

SUPCRT92: A SOFTWARE PACKAGE FOR CALCULATING THE STANDARD MOLAL THERMODYNAMIC PROPERTIES OF MINERALS, GASES, AQUEOUS SPECIES, AND REACTIONS FROM 1 TO 5000 BAR AND 0 TO 1000°C*

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Abstract—Recent advances in theoretical geochemistry permit calculation of the standard molal thermodynamic properties of a wide variety of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. The SUPCRT92 software package facilitates practical application of these recent theories, equations, and data to define equilibrium constraints on geochemical processes in a wide variety of geologic systems.

The SUPCRT92 package is composed of three interactive FORTRAN 77 programs, SUPCRT92, MPRONS92, and CPRONS92, and a sequential-access thermodynamic database, SPRONS92.DAT. The SUPCRT92 program reads or permits user-generation of its two input files, CON and RXN, retrieves data from the direct-access equivalent of SPRONS92.DAT, calculates the standard molal Gibbs free energy, enthalpy, entropy, heat capacity, and volume of each reaction specified on the RXN file through a range of conditions specified on the CON file, and writes the calculated reaction properties to the output TAB file and, optionally, to PLT files that facilitate their graphical depiction. Calculations can be performed along the liquid side of the H₂O vaporization boundary by specifying either temperature (*T*) or pressure (*P*), and in the single-phase regions of fluid H₂O by specifying either *T* and *P*, *T* and H₂O density, *T* and log *K*, or *P* and log *K*. SPRONS92.DAT, which contains standard molal thermodynamic properties at 25°C and 1 bar, equation-of-state parameters, heat capacity coefficients, and phase transition data for approximately 500 minerals, gases, and aqueous species, can be augmented or otherwise modified using MPRONS92, and converted to its direct-access equivalent using CPRONS92.

Key Words: SUPCRT92, Equations of state, Standard molal thermodynamic properties, Chemical equilibrium, Minerals, Gases, Aqueous species, H₂O, Thermodynamics, Geochemistry.

INTRODUCTION

Recent theories, equations, and data that permit calculation of the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions as a function of temperature and pressure (Helgeson and others, 1978; Levelt Sengers and others, 1983; Haar, Gallagher, and Kell, 1984; Tanger and Helgeson, 1988; Shock and Helgeson, 1988, 1990; Shock, Helgeson, and Sverjensky, 1989; Johnson and Norton, 1991; Shock and others, 1992; Sverjensky, Shock, and Helgeson, 1993) can be used to define equilibrium constraints on geochemical processes in many different geologic environments.

However, practical application of these predictive tools to solve geochemical problems requires their incorporation into reliable and efficient software. This requirement inspired creation of the original SUPCRT computer program (SUPCRT is an abbreviation for "supercritical"), which was written during 1974 and 1975 by J. V. Walther, D. H. Kirkham, and H. C. Helgeson of the Laboratory of Theoretical Geochemistry (a.k.a. Prediction Central), Department of Geology and Geophysics, University of California, Berkeley.

The inaugural SUPCRT program encoded equations and data given by Keenan and others (1969) and Helgeson and Kirkham (1974a, 1974b) for calculating the requisite electrostatic and standard molal thermodynamic properties of fluid H₂O (hereinafter, H₂O refers implicitly to the fluid phases of H₂O); those under development by Helgeson and Kirkham (1976) and Helgeson, Kirkham, and Flowers (1981) for describing the corresponding thermodynamic properties of aqueous species other than H₂O (hereinafter, "aqueous species other than H₂O" and "aqueous solute species" are used interchangeably); and those under development by

*The SUPCRT92 software package supersedes all previous versions of the SUPCRT computer program developed and distributed by H. C. Helgeson and his coworkers in the Laboratory of Theoretical Geochemistry, University of California, Berkeley. The SUPCRT92 package is available on a 5.25 in. 1.2 Mbyte DOS disk which can be obtained at no cost from the Laboratory of Theoretical Geochemistry.

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Helgeson and others (1978) for calculating the standard molal thermodynamic properties of minerals and gases. Since 1975, SUPCRT has been updated repeatedly by numerous students and colleagues of Prediction Central to incorporate new and revised equations and data that facilitate improved description and predictive extrapolation of the thermodynamic properties of minerals, gases, aqueous species, and reactions. Throughout this evolution, SUPCRT has been distributed widely among the geochemical community, where it has become a standard computational tool.

The SUPCRT92 software package supersedes all previously distributed versions of SUPCRT. Relative to its predecessors, SUPCRT92 incorporates new and revised equations and data that permit significantly improved representation of the standard molal thermodynamic properties of aqueous species for a substantially wider range of temperature. Specifically, SUPCRT92 encodes equations of state for H₂O developed by Levelt Sengers and others (1983) and Haar, Gallagher, and Kell (1984), the H₂O dielectric formulation given by Johnson and Norton (1991), and the revised HKF (Helgeson, Kirkham, and Flowers, 1981) equation of state for aqueous solute species presented by Tanger and Helgeson (1988) and Shock and others (1992). These new and revised equations facilitate calculation of the standard molal thermodynamic properties of aqueous species other than H₂O to 1000°C; such calculations were limited previously to 600°C (Helgeson, Kirkham, and Flowers, 1981). In addition, the revised HKF equation of state can be applied to a substantially expanded inventory of these aqueous solute species. Of particular importance are the data now available for aqueous organic species (Shock and Helgeson, 1990), inorganic neutral species (Shock, Helgeson, and Sverjensky, 1989), and inorganic metal complexes (Sverjensky, Shock, and Helgeson, 1993).

