r,T_r}$	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$, ω	38, 51
$Fe(CH_3COO)^+$, $Fe(CH_3COO)_2^0$	ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$	39, 40, 42
$Zn(CH_3COO)^+$, $Zn(CH_3COO)_2$, $Zn(CH_3COO)_3^-$	ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$	39, 40, 42
$Ag(CO_3)^-$, $Ag(CO_3)_2^{3-}$	$\overline{C}^0_{P_r,T_r}$, ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$	39, 40[2]
$MgCO_3^0$, $CaCO_3^0$, $SrCO_3^0$, $BaCO_3^0$	$\overline{C}^0_{P_r,T_r}$, ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$	39, 42[2]
MgF^+, CaF^+	ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$	39, 40
SrF^+, BaF^+, $SrCl^+$, $BaCl^+$, $MnCl^+$, $CaCl^+$	$\overline{C}^0_{P_r,T_r}$, ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$	39, 40, 53-59
$FeCl_2^0$	ω, $\overline{V}^0_{P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$	39, 42, 53-59, 62
$Na(HSiO_3)°$, $ZnCl_3^-$	$\overline{C}^0_{P_r,T_r}$, ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$	39, 42, 53-59
$CaCl_2^0$, $MnSO_4^0$, $AgNO_3^0$	$\overline{C}^0_{P_r,T_r}$, ω	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$	39, 42
$K(HSO_4)°$	$\overline{V}^0_{P_r,T_r}$, $\overline{C}^0_{P_r,T_r}$	$\Delta\overline{G}^0_{f,P_r,T_r}$, $\overline{S}^0_{P_r,T_r}$, ω	38, 42, 53-59

[1]For sources of dissociation constant data at low temperatures (near 25°C), see the figures below. [2]Values of $\overline{C}^0_{P_r,T_r}$ were estimated assuming that the standard partial molal heat capacities of association for carbonate complexes are the same as those for sulfate complexes (see text).

TABLE 5. Logarithms of the dissociation constants of aqueous complexes listed in Table 2 at temperatures ranging from 0 to 350°C and P_{SAT} (see text).

Species	0	25	50	75	100	125	150	175	200	225	250	275	300	325	350
$NaCl^0$	0.83	0.78	0.69	0.59	0.47	0.35	0.21	0.07	-0.09	-0.27	-0.48	-0.72	-1.01	-1.38	-1.93
$AgCl^0$	-3.57	-3.3	-3.11	-2.98	-2.9	-2.85	-2.83	-2.85	-2.89	-2.96	-3.07	-3.22	-3.43	-3.73	-4.19
$AgCl_2^-$	-5.79	-5.3	-4.97	-4.74	-4.6	-4.53	-4.51	-4.53	-4.61	-4.72	-4.89	-5.12	-5.41	-5.81	-6.39
$ZnCl^+$	0.44	-0.2	-0.82	-1.41	-1.98	-2.52	-3.04	-3.56	-4.07	-4.58	-5.11	-5.67	-6.27	-6.92	-7.65
$ZnCl_2^0$	0.15	-0.25	-0.74	-1.26	-1.8	-2.36	-2.93	-3.52	-4.14	-4.79	-5.49	-6.27	-7.14	-8.14	-9.41
$PbCl^+$	-1.41	-1.44	-1.53	-1.66	-1.81	-1.99	-2.19	-2.4	-2.64	-2.9	-3.2	-3.54	-3.94	-4.41	-5.03
$PbCl_2^0$	-1.94	-2	-2.16	-2.37	-2.63	-2.91	-3.23	-3.58	-3.97	-4.4	-4.89	-5.46	-6.13	-6.96	-8.1
$PbCl_3^-$	-1.65	-1.69	-1.85	-2.09	-2.38	-2.71	-3.08	-3.49	-3.94	-4.45	-5.02	-5.68	-6.47	-7.43	-8.73
$NiCl^+$	1.04	1	0.88	0.74	0.56	0.37	0.16	-0.07	-0.31	-0.58	-0.88	-1.22	-1.61	-2.07	-2.66
$FeCl^+$	0.15	0.16	0.08	-0.05	-0.21	-0.39	-0.61	-0.84	-1.09	-1.37	-1.69	-2.04	-2.45	-2.92	-3.52
$MgCl^+$	0.1	0.14	0.08	-0.03	-0.17	-0.34	-0.54	-0.75	-0.99	-1.26	-1.55	-1.89	-2.28	-2.74	-3.34
MgF^+	-1.39	-1.35	-1.43	-1.57	-1.74	-1.94	-2.17	-2.42	-2.69	-2.99	-3.32	-3.7	-4.13	-4.63	-5.26
CaF^+	-0.66	-0.68	-0.8	-0.97	-1.17	-1.4	-1.65	-1.92	-2.22	-2.54	-2.89	-3.28	-3.73	-4.24	-4.88
$Fe(CH_3COO)^+$	-1.43	-1.29	-1.3	-1.38	-1.52	-1.69	-1.9	-2.13	-2.38	-2.67	-2.99	-3.35	-3.76	-4.24	-4.83
$Fe(CH_3COO)_2^0$	-2.98	-2.49	-2.33	-2.37	-2.54	-2.81	-3.15	-3.56	-4.03	-4.56	-5.16	-5.85	-6.65	-7.6	-8.83
$Zn(CH_3COO)^+$	-1.54	-1.61	-1.79	-2.03	-2.3	-2.6	-2.91	-3.25	-3.6	-3.97	-4.37	-4.81	-5.3	-5.84	-6.49
$Zn(CH_3COO)_2^0$	-3.81	-3.45	-3.43	-3.59	-3.87	-4.23	-4.67	-5.16	-5.71	-6.31	-6.99	-7.74	-8.61	-9.61	-10.9
$Zn(CH_3COO)_3^-$	-5.1	-4.2	-3.89	-3.91	-4.15	-4.55	-5.07	-5.69	-6.39	-7.16	-8.02	-8.98	-10.1	-11.3	-12.8
KSO_4^-	-0.89	-0.88	-0.95	-1.06	-1.2	-1.35	-1.52	-1.71	-1.92	-2.15	-2.42	-2.73	-3.09	-3.53	-4.13
$CaSO_4^0$	-2.07	-2.11	-2.21	-2.35	-2.51	-2.7	-2.91	-3.15	-3.43	-3.76	-4.14	-4.61	-5.19	-5.91	-6.91
$HSiO_3^-$	-9.81	-9.59	-9.33	-9.12	-8.96	-8.86	-8.8	-8.8	-8.83	-8.91	-9.04	-9.21	-9.43	-9.73	-10.2
$LiCl^0$	1.55	1.51	1.42	1.31	1.18	1.04	0.88	0.7	0.51	0.3	0.05	-0.23	-0.56	-0.97	-1.54
KCl^0	2.84	2.54	2.25	1.98	1.73	1.49	1.26	1.02	0.79	0.54	0.28	-0.01	-0.34	-0.75	-1.32
$RbCl^0$	1.16	0.96	0.77	0.6	0.43	0.27	0.11	-0.05	-0.22	-0.39	-0.59	-0.81	-1.09	-1.43	-1.93
$CsCl^0$	0.28	0.14	0	-0.14	-0.26	-0.38	-0.5	-0.63	-0.75	-0.89	-1.04	-1.22	-1.43	-1.69	-2.07
NaF^0	1.08	1	0.88	0.76	0.62	0.48	0.34	0.18	0.01	-0.18	-0.4	-0.65	-0.96	-1.34	-1.86
RbF^0	-0.94	-0.96	-1	-1.04	-1.09	-1.15	-1.22	-1.31	-1.4	-1.52	-1.67	-1.85	-2.08	-2.38	-2.81
$NaBr^0$	1.46	1.36	1.23	1.09	0.94	0.8	0.64	0.48	0.3	0.11	-0.11	-0.36	-0.66	-1.04	-1.59
KBr^0	1.95	1.74	1.53	1.33	1.14	0.95	0.76	0.57	0.37	0.16	-0.06	-0.32	-0.61	-0.98	-1.51
$RbBr^0$	1.43	1.22	1.02	0.83	0.66	0.49	0.33	0.16	-0.01	-0.19	-0.38	-0.61	-0.87	-1.21	-1.71
$CsBr^0$	0.08	-0.02	-0.12	-0.22	-0.31	-0.4	-0.5	-0.59	-0.7	-0.81	-0.95	-1.12	-1.33	-1.61	-2.05
NaI^0	1.62	1.54	1.43	1.31	1.18	1.04	0.89	0.73	0.56	0.38	0.17	-0.07	-0.36	-0.72	-1.24
KI^0	1.72	1.6	1.47	1.33	1.2	1.05	0.9	0.75	0.58	0.4	0.2	-0.03	-0.31	-0.66	-1.17
RbI^0	1.08	0.96	0.84	0.73	0.61	0.49	0.37	0.24	0.1	-0.05	-0.22	-0.42	-0.67	-0.98	-1.46
CsI^0	-1.02	-0.98	-0.96	-0.96	-0.97	-0.98	-1.01	-1.05	-1.1	-1.17	-1.26	-1.38	-1.54	-1.77	-2.13

Table 6. Logarithms of the dissociation constants of aqueous complexes listed in Table 2 at temperatures ranging from 100 to 450°C at 0.5 kb (see text).

Species	100	150	200	250	300	350	400	450
$NaCl^0$	0.53	0.3	0.03	-0.29	-0.67	-1.18	-1.74	-3.05
$AgCl^0$	-2.82	-2.74	-2.76	-2.88	-3.1	-3.47	-3.93	-5.2
$AgCl_2^-$	-4.45	-4.34	-4.4	-4.61	-4.96	-5.51	-6.08	-7.45
$ZnCl^+$	-1.91	-2.94	-3.91	-4.85	-5.81	-6.87	-7.55	-8.24
$ZnCl_2^0$	-1.66	-2.74	-3.86	-5.04	-6.34	-7.89	-9.16	-11.2
$PbCl^+$	-1.75	-2.09	-2.49	-2.96	-3.51	-4.22	-4.77	-5.75
$PbCl_2^0$	-2.48	-3.04	-3.69	-4.46	-5.38	-6.58	-7.7	-10.1
$PbCl_3^-$	-2.14	-2.79	-3.57	-4.47	-5.55	-6.96	-8.24	-10.9
$NiCl^+$	0.62	0.24	-0.19	-0.67	-1.23	-1.92	-2.5	-3.52
$FeCl^+$	-0.15	-0.52	-0.96	-1.47	-2.06	-2.79	-3.36	-4.3
$MgCl^+$	-0.12	-0.46	-0.87	-1.34	-1.9	-2.59	-3.18	-4.22
MgF^+	-1.68	-2.08	-2.55	-3.09	-3.72	-4.48	-5.08	-6.07
CaF^+	-1.11	-1.57	-2.08	-2.67	-3.33	-4.13	-4.74	-5.67
$Fe(CH_3COO)^+$	-1.45	-1.8	-2.24	-2.76	-3.37	-4.11	-4.68	-5.53
$Fe(CH_3COO)_2^0$	-2.36	-2.92	-3.72	-4.7	-5.87	-7.34	-8.64	-10.9
$Zn(CH_3COO)^+$	-2.23	-2.82	-3.45	-4.14	-4.88	-5.76	-6.38	-7.14
$Zn(CH_3COO)_2^0$	-3.7	-4.45	-5.41	-6.53	-7.83	-9.41	-10.8	-13.1
$Zn(CH_3COO)_3^-$	-3.86	-4.74	-5.99	-7.48	-9.2	-11.2	-13.1	-15.8
KSO_4^-	-1.17	-1.47	-1.82	-2.23	-2.72	-3.35	-3.9	-5.01
$CaSO_4^0$	-2.44	-2.78	-3.21	-3.75	-4.44	-5.42	-6.17	-7.83
$HSiO_3^-$	-8.77	-8.61	-8.63	-8.78	-9.07	-9.53	-10.0	-11.1
$LiCl^0$	1.29	1.01	0.68	0.29	-0.16	-0.76	-1.35	-2.61
KCl^0	1.83	1.36	0.93	0.48	0	-0.59	-1.24	-2.67
$RbCl^0$	0.52	0.21	-0.08	-0.4	-0.76	-1.23	-1.76	-3.06
$CsCl^0$	-0.19	-0.42	-0.65	-0.88	-1.16	-1.52	-1.89	-2.78
NaF^0	0.69	0.43	0.15	-0.18	-0.57	-1.1	-1.52	-2.43
RbF^0	-1.03	-1.14	-1.28	-1.47	-1.72	-2.12	-2.44	-3.24
$NaBr^0$	1.01	0.72	0.42	0.08	-0.31	-0.84	-1.43	-2.85
KBr^0	1.23	0.87	0.51	0.14	-0.28	-0.81	-1.41	-2.78
$RbBr^0$	0.74	0.43	0.12	-0.19	-0.55	-1.02	-1.57	-2.91
$CsBr^0$	-0.23	-0.4	-0.57	-0.77	-1.02	-1.38	-1.83	-3.07
NaI^0	1.23	0.96	0.67	0.34	-0.05	-0.56	-1.13	-2.47
KI^0	1.3	1.01	0.72	0.39	0.01	-0.49	-1.08	-2.48
RbI^0	0.71	0.48	0.24	-0.03	-0.35	-0.79	-1.32	-2.67
CsI^0	-0.87	-0.9	-0.97	-1.09	-1.26	-1.54	-1.92	-2.98

Table 7. Logarithms of the dissociation constants of aqueous complexes listed in Table 2 at temperatures ranging from 100 to 600°C at 1.0 kb (see text).

Species	100	150	200	250	300	350	400	450	500	550	600
$NaCl^0$	0.58	0.36	0.11	-0.15	-0.45	-0.79	-1.18	-1.66	-2.26	-3.01	-3.82
$AgCl^0$	-2.77	-2.67	-2.67	-2.74	-2.88	-3.09	-3.37	-3.76	-4.3	-4.98	-5.75
$AgCl_2^-$	-4.33	-4.2	-4.23	-4.39	-4.65	-4.99	-5.43	-5.98	-6.67	-7.53	-8.45
$ZnCl^+$	-1.87	-2.87	-3.79	-4.67	-5.52	-6.35	-7.16	-7.96	-8.75	-9.51	-10.2
$ZnCl_2^0$	-1.56	-2.6	-3.65	-4.73	-5.84	-7	-8.21	-9.51	-10.9	-12.5	-14.0
$PbCl^+$	-1.7	-2.01	-2.38	-2.79	-3.25	-3.74	-4.27	-4.86	-5.53	-6.26	-7.01
$PbCl_2^0$	-2.37	-2.89	-3.48	-4.15	-4.9	-5.72	-6.64	-7.71	-8.98	-10.5	-12.1
$PbCl_3^-$	-1.95	-2.57	-3.28	-4.07	-4.96	-5.93	-7.01	-8.25	-9.72	-11.4	-13.2
$NiCl^+$	0.65	0.3	-0.09	-0.53	-0.99	-1.49	-2.03	-2.62	-3.29	-4.03	-4.78
$FeCl^+$	-0.1	-0.45	-0.86	-1.32	-1.81	-2.34	-2.91	-3.53	-4.21	-4.95	-5.68
$MgCl^+$	-0.08	-0.4	-0.77	-1.19	-1.66	-2.16	-2.71	-3.31	-3.99	-4.75	-5.52
MgF^+	-1.63	-2.01	-2.45	-2.93	-3.46	-4.01	-4.61	-5.26	-5.97	-6.74	-7.52
CaF^+	-1.07	-1.5	-1.98	-2.51	-3.07	-3.67	-4.3	-4.97	-5.69	-6.47	-7.22
$Fe(CH_3COO)^+$	-1.41	-1.73	-2.14	-2.61	-3.12	-3.67	-4.26	-4.89	-5.57	-6.29	-6.98
$Fe(CH_3COO)_2^0$	-2.23	-2.75	-3.48	-4.36	-5.36	-6.46	-7.66	-8.98	-10.5	-12.1	-13.8
$Zn(CH_3COO)^+$	-2.19	-2.74	-3.34	-3.97	-4.62	-5.29	-5.98	-6.69	-7.42	-8.16	-8.85
$Zn(CH_3COO)_2^0$	-3.58	-4.29	-5.18	-6.21	-7.33	-8.54	-9.84	-11.3	-12.8	-14.6	-16.3
$Zn(CH_3COO)_3^-$	-3.64	-4.49	-5.68	-7.08	-8.63	-10.3	-12.0	-13.9	-15.9	-18.1	-20.2
KSO_4^-	-1.18	-1.45	-1.77	-2.12	-2.5	-2.93	-3.41	-3.95	-4.59	-5.34	-6.11
$CaSO_4^0$	-2.4	-2.7	-3.06	-3.49	-4	-4.58	-5.25	-6.05	-7.02	-8.15	-9.31
$HSiO_3^-$	-8.59	-8.44	-8.44	-8.57	-8.8	-9.12	-9.52	-10.0	-10.6	-11.3	-12.1
$LiCl^0$	1.38	1.12	0.81	0.48	0.1	-0.31	-0.77	-1.31	-1.97	-2.74	-3.57
KCl^0	1.9	1.45	1.04	0.63	0.23	-0.2	-0.67	-1.21	-1.87	-2.67	-3.54
$RbCl^0$	0.58	0.29	0.02	-0.26	-0.54	-0.86	-1.22	-1.66	-2.22	-2.92	-3.69
$CsCl^0$	-0.14	-0.36	-0.56	-0.77	-0.99	-1.22	-1.49	-1.81	-2.22	-2.71	-3.26
NaF^0	0.75	0.51	0.25	-0.02	-0.32	-0.65	-1.02	-1.46	-1.97	-2.57	-3.19
RbF^0	-0.98	-1.07	-1.18	-1.32	-1.5	-1.71	-1.97	-2.3	-2.71	-3.21	-3.73
$NaBr^0$	1.06	0.78	0.51	0.22	-0.1	-0.45	-0.85	-1.35	-1.98	-2.76	-3.61
KBr^0	1.3	0.95	0.61	0.28	-0.07	-0.44	-0.85	-1.35	-1.96	-2.72	-3.55
$RbBr^0$	0.81	0.5	0.22	-0.06	-0.35	-0.66	-1.02	-1.46	-2.03	-2.74	-3.52
$CsBr^0$	-0.17	-0.33	-0.48	-0.64	-0.82	-1.04	-1.3	-1.65	-2.13	-2.75	-3.46
NaI^0	1.27	1.01	0.74	0.46	0.14	-0.21	-0.6	-1.09	-1.69	-2.44	-3.26
KI^0	1.37	1.1	0.82	0.53	0.22	-0.13	-0.53	-1.01	-1.62	-2.38	-3.22
RbI^0	0.79	0.57	0.34	0.11	-0.15	-0.44	-0.78	-1.2	-1.76	-2.46	-3.25
CsI^0	-0.79	-0.82	-0.88	-0.96	-1.07	-1.23	-1.44	-1.73	-2.14	-2.68	-3.29

Table 8. Logarithms of the dissociation constants of aqueous complexes listed in Table 2 at temperatures ranging from 100 to 950°C at 2.0 kb (see text).

Species	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950
$NaCl^0$	0.64	0.44	0.24	0.02	-0.21	-0.45	-0.71	-0.98	-1.29	-1.62	-1.97	-2.34	-2.71	-3.07	-3.41	-3.72	-4	-4.26
$AgCl^0$	-2.69	-2.57	-2.53	-2.56	-2.63	-2.75	-2.9	-3.1	-3.33	-3.59	-3.89	-4.22	-4.55	-4.87	-5.18	-5.46	-5.72	-5.95
$AgCl_2^-$	-4.15	-3.99	-3.99	-4.09	-4.27	-4.51	-4.8	-5.14	-5.52	-5.94	-6.4	-6.89	-7.38	-7.86	-8.32	-8.76	-9.16	-9.54
$ZnCl^+$	-1.82	-2.77	-3.64	-4.44	-5.2	-5.92	-6.61	-7.28	-7.94	-8.6	-9.25	-9.88	-10.5	-11.1	-11.7	-12.2	-12.7	-13.2
$ZnCl_2^0$	-1.43	-2.4	-3.36	-4.31	-5.27	-6.22	-7.18	-8.16	-9.15	-10.2	-11.2	-12.3	-13.3	-14.3	-15.3	-16.2	-17	-17.8
$PbCl^+$	-1.63	-1.92	-2.23	-2.57	-2.94	-3.32	-3.72	-4.14	-4.58	-5.04	-5.52	-6.01	-6.5	-6.97	-7.42	-7.85	-8.25	-8.63
$PbCl_2^0$	-2.21	-2.68	-3.19	-3.75	-4.34	-4.97	-5.63	-6.33	-7.07	-7.87	-8.7	-9.56	-10.4	-11.3	-12.1	-12.8	-13.5	-14.1
$PbCl_3^-$	-1.68	-2.23	-2.86	-3.53	-4.24	-4.99	-5.79	-6.62	-7.5	-8.44	-9.43	-10.4	-11.5	-12.4	-13.4	-14.2	-15.0	-15.8
$NiCl^+$	0.69	0.37	0.03	-0.34	-0.73	-1.13	-1.54	-1.97	-2.41	-2.88	-3.36	-3.85	-4.33	-4.8	-5.25	-5.67	-6.07	-6.44
$FeCl^+$	-0.05	-0.37	-0.73	-1.12	-1.53	-1.97	-2.41	-2.88	-3.36	-3.86	-4.37	-4.89	-5.4	-5.9	-6.38	-6.83	-7.26	-7.66
$MgCl^+$	-0.03	-0.32	-0.65	-1.01	-1.39	-1.8	-2.22	-2.65	-3.11	-3.59	-4.08	-4.58	-5.08	-5.56	-6.03	-6.46	-6.87	-7.26
MgF^+	-1.57	-1.91	-2.3	-2.72	-3.16	-3.61	-4.08	-4.56	-5.06	-5.58	-6.12	-6.66	-7.19	-7.71	-8.21	-8.68	-9.12	-9.54
CaF^+	-1.01	-1.41	-1.84	-2.3	-2.78	-3.28	-3.78	-4.3	-4.83	-5.38	-5.94	-6.5	-7.06	-7.6	-8.11	-8.6	-9.07	-9.51
$Fe(CH_3COO)^+$	-1.36	-1.65	-2	-2.41	-2.84	-3.3	-3.77	-4.25	-4.76	-5.28	-5.81	-6.35	-6.88	-7.39	-7.88	-8.35	-8.8	-9.22
$Fe(CH_3COO)_2^0$	-2.06	-2.51	-3.16	-3.92	-4.77	-5.68	-6.63	-7.63	-8.66	-9.74	-10.9	-12.0	-13.1	-14.2	-15.2	-16.2	-17.2	-18.1
$Zn(CH_3COO)^+$	-2.15	-2.66	-3.2	-3.76	-4.33	-4.9	-5.47	-6.05	-6.63	-7.22	-7.82	-8.41	-8.99	-9.56	-10.1	-10.6	-11.1	-11.6
$Zn(CH_3COO)_2^0$	-3.43	-4.07	-4.88	-5.78	-6.76	-7.78	-8.83	-9.91	-11.0	-12.2	-13.4	-14.6	-15.8	-16.9	-18	-19.1	-20.0	-21.0
$Zn(CH_3COO)_3^-$	-3.34	-4.12	-5.23	-6.53	-7.93	-9.41	-10.9	-12.5	-14.1	-15.7	-17.3	-19.0	-20.6	-22.1	-23.7	-25.1	-26.5	-27.8
KSO_4^-	-1.25	-1.49	-1.74	-2.02	-2.32	-2.63	-2.97	-3.32	-3.7	-4.1	-4.52	-4.96	-5.4	-5.82	-6.22	-6.6	-6.95	-7.28
$CaSO_4^0$	-2.4	-2.64	-2.9	-3.2	-3.53	-3.91	-4.33	-4.79	-5.3	-5.87	-6.48	-7.12	-7.76	-8.39	-8.98	-9.53	-10.4	-10.5
$HSiO_3^-$	-8.26	-8.13	-8.13	-8.23	-8.42	-8.67	-8.97	-9.32	-9.7	-10.1	-10.6	-11.0	-11.5	-12.0	-12.4	-12.9	-13.3	-13.7
$LiCl^0$	1.54	1.3	1.03	0.74	0.44	0.12	-0.21	-0.56	-0.94	-1.34	-1.76	-2.19	-2.62	-3.04	-3.44	-3.81	-4.15	-4.46
KCl^0	2.01	1.58	1.19	0.84	0.49	0.16	-0.18	-0.52	-0.88	-1.26	-1.65	-2.06	-2.46	-2.85	-3.21	-3.54	-3.84	-4.11
$RbCl^0$	0.67	0.4	0.16	-0.07	-0.29	-0.52	-0.76	-1.01	-1.28	-1.57	-1.88	-2.21	-2.53	-2.85	-3.14	-3.41	-3.65	-3.86
$CsCl^0$	-0.09	-0.29	-0.46	-0.63	-0.8	-0.96	-1.13	-1.32	-1.51	-1.73	-1.96	-2.19	-2.43	-2.67	-2.88	-3.08	-3.26	-3.42
NaF^0	0.84	0.62	0.41	0.19	-0.03	-0.26	-0.51	-0.77	-1.05	-1.36	-1.68	-2.02	-2.36	-2.69	-3	-3.28	-3.55	-3.79
RbF^0	-0.92	-0.98	-1.05	-1.13	-1.24	-1.36	-1.5	-1.67	-1.85	-2.07	-2.31	-2.56	-2.82	-3.07	-3.3	-3.52	-3.72	-3.89
$NaBr^0$	1.12	0.87	0.63	0.39	0.14	-0.11	-0.38	-0.66	-0.97	-1.31	-1.66	-2.04	-2.41	-2.78	-3.12	-3.43	-3.71	-3.96
KBr^0	1.41	1.07	0.77	0.47	0.19	-0.1	-0.39	-0.69	-1.01	-1.35	-1.71	-2.08	-2.45	-2.81	-3.14	-3.45	-3.72	-3.97
$RbBr^0$	0.89	0.61	0.36	0.12	-0.11	-0.34	-0.57	-0.82	-1.09	-1.38	-1.69	-2.01	-2.33	-2.64	-2.93	-3.2	-3.43	-3.63
$CsBr^0$	-0.1	-0.24	-0.36	-0.48	-0.6	-0.73	-0.87	-1.04	-1.22	-1.43	-1.67	-1.92	-2.17	-2.42	-2.65	-2.86	-3.04	-3.19
NaI^0	1.3	1.07	0.83	0.59	0.35	0.09	-0.18	-0.47	-0.78	-1.12	-1.47	-1.84	-2.21	-2.57	-2.91	-3.22	-3.5	-3.75
KI^0	1.47	1.22	0.97	0.71	0.46	0.19	-0.08	-0.37	-0.68	-1.02	-1.37	-1.74	-2.11	-2.47	-2.81	-3.11	-3.39	-3.64
RbI^0	0.89	0.69	0.49	0.29	0.09	-0.11	-0.33	-0.57	-0.83	-1.11	-1.42	-1.74	-2.06	-2.37	-2.66	-2.93	-3.16	-3.37
CsI^0	-0.7	-0.72	-0.75	-0.8	-0.86	-0.95	-1.05	-1.18	-1.33	-1.51	-1.71	-1.93	-2.16	-2.38	-2.58	-2.77	-2.93	-3.07

TABLE 9. **Logarithms of the dissociation constants of aqueous complexes listed in Table 2 at temperatures ranging from 100 to 1,000°C at 3.0 kb (see text).**

Species	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
$NaCl^0$	0.67	0.49	0.31	0.13	-0.06	-0.25	-0.44	-0.65	-0.86	-1.09	-1.33	-1.58	-1.84	-2.11	-2.38	-2.64	-2.89	-3.12	-3.34
$AgCl^0$	-2.64	-2.5	-2.44	-2.44	-2.47	-2.54	-2.64	-2.76	-2.91	-3.08	-3.27	-3.47	-3.69	-3.93	-4.16	-4.39	-4.62	-4.83	-5.02
$AgCl_2^-$	-4.02	-3.85	-3.82	-3.89	-4.02	-4.2	-4.43	-4.68	-4.97	-5.28	-5.62	-5.97	-6.35	-6.73	-7.13	-7.51	-7.89	-8.25	-8.59
$ZnCl^+$	-1.8	-2.72	-3.55	-4.3	-4.99	-5.64	-6.26	-6.85	-7.43	-7.99	-8.55	-9.1	-9.66	-10.2	-10.8	-11.3	-11.8	-12.3	-12.8
$ZnCl_2^0$	-1.36	-2.28	-3.17	-4.04	-4.9	-5.74	-6.57	-7.39	-8.22	-9.05	-9.89	-10.8	-11.6	-12.5	-13.4	-14.2	-15	-15.8	-16.6
$PbCl^+$	-1.6	-1.86	-2.14	-2.43	-2.74	-3.06	-3.39	-3.73	-4.08	-4.44	-4.81	-5.2	-5.59	-6	-6.41	-6.81	-7.21	-7.58	-7.93
$PbCl_2^0$	-2.12	-2.54	-3	-3.48	-3.98	-4.5	-5.04	-5.59	-6.16	-6.75	-7.37	-8.02	-8.68	-9.35	-10	-10.7	-11.3	-11.9	-12.5
$PbCl_3^-$	-1.49	-2	-2.56	-3.15	-3.77	-4.4	-5.05	-5.72	-6.41	-7.12	-7.86	-8.63	-9.42	-10.2	-11	-11.8	-12.6	-13.3	-14
$NiCl^+$	0.7	0.41	0.1	-0.23	-0.56	-0.91	-1.25	-1.61	-1.97	-2.34	-2.71	-3.1	-3.5	-3.91	-4.31	-4.71	-5.1	-5.46	-5.81
$FeCl^+$	-0.03	-0.32	-0.65	-1	-1.36	-1.74	-2.12	-2.51	-2.9	-3.31	-3.72	-4.15	-4.58	-5.02	-5.46	-5.9	-6.32	-6.72	-7.1
$MgCl^+$	-0.02	-0.27	-0.57	-0.89	-1.22	-1.57	-1.93	-2.29	-2.66	-3.04	-3.43	-3.83	-4.25	-4.66	-5.08	-5.49	-5.89	-6.27	-6.63
MgF^+	-1.52	-1.84	-2.2	-2.57	-2.96	-3.35	-3.75	-4.16	-4.57	-4.99	-5.42	-5.87	-6.32	-6.77	-7.23	-7.68	-8.12	-8.54	-8.94
CaF^+	-0.96	-1.34	-1.75	-2.16	-2.59	-3.03	-3.47	-3.91	-4.35	-4.81	-5.27	-5.74	-6.22	-6.7	-7.18	-7.66	-8.13	-8.57	-8.99
$Fe(CH_3COO)^+$	-1.36	-1.61	-1.93	-2.29	-2.67	-3.07	-3.48	-3.89	-4.31	-4.74	-5.18	-5.63	-6.09	-6.55	-7.02	-7.48	-7.92	-8.35	-8.75
$Fe(CH_3COO)_2^0$	-1.97	-2.37	-2.95	-3.64	-4.4	-5.2	-6.03	-6.88	-7.75	-8.64	-9.55	-10.5	-11.4	-12.4	-13.3	-14.3	-15.2	-16.1	-16.9
$Zn(CH_3COO)^+$	-2.15	-2.62	-3.13	-3.64	-4.15	-4.66	-5.17	-5.67	-6.17	-6.67	-7.18	-7.69	-8.21	-8.73	-9.25	-9.76	-10.3	-10.7	-11.2
$Zn(CH_3COO)_2^0$	-3.37	-3.95	-4.69	-5.52	-6.4	-7.31	-8.23	-9.17	-10.1	-11.1	-12.1	-13.1	-14.1	-15.1	-16.1	-17.1	-18.1	-19	-19.9
$Zn(CH_3COO)_3^-$	-3.15	-3.88	-4.94	-6.16	-7.48	-8.85	-10.2	-11.7	-13.1	-14.5	-16	-17.4	-18.9	-20.3	-21.7	-23.1	-24.5	-25.8	-27.1
KSO_4^-	-1.37	-1.57	-1.79	-2.02	-2.25	-2.5	-2.76	-3.03	-3.3	-3.6	-3.9	-4.23	-4.56	-4.9	-5.25	-5.59	-5.92	-6.23	-6.52
$CaSO_4^0$	-2.46	-2.65	-2.84	-3.05	-3.28	-3.54	-3.82	-4.12	-4.46	-4.82	-5.22	-5.66	-6.13	-6.62	-7.12	-7.62	-8.11	-8.57	-8.99
$HSiO_3^-$	-7.95	-7.85	-7.85	-7.95	-8.12	-8.34	-8.6	-8.89	-9.21	-9.56	-9.92	-10.3	-10.7	-11.1	-11.5	-11.9	-12.3	-12.7	-13
$LiCl^0$	1.68	1.45	1.2	0.94	0.68	0.41	0.14	-0.14	-0.43	-0.73	-1.04	-1.36	-1.69	-2.03	-2.37	-2.7	-3.01	-3.31	-3.59
KCl^0	2.08	1.66	1.3	0.97	0.67	0.38	0.1	-0.18	-0.46	-0.73	-1.02	-1.31	-1.6	-1.89	-2.18	-2.46	-2.73	-2.97	-3.2
$RbCl^0$	0.72	0.47	0.25	0.05	-0.14	-0.32	-0.5	-0.68	-0.87	-1.07	-1.27	-1.49	-1.71	-1.93	-2.16	-2.38	-2.58	-2.77	-2.94
$CsCl^0$	-0.08	-0.25	-0.41	-0.55	-0.68	-0.81	-0.94	-1.07	-1.2	-1.34	-1.49	-1.65	-1.81	-1.98	-2.15	-2.31	-2.47	-2.61	-2.74
NaF^0	0.9	0.7	0.52	0.34	0.16	-0.01	-0.19	-0.38	-0.58	-0.79	-1.01	-1.25	-1.49	-1.75	-2.01	-2.27	-2.53	-2.76	-2.98
RbF^0	-0.89	-0.92	-0.96	-1.01	-1.07	-1.14	-1.22	-1.32	-1.43	-1.55	-1.69	-1.85	-2.02	-2.21	-2.4	-2.59	-2.77	-2.94	-3.09
$NaBr^0$	1.15	0.92	0.71	0.5	0.29	0.09	-0.12	-0.33	-0.55	-0.78	-1.02	-1.27	-1.53	-1.79	-2.06	-2.31	-2.56	-2.78	-2.99
KBr^0	1.48	1.16	0.87	0.6	0.35	0.11	-0.13	-0.37	-0.61	-0.85	-1.1	-1.36	-1.63	-1.89	-2.15	-2.4	-2.65	-2.87	-3.07
$RbBr^0$	0.93	0.67	0.44	0.23	0.04	-0.15	-0.33	-0.51	-0.7	-0.89	-1.09	-1.3	-1.52	-1.74	-1.95	-2.17	-2.36	-2.55	-2.71
$CsBr^0$	-0.08	-0.19	-0.29	-0.38	-0.47	-0.56	-0.65	-0.75	-0.86	-0.97	-1.1	-1.25	-1.4	-1.55	-1.71	-1.86	-2	-2.13	-2.25
NaI^0	1.31	1.09	0.88	0.67	0.46	0.25	0.04	-0.18	-0.41	-0.65	-0.89	-1.15	-1.41	-1.68	-1.94	-2.2	-2.45	-2.68	-2.89
KI^0	1.53	1.29	1.06	0.83	0.61	0.38	0.16	-0.07	-0.3	-0.54	-0.79	-1.05	-1.31	-1.57	-1.83	-2.09	-2.33	-2.56	-2.76
RbI^0	0.95	0.76	0.58	0.41	0.24	0.07	-0.1	-0.27	-0.45	-0.64	-0.84	-1.05	-1.27	-1.49	-1.7	-1.91	-2.11	-2.3	-2.46
CsI^0	-0.66	-0.66	-0.68	-0.7	-0.74	-0.79	-0.85	-0.92	-1.01	-1.1	-1.22	-1.34	-1.47	-1.61	-1.75	-1.89	-2.02	-2.14	-2.25

TABLE 10. Logarithms of the dissociation constants of aqueous complexes listed in Table 2 at temperatures ranging from 100 to 1,000°C at 4.0 kb (see text).