The pressing need for a modern software tool that incorporated these improved equations and data for H₂O and other aqueous species together with their counterparts for minerals and gases (Helgeson and others, 1978) catalyzed the development of SUPCRT92. Additional incentive to redesign the new code relative to previous releases, and to develop the auxiliary software included in the package, was provided by an equally pressing need to improve the ease of verification, maintenance, and update procedures, improve the user interface, expand the flexibility of input, run-time, and output options, improve run-time efficiency, and facilitate portability to diverse computing environments. We hope that each of these goals has been met; keep in mind, however, that software is never completed, only abandoned!

The purpose of the present communication is to provide (1) a succinct yet comprehensive summary of the new and revised equations and data as referenced; (2) documentation for the SUPCRT92 software package: its design, individual modules, input and output

specifications, installation, operation, and accuracy verification; and (3) a suite of generic interactive sessions with the programs that facilitate expeditious use of SUPCRT92 to solve geochemical problems. Readers intimately familiar with earlier versions of SUPCRT and the recent advances noted here are invited to leapfrog the following text to Appendices 1–8, which present installation instructions for the SUPCRT92 package, generic sessions with the interactive programs, and example input and output files.

CONVENTIONS, EQUATIONS, AND DATA USED IN SUPCRT92

In this section we present a resume of the conventions, equations, and data used in SUPCRT92 to calculate the standard molal Gibbs free energies, enthalpies, entropies, volumes, and heat capacities of minerals, gases, aqueous species, and reactions as a function of temperature and pressure. The theoretical development and practical implementation of these equations has been described by Helgeson and Kirkham (1974a, 1974b, 1976), Helgeson, Kirkham, and Flowers (1981), Helgeson and others (1978), Uematsu and Franck (1980), Pitzer (1983), Levelt Sengers and others (1983), Haar, Gallagher, and Kell (1984), Tanger and Helgeson (1988), Shock and Helgeson (1988, 1990), Shock, Helgeson, and Sverjensky (1989), Johnson and Norton (1991), Shock and others (1992), and Sverjensky, Shock, and Helgeson (1993).

Standard state, H₂O triple point, and unit conventions

The standard state convention adopted for thermodynamic components that correspond to stoichiometric minerals or pure liquids (including water) calls for unit activity of the pure component at all pressures and temperatures. For gases (including stable and metastable steam), the standard state is unit fugacity of the hypothetical gas at 1 bar and any temperature; for aqueous species other than H₂O, it is unit activity of the species in a hypothetical 1 molal solution referenced to infinite dilution at any pressure and temperature (Helgeson and Kirkham, 1974a; Helgeson, Kirkham, and Flowers, 1981; Helgeson and others, 1978; Tanger and Helgeson, 1988).

The standard molal Gibbs free energies and enthalpies of minerals, gases, and aqueous species are represented as *apparent* standard molal Gibbs free energies ($\Delta G_{P,T}^\circ$) and enthalpies ($\Delta H_{P,T}^\circ$) of formation from the elements at the subscripted pressure (P) and temperature (T). These apparent standard molal properties, as defined by Benson (1968), Helgeson and others (1978), and Helgeson, Kirkham, and Flowers (1981), can be written as

$$\Delta G_{P,T}^\circ \equiv \Delta G_f^\circ + (G_{P,T}^\circ - G_{P,T}^\circ) \quad (1)$$

and

$$\Delta H_{P,T}^\circ \equiv \Delta H_f^\circ + (H_{P,T}^\circ - H_{P,T}^\circ), \quad (2)$$

where ΔG_f° and ΔH_f° denote the standard molal Gibbs free energy and enthalpy of formation of the species from its elements in their stable phase at the reference pressure ($P_r = 1$ bar) and temperature ($T_r = 298.15$ K), and $G_{P,T}^\circ - G_{P_r,T_r}^\circ$ and $H_{P,T}^\circ - H_{P_r,T_r}^\circ$ refer to differences in the standard molal Gibbs free energy and enthalpy of the species that arise from changes in pressure ($P - P_r$) and temperature ($T - T_r$). The standard molal entropies, isobaric heat capacities, and volumes of minerals, gases, and aqueous species are designated by $S_{P,T}^\circ$, $C_{P,T}^\circ$, and $V_{P,T}^\circ$, respectively.

Thermodynamic properties of the j th aqueous species other than H_2O are represented as *conventional* standard molal properties, which are related to the corresponding *absolute* properties by (Helgeson, Kirkham, and Flowers, 1981; Tanger and Helgeson, 1988)

$$\Delta \Xi_{j,P,T}^\circ \equiv \Delta \Xi_{H^+,P,T}^{\circ,abs} - Z_j \Delta \Xi_{H^+,P,T}^{\circ,abs} \quad (3)$$

and

$$\Xi_{j,P,T}^\circ \equiv \Xi_{j,P,T}^{\circ,abs} - Z_j \Xi_{H^+,P,T}^{\circ,abs}, \quad (4)$$

where $\Delta \Xi_{j,P,T}^\circ$ and $\Delta \Xi_{j,P,T}^{\circ,abs}$ refer to the conventional and absolute apparent standard molal Gibbs free energy and enthalpy of formation of the j th species, $\Xi_{j,P,T}^\circ$ and $\Xi_{j,P,T}^{\circ,abs}$ stand for the conventional and absolute standard molal entropy, heat capacity, and volume of this species, and Z_j represents the species charge. Hence, the conventional standard molal properties of the hydrogen ion are zero at any pressure and temperature, the corresponding properties of aqueous anions are equivalent to those of the associated acid electrolyte ($H_{Z_{A^-}|v_{A^-}}^+$, where v_{A^-} represents the stoichiometric number of moles of anion A^- in 1 mol of the electrolyte), and those of any aqueous electrolyte ($C_{v_{C^+}}^+ A_{v_{A^-}}^-$, where v_{C^+} represents the stoichiometric number of moles of cation C^+ in 1 mol of the electrolyte) are equivalent to the stoichiometric sum of the corresponding properties of the cation and anion (Helgeson, Kirkham, and Flowers, 1981; Tanger and Helgeson, 1988). Note that the conventional standard molal properties of aqueous solute species are equivalent to their conventional standard *partial* molal analogs; that is $\Delta \Xi_{j,P,T}^\circ = \Delta \bar{\Xi}_{j,P,T}^\circ$ and $\Xi_{j,P,T}^\circ = \bar{\Xi}_{j,P,T}^\circ$ (Helgeson, Kirkham, and Flowers, 1981).

For the stable phase of H_2O at any temperature and pressure, the apparent standard molal Gibbs free energy and enthalpy of formation and the standard molal entropy ($\Delta G_{H_2O,P,T}^\circ$, $\Delta H_{H_2O,P,T}^\circ$, and $S_{H_2O,P,T}^\circ$) are referenced to nonzero values for the corresponding molal properties of liquid H_2O at its triple point (Helgeson and Kirkham, 1974a), which are designated by the subscript *tr* ($H_{H_2O,tr}$, $G_{H_2O,tr}$, and $S_{H_2O,tr}$). Calculation of these apparent standard molal and standard molal properties requires conversion from the molal Gibbs free energy ($G_{H_2O,P,T}^\circ - G_{H_2O,tr}$), enthalpy ($H_{H_2O,P,T}^\circ - H_{H_2O,tr}$), and entropy ($S_{H_2O,P,T}^\circ - S_{H_2O,tr}$) computed using equations of state

given by Levelt Sengers and others (1983) and Haar, Gallagher, and Kell (1984), both of which are predicted on the typical steam-table convention $S_{H_2O,tr} = G_{H_2O,tr} = H_{H_2O,tr} = 0$. This conversion of the triple-point reference frame is accomplished using (Helgeson and Kirkham, 1974a)

$$\begin{aligned} S_{H_2O,P,T}^\circ &= S_{H_2O,P,T} \\ &= (S_{H_2O,P,T} - S_{H_2O,tr}) + S_{H_2O,tr}, \end{aligned} \quad (5)$$

$$\begin{aligned} \Delta H_{H_2O,P,T}^\circ &= \Delta H_{H_2O,P,T} \\ &= (H_{H_2O,P,T} - H_{H_2O,tr}) + H_{H_2O,tr}, \end{aligned} \quad (6)$$

and

$$\begin{aligned} \Delta G_{H_2O,P,T}^\circ &= \Delta G_{H_2O,P,T} = (H_{H_2O,P,T} - H_{H_2O,tr}) \\ &\quad - TS_{H_2O,P,T} + T_{tr} S_{H_2O,tr} + G_{H_2O,tr} \\ &= (G_{H_2O,P,T} - G_{H_2O,tr}) \\ &\quad + T_{tr} S_{H_2O,tr} + G_{H_2O,tr}, \end{aligned} \quad (7)$$

where $S_{H_2O,P,T}$ designates the molal entropy, $\Delta H_{H_2O,P,T}$ and $\Delta G_{H_2O,P,T}$ refer to the apparent molal enthalpy and Gibbs free energy of formation, $T_{tr} = 273.16$ K, $S_{H_2O,tr} = 15.132$ cal mol⁻¹ K⁻¹, $H_{H_2O,tr} = -68,767$ cal/mol, and $G_{H_2O,tr} = -56,290$ cal/mol (Helgeson and Kirkham, 1974a). The first equality in Equations (5)–(7) follows from the standard state convention adopted for liquid H_2O .

All of the equations given below that represent the apparent standard molal and standard molal properties of minerals, gases, aqueous species, and reactions are cast in terms of the following unit conventions: temperature in Kelvin (K), pressure in bar, energy in thermochemical calories (cal or kcal), mass in moles (mol), and volume in cubic centimeters (cm³).

Thermodynamic and electrostatic properties of H_2O

Thermodynamic and electrostatic properties of H_2O are calculated in SUPCRT92 using equations and data given by Helgeson and Kirkham (1974a), Uematsu and Franck (1980), Levelt Sengers and others (1983), Pitzer (1983), Haar, Gallagher, and Kell (1984), and Johnson and Norton (1991). Within the critical region for H_2O (Fig. 1), thermodynamic properties are obtained from the nonclassical scaled equation of state developed by Levelt Sengers and others (1983); outside the critical region, these properties are calculated using the classical virial equation of state developed by Haar, Gallagher, and Kell (1984). In lieu of an alternative computationally convenient approach, transition between these two formulations is accomplished by a simple switch function along the T - P - ρ_{H_2O} boundary of the critical region, where ρ_{H_2O} refers to the density of H_2O (hereinafter, ρ refers implicitly to ρ_{H_2O}). Although this algorithm necessarily imposes discontinuities in computed H_2O properties across the critical-region boundary (Johnson and Norton, 1991), such discontinuities are sufficiently small to be considered negligible in SUPCRT92 applications.