Species	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
$NaCl^0$	0.69	0.53	0.37	0.21	0.05	-0.11	-0.27	-0.43	-0.6	-0.77	-0.95	-1.15	-1.35	-1.56	-1.77	-1.99	-2.2	-2.41	-2.61
$AgCl^0$	-2.61	-2.46	-2.38	-2.35	-2.36	-2.4	-2.46	-2.55	-2.65	-2.77	-2.9	-3.05	-3.22	-3.39	-3.58	-3.77	-3.96	-4.15	-4.33
$AgCl_2^-$	-3.93	-3.74	-3.69	-3.73	-3.83	-3.98	-4.16	-4.37	-4.6	-4.86	-5.13	-5.42	-5.73	-6.05	-6.38	-6.72	-7.06	-7.39	-7.71
$ZnCl^+$	-1.8	-2.69	-3.49	-4.2	-4.85	-5.45	-6.02	-6.55	-7.07	-7.57	-8.06	-8.56	-9.05	-9.54	-10.0	-10.5	-11	-11.5	-11.9
$ZnCl_2^0$	-1.34	-2.2	-3.05	-3.86	-4.65	-5.41	-6.15	-6.88	-7.6	-8.32	-9.04	-9.78	-10.5	-11.3	-12.0	-12.8	-13.5	-14.3	-15.0
$PbCl^+$	-1.59	-1.82	-2.07	-2.34	-2.61	-2.89	-3.17	-3.45	-3.74	-4.04	-4.35	-4.67	-5	-5.34	-5.69	-6.05	-6.39	-6.74	-7.06
$PbCl_2^0$	-2.07	-2.45	-2.86	-3.29	-3.73	-4.18	-4.64	-5.1	-5.57	-6.05	-6.56	-7.08	-7.62	-8.18	-8.74	-9.32	-9.88	-10.4	-11.0
$PbCl_3^-$	-1.37	-1.83	-2.35	-2.88	-3.43	-3.98	-4.54	-5.1	-5.68	-6.27	-6.88	-7.51	-8.16	-8.84	-9.52	-10.2	-10.9	-11.6	-12.2
$NiCl^+$	0.69	0.43	0.14	-0.16	-0.46	-0.76	-1.06	-1.37	-1.68	-1.99	-2.31	-2.64	-2.97	-3.32	-3.67	-4.02	-4.36	-4.7	-5.03
$FeCl^+$	-0.04	-0.3	-0.6	-0.91	-1.24	-1.58	-1.91	-2.26	-2.6	-2.95	-3.31	-3.67	-4.04	-4.42	-4.81	-5.2	-5.58	-5.95	-6.31
$MgCl^+$	-0.02	-0.25	-0.52	-0.81	-1.11	-1.42	-1.73	-2.05	-2.36	-2.69	-3.02	-3.36	-3.71	-4.07	-4.44	-4.8	-5.16	-5.51	-5.85
MgF^+	-1.49	-1.79	-2.12	-2.47	-2.82	-3.17	-3.52	-3.88	-4.24	-4.6	-4.97	-5.35	-5.74	-6.13	-6.53	-6.93	-7.33	-7.72	-8.09
CaF^+	-0.93	-1.29	-1.67	-2.06	-2.46	-2.85	-3.24	-3.64	-4.03	-4.42	-4.83	-5.23	-5.65	-6.07	-6.5	-6.93	-7.35	-7.76	-8.16
$Fe(CH_3COO)^+$	-1.38	-1.6	-1.89	-2.22	-2.56	-2.92	-3.28	-3.65	-4.02	-4.39	-4.78	-5.17	-5.57	-5.97	-6.38	-6.79	-7.2	-7.6	-7.98
$Fe(CH_3COO)_2^0$	-1.95	-2.29	-2.82	-3.45	-4.14	-4.87	-5.61	-6.37	-7.15	-7.93	-8.73	-9.55	-10.	-11.2	-12.1	-12.9	-13.8	-14.6	-15.4
$Zn(CH_3COO)^+$	-2.17	-2.61	-3.09	-3.56	-4.03	-4.5	-4.96	-5.41	-5.86	-6.31	-6.75	-7.2	-7.66	-8.12	-8.59	-9.05	-9.5	-9.95	-10.4
$Zn(CH_3COO)_2^0$	-3.36	-3.88	-4.57	-5.34	-6.15	-6.99	-7.83	-8.68	-9.54	-10.4	-11.3	-12.2	-13.0	-13.9	-14.9	-15.8	-16.6	-17.5	-18.3
$Zn(CH_3COO)_3^-$	-3.05	-3.73	-4.73	-5.9	-7.15	-8.45	-9.78	-11.1	-12.4	-13.8	-15.1	-16.4	-17.8	-19.1	-20.4	-21.7	-23.0	-24.3	-25.5
KSO_4^-	-1.53	-1.7	-1.88	-2.06	-2.25	-2.45	-2.66	-2.87	-3.09	-3.32	-3.56	-3.81	-4.07	-4.35	-4.63	-4.92	-5.21	-5.49	-5.75
$CaSO_4^0$	-2.56	-2.7	-2.84	-2.99	-3.14	-3.31	-3.5	-3.7	-3.93	-4.18	-4.46	-4.77	-5.11	-5.47	-5.86	-6.27	-6.67	-7.07	-7.45
$HSiO_3^-$	-7.66	-7.59	-7.6	-7.7	-7.86	-8.06	-8.3	-8.57	-8.86	-9.16	-9.49	-9.82	-10.2	-10.5	-10.9	-11.3	-11.6	-12.0	-12.3
$LiCl^0$	1.79	1.58	1.35	1.11	0.87	0.63	0.4	0.16	-0.09	-0.34	-0.59	-0.85	-1.13	-1.4	-1.69	-1.97	-2.25	-2.53	-2.79
KCl^0	2.12	1.73	1.38	1.07	0.79	0.53	0.28	0.05	-0.19	-0.42	-0.65	-0.88	-1.11	-1.35	-1.59	-1.83	-2.06	-2.29	-2.5
$RbCl^0$	0.74	0.51	0.31	0.14	-0.03	-0.18	-0.33	-0.47	-0.62	-0.77	-0.92	-1.08	-1.25	-1.42	-1.6	-1.78	-1.95	-2.12	-2.28
$CsCl^0$	-0.09	-0.25	-0.39	-0.51	-0.62	-0.72	-0.82	-0.91	-1.01	-1.11	-1.22	-1.33	-1.45	-1.58	-1.71	-1.84	-1.97	-2.1	-2.22
NaF^0	0.96	0.77	0.6	0.45	0.31	0.17	0.03	-0.12	-0.26	-0.41	-0.58	-0.75	-0.94	-1.14	-1.35	-1.56	-1.77	-1.98	-2.18
RbF^0	-0.87	-0.88	-0.9	-0.93	-0.95	-0.99	-1.03	-1.09	-1.15	-1.22	-1.31	-1.41	-1.53	-1.66	-1.8	-1.94	-2.09	-2.23	-2.37
$NaBr^0$	1.17	0.95	0.75	0.57	0.39	0.22	0.06	-0.11	-0.29	-0.46	-0.65	-0.84	-1.04	-1.24	-1.45	-1.66	-1.87	-2.08	-2.27
KBr^0	1.52	1.21	0.94	0.69	0.47	0.25	0.05	-0.16	-0.35	-0.55	-0.75	-0.96	-1.17	-1.38	-1.59	-1.81	-2.02	-2.22	-2.41
$RbBr^0$	0.95	0.71	0.49	0.31	0.14	-0.02	-0.17	-0.31	-0.46	-0.6	-0.76	-0.91	-1.08	-1.24	-1.41	-1.58	-1.75	-1.91	-2.07
$CsBr^0$	-0.08	-0.18	-0.26	-0.33	-0.39	-0.45	-0.51	-0.57	-0.64	-0.71	-0.79	-0.88	-0.98	-1.08	-1.19	-1.31	-1.42	-1.53	-1.63
NaI^0	1.28	1.08	0.89	0.71	0.53	0.35	0.17	-0.01	-0.19	-0.38	-0.57	-0.77	-0.98	-1.19	-1.41	-1.63	-1.84	-2.05	-2.25
KI^0	1.56	1.33	1.11	0.91	0.71	0.51	0.32	0.13	-0.07	-0.26	-0.46	-0.67	-0.88	-1.09	-1.31	-1.52	-1.73	-1.94	-2.13
RbI^0	0.97	0.8	0.64	0.49	0.34	0.2	0.06	-0.08	-0.22	-0.37	-0.52	-0.68	-0.84	-1.01	-1.19	-1.36	-1.53	-1.69	-1.85
CsI^0	-0.66	-0.64	-0.64	-0.65	-0.67	-0.69	-0.72	-0.76	-0.81	-0.87	-0.94	-1.02	-1.1	-1.2	-1.3	-1.41	-1.51	-1.61	-1.71

TABLE 11. **Logarithms of the dissociation constants of aqueous complexes listed in Table 2 at temperatures ranging from 100 to 1,000°C at 5.0 kb (see text).**

Species	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
$NaCl^0$	0.69	0.55	0.4	0.26	0.12	-0.01	-0.14	-0.27	-0.41	-0.55	-0.7	-0.86	-1.02	-1.2	-1.39	-1.58	-1.78	-1.99	-2.2
$AgCl^0$	-2.6	-2.42	-2.33	-2.29	-2.28	-2.29	-2.33	-2.39	-2.46	-2.55	-2.65	-2.77	-2.9	-3.05	-3.21	-3.38	-3.55	-3.74	-3.93
$AgCl_2^-$	-3.87	-3.65	-3.59	-3.61	-3.69	-3.81	-3.96	-4.14	-4.34	-4.55	-4.79	-5.04	-5.31	-5.59	-5.89	-6.2	-6.52	-6.85	-7.18
$ZnCl^+$	-1.82	-2.69	-3.45	-4.13	-4.75	-5.32	-5.84	-6.34	-6.81	-7.27	-7.72	-8.16	-8.61	-9.06	-9.51	-9.97	-10.4	-10.9	-11.3
$ZnCl_2^0$	-1.34	-2.16	-2.97	-3.73	-4.47	-5.17	-5.85	-6.51	-7.16	-7.8	-8.45	-9.1	-9.77	-10.5	-11.1	-11.9	-12.6	-13.3	-14.0
$PbCl^+$	-1.6	-1.8	-2.03	-2.27	-2.51	-2.76	-3.01	-3.25	-3.51	-3.76	-4.03	-4.31	-4.6	-4.9	-5.21	-5.53	-5.86	-6.2	-6.54
$PbCl_2^0$	-2.05	-2.39	-2.77	-3.16	-3.55	-3.94	-4.34	-4.74	-5.15	-5.56	-5.99	-6.44	-6.91	-7.4	-7.9	-8.43	-8.96	-9.51	-10.1
$PbCl_3^-$	-1.29	-1.71	-2.19	-2.67	-3.17	-3.66	-4.15	-4.65	-5.15	-5.66	-6.19	-6.74	-7.31	-7.9	-8.51	-9.15	-9.79	-10.5	-11.1
$NiCl^+$	0.66	0.43	0.16	-0.11	-0.38	-0.65	-0.93	-1.2	-1.47	-1.75	-2.03	-2.32	-2.62	-2.92	-3.24	-3.56	-3.89	-4.23	-4.56
$FeCl^+$	-0.05	-0.29	-0.56	-0.86	-1.16	-1.46	-1.77	-2.08	-2.38	-2.7	-3.01	-3.34	-3.67	-4.02	-4.37	-4.73	-5.1	-5.46	-5.83
$MgCl^+$	-0.03	-0.24	-0.49	-0.76	-1.03	-1.31	-1.59	-1.87	-2.15	-2.44	-2.74	-3.04	-3.35	-3.67	-4	-4.34	-4.69	-5.03	-5.38
MgF^+	-1.47	-1.75	-2.06	-2.38	-2.71	-3.03	-3.35	-3.67	-3.99	-4.32	-4.65	-4.99	-5.33	-5.69	-6.05	-6.43	-6.81	-7.19	-7.57
CaF^+	-0.92	-1.26	-1.62	-1.99	-2.35	-2.72	-3.08	-3.44	-3.79	-4.15	-4.51	-4.88	-5.26	-5.64	-6.03	-6.43	-6.84	-7.24	-7.65
$Fe(CH_3COO)^+$	-1.43	-1.61	-1.88	-2.18	-2.49	-2.82	-3.14	-3.48	-3.81	-4.15	-4.49	-4.84	-5.2	-5.57	-5.95	-6.34	-6.72	-7.12	-7.51
$Fe(CH_3COO)_2^0$	-1.96	-2.25	-2.74	-3.32	-3.96	-4.63	-5.32	-6.01	-6.72	-7.43	-8.16	-8.9	-9.66	-10.4	-11.2	-12.0	-12.8	-13.6	-14.4
$Zn(CH_3COO)^+$	-2.22	-2.63	-3.07	-3.52	-3.96	-4.39	-4.81	-5.23	-5.64	-6.05	-6.45	-6.86	-7.28	-7.7	-8.13	-8.56	-9	-9.44	-9.87
$Zn(CH_3COO)_2^0$	-3.4	-3.86	-4.51	-5.23	-5.99	-6.76	-7.55	-8.33	-9.12	-9.91	-10.7	-11.5	-12.3	-13.2	-14.0	-14.9	-15.7	-16.6	-17.4
$Zn(CH_3COO)_3^-$	-3.01	-3.62	-4.58	-5.71	-6.91	-8.16	-9.43	-10.7	-12.0	-13.	-14.5	-15.7	-17	-18.3	-19.5	-20.8	-22.0	-23.3	-24.5
KSO_4^-	-1.72	-1.85	-2	-2.15	-2.3	-2.46	-2.62	-2.79	-2.97	-3.15	-3.34	-3.55	-3.77	-4.01	-4.25	-4.51	-4.77	-5.05	-5.32
$CaSO_4^0$	-2.69	-2.8	-2.89	-2.98	-3.08	-3.18	-3.3	-3.43	-3.58	-3.75	-3.95	-4.17	-4.43	-4.72	-5.04	-5.39	-5.76	-6.14	-6.54
$HSiO_3^-$	-7.39	-7.34	-7.37	-7.48	-7.63	-7.83	-8.05	-8.3	-8.57	-8.86	-9.16	-9.47	-9.79	-10.1	-10.5	-10.8	-11.2	-11.5	-11.9
$LiCl^0$	1.9	1.7	1.47	1.25	1.03	0.81	0.6	0.39	0.18	-0.04	-0.26	-0.49	-0.73	-0.98	-1.23	-1.49	-1.76	-2.03	-2.3
KCl^0	2.15	1.77	1.44	1.14	0.88	0.64	0.42	0.21	0.01	-0.19	-0.39	-0.59	-0.8	-1.01	-1.22	-1.44	-1.66	-1.88	-2.1
$RbCl^0$	0.75	0.54	0.36	0.2	0.05	-0.08	-0.2	-0.32	-0.44	-0.56	-0.69	-0.81	-0.95	-1.09	-1.25	-1.4	-1.56	-1.73	-1.9
$CsCl^0$	-0.12	-0.26	-0.38	-0.48	-0.57	-0.66	-0.73	-0.81	-0.88	-0.96	-1.04	-1.13	-1.22	-1.32	-1.43	-1.55	-1.67	-1.79	-1.91
NaF^0	1	0.82	0.67	0.54	0.42	0.3	0.19	0.08	-0.03	-0.15	-0.27	-0.41	-0.56	-0.72	-0.9	-1.09	-1.28	-1.48	-1.69
RbF^0	-0.87	-0.86	-0.86	-0.86	-0.87	-0.88	-0.89	-0.92	-0.95	-0.99	-1.04	-1.11	-1.19	-1.29	-1.4	-1.52	-1.65	-1.79	-1.94
$NaBr^0$	1.17	0.97	0.79	0.62	0.47	0.32	0.18	0.04	-0.1	-0.25	-0.4	-0.55	-0.72	-0.89	-1.07	-1.26	-1.46	-1.66	-1.86
KBr^0	1.54	1.25	0.99	0.76	0.55	0.36	0.17	0	-0.17	-0.34	-0.52	-0.69	-0.87	-1.05	-1.24	-1.44	-1.64	-1.84	-2.04
$RbBr^0$	0.94	0.72	0.53	0.36	0.21	0.07	-0.05	-0.17	-0.29	-0.41	-0.53	-0.66	-0.79	-0.93	-1.08	-1.23	-1.38	-1.54	-1.7
$CsBr^0$	-0.1	-0.18	-0.25	-0.3	-0.34	-0.38	-0.41	-0.45	-0.49	-0.53	-0.58	-0.64	-0.71	-0.79	-0.88	-0.97	-1.07	-1.18	-1.29
NaI^0	1.25	1.07	0.89	0.72	0.56	0.41	0.26	0.11	-0.05	-0.2	-0.36	-0.53	-0.71	-0.89	-1.08	-1.27	-1.48	-1.68	-1.89
KI^0	1.57	1.35	1.15	0.96	0.77	0.6	0.43	0.26	0.1	-0.07	-0.24	-0.42	-0.6	-0.79	-0.98	-1.18	-1.38	-1.58	-1.78
RbI^0	0.97	0.82	0.67	0.54	0.41	0.29	0.17	0.05	-0.06	-0.18	-0.31	-0.44	-0.57	-0.72	-0.87	-1.02	-1.18	-1.34	-1.51
CsI^0	-0.68	-0.65	-0.63	-0.62	-0.62	-0.63	-0.64	-0.66	-0.68	-0.72	-0.76	-0.81	-0.87	-0.95	-1.03	-1.12	-1.21	-1.31	-1.41

TABLE 12. Equations of state parameters and standard partial molal properties referring to 25°C and 1 bar of aqueous complexes computed using equations and data summarized in the text. Unless otherwise noted, the standard partial molal Gibbs free energies of formation of the complexes were obtained from dissociation constants at 25°C and 1 bar given by Turner et al. (1981).