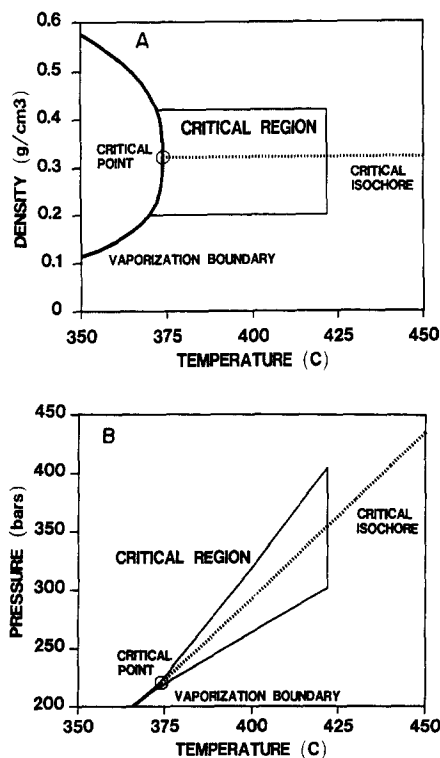


Figure 1. H₂O critical region in T - ρ (A) and T - P (B) coordinates. Critical region is bound by 421.85°C isotherm, 0.20 and 0.42 g/cm³ isochores, and segment of vaporization boundary that bridges these isochores (Levelt Sengers and others, 1983). Vaporization boundary, critical point (373.917°C, 220.46 bar, 0.322778 g/cm³), and critical isochore (0.322778 g/cm³) also are illustrated for reference.

Both within and beyond the critical region, electrostatic properties are obtained from an empirical expression for the dielectric constant that was proposed originally by Uematsu and Franck (1980), but since has been modified by Johnson and Norton (1991). These modifications facilitate the smooth confluence of properties described at low temperatures ($\leq 350^\circ\text{C}$) by the Helgeson-Kirkham (1974) equation and those predicted at high temperatures ($\geq 550^\circ\text{C}$) by the revised Kirkwood (1939) equation developed by Pitzer (1983).

Thermodynamic properties are represented from the fusion boundaries to 2250°C, from 10^{-4} to 30,000 bar, and from H₂O densities of 10^{-7} to 1.38 g/cm³. The corresponding range of conditions for which electrostatic properties can be calculated is relatively small: from 0 to 1000°C, 1 to 5000 bar, and H₂O densities from 0.05 to 1.1 g/cm³ (Fig. 2). This comparatively restricted range reflects the present limits on experimental measurements of the dielectric constant (e.g., Oshry, 1949; Owen and others, 1961; Heger, 1969; Heger, Uematsu, and Franck, 1980) and on theoretical extrapolation of these data to higher temperatures (e.g. Pitzer, 1983).

Equations of state and the standard molal volume. The equation of state used for H₂O in its critical region can be expressed as (Johnson and Norton, 1991)

$$\rho = \rho_c \left(\frac{\partial \tilde{P}}{\partial \tilde{\mu}} \right)_T, \quad (8)$$

where ρ stands for the density of H₂O (g/cm³), and the dimensionless properties \tilde{P} , $\tilde{\mu}$, and \tilde{T} are defined by (Levelt Sengers and others, 1983)

$$\tilde{P} \equiv \frac{T_c}{P_c} \left(\frac{P}{T} \right), \quad (9)$$

$$\tilde{\mu} \equiv \frac{\rho_c T_c}{P_c} \left(\frac{\mu}{T} \right), \quad (10)$$

and

$$\tilde{T} = - \left(\frac{T_c}{T} \right), \quad (11)$$

where μ denotes the chemical potential of H₂O, and the subscript c designates properties at the H₂O critical point: $T_c = 647.067 \text{ K}$ (373.917°C), $P_c = 220.46 \text{ bar}$, and $\rho_c = 0.322778 \text{ g/cm}^3$ (Levelt Sengers and others, 1983). The analogous equation

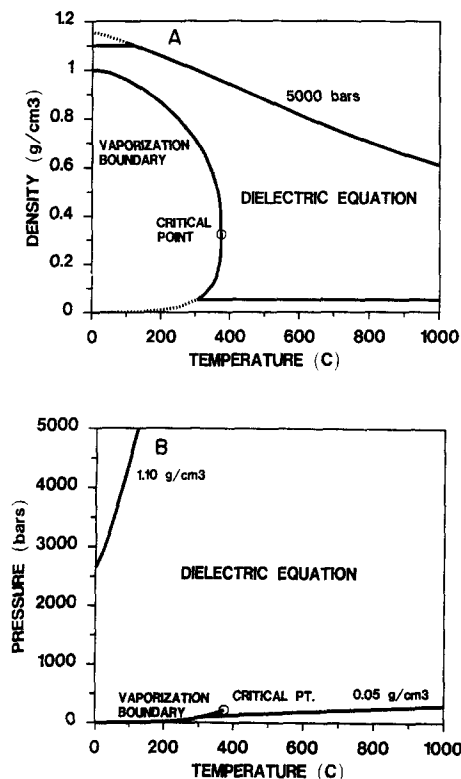


Figure 2. Range of conditions in T - ρ (A) and T - P (B) coordinates for which dielectric constant and Born functions of H₂O can be calculated using Equations (32)–(44) and coefficients given in Table 1. This range is bound by 5000-bar isobar, 0 and 1000°C isotherms, 0.05 and 1.10 g/cm³ isochores, and vaporization boundary. Calculation of standard molal thermodynamic properties of neutral aqueous solute species using Equations (45) and (59)–(62) also is restricted to this T - P - ρ region as consequence of their implicit dependence on Equations (32)–(44).

used outside the critical region can be written as (Johnson and Norton, 1991)

$$\rho = (PCM)^{1/2} \left(\frac{\partial A}{\partial \rho} \right)_T^{-1/2}, \quad (12)$$

where A refers to the molal Helmholtz function for H_2O developed by Haar, Gallagher, and Kell (1984), C represents a conversion factor ($0.02390054 \text{ cal bar}^{-1} \text{ cm}^{-3}$), and M stands for the molecular weight of H_2O (18.0152 g/mol). Values for the standard molal volume of H_2O (V°) can be obtained from either Equation (8) or Equation (12), together with $V^\circ = M/\rho$.

Calculation of the electrostatic properties of H_2O , which are needed to describe the standard molal thermodynamic properties of aqueous solute species (see next), requires values for the isothermal compressibility (β), isobaric expansivity (α), and $(\partial\alpha/\partial T)_P$ of H_2O , which are defined by

$$\beta \equiv \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T = -\frac{1}{V^\circ} \left(\frac{\partial V^\circ}{\partial P} \right)_T, \quad (13)$$

$$\alpha \equiv -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P = \frac{1}{V^\circ} \left(\frac{\partial V^\circ}{\partial T} \right)_P, \quad (14)$$

and

$$\left(\frac{\partial \alpha}{\partial T} \right)_P = \alpha^2 - \frac{1}{\rho} \left(\frac{\partial^2 \rho}{\partial T^2} \right)_P = -\alpha^2 + \frac{1}{V^\circ} \left(\frac{\partial^2 V^\circ}{\partial T^2} \right)_P. \quad (15)$$

Within the critical region, specific statements of Equations (13)–(15) can be cast in terms of Equation (8) and its partial derivatives, which leads to (Johnson and Norton, 1991)

$$\beta = -\frac{\tilde{T}}{\tilde{\rho}^2 P_c} \left(\frac{\partial^2 \Delta \tilde{P}}{\partial \Delta \tilde{\mu}^2} \right)_{\Delta \tilde{T}}, \quad (16)$$

$$\alpha = -\frac{\tilde{T}}{\tilde{\rho}^2 T_c} \left(\frac{\partial^2 \Delta \tilde{P}}{\partial \Delta \tilde{\mu}^2} \right)_{\Delta \tilde{T}} \left\{ \tilde{P} + \tilde{T} \left(\frac{\partial \tilde{P}}{\partial \tilde{T}} \right)_\rho \right\}, \quad (17)$$

and

$$\begin{aligned} \left(\frac{\partial \alpha}{\partial T} \right)_P = & \frac{\tilde{T}^2}{\tilde{\rho}^2 T_c} \left\{ \left[\frac{P}{P_c} + \left(\frac{\partial \tilde{P}}{\partial \tilde{T}} \right)_\rho \right] \left\{ 2 \left(\frac{\partial^2 \Delta \tilde{P}}{\partial \Delta \tilde{\mu}^2} \right)_{\Delta \tilde{T}} \left\{ \alpha - \frac{1}{T} \right\} \right. \right. \\ & \left. \left. - \frac{\tilde{T}}{T} \left(\frac{\partial^3 \Delta \tilde{P}}{\partial \Delta \tilde{\mu}^2 \partial \Delta \tilde{T}} \right)_{\Delta \tilde{T}, \Delta \tilde{T}, P} \right\} \right. \\ & \left. - \frac{\tilde{T}}{T} \left(\frac{\partial^2 \Delta \tilde{P}}{\partial \Delta \tilde{\mu}^2} \right)_{\Delta \tilde{T}} \left(\frac{\partial^2 \tilde{P}}{\partial \tilde{T}^2} \right)_{\rho, P} \right\}, \quad (18) \end{aligned}$$

where $\tilde{\rho} = \rho/\rho_c$, $\Delta \tilde{T} = \tilde{T} + 1$, $\Delta \tilde{\mu}$ represents the difference between $\tilde{\mu}(\rho, T)$ and $\tilde{\mu}(\rho_c, T)$, and $\Delta \tilde{P}$ denotes the sum of scaling and correction-to-scaling contributions to \tilde{P} that account for asymptotic critical behavior (Levelt Sengers and others, 1983). Outside the critical region, specific statements of Equations (13)–(15) can be cast in terms of Equation (12) and its partial derivatives, which leads to (Johnson and Norton, 1991)

$$\beta = CM \left\{ 2\rho^2 \left(\frac{\partial A}{\partial \rho} \right)_T + \rho^3 \left(\frac{\partial^2 A}{\partial \rho^2} \right)_T \right\}^{-1}, \quad (19)$$

$$\alpha = \left(\frac{\partial^2 A}{\partial \rho \partial T} \right)_{T, \rho} \left\{ 2 \left(\frac{\partial A}{\partial \rho} \right)_T + \rho \left(\frac{\partial^2 A}{\partial \rho^2} \right)_T \right\}^{-1}, \quad (20)$$

and

$$\begin{aligned} \left(\frac{\partial \alpha}{\partial T} \right)_P = & \alpha \left(\frac{\partial^2 A}{\partial \rho \partial T} \right)_{T, \rho}^{-1} \left\{ \left(\frac{\partial^3 A}{\partial \rho \partial T^2} \right)_{T, \rho, P} \right. \\ & \left. - \alpha \left[2 \left(\frac{\partial^2 A}{\partial \rho \partial T} \right)_{T, P} + \rho \left(\frac{\partial^3 A}{\partial \rho^2 \partial T} \right)_{T, T, P} \right. \right. \\ & \left. \left. - \rho \alpha \left(\frac{\partial^2 A}{\partial \rho^2} \right)_T \right] \right\}. \quad (21) \end{aligned}$$

Other standard molal thermodynamic properties.