Species	ΔG^o_f [a]	ΔH^o_f [a]	S^o [b]	C^o_{pr} [b]	V^o [c]	a_1 [d] x 10	a_2 [a] x 10^{-2}	a_3 [e]	a_4 [f] x 10^{-4}	c_1 [b]	c_2 [f] x 10^{-4}	ω [a] x 10^{-5}
$BeCl^+$	-115316	-124998	92.31	31.19	-2.06	1.1974	-4.8548	7.6512	-2.5783	16.6475	3.3197	-0.8467
$BeCl_2$	-145521	-156432	130.44	57.74	23.95	5.0297	4.5026	3.9733	-2.9651	39.653	8.7262	-0.038
$FeCl^{++}$	-37518	-50820	-42.74	3.37	-22.34	-0.7164	-9.5277	9.4878	-2.3851	23.8149	-2.3482	1.7013
$CoCl^+$	-45157	-53965	-11.27	17.02	-1.5	1.8028	-3.3766	7.0702	-2.6394	22.7656	0.4323	0.7191
CuCl	-22608	-26338	22.06	19.64	17.22	4.1084	2.253	4.8575	-2.8721	17.3292	0.967	-0.038
$CuCl_2^-$	-58038	-72903	26.96	32.99	45.43	8.3943	12.7182	0.7442	-3.3047	36.7555	3.6846	1.2219
$CuCl_3^{2-}$	-89963	-118524	23.28	53.72	76.86	13.2482	24.57	-3.914	-3.7947	63.9808	7.9089	2.8579
$CuCl^+$	-16250	-23847	-6.51	29.39	-1.72	1.748	-3.5103	7.1228	-2.6338	29.356	2.953	0.6472
$CuCl_2$	-46142 [g]	-64160	0.78	54.22	24.32	5.0806	4.627	3.9244	-2.9702	37.5948	8.0108	-0.038
$CuCl_3^-$	-75338 [g]	-106846	-2.21	72.39	53.34	9.6259	15.7252	-0.4377	-3.429	63.8881	11.7108	1.6605
$CuCl_4^{2-}$	-103579 [g]	-152534	-18.48	83.89	85.68	14.6696	28.0407	-5.2782	-3.9382	87.5037	14.0532	3.4923
$CdCl^+$	-52627	-59392	0.75	26.47	8.42	3.099	-0.2116	5.8262	-2.7702	26.6485	2.3572	0.5394
$CdCl_2$	-84851	-101362	10.31	48.52	35.62	6.6265	8.4016	2.4408	-3.1263	34.2501	6.8482	-0.038
$CdCl_3^-$	-115971	-144916	10.86	62.74	65.93	11.2826	19.7705	-2.0276	-3.5963	56.4451	9.7459	1.4662
$CdCl_4^{2-}$	-146081	-190793	0.23	69.14	99.7	16.4919	32.4903	-7.0271	-4.1221	76.2256	11.0502	3.206
TlCl	-39815	-37819	48.69	-20.63	46.52	8.1182	12.044	1.0092	-3.2768	-6.2744	-7.237	-0.038
$TlCl^{++}$	9375	671	-18.52	-8.56	-18.32	-0.2904	-8.4877	9.079	-2.4281	13.4748	-4.7774	1.3375
AuCl	-3184 [h]	-2140	41.47	-9.83	38.61	7.0357	9.4008	2.0481	-3.1676	0.0551	-5.0371	-0.038
$AuCl_2^-$	-36781 [g]	-44725	53.6	-24.52	69.26	11.5192	20.3482	-2.2547	-3.6201	-0.6764	-8.03	0.8173
$AuCl_3^{2-}$	-67811 [h]	-86023	61.39	-43.48	103.42	16.6878	32.9687	-7.2151	-4.1419	1.7155	-11.891	2.2827
$AuCl_4^-$	35332	23573	-32.72	-1.36	-20.66	-0.5361	-9.0876	9.3148	-2.4033	19.7251	-3.3107	1.5579
$HgCl^+$	-2155	-7374	11.67	39.07	4.41	2.4941	-1.6886	6.4067	-2.7091	32.5048	4.9238	0.3735
$HgCl_2$	-42838	-56787	24.64	73.1	31.15	6.015	6.9084	3.0277	-3.0645	48.6578	11.856	-0.038
$HgCl_3^-$	-74504	-99299	30.51	104.29	60.95	10.5003	17.8603	-1.2769	-3.5173	78.0458	18.2101	1.1676
$HgCl_4^{2-}$	-106988	-145023	28.36	132.65	94.15	15.5903	30.2888	-6.1618	-4.0311	109.561	23.986	2.7846
$InCl^{++}$	-59226	-66209	-38.8	1.57	-21.67	-0.6441	-9.3513	9.4185	-2.3924	22.2354	-2.7149	1.6444
BeF^+	-158493	-177322	59.2	35.46	-21.26	-1.2603	-10.856	10.0098	-2.3302	23.774	4.1893	-0.3447
BeF_2	-231386	-258350	71.72	67.93	-16.64	-0.525	-9.0604	9.3042	-2.4044	45.6271	10.8026	-0.038
BeF_3^-	-302532	-331512	104.78	96.1	-11.5	0.2052	-7.2776	8.6034	-2.4781	62.8555	16.5406	0.0401
BeF_4^{2-}	-370691	-386096	190.12	119.97	-5.77	1.0882	-5.1214	7.756	-2.5672	79.5432	21.4033	0.3329
MnF^+	-123641	-132454	-13.3	29.39	-12.46	0.3136	-7.0128	8.4994	-2.489	30.284	2.9518	0.7483
FeF^+	-91157	-101452	-20.92	20.84	-18.14	-0.4234	-8.8124	9.2067	-2.4146	26.3785	1.2102	0.8683
FeF^{++}	-79645	-87141	-25.7	7.64	-41.54	-3.4294	-16.152	12.0915	-2.1112	23.9805	-1.4787	1.4477
CoF^+	-81732	-93191	-22.6	21.29	-20.7	-0.7659	-9.6486	9.5354	-2.3801	26.8657	1.3018	0.8926
NiF^+	-79768	-92315	-26.36	12.51	-25.83	-1.4455	-11.308	10.1875	-2.3115	22.317	-0.4857	0.957
CuF^+	-53739	-64285	-18.84	33.66	-20.92	-0.8164	-9.7719	9.5838	-2.375	33.5733	3.8226	0.8334
ZnF^+	-104109	-116131	-21.81	24.44	-20.48	-0.7395	-9.5843	9.5101	-2.3827	28.5991	1.9435	0.8803
AgF	-49459	-54722	16.74	10.86	6.04	2.5788	-1.4818	6.3255	-2.7177	12.1829	-0.8218	-0.038
CdF^+	-87373	-97544	-13.11	30.74	-10.78	0.5423	-6.4544	8.2799	-2.5121	31.0752	3.2268	0.7483
CdF_2	-155164	-180369	-23.72	58.71	-4.97	1.0718	-5.1614	7.7717	-2.5656	40.2242	8.9247	-0.038
BaF^+	-201807	-206931	6.38	10.94	-7.33	0.916	-5.542	7.9213	-2.5498	16.7731	-0.8065	0.4555
TlF	-75216	-77118	33.18	-16.36	27.32	5.4909	5.6287	3.5307	-3.0116	-3.7726	-6.3675	-0.038
HgF^+	-30204	-39512	-4.48	43.34	-14.79	-0.0492	-7.8986	8.8475	-2.4524	37.2987	5.7934	0.6223
InF^{++}	-97016	-98718	-23.53	5.84	-40.87	-3.3507	-15.96	12.016	-2.1192	22.5771	-1.8453	1.4099
PbF^+	-75860	-80591	8.26	10.04	-10.67	0.4488	-6.6827	8.3696	-2.5027	15.9794	-0.9898	0.4266
PbF_2	-145056	-162783	4.48	18.32	-4.85	1.0888	-5.1199	7.7554	-2.5673	16.5543	0.6976	-0.038
$Ag(HS)_2^-$	0 [i]	-8200	44.68	38.1	60.5	10.3654	17.5311	-1.1475	-3.5037	37.2753	4.7273	0.9527
$Au(HS)_2^-$	2429 [j]	-2509	56.77	6.06	75.39	12.342	22.3572	-3.0443	-3.7032	16.8038	-1.8007	0.7693
$Pb(HS)_2$	-20058 [k]	-22851	52.56	38.71	41.88	7.4825	10.4917	1.6193	-3.2127	28.5025	4.8505	-0.038
$Pb(HS)_3^-$	-18971 [k]	-28704	68.08	47.8	75.8	12.3397	22.3518	-3.0422	-3.703	39.6902	6.7025	0.598
$Mg(HSiO_3)^+$	-353025	-385700	-23.78	37.82	-10.57	0.6289	-6.2428	8.1967	-2.5209	36.7882	4.6702	0.9177
$Ca(HSiO_3)^+$	-376299	-403109	-1.99	32.87	-6.56	1.0647	-5.1787	7.7785	-2.5649	30.8048	3.6619	0.5831

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.Nikolaeva et al. (1972) h. Retrieved from experimental data reported by Gammons and Williams-Jones (1995) for 300°C and Psat. i. Gammons and Barnes (1989). j. Retrieved from experimental data reported by Shenberger and Barnes (1989) for 250°C and P_{SAT}. k. Hemley (1953).

TABLE 13. **Logarithms of the dissociation constants of aqueous complexes listed in Table 12 at temperatures ranging from 0 to 350°C and P_{SAT} (see text).**

Species	0	25	50	75	100	125	150	175	200	225	250	275	300	325	350
$BeCl^+$	2.28	-0.32	-2.61	-4.64	-6.45	-8.09	-9.61	-11	-12.3	-13.6	-14.8	-16.1	-17.4	-18.7	-20.2
$BeCl_2$	3.65	0.54	-2.27	-4.79	-7.09	-9.19	-11.1	-13	-14.7	-16.4	-18	-19.6	-21.2	-22.9	-24.8
$FeCl^{++}$	-1.48	-1.48	-1.58	-1.73	-1.92	-2.14	-2.39	-2.66	-2.95	-3.28	-3.63	-4.03	-4.47	-4.98	-5.57
$CoCl^+$	-0.63	-0.57	-0.6	-0.68	-0.8	-0.94	-1.12	-1.31	-1.54	-1.79	-2.07	-2.39	-2.77	-3.22	-3.8
CuCl	-2.6	-2.33	-2.15	-2.04	-1.97	-1.94	-1.95	-1.99	-2.06	-2.16	-2.3	-2.48	-2.72	-3.05	-3.56
$CuCl_2^-$	-6.06	-5.3	-4.77	-4.4	-4.15	-3.99	-3.9	-3.87	-3.9	-3.99	-4.13	-4.33	-4.6	-4.97	-5.51
$CuCl_3^{2-}$	-6.89	-5.7	-4.88	-4.31	-3.93	-3.68	-3.54	-3.49	-3.52	-3.62	-3.78	-4.02	-4.33	-4.74	-5.33
$CuCl^+$	-0.43	-0.4	-0.46	-0.58	-0.73	-0.91	-1.11	-1.34	-1.6	-1.87	-2.19	-2.54	-2.95	-3.42	-4.01
$CuCl_2$	0.58	0.69	0.62	0.43	0.17	-0.15	-0.52	-0.93	-1.4	-1.92	-2.51	-3.18	-3.96	-4.89	-6.09
$CuCl_3^-$	1.95	2.29	2.34	2.22	1.98	1.64	1.23	0.76	0.23	-0.36	-1.03	-1.78	-2.64	-3.65	-4.93
$CuCl_4^{2-}$	3.82	4.59	4.94	5.04	4.95	4.73	4.4	3.98	3.49	2.92	2.26	1.51	0.65	-0.38	-1.71
$CdCl^+$	-2.12	-1.97	-1.93	-1.96	-2.04	-2.16	-2.31	-2.48	-2.69	-2.93	-3.2	-3.52	-3.89	-4.33	-4.92
$CdCl_2$	-2.92	-2.59	-2.47	-2.48	-2.59	-2.78	-3.03	-3.34	-3.7	-4.13	-4.63	-5.22	-5.93	-6.79	-7.95
$CdCl_3^-$	-3.02	-2.4	-2.1	-2.01	-2.06	-2.22	-2.47	-2.8	-3.2	-3.68	-4.23	-4.88	-5.65	-6.58	-7.8
$CdCl_4^{2-}$	-2.52	-1.47	-0.86	-0.53	-0.41	-0.44	-0.59	-0.84	-1.19	-1.63	-2.16	-2.79	-3.54	-4.47	-5.7
TlCl	-0.47	-0.51	-0.57	-0.63	-0.7	-0.78	-0.86	-0.96	-1.07	-1.19	-1.34	-1.53	-1.77	-2.08	-2.56
$TlCl^{++}$	-8.22	-7.73	-7.41	-7.19	-7.06	-6.99	-6.98	-7.02	-7.11	-7.24	-7.42	-7.66	-7.96	-8.33	-8.8
AuCl	-8.60	-7.92	-7.38	-6.93	-6.57	-6.27	-6.03	-5.84	-5.69	-5.59	-5.54	-5.54	-5.62	-5.78	-6.13
$AuCl_2^-$	-10.4	-9.55	-8.87	-8.32	-7.88	-7.52	-7.24	-7.03	-6.88	-6.78	-6.75	-6.79	-6.92	-7.16	-7.60
$AuCl_3^{2-}$	-10.3	-9.29	-8.54	-7.94	-7.46	-7.08	-6.79	-6.57	-6.41	-6.32	-6.29	-6.33	-6.45	-6.68	-7.09
$AuCl_4^-$	45.1	42	39.1	36.5	34.1	31.9	29.8	27.8	25.9	24	22.2	20.2	18.2	16	13.2
$HgCl^+$	-8.04	-7.43	-7.01	-6.72	-6.53	-6.42	-6.36	-6.37	-6.42	-6.52	-6.68	-6.89	-7.17	-7.54	-8.05
$HgCl_2$	-15.6	-14.2	-13.3	-12.7	-12.2	-11.9	-11.8	-11.7	-11.8	-11.9	-12.2	-12.6	-13.1	-13.8	-14.8
$HgCl_3^-$	-16	-14.5	-13.4	-12.8	-12.3	-12.1	-12	-12.1	-12.2	-12.5	-12.9	-13.5	-14.1	-15	-16.1
$HgCl_4^{2-}$	-17.2	-15.3	-14	-13.1	-12.5	-12.2	-12.1	-12.2	-12.4	-12.7	-13.1	-13.7	-14.4	-15.4	-16.6
$InCl^{++}$	-3.41	-3.26	-3.23	-3.27	-3.37	-3.5	-3.67	-3.87	-4.1	-4.36	-4.66	-5.01	-5.41	-5.88	-6.46
BeF^+	-3.83	-5.61	-7.21	-8.65	-9.95	-11.2	-12.3	-13.3	-14.3	-15.3	-16.2	-17.2	-18.2	-19.2	-20.3
BeF_2	-8.02	-9.68	-11.3	-12.8	-14.2	-15.5	-16.7	-17.9	-19.1	-20.3	-21.5	-22.7	-24	-25.4	-26.9
BeF_3^-	-10.4	-12.5	-14.5	-16.4	-18.2	-19.9	-21.6	-23.2	-24.7	-26.3	-27.9	-29.6	-31.3	-33.2	-35.4
BeF_4^{2-}	-9.33	-13.1	-16.6	-19.8	-22.8	-25.6	-28.2	-30.7	-33.1	-35.5	-37.8	-40.2	-42.7	-45.4	-48.4
MnF^+	-1.35	-1.32	-1.38	-1.5	-1.65	-1.82	-2.03	-2.25	-2.5	-2.78	-3.08	-3.44	-3.85	-4.32	-4.91
FeF^+	-1.46	-1.43	-1.48	-1.58	-1.72	-1.88	-2.06	-2.27	-2.5	-2.75	-3.04	-3.38	-3.77	-4.23	-4.81
FeF^{++}	-5.74	-6	-6.32	-6.66	-7.02	-7.39	-7.76	-8.15	-8.55	-8.97	-9.42	-9.91	-10.4	-11	-11.6
CoF^+	-1.02	-1.02	-1.11	-1.23	-1.39	-1.58	-1.78	-2	-2.25	-2.52	-2.82	-3.16	-3.56	-4.03	-4.63
NiF^+	-1.12	-1.12	-1.19	-1.31	-1.45	-1.62	-1.8	-2.01	-2.24	-2.49	-2.77	-3.1	-3.48	-3.94	-4.53
CuF^+	-1.57	-1.52	-1.57	-1.67	-1.82	-1.99	-2.18	-2.4	-2.65	-2.92	-3.22	-3.57	-3.98	-4.45	-5.04
ZnF^+	-1.16	-1.15	-1.23	-1.35	-1.5	-1.68	-1.88	-2.11	-2.35	-2.62	-2.93	-3.28	-3.68	-4.15	-4.75
AgF	-0.42	-0.4	-0.43	-0.48	-0.56	-0.64	-0.75	-0.87	-1.01	-1.17	-1.37	-1.6	-1.89	-2.24	-2.75
CdF^+	-1.09	-1.08	-1.16	-1.29	-1.46	-1.65	-1.86	-2.09	-2.35	-2.63	-2.94	-3.3	-3.7	-4.18	-4.79
CdF_2	-1.66	-1.41	-1.38	-1.46	-1.64	-1.88	-2.18	-2.53	-2.94	-3.42	-3.96	-4.6	-5.36	-6.25	-7.39
BaF^+	-0.25	-0.32	-0.45	-0.61	-0.8	-1.01	-1.23	-1.47	-1.74	-2.02	-2.33	-2.69	-3.1	-3.57	-4.18
TlF	0.0	-0.1	-0.21	-0.32	-0.42	-0.53	-0.65	-0.77	-0.91	-1.06	-1.24	-1.45	-1.71	-2.04	-2.51
HgF^+	-1.7	-1.63	-1.67	-1.78	-1.92	-2.1	-2.31	-2.54	-2.8	-3.08	-3.4	-3.76	-4.18	-4.66	-5.28
InF^{++}	-4.24	-4.6	-5.01	-5.43	-5.85	-6.27	-6.69	-7.12	-7.55	-8	-8.48	-8.99	-9.54	-10.1	-10.8
PbF^+	-2.15	-2.06	-2.05	-2.1	-2.18	-2.29	-2.43	-2.59	-2.78	-3	-3.25	-3.55	-3.91	-4.34	-4.88
PbF_2	-3.69	-3.42	-3.32	-3.32	-3.4	-3.53	-3.72	-3.96	-4.25	-4.61	-5.04	-5.56	-6.19	-6.97	-8.02
$Ag(HS)_2^-$	-19.5	-17.7	-16.3	-15.1	-14.2	-13.5	-12.8	-12.3	-11.9	-11.6	-11.4	-11.3	-11.3	-11.4	-11.7
$Au(HS)_2^-$	-33.9	-31.0	-28.6	-26.6	-25.0	-23.5	-22.3	-21.3	-20.4	-19.6	-19.0	-18.5	-18.1	-17.9	-18.0
$Pb(HS)_2$	-15.8	-14.7	-13.9	-13.3	-12.9	-12.6	-12.4	-12.3	-12.2	-12.3	-12.5	-12.8	-13.2	-13.8	-14.7
$Pb(HS)_3^-$	-17.3	-16	-15.1	-14.5	-14	-13.7	-13.5	-13.5	-13.5	-13.7	-13.9	-14.3	-14.8	-15.6	-16.7
$Mg(HSiO_3)^+$	-1.36	-1.26	-1.27	-1.35	-1.46	-1.6	-1.77	-1.96	-2.17	-2.41	-2.68	-2.99	-3.36	-3.81	-4.4
$Ca(HSiO_3)^+$	-1.03	-1.01	-1.08	-1.2	-1.36	-1.55	-1.76	-1.99	-2.25	-2.52	-2.84	-3.19	-3.6	-4.07	-4.69

Table 14. Logarithms of the dissociation constants of aqueous complexes listed in Table 12 at temperatures ranging from 100 to 450°C at 0.5 kb (see text).

Species	100	150	200	250	300	350	400	450
$BeCl^+$	-6.36	-9.46	-12.1	-14.5	-16.7	-18.9	-20.5	-22.2
$BeCl_2$	-6.94	-10.9	-14.4	-17.5	-20.4	-23.3	-25.5	-27.7
$FeCl^{++}$	-1.88	-2.31	-2.82	-3.41	-4.07	-4.87	-5.35	-5.82
$CoCl^+$	-0.73	-1.02	-1.39	-1.84	-2.37	-3.06	-3.59	-4.48
CuCl	-1.9	-1.86	-1.93	-2.1	-2.37	-2.81	-3.31	-4.58
$CuCl_2^-$	-4.01	-3.74	-3.71	-3.87	-4.19	-4.71	-5.25	-6.49
$CuCl_3^{2-}$	-3.7	-3.31	-3.27	-3.48	-3.89	-4.53	-5.25	-6.7
$CuCl^+$	-0.67	-1.03	-1.46	-1.96	-2.55	-3.28	-3.82	-4.63
$CuCl_2$	0.31	-0.33	-1.12	-2.06	-3.17	-4.58	-5.71	-7.67
$CuCl_3^-$	2.18	1.48	0.56	-0.55	-1.84	-3.44	-4.83	-7.14
$CuCl_4^{2-}$	5.25	4.72	3.87	2.77	1.45	-0.19	-1.82	-4.69
$CdCl^+$	-1.96	-2.2	-2.54	-2.96	-3.49	-4.16	-4.72	-5.72
$CdCl_2$	-2.43	-2.81	-3.4	-4.17	-5.14	-6.42	-7.56	-9.78
$CdCl_3^-$	-1.81	-2.18	-2.84	-3.72	-4.83	-6.26	-7.56	-9.9
$CdCl_4^{2-}$	-0.06	-0.22	-0.76	-1.6	-2.7	-4.15	-5.59	-8.28
TlCl	-0.61	-0.76	-0.93	-1.15	-1.43	-1.84	-2.34	-3.63
$TlCl^{++}$	-7.01	-6.9	-6.97	-7.19	-7.55	-8.08	-8.36	-8.7
AuCl	-6.49	-5.93	-5.56	-5.34	-5.28	-5.41	-5.66	-6.75
$AuCl_2^-$	-7.70	-7.05	-6.65	-6.45	-6.44	-6.67	-6.97	-8.17
$AuCl_3^{2-}$	-7.18	-6.5	-6.1	-5.91	-5.92	-6.17	-6.42	-7.38
$AuCl_4^-$	33.8	29.7	26	22.5	19.2	15.6	12.2	6.64
$HgCl^+$	-6.47	-6.27	-6.28	-6.45	-6.77	-7.29	-7.71	-8.58
$HgCl_2$	-12.1	-11.6	-11.5	-11.8	-12.3	-13.3	-14.2	-16.3
$HgCl_3^-$	-12.1	-11.8	-11.9	-12.4	-13.3	-14.6	-15.8	-18.1
$HgCl_4^{2-}$	-12.2	-11.8	-11.9	-12.6	-13.6	-15	-16.4	-18.9
$InCl^{++}$	-3.33	-3.6	-3.98	-4.45	-5.02	-5.74	-6.25	-6.99
BeF^+	-9.87	-12.1	-14.1	-15.9	-17.6	-19.3	-20.2	-20.2
BeF_2	-14	-16.5	-18.8	-21	-23.1	-25.4	-26.7	-27.6
BeF_3^-	-18	-21.3	-24.3	-27.2	-30.1	-33.2	-35.4	-38
BeF_4^{2-}	-22.5	-27.8	-32.6	-37	-41.2	-45.6	-49	-53
MnF^+	-1.58	-1.93	-2.35	-2.85	-3.42	-4.15	-4.64	-5.34
FeF^+	-1.66	-1.97	-2.36	-2.81	-3.35	-4.04	-4.54	-5.36
FeF^{++}	-6.97	-7.67	-8.4	-9.16	-9.98	-10.9	-11.2	-10.9
CoF^+	-1.32	-1.68	-2.09	-2.58	-3.14	-3.85	-4.37	-5.22
NiF^+	-1.4	-1.72	-2.1	-2.55	-3.08	-3.75	-4.27	-5.19
CuF^+	-1.76	-2.09	-2.5	-2.99	-3.56	-4.28	-4.77	-5.5
ZnF^+	-1.44	-1.8	-2.21	-2.7	-3.27	-3.98	-4.51	-5.37
AgF	-0.48	-0.65	-0.87	-1.15	-1.51	-2	-2.43	-3.38
CdF^+	-1.38	-1.75	-2.19	-2.7	-3.29	-4.02	-4.58	-5.53
CdF_2	-1.48	-1.96	-2.63	-3.47	-4.49	-5.83	-6.75	-8.19
BaF^+	-0.75	-1.16	-1.61	-2.12	-2.71	-3.43	-3.97	-4.83
TlF	-0.33	-0.54	-0.76	-1.01	-1.33	-1.78	-2.16	-3.06
HgF^+	-1.86	-2.21	-2.65	-3.17	-3.77	-4.52	-5.09	-5.99
InF^{++}	-5.8	-6.6	-7.4	-8.22	-9.09	-10.1	-10.5	-10.6
PbF^+	-2.11	-2.33	-2.63	-3.02	-3.49	-4.11	-4.52	-5.17
PbF_2	-3.26	-3.52	-3.96	-4.57	-5.36	-6.48	-7.25	-8.72
$Ag(HS)_2^-$	-14.1	-12.7	-11.8	-11.2	-10.9	-10.8	-11.0	-11.9
$Au(HS)_2^-$	-24.8	-22.1	-20.2	-18.7	-17.6	-17	-16.6	-17.2
$Pb(HS)_2$	-12.7	-12.2	-12	-12.1	-12.4	-13.2	-13.9	-16
$Pb(HS)_3^-$	-13.8	-13.2	-13.1	-13.4	-13.9	-14.9	-15.9	-18.4
$Mg(HSiO_3)^+$	-1.4	-1.68	-2.04	-2.47	-2.98	-3.63	-4.2	-5.28
$Ca(HSiO_3)^+$	-1.31	-1.68	-2.12	-2.62	-3.21	-3.94	-4.54	-5.57

Table 15. Logarithms of the dissociation constants of aqueous complexes listed in Table 12 at temperatures ranging from 100 to 600°C at 1.0 kb (see text).

Species	100	150	200	250	300	350	400	450	500	550	600
$BeCl^+$	-6.3	-9.36	-11.9	-14.2	-16.2	-18.1	-19.8	-21.5	-23.1	-24.6	-26
$BeCl_2$	-6.83	-10.8	-14.2	-17.2	-19.9	-22.4	-24.7	-27	-29.1	-31.1	-33
$FeCl^{++}$	-1.85	-2.26	-2.73	-3.26	-3.82	-4.41	-5.02	-5.65	-6.28	-6.89	-7.41
$CoCl^+$	-0.68	-0.94	-1.28	-1.68	-2.12	-2.6	-3.13	-3.71	-4.35	-5.06	-5.75
CuCl	-1.85	-1.79	-1.83	-1.96	-2.15	-2.41	-2.74	-3.18	-3.76	-4.48	-5.29
$CuCl_2^-$	-3.9	-3.62	-3.57	-3.67	-3.91	-4.24	-4.67	-5.21	-5.89	-6.7	-7.58
$CuCl_3^{2-}$	-3.52	-3.12	-3.07	-3.24	-3.58	-4.05	-4.64	-5.34	-6.2	-7.2	-8.27
$CuCl^+$	-0.63	-0.96	-1.36	-1.81	-2.3	-2.83	-3.39	-4	-4.65	-5.35	-6.02
$CuCl_2$	0.41	-0.18	-0.91	-1.74	-2.67	-3.68	-4.77	-5.98	-7.33	-8.81	-10.3
$CuCl_3^-$	2.34	1.68	0.81	-0.2	-1.32	-2.54	-3.84	-5.27	-6.86	-8.6	-10.3
$CuCl_4^{2-}$	5.48	4.98	4.18	3.16	2	0.71	-0.71	-2.29	-4.08	-6.09	-8.18
$CdCl^+$	-1.91	-2.12	-2.42	-2.8	-3.23	-3.71	-4.24	-4.83	-5.5	-6.25	-7
$CdCl_2$	-2.31	-2.65	-3.18	-3.84	-4.63	-5.52	-6.53	-7.68	-9.02	-10.6	-12.2
$CdCl_3^-$	-1.62	-1.96	-2.56	-3.35	-4.28	-5.33	-6.51	-7.83	-9.34	-11	-12.8
$CdCl_4^{2-}$	0.22	0.09	-0.41	-1.17	-2.11	-3.21	-4.45	-5.87	-7.51	-9.39	-11.3
TlCl	-0.54	-0.67	-0.82	-1	-1.21	-1.46	-1.77	-2.17	-2.7	-3.39	-4.15
$TlCl^{++}$	-6.98	-6.85	-6.88	-7.04	-7.29	-7.62	-8	-8.44	-8.9	-9.38	-9.81
AuCl	-6.42	-5.85	-5.46	-5.2	-5.06	-5.02	-5.09	-5.29	-5.65	-6.19	-6.82
$AuCl_2^-$	-7.56	-6.90	-6.47	-6.22	-6.11	-6.13	-6.28	-6.57	-7.04	-7.70	-8.45
$AuCl_3^{2-}$	-6.94	-6.26	-5.84	-5.61	-5.53	-5.58	-5.75	-6.04	-6.48	-7.08	-7.74
$AuCl_4^-$	33.5	29.4	25.9	22.7	19.6	16.7	13.8	10.8	7.56	3.97	0.3
$HgCl^+$	-6.42	-6.2	-6.18	-6.29	-6.52	-6.84	-7.23	-7.72	-8.29	-8.96	-9.65
$HgCl_2$	-12	-11.4	-11.3	-11.4	-11.8	-12.4	-13.2	-14.1	-15.3	-16.7	-18.3
$HgCl_3^-$	-11.9	-11.5	-11.6	-12.1	-12.7	-13.6	-14.7	-15.9	-17.4	-19.1	-20.9
$HgCl_4^{2-}$	-11.9	-11.5	-11.6	-12.2	-13	-14	-15.3	-16.8	-18.4	-20.4	-22.4
$InCl^{++}$	-3.3	-3.55	-3.89	-4.31	-4.78	-5.3	-5.85	-6.45	-7.1	-7.78	-8.42
BeF^+	-9.81	-12	-13.9	-15.6	-17.2	-18.6	-19.9	-21.1	-22.1	-22.9	-23.4
BeF_2	-13.9	-16.4	-18.6	-20.6	-22.5	-24.4	-26.1	-27.8	-29.3	-30.7	-31.8
BeF_3^-	-17.9	-21.1	-24	-26.7	-29.3	-31.8	-34.2	-36.7	-39.1	-41.5	-43.6
BeF_4^{2-}	-22.3	-27.6	-32.2	-36.3	-40.2	-43.9	-47.5	-50.9	-54.4	-57.8	-60.9
MnF^+	-1.53	-1.86	-2.24	-2.68	-3.16	-3.67	-4.21	-4.8	-5.42	-6.08	-6.7
FeF^+	-1.61	-1.9	-2.25	-2.65	-3.09	-3.57	-4.09	-4.66	-5.28	-5.96	-6.62
FeF^{++}	-6.94	-7.6	-8.28	-8.97	-9.68	-10.4	-11.1	-11.7	-12.2	-12.6	-12.7
CoF^+	-1.27	-1.6	-1.98	-2.41	-2.87	-3.37	-3.91	-4.49	-5.14	-5.83	-6.51
NiF^+	-1.36	-1.66	-2	-2.39	-2.82	-3.29	-3.8	-4.36	-4.99	-5.69	-6.39
CuF^+	-1.71	-2.02	-2.4	-2.82	-3.3	-3.8	-4.34	-4.92	-5.55	-6.21	-6.84
ZnF^+	-1.4	-1.73	-2.11	-2.54	-3.01	-3.51	-4.05	-4.64	-5.29	-5.99	-6.68
AgF	-0.42	-0.57	-0.76	-0.99	-1.26	-1.57	-1.93	-2.36	-2.88	-3.49	-4.13
CdF^+	-1.32	-1.66	-2.07	-2.52	-3.01	-3.54	-4.11	-4.72	-5.4	-6.14	-6.87
CdF_2	-1.36	-1.79	-2.38	-3.11	-3.94	-4.85	-5.85	-6.95	-8.15	-9.44	-10.7
BaF^+	-0.73	-1.11	-1.53	-1.98	-2.47	-2.98	-3.53	-4.13	-4.78	-5.48	-6.17
TlF	-0.26	-0.45	-0.64	-0.85	-1.08	-1.35	-1.66	-2.03	-2.49	-3.05	-3.63
HgF^+	-1.81	-2.14	-2.55	-3.01	-3.51	-4.05	-4.64	-5.26	-5.95	-6.69	-7.42
InF^{++}	-5.77	-6.54	-7.29	-8.05	-8.8	-9.54	-10.3	-10.9	-11.6	-12.1	-12.4
PbF^+	-2.06	-2.26	-2.52	-2.84	-3.22	-3.63	-4.09	-4.59	-5.14	-5.73	-6.29
PbF_2	-3.15	-3.37	-3.74	-4.23	-4.83	-5.53	-6.33	-7.24	-8.29	-9.46	-10.6
$Ag(HS)_2^-$	-14.0	-12.6	-11.6	-11.0	-10.6	-10.3	-10.3	-10.5	-10.8	-11.4	-12.0
$Au(HS)_2^-$	-24.7	-22.0	-20.0	-18.5	-17.3	-16.5	-15.9	-15.5	-15.5	-15.7	-16.1
$Pb(HS)_2$	-12.6	-12	-11.8	-11.8	-12	-12.3	-12.9	-13.6	-14.7	-15.9	-17.3
$Pb(HS)_3^-$	-13.6	-13	-12.9	-13	-13.3	-13.8	-14.6	-15.6	-16.9	-18.5	-20.2
$Mg(HSiO_3)^+$	-1.36	-1.62	-1.95	-2.32	-2.74	-3.2	-3.7	-4.28	-4.94	-5.69	-6.47
$Ca(HSiO_3)^+$	-1.27	-1.62	-2.03	-2.48	-2.97	-3.5	-4.07	-4.7	-5.4	-6.17	-6.95

TABLE 16. Logarithms of the dissociation constants of aqueous complexes listed in Table 12 at temperatures ranging from 100 to 950°C at 2.0 kb (see text).