Within the critical region, $\Delta G_{P,T}^\circ$, $\Delta H_{P,T}^\circ$, and $S_{P,T}^\circ$ of H_2O consistent with the thermodynamic potential given by Levelt Sengers and others (1983) can be calculated from Equations (5)–(7), together with (Johnson and Norton, 1991)

$$\begin{aligned} G_{P,T} - G_u = & \frac{CMP_c}{\rho_c} \left(\frac{\partial \tilde{P}}{\partial \tilde{\mu}} \right)_T^{-1} \left\{ \left(\frac{1}{\tilde{T}} + 1 \right) \tilde{P} \right. \\ & \left. - (\tilde{T} + 1) \left(\frac{\partial \tilde{P}}{\partial \tilde{T}} \right)_\mu - \left(\frac{\tilde{\mu}}{\tilde{T}} \right) \left(\frac{\partial \tilde{P}}{\partial \tilde{\mu}} \right)_T \right\}, \quad (22) \end{aligned}$$

$$H_{P,T} - H_u = \frac{CMP_c}{\rho_c} \left(\frac{\partial \tilde{P}}{\partial \tilde{\mu}} \right)_T^{-1} \left\{ \tilde{P} - \tilde{T} \left(\frac{\partial \tilde{P}}{\partial \tilde{T}} \right)_\mu \right\}, \quad (23)$$

and

$$\begin{aligned} S_{P,T} - S_u = & \frac{CMP_c}{T_c \rho_c} \left(\frac{\partial \tilde{P}}{\partial \tilde{\mu}} \right)_T^{-1} \\ & \times \left\{ \tilde{P} - \tilde{T} \left(\frac{\partial \tilde{P}}{\partial \tilde{T}} \right)_\mu - \left(\frac{\partial \tilde{P}}{\partial \tilde{\mu}} \right)_T \right\}. \quad (24) \end{aligned}$$

The associated standard molal isobaric heat capacity of H_2O ($C_{P,P,T}^\circ$) can be obtained from

$$\begin{aligned} C_{P,P,T}^\circ = & C_{V,P,T}^\circ + \frac{CMP_c}{T_c \rho_c} \left(\frac{\partial \tilde{P}}{\partial \tilde{\mu}} \right)_T^{-1} \\ & \times \left\{ \left(\frac{\partial^2 \tilde{P}}{\partial \tilde{\mu}^2} \right)_T \left(\frac{\partial \tilde{P}}{\partial \tilde{\mu}} \right)_T^{-2} \left[\tilde{P} - \tilde{T} \left(\frac{\partial \tilde{P}}{\partial \tilde{T}} \right)_\mu \right]^2 \right\}, \quad (25) \end{aligned}$$

where the corresponding standard molal isochoric heat capacity ($C_{V,P,T}^\circ$) can be expressed as

$$\begin{aligned} C_{V,P,T}^\circ = & \frac{CMP_c}{T_c \rho_c} \tilde{T}^2 \left(\frac{\partial \tilde{P}}{\partial \tilde{\mu}} \right)_T^{-1} \\ & \left\{ \left(\frac{\partial^2 \tilde{P}}{\partial \tilde{T}^2} \right)_\mu - \left(\frac{\partial^2 \tilde{P}}{\partial \tilde{\mu}^2} \right)_T \left(\frac{\partial^2 \tilde{P}}{\partial \tilde{T} \partial \tilde{\mu}} \right)_{\mu, T} \right\}. \quad (26) \end{aligned}$$

Outside the critical region, values for $\Delta G_{P,T}^\circ$, $\Delta H_{P,T}^\circ$, and $S_{P,T}^\circ$ of H_2O consistent with the Helmholtz function developed by Haar, Gallagher, and Kell (1984) can be calculated using Equations (5)–(7), together with (Johnson and Norton, 1991)

$$G_{P,T} - G_u = A + \rho \left(\frac{\partial A}{\partial \rho} \right)_T, \quad (27)$$

$$H_{P,T} - H_u = A - T \left(\frac{\partial A}{\partial T} \right)_\rho + \rho \left(\frac{\partial A}{\partial \rho} \right)_T, \quad (28)$$

and

$$S_{p,T} - S_r = - \left(\frac{\partial A}{\partial T} \right)_p. \quad (29)$$

The associated standard molal isobaric heat capacity of H₂O can be obtained from

$$C_{p,T}^\circ = C_{v,T}^\circ + T\rho^2 \left(\frac{\partial^2 A}{\partial \rho \partial T} \right)_{T,\rho}^2 \times \left\{ 2\rho \left(\frac{\partial A}{\partial \rho} \right)_T + \rho^2 \left(\frac{\partial^2 A}{\partial \rho^2} \right)_T \right\}^{-1}, \quad (30)$$

where

$$C_{v,T}^\circ = -T \left(\frac{\partial^2 A}{\partial T^2} \right)_p. \quad (31)$$

Electrostatic properties. Calculation of the standard molal thermodynamic properties of aqueous solute species using electrostatic models of ion solvation (e.g. Helgeson and Kirkham, 1974b, 1976; Helgeson, Kirkham, and Flowers, 1981; Tanger and Helgeson, 1988; Shock and others, 1992) requires values for the negative reciprocal of the dielectric constant of H₂O ($-1/\epsilon$) and its partial derivatives, which are defined by the following Born functions (Helgeson and Kirkham, 1974a; Helgeson, Kirkham, and Flowers, 1981):

$$Z \equiv -\frac{1}{\epsilon}, \quad (32)$$

$$Q \equiv \left(\frac{\partial Z}{\partial P} \right)_T = \frac{1}{\epsilon^2} \left(\frac{\partial \epsilon}{\partial P} \right)_T, \quad (33)$$

$$Y \equiv \left(\frac{\partial Z}{\partial T} \right)_P = \frac{1}{\epsilon^2} \left(\frac{\partial \epsilon}{\partial T} \right)_P, \quad (34)$$

and

$$X \equiv \left(\frac{\partial Y}{\partial T} \right)_P = \left(\frac{\partial^2 Z}{\partial T^2} \right)_P = \frac{1}{\epsilon^2} \left(\frac{\partial^2 \epsilon}{\partial T^2} \right)_P - 2\epsilon Y^2. \quad (35)$$