Species	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950
$BeCl^+$	-6.23	-9.22	-11.7	-13.8	-15.7	-17.4	-18.9	-20.4	-21.7	-23.1	-24.3	-25.5	-26.6	-27.7	-28.7	-29.7	-30.6	-31.4
$BeCl_2$	-6.7	-10.6	-13.8	-16.7	-19.3	-21.6	-23.7	-25.7	-27.6	-29.4	-31.1	-32.7	-34.3	-35.8	-37.2	-38.5	-39.8	-40.9
$FeCl^{++}$	-1.83	-2.2	-2.62	-3.07	-3.54	-4.03	-4.54	-5.05	-5.58	-6.11	-6.66	-7.2	-7.73	-8.25	-8.74	-9.22	-9.68	-10.1
$CoCl^+$	-0.62	-0.85	-1.14	-1.47	-1.83	-2.21	-2.62	-3.04	-3.49	-3.95	-4.43	-4.92	-5.41	-5.88	-6.33	-6.76	-7.17	-7.55
CuCl	-1.78	-1.7	-1.7	-1.77	-1.89	-2.06	-2.26	-2.5	-2.77	-3.09	-3.43	-3.79	-4.17	-4.53	-4.88	-5.2	-5.5	-5.77
$CuCl_2^-$	-3.74	-3.44	-3.35	-3.41	-3.57	-3.81	-4.11	-4.46	-4.86	-5.31	-5.79	-6.3	-6.81	-7.32	-7.81	-8.27	-8.71	-9.13
$CuCl_3^{2-}$	-3.24	-2.83	-2.76	-2.89	-3.17	-3.56	-4.03	-4.55	-5.13	-5.76	-6.43	-7.11	-7.81	-8.49	-9.16	-9.8	-10.4	-11
$CuCl^+$	-0.58	-0.88	-1.23	-1.61	-2.02	-2.45	-2.89	-3.35	-3.83	-4.32	-4.83	-5.34	-5.85	-6.34	-6.81	-7.26	-7.68	-8.09
$CuCl_2$	0.54	0.01	-0.62	-1.33	-2.09	-2.9	-3.75	-4.63	-5.55	-6.52	-7.52	-8.53	-9.54	-10.5	-11.4	-12.3	-13.2	-14
$CuCl_3^-$	2.56	1.95	1.17	0.27	-0.7	-1.73	-2.8	-3.9	-5.04	-6.23	-7.44	-8.66	-9.87	-11.1	-12.2	-13.3	-14.3	-15.2
$CuCl_4^{2-}$	5.84	5.38	4.63	3.71	2.68	1.56	0.38	-0.84	-2.12	-3.44	-4.8	-6.18	-7.54	-8.88	-10.2	-11.4	-12.5	-13.6
$CdCl^+$	-1.84	-2.01	-2.27	-2.58	-2.93	-3.31	-3.72	-4.15	-4.6	-5.08	-5.57	-6.08	-6.58	-7.07	-7.54	-7.99	-8.4	-8.8
$CdCl_2$	-2.14	-2.42	-2.86	-3.41	-4.04	-4.73	-5.48	-6.28	-7.13	-8.04	-8.99	-9.97	-10.9	-11.9	-12.8	-13.7	-14.5	-15.2
$CdCl_3^-$	-1.34	-1.62	-2.15	-2.82	-3.61	-4.48	-5.41	-6.39	-7.43	-8.52	-9.65	-10.8	-11.9	-13.1	-14.1	-15.2	-16.1	-17
$CdCl_4^{2-}$	0.65	0.56	0.11	-0.55	-1.37	-2.29	-3.29	-4.36	-5.5	-6.7	-7.94	-9.2	-10.5	-11.7	-12.9	-14	-15.1	-16.1
TlCl	-0.43	-0.55	-0.67	-0.8	-0.95	-1.11	-1.29	-1.5	-1.73	-1.99	-2.27	-2.58	-2.88	-3.18	-3.47	-3.72	-3.95	-4.14
$TlCl^{++}$	-6.96	-6.78	-6.76	-6.84	-7.01	-7.24	-7.51	-7.82	-8.17	-8.55	-8.95	-9.36	-9.78	-10.2	-10.6	-11	-11.3	-11.7
AuCl	-6.33	-5.73	-5.31	-5.0	-4.8	-4.68	-4.62	-4.62	-4.67	-4.79	-4.94	-5.13	-5.34	-5.56	-5.76	-5.95	-6.11	-6.26
$AuCl_2^-$	-7.34	-6.66	-6.19	-5.89	-5.70	-5.61	-5.61	-5.68	-5.81	-6.01	-6.26	-6.55	-6.86	-7.17	-7.47	-7.75	-8.01	-8.24
$AuCl_3^{2-}$	-6.56	-5.88	-5.43	-5.16	-5.02	-4.97	-5.01	-5.12	-5.29	-5.52	-5.8	-6.11	-6.44	-6.78	-7.1	-7.41	-7.7	-8.0
$AuCl_4^-$	32.8	28.9	25.6	22.6	19.9	17.4	15	12.7	10.5	8.24	6.01	3.81	1.67	-0.37	-2.28	-4.06	-5.7	-7.21
$HgCl^+$	-6.36	-6.11	-6.04	-6.09	-6.24	-6.45	-6.72	-7.04	-7.4	-7.8	-8.23	-8.68	-9.13	-9.58	-10	-10.4	-10.8	-11.2
$HgCl_2$	-11.8	-11.2	-11	-11.1	-11.3	-11.7	-12.1	-12.7	-13.4	-14.2	-15	-15.9	-16.8	-17.7	-18.5	-19.3	-20.1	-20.8
$HgCl_3^-$	-11.7	-11.2	-11.2	-11.6	-12.1	-12.8	-13.6	-14.5	-15.4	-16.5	-17.6	-18.8	-20	-21.2	-22.3	-23.4	-24.4	-25.4
$HgCl_4^{2-}$	-11.5	-11	-11.1	-11.5	-12.2	-13.1	-14.1	-15.2	-16.4	-17.7	-19.1	-20.5	-21.9	-23.3	-24.6	-25.9	-27.1	-28.3
$InCl^{++}$	-3.28	-3.49	-3.78	-4.13	-4.51	-4.93	-5.37	-5.83	-6.31	-6.81	-7.33	-7.85	-8.37	-8.87	-9.36	-9.82	-10.3	-10.7
BeF^+	-9.73	-11.9	-13.7	-15.3	-16.7	-18	-19.1	-20.2	-21.3	-22.3	-23.2	-24.1	-25	-25.8	-26.5	-27.2	-27.9	-28.6
BeF_2	-13.8	-16.1	-18.2	-20.1	-21.8	-23.5	-25	-26.5	-27.9	-29.3	-30.6	-32	-33.2	-34.4	-35.5	-36.6	-37.7	-38.7
BeF_3^-	-17.6	-20.7	-23.5	-26	-28.4	-30.6	-32.7	-34.7	-36.7	-38.6	-40.6	-42.5	-44.3	-46	-47.6	-49.2	-50.7	-52.1
BeF_4^{2-}	-22	-27.1	-31.6	-35.5	-39.1	-42.4	-45.5	-48.5	-51.3	-54.1	-56.8	-59.4	-61.9	-64.3	-66.6	-68.7	-70.7	-72.6
MnF^+	-1.46	-1.75	-2.08	-2.45	-2.84	-3.26	-3.68	-4.12	-4.58	-5.06	-5.55	-6.05	-6.54	-7.01	-7.47	-7.9	-8.32	-8.71
FeF^+	-1.54	-1.8	-2.1	-2.43	-2.79	-3.17	-3.56	-3.98	-4.41	-4.86	-5.33	-5.8	-6.28	-6.74	-7.18	-7.59	-7.99	-8.36
FeF^{++}	-6.9	-7.52	-8.13	-8.73	-9.34	-9.94	-10.5	-11.1	-11.7	-12.2	-12.8	-13.3	-13.9	-14.4	-14.9	-15.3	-15.8	-16.3
CoF^+	-1.2	-1.49	-1.82	-2.17	-2.56	-2.95	-3.37	-3.8	-4.24	-4.71	-5.19	-5.68	-6.16	-6.63	-7.08	-7.5	-7.91	-8.29
NiF^+	-1.3	-1.57	-1.86	-2.19	-2.53	-2.89	-3.27	-3.67	-4.08	-4.52	-4.98	-5.44	-5.91	-6.36	-6.78	-7.19	-7.57	-7.93
CuF^+	-1.65	-1.93	-2.25	-2.61	-2.99	-3.4	-3.81	-4.25	-4.7	-5.18	-5.66	-6.16	-6.64	-7.12	-7.57	-8	-8.41	-8.8
ZnF^+	-1.34	-1.63	-1.96	-2.32	-2.71	-3.11	-3.53	-3.96	-4.41	-4.88	-5.36	-5.86	-6.35	-6.82	-7.27	-7.7	-8.11	-8.49
AgF	-0.32	-0.45	-0.6	-0.78	-0.97	-1.19	-1.42	-1.68	-1.96	-2.27	-2.6	-2.94	-3.29	-3.63	-3.95	-4.24	-4.51	-4.76
CdF^+	-1.23	-1.54	-1.9	-2.28	-2.69	-3.12	-3.56	-4.02	-4.49	-4.98	-5.49	-6.01	-6.51	-7.01	-7.48	-7.93	-8.35	-8.74
CdF_2	-1.18	-1.54	-2.04	-2.62	-3.28	-4	-4.75	-5.55	-6.4	-7.29	-8.21	-9.15	-10.1	-11	-11.9	-12.7	-13.5	-14.2
BaF^+	-0.71	-1.06	-1.43	-1.81	-2.21	-2.63	-3.05	-3.49	-3.95	-4.42	-4.91	-5.4	-5.89	-6.36	-6.81	-7.24	-7.65	-8.03
TlF	-0.13	-0.3	-0.46	-0.62	-0.78	-0.95	-1.14	-1.35	-1.57	-1.83	-2.1	-2.38	-2.67	-2.95	-3.21	-3.45	-3.67	-3.86
HgF^+	-1.73	-2.03	-2.39	-2.79	-3.21	-3.65	-4.11	-4.59	-5.08	-5.59	-6.12	-6.66	-7.18	-7.7	-8.19	-8.65	-9.1	-9.52
InF^{++}	-5.73	-6.45	-7.15	-7.82	-8.47	-9.11	-9.73	-10.3	-10.9	-11.6	-12.1	-12.7	-13.3	-13.8	-14.3	-14.8	-15.3	-15.8
PbF^+	-1.98	-2.15	-2.36	-2.61	-2.9	-3.22	-3.55	-3.91	-4.29	-4.69	-5.11	-5.54	-5.96	-6.38	-6.78	-7.15	-7.51	-7.85
PbF_2	-2.99	-3.14	-3.42	-3.78	-4.21	-4.71	-5.26	-5.86	-6.51	-7.22	-7.97	-8.74	-9.52	-10.3	-11	-11.7	-12.3	-12.9
$Ag(HS)_2^-$	-13.8	-12.4	-11.4	-10.7	-10.2	-9.9	-9.72	-9.66	-9.69	-9.81	-10.0	-10.2	-10.5	-10.8	-11.1	-11.4	-11.6	-11.9
$Au(HS)_2^-$	-24.5	-21.8	-19.7	-18.2	-16.9	-16.0	-15.2	-14.7	-14.2	-14.0	-13.8	-13.7	-13.7	-13.7	-13.7	-13.8	-13.8	-13.8
$Pb(HS)_2$	-12.5	-11.8	-11.5	-11.4	-11.4	-11.6	-11.9	-12.3	-12.8	-13.3	-13.9	-14.6	-15.3	-16	-16.7	-17.3	-17.9	-18.5
$Pb(HS)_3^-$	-13.3	-12.7	-12.5	-12.4	-12.6	-12.9	-13.4	-13.9	-14.6	-15.3	-16.1	-17	-17.9	-18.8	-19.7	-20.5	-21.3	-22
$Mg(HSiO_3)^+$	-1.32	-1.55	-1.83	-2.13	-2.47	-2.83	-3.21	-3.6	-4.02	-4.46	-4.93	-5.4	-5.87	-6.33	-6.76	-7.18	-7.56	-7.92
$Ca(HSiO_3)^+$	-1.23	-1.55	-1.91	-2.3	-2.71	-3.14	-3.58	-4.05	-4.52	-5.02	-5.54	-6.06	-6.58	-7.08	-7.56	-8.01	-8.44	-8.84

TABLE 17. Logarithms of the dissociation constants of aqueous complexes listed in Table 12 at temperatures ranging from 100 to 1,000°C at 3.0 kb (see text).

Species	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
$BeCl^+$	-6.2	-9.14	-11.6	-13.6	-15.4	-17	-18.4	-19.7	-20.9	-22.1	-23.2	-24.2	-25.3	-26.3	-27.3	-28.2	-29.1	-30	-30.8
$BeCl_2$	-6.62	-10.4	-13.7	-16.4	-18.9	-21.1	-23.1	-24.9	-26.6	-28.2	-29.8	-31.3	-32.8	-34.2	-35.5	-36.9	-38.1	-39.4	-40.5
$FeCl^{++}$	-1.85	-2.18	-2.55	-2.95	-3.37	-3.8	-4.24	-4.68	-5.12	-5.58	-6.04	-6.51	-6.99	-7.48	-7.98	-8.47	-8.94	-9.4	-9.84
$CoCl^+$	-0.6	-0.8	-1.05	-1.34	-1.65	-1.97	-2.31	-2.66	-3.02	-3.39	-3.78	-4.17	-4.58	-4.99	-5.41	-5.82	-6.22	-6.61	-6.97
$CuCl$	-1.74	-1.64	-1.61	-1.65	-1.73	-1.84	-1.99	-2.15	-2.34	-2.55	-2.78	-3.03	-3.29	-3.56	-3.84	-4.11	-4.38	-4.63	-4.86
$CuCl_2^-$	-3.64	-3.31	-3.2	-3.22	-3.34	-3.53	-3.77	-4.05	-4.37	-4.71	-5.08	-5.48	-5.89	-6.31	-6.74	-7.17	-7.59	-7.99	-8.37
$CuCl_3^{2-}$	-3.03	-2.61	-2.52	-2.63	-2.88	-3.23	-3.64	-4.11	-4.61	-5.14	-5.7	-6.28	-6.88	-7.48	-8.09	-8.68	-9.27	-9.84	-10.4
$CuCl^+$	-0.57	-0.84	-1.15	-1.49	-1.84	-2.21	-2.59	-2.97	-3.37	-3.77	-4.18	-4.61	-5.04	-5.48	-5.92	-6.36	-6.79	-7.2	-7.58
$CuCl_2$	0.61	0.13	-0.44	-1.06	-1.73	-2.42	-3.13	-3.87	-4.62	-5.39	-6.19	-7.01	-7.85	-8.7	-9.56	-10.4	-11.2	-12	-12.7
$CuCl_3^-$	2.7	2.14	1.41	0.59	-0.3	-1.22	-2.16	-3.12	-4.1	-5.1	-6.11	-7.14	-8.18	-9.23	-10.3	-11.3	-12.3	-13.2	-14.2
$CuCl_4^{2-}$	6.09	5.66	4.96	4.1	3.14	2.11	1.05	-0.04	-1.16	-2.29	-3.44	-4.61	-5.79	-6.97	-8.13	-9.28	-10.4	-11.5	-12.5
$CdCl^+$	-1.81	-1.95	-2.17	-2.44	-2.74	-3.06	-3.4	-3.76	-4.13	-4.51	-4.9	-5.31	-5.73	-6.16	-6.58	-7.01	-7.42	-7.81	-8.18
$CdCl_2$	-2.05	-2.27	-2.65	-3.12	-3.65	-4.24	-4.86	-5.51	-6.19	-6.9	-7.64	-8.41	-9.2	-10	-10.8	-11.6	-12.4	-13.1	-13.8
$CdCl_3^-$	-1.16	-1.39	-1.86	-2.47	-3.17	-3.93	-4.74	-5.58	-6.45	-7.35	-8.27	-9.22	-10.2	-11.2	-12.2	-13.1	-14.1	-15	-15.8
$CdCl_4^{2-}$	0.96	0.9	0.5	-0.11	-0.85	-1.68	-2.57	-3.51	-4.49	-5.49	-6.53	-7.59	-8.67	-9.76	-10.8	-11.9	-12.9	-13.9	-14.9
$TlCl$	-0.36	-0.46	-0.56	-0.67	-0.78	-0.89	-1.02	-1.16	-1.31	-1.47	-1.65	-1.83	-2.03	-2.24	-2.45	-2.65	-2.84	-3.02	-3.18
$TlCl^{++}$	-6.96	-6.75	-6.69	-6.73	-6.84	-7	-7.21	-7.44	-7.71	-8	-8.32	-8.66	-9.02	-9.4	-9.79	-10.2	-10.6	-10.9	-11.3
$AuCl$	-6.26	-5.65	-5.2	-4.87	-4.63	-4.46	-4.35	-4.28	-4.25	-4.27	-4.31	-4.39	-4.49	-4.61	-4.74	-4.87	-5.0	-5.13	-5.24
$AuCl_2^-$	-7.18	-6.48	-5.99	-5.65	-5.42	-5.28	-5.20	-5.19	-5.22	-5.30	-5.42	-5.58	-5.77	-5.98	-6.20	-6.43	-6.66	-6.87	-7.07
$AuCl_3^{2-}$	-6.27	-5.58	-5.12	-4.82	-4.64	-4.55	-4.53	-4.56	-4.65	-4.78	-4.94	-5.15	-5.38	-5.63	-5.9	-6.17	-6.44	-6.7	-6.94
$AuCl_4^-$	32	28.4	25.2	22.4	19.9	17.6	15.5	13.5	11.6	9.73	7.92	6.13	4.38	2.66	0.98	-0.64	-2.18	-3.62	-4.97
$HgCl^+$	-6.33	-6.05	-5.95	-5.96	-6.05	-6.21	-6.42	-6.66	-6.93	-7.23	-7.56	-7.91	-8.28	-8.67	-9.06	-9.46	-9.85	-10.2	-10.6
$HgCl_2$	-11.8	-11.1	-10.8	-10.8	-10.9	-11.2	-11.5	-12	-12.5	-13.1	-13.7	-14.3	-15	-15.8	-16.5	-17.3	-18	-18.7	-19.4
$HgCl_3^-$	-11.5	-11	-11	-11.2	-11.6	-12.2	-12.9	-13.6	-14.4	-15.3	-16.2	-17.2	-18.2	-19.2	-20.2	-21.3	-22.3	-23.2	-24.1
$HgCl_4^{2-}$	-11.2	-10.7	-10.7	-11.1	-11.7	-12.5	-13.4	-14.4	-15.4	-16.5	-17.7	-18.9	-20.1	-21.3	-22.5	-23.8	-25	-26.1	-27.2
$InCl^{++}$	-3.29	-3.47	-3.72	-4.02	-4.35	-4.71	-5.08	-5.47	-5.87	-6.28	-6.7	-7.14	-7.59	-8.04	-8.5	-8.96	-9.41	-9.83	-10.2
BeF^+	-9.68	-11.8	-13.5	-15.1	-16.4	-17.6	-18.6	-19.6	-20.6	-21.5	-22.3	-23.2	-24	-24.8	-25.6	-26.4	-27.2	-27.9	-28.6
BeF_2	-13.7	-16	-18	-19.8	-21.4	-22.9	-24.3	-25.6	-26.9	-28.1	-29.3	-30.5	-31.7	-32.8	-34	-35.1	-36.2	-37.3	-38.3
BeF_3^-	-17.5	-20.5	-23.2	-25.6	-27.7	-29.8	-31.7	-33.5	-35.2	-36.9	-38.6	-40.2	-41.8	-43.5	-45.1	-46.6	-48.1	-49.6	-50.9
BeF_4^{2-}	-21.8	-26.9	-31.1	-34.9	-38.3	-41.4	-44.3	-47	-49.5	-51.9	-54.3	-56.6	-58.9	-61.1	-63.3	-65.4	-67.4	-69.3	-71.1
MnF^+	-1.41	-1.67	-1.97	-2.3	-2.64	-2.99	-3.35	-3.71	-4.09	-4.47	-4.87	-5.28	-5.7	-6.13	-6.56	-6.99	-7.41	-7.81	-8.19
FeF^+	-1.5	-1.73	-2	-2.29	-2.59	-2.91	-3.24	-3.57	-3.92	-4.27	-4.64	-5.03	-5.42	-5.83	-6.23	-6.64	-7.03	-7.41	-7.76
FeF^{++}	-6.88	-7.47	-8.03	-8.58	-9.11	-9.64	-10.2	-10.7	-11.2	-11.7	-12.2	-12.7	-13.2	-13.7	-14.3	-14.8	-15.3	-15.8	-16.3
CoF^+	-1.16	-1.41	-1.71	-2.02	-2.35	-2.69	-3.03	-3.38	-3.74	-4.11	-4.49	-4.89	-5.29	-5.71	-6.12	-6.53	-6.93	-7.32	-7.67
NiF^+	-1.27	-1.51	-1.77	-2.05	-2.34	-2.64	-2.95	-3.27	-3.6	-3.94	-4.29	-4.66	-5.03	-5.42	-5.81	-6.19	-6.57	-6.93	-7.26
CuF^+	-1.61	-1.86	-2.15	-2.46	-2.79	-3.13	-3.49	-3.84	-4.21	-4.59	-4.98	-5.39	-5.8	-6.23	-6.66	-7.08	-7.5	-7.9	-8.27
ZnF^+	-1.3	-1.57	-1.86	-2.18	-2.51	-2.85	-3.2	-3.56	-3.92	-4.29	-4.68	-5.08	-5.49	-5.91	-6.32	-6.74	-7.15	-7.53	-7.89
AgF	-0.25	-0.36	-0.49	-0.62	-0.78	-0.94	-1.11	-1.3	-1.5	-1.71	-1.94	-2.18	-2.44	-2.7	-2.97	-3.24	-3.5	-3.74	-3.97
CdF^+	-1.18	-1.46	-1.78	-2.12	-2.48	-2.85	-3.23	-3.61	-4	-4.39	-4.8	-5.22	-5.65	-6.08	-6.51	-6.94	-7.36	-7.76	-8.13
CdF_2	-1.07	-1.37	-1.79	-2.29	-2.84	-3.44	-4.06	-4.71	-5.38	-6.08	-6.81	-7.58	-8.37	-9.18	-10	-10.8	-11.6	-12.4	-13.1
BaF^+	-0.72	-1.05	-1.38	-1.72	-2.07	-2.42	-2.78	-3.14	-3.51	-3.88	-4.27	-4.67	-5.08	-5.49	-5.91	-6.32	-6.73	-7.11	-7.47
TlF	-0.04	-0.19	-0.32	-0.45	-0.57	-0.7	-0.83	-0.96	-1.11	-1.27	-1.44	-1.63	-1.83	-2.03	-2.25	-2.46	-2.66	-2.85	-3.02
HgF^+	-1.68	-1.96	-2.29	-2.64	-3.01	-3.39	-3.79	-4.19	-4.6	-5.02	-5.44	-5.89	-6.34	-6.79	-7.25	-7.7	-8.14	-8.57	-8.96
InF^{++}	-5.72	-6.41	-7.06	-7.67	-8.26	-8.83	-9.38	-9.91	-10.4	-11	-11.5	-12	-12.6	-13.1	-13.6	-14.2	-14.7	-15.2	-15.7
PbF^+	-1.93	-2.07	-2.25	-2.46	-2.69	-2.95	-3.21	-3.49	-3.79	-4.09	-4.42	-4.76	-5.12	-5.48	-5.86	-6.23	-6.59	-6.94	-7.27
PbF_2	-2.87	-2.98	-3.19	-3.47	-3.8	-4.18	-4.6	-5.04	-5.52	-6.04	-6.59	-7.18	-7.8	-8.44	-9.1	-9.76	-10.4	-11	-11.6
$Ag(HS)_2^-$	-13.7	-12.3	-11.2	-10.5	-10.0	-9.62	-9.38	-9.24	-9.17	-9.18	-9.25	-9.37	-9.53	-9.72	-9.94	-10.2	-10.4	-10.6	-10.8
$Au(HS)_2^-$	-24.3	-21.6	-19.6	-17.9	-16.7	-15.7	-14.8	-14.2	-13.7	-13.3	-13.0	-12.7	-12.6	-12.5	-12.4	-12.4	-12.4	-12.4	-12.4
$Pb(HS)_2$	-12.4	-11.8	-11.3	-11.2	-11.1	-11.2	-11.3	-11.6	-11.9	-12.2	-12.6	-13.1	-13.6	-14.2	-14.7	-15.3	-15.8	-16.3	-16.8
$Pb(HS)_3^-$	-13.2	-12.5	-12.2	-12.1	-12.2	-12.4	-12.6	-13	-13.5	-14	-14.5	-15.2	-15.8	-16.6	-17.3	-18	-18.7	-19.4	-20
$Mg(HSiO_3)^+$	-1.31	-1.51	-1.76	-2.02	-2.31	-2.61	-2.92	-3.24	-3.57	-3.91	-4.26	-4.63	-5.01	-5.4	-5.78	-6.16	-6.53	-6.89	-7.21
$Ca(HSiO_3)^+$	-1.23	-1.52	-1.85	-2.19	-2.55	-2.92	-3.3	-3.69	-4.08	-4.48	-4.89	-5.31	-5.74	-6.18	-6.62	-7.05	-7.47	-7.87	-8.24

TABLE 18. Logarithms of the dissociation constants of aqueous complexes listed in Table 12 at temperatures ranging from 100 to 1,000°C at 4.0 kb (see text).

Species	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
$BeCl^+$	-6.2	-9.1	-11.5	-13.5	-15.2	-16.7	-18	-19.2	-20.4	-21.4	-22.4	-23.4	-24.3	-25.2	-26.1	-26.9	-27.8	-28.6	-29.3
$BeCl_2$	-6.59	-10.4	-13.5	-16.2	-18.6	-20.7	-22.6	-24.3	-25.9	-27.5	-28.9	-30.3	-31.6	-32.9	-34.2	-35.4	-36.6	-37.7	-38.8
$FeCl^{++}$	-1.88	-2.18	-2.52	-2.89	-3.26	-3.65	-4.03	-4.42	-4.81	-5.21	-5.61	-6.03	-6.45	-6.88	-7.32	-7.76	-8.19	-8.62	-9.03
$CoCl^+$	-0.61	-0.77	-0.99	-1.25	-1.52	-1.81	-2.1	-2.4	-2.71	-3.03	-3.35	-3.69	-4.04	-4.39	-4.75	-5.12	-5.48	-5.83	-6.17
$CuCl$	-1.72	-1.6	-1.55	-1.57	-1.62	-1.7	-1.8	-1.92	-2.07	-2.22	-2.4	-2.59	-2.79	-3.01	-3.23	-3.46	-3.69	-3.91	-4.13
$CuCl_2^-$	-3.57	-3.22	-3.09	-3.09	-3.18	-3.33	-3.53	-3.77	-4.04	-4.33	-4.64	-4.98	-5.33	-5.69	-6.07	-6.45	-6.83	-7.2	-7.57
$CuCl_3^{2-}$	-2.87	-2.44	-2.34	-2.44	-2.66	-2.98	-3.36	-3.79	-4.25	-4.74	-5.25	-5.77	-6.31	-6.86	-7.42	-7.98	-8.53	-9.07	-9.6
$CuCl^+$	-0.57	-0.81	-1.1	-1.41	-1.73	-2.05	-2.38	-2.72	-3.06	-3.41	-3.76	-4.12	-4.5	-4.88	-5.26	-5.65	-6.04	-6.41	-6.78
$CuCl_2$	0.63	0.21	-0.31	-0.88	-1.47	-2.09	-2.71	-3.35	-4	-4.66	-5.34	-6.04	-6.75	-7.49	-8.23	-8.98	-9.72	-10.4	-11.1
$CuCl_3^-$	2.79	2.27	1.58	0.81	-0.01	-0.86	-1.72	-2.59	-3.47	-4.36	-5.26	-6.18	-7.1	-8.04	-8.97	-9.91	-10.8	-11.7	-12.6
$CuCl_4^{2-}$	6.27	5.87	5.2	4.39	3.48	2.52	1.53	0.51	-0.51	-1.55	-2.6	-3.65	-4.72	-5.78	-6.85	-7.91	-8.95	-9.97	-11
$CdCl^+$	-1.8	-1.91	-2.1	-2.34	-2.61	-2.89	-3.19	-3.5	-3.82	-4.14	-4.48	-4.83	-5.18	-5.55	-5.92	-6.3	-6.67	-7.04	-7.39
$CdCl_2$	-2	-2.17	-2.5	-2.92	-3.39	-3.9	-4.43	-4.99	-5.57	-6.17	-6.8	-7.44	-8.11	-8.79	-9.49	-10.2	-10.9	-11.6	-12.2
$CdCl_3^-$	-1.04	-1.23	-1.65	-2.21	-2.84	-3.54	-4.26	-5.02	-5.79	-6.59	-7.4	-8.23	-9.08	-9.95	-10.8	-11.7	-12.6	-13.4	-14.2
$CdCl_4^{2-}$	1.19	1.17	0.8	0.23	-0.46	-1.23	-2.05	-2.91	-3.8	-4.71	-5.64	-6.59	-7.56	-8.53	-9.52	-10.5	-11.5	-12.4	-13.3
$TlCl$	-0.31	-0.39	-0.48	-0.56	-0.65	-0.74	-0.83	-0.93	-1.04	-1.15	-1.28	-1.41	-1.56	-1.71	-1.87	-2.03	-2.19	-2.34	-2.49
$TlCl^{++}$	-6.99	-6.75	-6.65	-6.65	-6.72	-6.84	-7	-7.18	-7.39	-7.63	-7.89	-8.16	-8.47	-8.79	-9.12	-9.46	-9.81	-10.2	-10.5
$AuCl$	-6.22	-5.59	-5.13	-4.78	-4.51	-4.31	-4.16	-4.05	-3.99	-3.95	-3.94	-3.96	-4.01	-4.07	-4.15	-4.25	-4.35	-4.45	-4.55
$AuCl_2^-$	-7.06	-6.34	-5.83	-5.47	-5.21	-5.03	-4.91	-4.85	-4.83	-4.85	-4.91	-4.99	-5.11	-5.26	-5.42	-5.60	-5.78	-5.97	-6.15
$AuCl_3^{2-}$	-6.03	-5.33	-4.86	-4.55	-4.35	-4.23	-4.17	-4.16	-4.2	-4.27	-4.38	-4.52	-4.69	-4.89	-5.1	-5.32	-5.55	-5.79	-6.01
$AuCl_4^-$	31.3	27.8	24.7	22.1	19.8	17.7	15.7	13.9	12.2	10.5	8.92	7.37	5.84	4.34	2.86	1.42	0.03	-1.32	-2.6
$HgCl^+$	-6.33	-6.02	-5.89	-5.87	-5.93	-6.05	-6.21	-6.4	-6.62	-6.86	-7.13	-7.42	-7.73	-8.06	-8.39	-8.74	-9.09	-9.43	-9.77
$HgCl_2$	-11.7	-11	-10.7	-10.6	-10.7	-10.8	-11.1	-11.5	-11.9	-12.3	-12.8	-13.4	-14	-14.6	-15.2	-15.9	-16.5	-17.2	-17.8
$HgCl_3^-$	-11.4	-10.9	-10.8	-10.9	-11.3	-11.8	-12.4	-13.1	-13.8	-14.5	-15.3	-16.2	-17.1	-17.9	-18.9	-19.8	-20.7	-21.6	-22.5
$HgCl_4^{2-}$	-11	-10.5	-10.4	-10.8	-11.3	-12	-12.9	-13.8	-14.7	-15.7	-16.7	-17.8	-18.9	-20	-21.2	-22.3	-23.4	-24.5	-25.6
$InCl^{++}$	-3.32	-3.47	-3.69	-3.96	-4.25	-4.56	-4.89	-5.22	-5.57	-5.92	-6.29	-6.66	-7.05	-7.45	-7.85	-8.26	-8.66	-9.06	-9.45
BeF^+	-9.65	-11.7	-13.4	-14.9	-16.1	-17.3	-18.3	-19.2	-20.1	-20.9	-21.6	-22.4	-23.1	-23.9	-24.6	-25.3	-26	-26.7	-27.4
BeF_2	-13.6	-15.9	-17.8	-19.5	-21.1	-22.5	-23.8	-25	-26.1	-27.2	-28.3	-29.4	-30.4	-31.5	-32.5	-33.6	-34.6	-35.6	-36.5
BeF_3^-	-17.4	-20.4	-22.9	-25.2	-27.3	-29.2	-31	-32.6	-34.2	-35.7	-37.2	-38.7	-40.1	-41.6	-43	-44.4	-45.8	-47.1	-48.4
BeF_4^{2-}	-21.7	-26.6	-30.9	-34.5	-37.8	-40.7	-43.4	-45.9	-48.2	-50.5	-52.6	-54.7	-56.7	-58.8	-60.7	-62.6	-64.5	-66.3	-68
MnF^+	-1.38	-1.62	-1.89	-2.19	-2.49	-2.8	-3.11	-3.42	-3.75	-4.07	-4.41	-4.76	-5.12	-5.48	-5.86	-6.24	-6.62	-6.98	-7.34
FeF^+	-1.48	-1.68	-1.93	-2.18	-2.45	-2.73	-3.01	-3.29	-3.58	-3.88	-4.19	-4.51	-4.85	-5.19	-5.54	-5.89	-6.24	-6.58	-6.92
FeF^{++}	-6.89	-7.44	-7.97	-8.47	-8.96	-9.43	-9.89	-10.3	-10.8	-11.2	-11.7	-12.1	-12.6	-13.1	-13.5	-14	-14.5	-15	-15.4
CoF^+	-1.14	-1.37	-1.63	-1.91	-2.2	-2.5	-2.8	-3.1	-3.4	-3.72	-4.04	-4.37	-4.71	-5.06	-5.42	-5.78	-6.14	-6.49	-6.83
NiF^+	-1.26	-1.47	-1.71	-1.95	-2.21	-2.47	-2.73	-3	-3.27	-3.56	-3.85	-4.15	-4.46	-4.79	-5.12	-5.45	-5.78	-6.11	-6.42
CuF^+	-1.59	-1.82	-2.08	-2.36	-2.65	-2.95	-3.25	-3.56	-3.88	-4.2	-4.53	-4.87	-5.22	-5.59	-5.96	-6.33	-6.71	-7.07	-7.42
ZnF^+	-1.28	-1.52	-1.79	-2.08	-2.37	-2.67	-2.97	-3.28	-3.59	-3.91	-4.23	-4.57	-4.91	-5.27	-5.63	-6	-6.36	-6.71	-7.05
AgF	-0.2	-0.29	-0.39	-0.51	-0.63	-0.76	-0.9	-1.04	-1.19	-1.35	-1.52	-1.7	-1.9	-2.11	-2.33	-2.55	-2.77	-2.98	-3.19
CdF^+	-1.15	-1.4	-1.69	-2.01	-2.33	-2.66	-2.99	-3.32	-3.66	-4	-4.35	-4.7	-5.07	-5.44	-5.82	-6.2	-6.58	-6.94	-7.3
CdF_2	-1	-1.25	-1.61	-2.05	-2.53	-3.04	-3.56	-4.11	-4.68	-5.27	-5.88	-6.51	-7.18	-7.87	-8.57	-9.28	-10	-10.7	-11.4
BaF^+	-0.76	-1.06	-1.37	-1.67	-1.98	-2.29	-2.6	-2.91	-3.22	-3.54	-3.87	-4.2	-4.55	-4.9	-5.26	-5.62	-5.98	-6.33	-6.67
TlF	0.04	-0.1	-0.22	-0.32	-0.42	-0.51	-0.6	-0.7	-0.8	-0.9	-1.02	-1.15	-1.29	-1.45	-1.61	-1.77	-1.94	-2.1	-2.26
HgF^+	-1.65	-1.91	-2.21	-2.53	-2.87	-3.21	-3.56	-3.91	-4.27	-4.63	-5	-5.38	-5.77	-6.16	-6.57	-6.97	-7.37	-7.76	-8.13
InF^{++}	-5.72	-6.38	-6.99	-7.57	-8.11	-8.63	-9.13	-9.61	-10.1	-10.5	-11	-11.5	-11.9	-12.4	-12.9	-13.4	-13.9	-14.3	-14.8
PbF^+	-1.9	-2.01	-2.17	-2.35	-2.54	-2.75	-2.97	-3.2	-3.44	-3.69	-3.96	-4.24	-4.53	-4.83	-5.15	-5.47	-5.79	-6.11	-6.41
PbF_2	-2.8	-2.86	-3.02	-3.24	-3.5	-3.8	-4.13	-4.48	-4.85	-5.25	-5.68	-6.14	-6.64	-7.16	-7.71	-8.26	-8.82	-9.37	-9.89
$Ag(HS)_2^-$	-13.7	-12.2	-11.2	-10.4	-9.83	-9.43	-9.15	-8.9	-8.84	-8.79	-8.79	-8.85	-8.94	-9.07	-9.23	-9.41	-9.6	-9.8	-10.0
$Au(HS)_2^-$	-24.3	-21.5	-19.4	-17.8	-16.5	-15.4	-14.6	-13.9	-13.3	-12.8	-12.5	-12.2	-11.9	-11.8	-11.7	-11.6	-11.6	-11.5	-11.5
$Pb(HS)_2$	-12.4	-11.7	-11.2	-11	-10.9	-10.9	-11	-11.1	-11.3	-11.6	-11.8	-12.2	-12.6	-13	-13.4	-13.9	-14.4	-14.8	-15.3
$Pb(HS)_3^-$	-13.1	-12.4	-12	-11.9	-11.9	-12	-12.2	-12.4	-12.8	-13.1	-13.6	-14.1	-14.6	-15.1	-15.7	-16.3	-17	-17.6	-18.2
$Mg(HSiO_3)^+$	-1.33	-1.5	-1.72	-1.96	-2.2	-2.46	-2.73	-3	-3.28	-3.56	-3.86	-4.16	-4.48	-4.8	-5.13	-5.46	-5.79	-6.11	-6.42
$Ca(HSiO_3)^+$	-1.24	-1.51	-1.81	-2.13	-2.45	-2.78	-3.11	-3.45	-3.79	-4.13	-4.48	-4.84	-5.21	-5.59	-5.97	-6.35	-6.73	-7.1	-7.45

TABLE 19. Logarithms of the dissociation constants of aqueous complexes listed in Table 12 at temperatures ranging from 100 to 1,000°C at 5.0 kb (see text).