Values of the dielectric constant and its partial derivatives in Equations (32)–(35) can be obtained from (Uematsu and Franck, 1980; Johnson and Norton, 1991)

$$\epsilon = \sum_{i=0}^4 k_i(\hat{T}) \hat{\rho}^i, \quad (36)$$

$$\left(\frac{\partial \epsilon}{\partial P} \right)_T = \beta \sum_{i=0}^4 i k_i(\hat{T}) \hat{\rho}^i, \quad (37)$$

$$\left(\frac{\partial \epsilon}{\partial T} \right)_P = \sum_{i=0}^4 \hat{\rho}^i \left\{ \left(\frac{\partial k_i(\hat{T})}{\partial T} \right)_P - i \alpha k_i(\hat{T}) \right\}, \quad (38)$$

and

$$\left(\frac{\partial^2 \epsilon}{\partial T^2} \right)_P = \sum_{i=0}^4 \hat{\rho}^i \left\{ \left(\frac{\partial^2 k_i(\hat{T})}{\partial T^2} \right)_P - i \left[\alpha \left(\frac{\partial k_i(\hat{T})}{\partial T} \right)_P + k_i(\hat{T}) \left(\frac{\partial \alpha}{\partial T} \right)_P \right] - i \alpha \left[\left(\frac{\partial k_i(\hat{T})}{\partial T} \right)_P - i \alpha k_i(\hat{T}) \right] \right\}, \quad (39)$$

Table 1. Dimensionless adjustable regression coefficients, $a_{\epsilon,i}$, used in Equations (40)–(44); modified from Johnson and Norton (1991, table 19)

i	$a_{\epsilon,i}$
1	0.1470333593(10 ²)
2	0.2128462733(10 ³)
3	-0.1154445173(10 ³)
4	0.1955210915(10 ²)
5	-0.8330347980(10 ²)
6	0.3213240048(10 ²)
7	-0.6694098645(10 ¹)
8	-0.3786202045(10 ²)
9	0.6887359646(10 ²)
10	-0.2729401652(10 ²)

where the dimensionless variables are defined by $\hat{T} \equiv T/T_r$ and $\hat{\rho} \equiv \rho/(1 \text{ g/cm}^3)$, and the $k_i(\hat{T})$ are given by

$$k_0(\hat{T}) = 1, \quad (40)$$

$$k_1(\hat{T}) = a_{\epsilon,1} \hat{T}^{-1}, \quad (41)$$

$$k_2(\hat{T}) = a_{\epsilon,2} \hat{T}^{-1} + a_{\epsilon,3} + a_{\epsilon,4} \hat{T}, \quad (42)$$

$$k_3(\hat{T}) = a_{\epsilon,5} \hat{T}^{-1} + a_{\epsilon,6} \hat{T} + a_{\epsilon,7} \hat{T}^2, \quad (43)$$

and

$$k_4(\hat{T}) = a_{\epsilon,8} \hat{T}^{-2} + a_{\epsilon,9} \hat{T}^{-1} + a_{\epsilon,10}, \quad (44)$$

where the $a_{\epsilon,1 \dots 10}$ stand for the dimensionless adjustable regression coefficients given in Table 1.

Thermodynamic properties of aqueous species other than H₂O

The apparent standard molal and standard molal thermodynamic properties of aqueous species other than H₂O are calculated in SUPCRT92 using the revised HKF equation of state (Tanger and Helgeson, 1988; Shock and others, 1992). The T – P – ρ region over which these calculations can be carried out for neutral species corresponds to that where Equations (32)–(44) can be used to describe the Born functions of H₂O (Fig. 2). For charged species, this region is restricted further to the T – P – ρ range over which the solvent function g and its partial derivatives (Tanger and Helgeson, 1988; Shock and others, 1992) can be represented using the equations given next. As a result, calculation of the apparent standard molal Gibbs free energy of formation of charged species is limited to $\rho \geq 0.35 \text{ g/cm}^3$, and to $T \leq 350$ or $\geq 400^\circ\text{C}$ for $P < 500$ bar. Calculation of the apparent standard molal enthalpy of formation and the standard molal entropy, heat capacity, and volume of these species is limited to $\rho \geq 0.35 \text{ g/cm}^3$, and to $T \leq 350^\circ\text{C}$ for $P < 1000$ bar. These restricted T – P – ρ regions within which the apparent standard molal and standard molal properties of charged species can be calculated are shown in Figure 3.