Species	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
$BeCl^+$	-6.22	-9.08	-11.4	-13.4	-15	-16.5	-17.8	-18.9	-20	-20.9	-21.9	-22.8	-23.6	-24.4	-25.3	-26.1	-26.9	-27.7	-28.4
$BeCl_2$	-6.6	-10.3	-13.4	-16.1	-18.4	-20.4	-22.3	-23.9	-25.5	-26.9	-28.3	-29.6	-30.8	-32	-33.2	-34.4	-35.5	-36.7	-37.8
$FeCl^{++}$	-1.92	-2.19	-2.51	-2.85	-3.19	-3.54	-3.89	-4.24	-4.59	-4.95	-5.31	-5.68	-6.06	-6.46	-6.86	-7.27	-7.68	-8.1	-8.52
$CoCl^+$	-0.64	-0.77	-0.96	-1.19	-1.44	-1.69	-1.95	-2.22	-2.49	-2.77	-3.06	-3.36	-3.66	-3.98	-4.31	-4.65	-4.99	-5.34	-5.69
$CuCl$	-1.72	-1.57	-1.51	-1.51	-1.54	-1.59	-1.67	-1.76	-1.87	-2	-2.14	-2.29	-2.46	-2.64	-2.84	-3.05	-3.26	-3.48	-3.71
$CuCl_2^-$	-3.52	-3.15	-3	-2.98	-3.05	-3.18	-3.35	-3.56	-3.8	-4.06	-4.33	-4.63	-4.95	-5.28	-5.62	-5.98	-6.35	-6.72	-7.09
$CuCl_3^{2-}$	-2.75	-2.3	-2.19	-2.27	-2.49	-2.79	-3.15	-3.55	-3.98	-4.44	-4.92	-5.41	-5.92	-6.44	-6.97	-7.51	-8.05	-8.59	-9.13
$CuCl^+$	-0.59	-0.81	-1.07	-1.35	-1.64	-1.94	-2.24	-2.54	-2.84	-3.15	-3.46	-3.79	-4.12	-4.46	-4.82	-5.18	-5.54	-5.91	-6.29
$CuCl_2$	0.62	0.24	-0.23	-0.75	-1.29	-1.85	-2.41	-2.98	-3.55	-4.14	-4.74	-5.36	-6	-6.66	-7.34	-8.03	-8.74	-9.45	-10.2
$CuCl_3^-$	2.83	2.35	1.71	0.98	0.21	-0.59	-1.39	-2.2	-3.02	-3.84	-4.67	-5.51	-6.36	-7.22	-8.1	-8.98	-9.87	-10.8	-11.7
$CuCl_4^{2-}$	6.4	6.04	5.4	4.61	3.74	2.83	1.89	0.93	-0.04	-1.01	-1.99	-2.98	-3.98	-4.99	-6	-7.01	-8.03	-9.04	-10.1
$CdCl^+$	-1.82	-1.89	-2.06	-2.27	-2.51	-2.77	-3.04	-3.31	-3.59	-3.88	-4.18	-4.49	-4.81	-5.14	-5.48	-5.83	-6.18	-6.54	-6.9
$CdCl_2$	-1.99	-2.11	-2.4	-2.77	-3.19	-3.64	-4.12	-4.62	-5.13	-5.66	-6.21	-6.77	-7.37	-7.98	-8.62	-9.27	-9.93	-10.6	-11.3
$CdCl_3^-$	-0.97	-1.11	-1.49	-2.01	-2.6	-3.24	-3.91	-4.6	-5.31	-6.04	-6.78	-7.54	-8.32	-9.11	-9.93	-10.8	-11.6	-12.4	-13.3
$CdCl_4^{2-}$	1.36	1.38	1.04	0.5	-0.15	-0.88	-1.65	-2.46	-3.29	-4.13	-5	-5.88	-6.78	-7.7	-8.63	-9.56	-10.5	-11.4	-12.4
$TlCl$	-0.27	-0.34	-0.41	-0.49	-0.55	-0.62	-0.69	-0.77	-0.85	-0.93	-1.03	-1.13	-1.24	-1.37	-1.5	-1.64	-1.79	-1.94	-2.1
$TlCl^{++}$	-7.03	-6.76	-6.64	-6.61	-6.65	-6.73	-6.85	-7	-7.17	-7.36	-7.58	-7.82	-8.07	-8.35	-8.65	-8.97	-9.29	-9.63	-9.97
$AuCl$	-6.19	-5.55	-5.07	-4.7	-4.42	-4.2	-4.02	-3.89	-3.79	-3.73	-3.69	-3.68	-3.69	-3.73	-3.78	-3.86	-3.94	-4.04	-4.15
$AuCl_2^-$	-6.97	-6.23	-5.71	-5.32	-5.04	-4.84	-4.69	-4.60	-4.54	-4.52	-4.54	-4.59	-4.67	-4.77	-4.90	-5.05	-5.22	-5.40	-5.60
$AuCl_3^{2-}$	-5.84	-5.12	-4.65	-4.32	-4.1	-3.96	-3.88	-3.85	-3.85	-3.9	-3.97	-4.07	-4.21	-4.36	-4.55	-4.75	-4.96	-5.19	-5.43
$AuCl_4^-$	30.5	27.1	24.2	21.7	19.5	17.5	15.7	14.0	12.5	11.0	9.51	8.1	6.72	5.35	3.99	2.64	1.31	-0.01	-1.31
$HgCl^+$	-6.33	-6.01	-5.85	-5.81	-5.84	-5.93	-6.05	-6.21	-6.4	-6.6	-6.83	-7.08	-7.35	-7.64	-7.95	-8.27	-8.6	-8.93	-9.28
$HgCl_2$	-11.7	-11	-10.6	-10.5	-10.5	-10.6	-10.8	-11.1	-11.5	-11.8	-12.3	-12.7	-13.2	-13.8	-14.4	-15	-15.6	-16.2	-16.9
$HgCl_3^-$	-11.3	-10.8	-10.6	-10.8	-11.1	-11.5	-12.1	-12.7	-13.3	-14	-14.7	-15.5	-16.3	-17.1	-17.9	-18.8	-19.7	-20.6	-21.5
$HgCl_4^{2-}$	-10.9	-10.3	-10.2	-10.5	-11	-11.7	-12.4	-13.3	-14.2	-15.1	-16.1	-17.1	-18.1	-19.1	-20.2	-21.3	-22.4	-23.5	-24.6
$InCl^{++}$	-3.37	-3.49	-3.68	-3.92	-4.18	-4.46	-4.75	-5.05	-5.36	-5.67	-6	-6.33	-6.68	-7.04	-7.41	-7.79	-8.18	-8.57	-8.96
BeF^+	-9.64	-11.7	-13.3	-14.8	-16	-17.1	-18	-18.9	-19.7	-20.4	-21.1	-21.8	-22.5	-23.2	-23.9	-24.5	-25.2	-25.9	-26.5
BeF_2	-13.6	-15.8	-17.7	-19.4	-20.8	-22.2	-23.4	-24.5	-25.6	-26.6	-27.6	-28.6	-29.5	-30.5	-31.5	-32.4	-33.4	-34.4	-35.3
BeF_3^-	-17.4	-20.2	-22.8	-25	-27	-28.8	-30.4	-32	-33.5	-34.9	-36.2	-37.6	-38.9	-40.2	-41.5	-42.9	-44.2	-45.5	-46.8
BeF_4^{2-}	-21.6	-26.5	-30.6	-34.2	-37.4	-40.2	-42.8	-45.1	-47.3	-49.4	-51.4	-53.4	-55.2	-57.1	-59	-60.8	-62.6	-64.4	-66.1
MnF^+	-1.36	-1.58	-1.83	-2.1	-2.38	-2.65	-2.93	-3.21	-3.49	-3.78	-4.08	-4.38	-4.7	-5.03	-5.37	-5.72	-6.08	-6.44	-6.81
FeF^+	-1.46	-1.65	-1.87	-2.1	-2.35	-2.59	-2.84	-3.09	-3.34	-3.6	-3.87	-4.15	-4.44	-4.74	-5.06	-5.38	-5.72	-6.05	-6.39
FeF^{++}	-6.91	-7.43	-7.93	-8.4	-8.85	-9.28	-9.7	-10.1	-10.5	-10.9	-11.3	-11.7	-12.1	-12.5	-13	-13.4	-13.9	-14.3	-14.8
CoF^+	-1.14	-1.33	-1.57	-1.83	-2.09	-2.36	-2.62	-2.89	-3.16	-3.43	-3.71	-4	-4.3	-4.62	-4.94	-5.27	-5.61	-5.96	-6.3
NiF^+	-1.25	-1.44	-1.66	-1.88	-2.11	-2.34	-2.57	-2.8	-3.04	-3.28	-3.53	-3.79	-4.07	-4.35	-4.65	-4.95	-5.27	-5.59	-5.91
CuF^+	-1.59	-1.79	-2.03	-2.28	-2.55	-2.81	-3.08	-3.35	-3.63	-3.91	-4.2	-4.5	-4.82	-5.14	-5.48	-5.82	-6.17	-6.53	-6.89
ZnF^+	-1.27	-1.49	-1.74	-2	-2.27	-2.54	-2.81	-3.08	-3.35	-3.63	-3.91	-4.21	-4.51	-4.83	-5.16	-5.49	-5.84	-6.18	-6.53
AgF	-0.15	-0.23	-0.32	-0.42	-0.52	-0.62	-0.73	-0.84	-0.96	-1.09	-1.22	-1.37	-1.53	-1.71	-1.89	-2.09	-2.3	-2.51	-2.72
CdF^+	-1.14	-1.36	-1.63	-1.92	-2.21	-2.51	-2.81	-3.11	-3.41	-3.71	-4.02	-4.34	-4.67	-5	-5.35	-5.7	-6.06	-6.42	-6.78
CdF_2	-0.95	-1.15	-1.48	-1.86	-2.29	-2.73	-3.19	-3.67	-4.16	-4.67	-5.2	-5.75	-6.34	-6.95	-7.58	-8.24	-8.91	-9.6	-10.3
BaF^+	-0.81	-1.09	-1.37	-1.66	-1.93	-2.21	-2.48	-2.75	-3.03	-3.31	-3.59	-3.88	-4.19	-4.5	-4.83	-5.16	-5.5	-5.84	-6.19
TlF	0.11	-0.02	-0.12	-0.21	-0.29	-0.36	-0.42	-0.49	-0.56	-0.64	-0.72	-0.82	-0.93	-1.05	-1.18	-1.32	-1.47	-1.63	-1.8
HgF^+	-1.63	-1.87	-2.15	-2.45	-2.76	-3.07	-3.39	-3.71	-4.03	-4.35	-4.68	-5.02	-5.37	-5.73	-6.1	-6.47	-6.85	-7.24	-7.62
InF^{++}	-5.74	-6.37	-6.96	-7.5	-8.01	-8.49	-8.94	-9.38	-9.81	-10.2	-10.6	-11.1	-11.5	-11.9	-12.4	-12.8	-13.3	-13.7	-14.2
PbF^+	-1.88	-1.97	-2.1	-2.26	-2.43	-2.61	-2.79	-2.99	-3.19	-3.4	-3.62	-3.86	-4.11	-4.38	-4.66	-4.95	-5.26	-5.56	-5.88
PbF_2	-2.74	-2.77	-2.89	-3.07	-3.28	-3.51	-3.77	-4.05	-4.35	-4.68	-5.03	-5.41	-5.83	-6.27	-6.75	-7.25	-7.77	-8.31	-8.86
$Ag(HS)_2^-$	-13.6	-12.2	-11.1	-10.3	-9.72	-9.29	-8.98	-8.75	-8.6	-8.52	-8.48	-8.5	-8.55	-8.64	-8.77	-8.92	-9.1	-9.29	-9.5
$Au(HS)_2^-$	-24.2	-21.4	-19.3	-17.7	-16.3	-15.3	-14.4	-13.6	-13.0	-12.5	-12.1	-11.8	-11.5	-11.3	-11.2	-11.1	-11.0	-11.0	-11.0
$Pb(HS)_2$	-12.4	-11.7	-11.2	-10.9	-10.7	-10.7	-10.7	-10.8	-10.9	-11.1	-11.3	-11.6	-11.9	-12.2	-12.6	-13	-13.5	-13.9	-14.4
$Pb(HS)_3^-$	-13.1	-12.3	-11.9	-11.7	-11.6	-11.7	-11.8	-12	-12.2	-12.5	-12.9	-13.3	-13.7	-14.2	-14.7	-15.3	-15.9	-16.5	-17.1
$Mg(HSiO_3)^+$	-1.35	-1.51	-1.7	-1.91	-2.14	-2.36	-2.6	-2.83	-3.07	-3.32	-3.57	-3.84	-4.12	-4.4	-4.7	-5	-5.32	-5.63	-5.95
$Ca(HSiO_3)^+$	-1.27	-1.52	-1.8	-2.09	-2.39	-2.68	-2.98	-3.28	-3.59	-3.89	-4.2	-4.52	-4.85	-5.19	-5.54	-5.89	-6.25	-6.62	-6.98

are not consistent with those adopted in the present study from Shock et al. (1989).

9.1. Uncertainties Associated with the Estimation of the Equilibrium Constants of Aqueous Metal Complexes at Elevated Temperatures and Pressures

Assessing the uncertainties associated with the predicted log β values at elevated temperatures and pressures is difficult. However, approximate estimates can be made by taking account of the principal sources of uncertainty. Three sources of uncertainty can be identified. First, the uncertainty in the log β values at 25°C and 1 bar which are used in the predictive calculations is transmitted to the log β values at elevated temperatures and pressures. For example, it can be seen in Figs. 4, 5, and 14–17 that the scatter of the data points at or near 25°C and 1 bar is commonly ± 0.3 of a log unit. A second source of uncertainty in log β values predicted at elevated temperatures and pressures arises from uncertainties in the equation of state coefficients estimated from the standard partial molal properties of the aqueous complexes (Eqns. 27–30 and Fig. 1). According to Shock and Helgeson (1988), combined uncertainties in estimated equation of state parameters may lead to uncertainties in $\Delta \bar{G}^0$ as large as ± 700 cal mol^{-1} at 500°C and 2 kb or ± 1500 cal mol^{-1} at 1000°C and 5 kb, corresponding to ± 0.2 and 0.3 units in log β, respectively. A third source of uncertainty in predicted log β values arises from the estimated conventional standard partial molal entropies ($\bar{S}^0$), volumes ($\bar{V}^0$), and heat capacities ($\bar{C}_P^0$) of aqueous metal complexes at 25°C and 1 bar used to obtain the equation of state coefficients. Based on the scatter of the data points in Figs. 9, 10, 12, and 18–25, it is possible that $\bar{S}^0$, $\bar{V}^0$, and $\bar{C}_P^0$ may be uncertain to the extent of ± 5 cal mol^{-1} K^{-1}, ± 5 cm^3 mol^{-1}, and ± 5 cal mol^{-1} K^{-1}, respectively. Of these, the uncertainties in the estimated values of $\bar{V}^0$ lead to negligible uncertainties in predicted log β values compared to those for $\bar{S}^0$ and $\bar{C}_P^0$. The latter uncertainties result in values of $\Delta \bar{G}^0$ calculated from Eqn. 38 which are uncertain to the extent of ± 2400 cal mol^{-1} and ± 1100 cal mol^{-1} at 500°C, which correspond to ± 0.7 and 0.3 log units, respectively, for predicted values of log β. Where comparisons can be made, the discrepancies between experimental and predicted values of log β are well within these estimated uncertainties, which are maximal but probably not typical.

10. CONCLUDING REMARKS

The equations, correlations, and parameters summarized above for aqueous metal complexes can be used together with corresponding values for cations and anions taken from Shock and Helgeson (1988) to calculate values of log K for a wide variety of metal ion complexes of geologic interest at high temperatures and pressures. Although provisional, the results of such calculations can be confirmed or refined by critical experiments. In the meantime, thermodynamic calculations using the equations of state parameters and standard partial molal thermodynamic properties at 25°C and 1 bar generated in the present study can be used to predict mineral solubilities in hydrothermal systems.

The correlations used to estimate the standard partial molal entropies, heat capacities and volumes of aqueous complexes and the associated equations of state coefficients for aqueous metal ion complexes have been incorporated in a computer program called PRONSPREP96, which is available from D. A. Sverjensky or E. L. Shock. The equations of state parameters have been incorporated in a revised version of computer program SUPCRT92, which can be obtained from the Laboratory of Theoretical Geochemistry at the University of California, Berkeley.

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