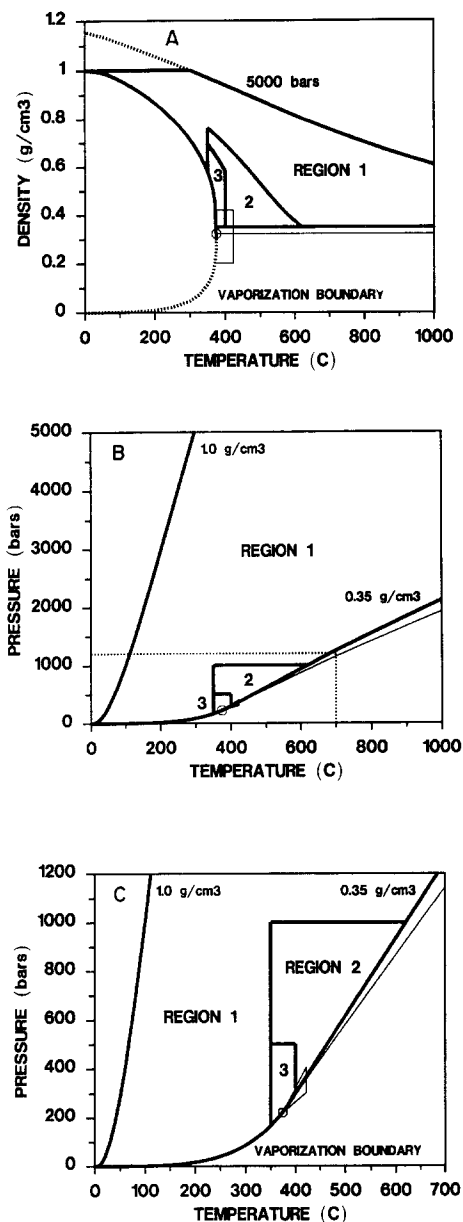


Figure 3. Range of conditions in T - ρ (A) and T - P (B-C) coordinates for which standard molal thermodynamic properties of charged aqueous species can be calculated using Equations (45)–(76) and coefficients given in Table 2. (Note that section of B which is delineated by dotted lines is expanded in C). All of these equations can be used without restriction within region 1, which is bound by 5000-bar isobar, 1000°C isotherm, 0.35 and 1.0 g/cm³ isochores, vaporization boundary, and analogous perimeter of region 2. However, owing to relatively large uncertainties in Equations (66)–(76), only apparent standard molal Gibbs free energy of charged aqueous species can be calculated within region 2, which is delineated by 1000-bar isobar, 350°C isotherm, 0.35 g/cm³ isochore, and vaporization boundary. Within region 3, which is localized by 350 and 400°C isotherms, 500-bar isobar, 0.35 g/cm³ isochore, and vaporization boundary, these uncertainties are sufficiently large to prohibit calculation of all standard molal thermodynamic properties of charged aqueous species. H₂O critical region and critical isochore are illustrated for reference in A–C.

Equation of state and the standard molal volume. The revised HKF equation of state for the j th aqueous solute species can be expressed as (Tanger and Helgeson, 1988)

$$V_{j,P,T}^{\circ} = \hat{C} \left[a_{1,j} + \frac{a_{2,j}}{\Psi + P} + \frac{a_{3,j}}{T - \Theta} + \frac{a_{4,j}}{(\Psi + P)(T - \Theta)} - \omega_j Q - (Z + 1) \left(\frac{\partial \omega_j}{\partial P} \right)_T \right], \quad (45)$$

where \hat{C} is a conversion factor (41.84 bar cm³ cal⁻¹), Ψ (2600 bar) and Θ (228 K) stand for constants characteristic of the solvent, Z and Q refer to the solvent Born functions defined by Equations (32) and (33), and the P/T -independent $a_{1,\dots,4,j}$ denote equation-of-state coefficients unique to the j th aqueous solute species. By analogy with Equations (1) and (2), the *conventional* Born coefficient of this species, ω_j , is defined by

$$\omega_j \equiv \omega_j^{\text{abs}} - Z_j \omega_{\text{H}^+}^{\text{abs}}, \quad (46)$$

and its *absolute* counterpart, ω_j^{abs} , is defined by

$$\omega_j^{\text{abs}} \equiv \frac{N^{\circ} e^2 Z_j^2}{2r_{e,j}} = \frac{\eta Z_j^2}{r_{e,j}}, \quad (47)$$

where N° stands for Avogadro's number [6.02252(10²³) mol⁻¹], e denotes the absolute electronic charge [4.80298(10⁻¹⁰) cm^{3/2} g^{1/2} s⁻¹], and η is a constant equal to 0.5 $N^{\circ} e^2$ [1.66027(10⁵) Å cal mol⁻¹]. The effective electrostatic radius of the j th aqueous solute species, $r_{e,j}$, can be expressed as

$$r_{e,j} = r_{e,j,P,T} + |Z_j|g \quad (48)$$

where g (in Å) designates a P/T -dependent solvent function (Tanger and Helgeson, 1988; Shock and others, 1992), which is given by (Shock and others, 1992)

$$g = a_g(1 - \hat{\rho})^{b_g} - f, \quad (49)$$

where

$$a_g = a_{g,1} + a_{g,2}T + a_{g,3}T^2, \quad (50)$$

$$b_g = b_{g,1} + b_{g,2}T + b_{g,3}T^2, \quad (51)$$

the $a_{g,1,\dots,3}$ and $b_{g,1,\dots,3}$ stand for the adjustable regression coefficients given in Table 2, and f (in Å) denotes a P/T -dependent difference function, which is given by

$$f = \left[\left(\frac{T - 155}{300} \right)^{4.8} + a_{f,1} \left(\frac{T - 155}{300} \right)^{16} \right] \times [a_{f,2}(1000 - P)^3 + a_{f,3}(1000 - P)^4], \quad (52)$$

where the $a_{f,1,\dots,3}$ stand for the adjustable regression coefficients given in Table 3. In practice, nonzero values of g calculated using Equation (49) are limited to $\rho < 1.0$ g/cm³, and nonzero values for f calculated using Equation (52) are restricted to temperatures between 155 and 355°C and pressures between the H₂O vaporization boundary and 1000 bar (Shock and others, 1992). Practical application of Equations

Table 2. Adjustable regression coefficients $a_{g,i}$ and $b_{g,i}$ used in Equations (49)–(51) and (66)–(73); modified from Shock and others (1992, table 3)

i	$a_{g,i}$	units	$b_{g,i}$	units
1	$-0.2037662(10^1)$	\AA	$0.6107361(10^1)$	—
2	$0.5747000(10^{-2})$	$\text{\AA}/^\circ\text{C}$	$-0.1074377(10^{-1})$	$^\circ\text{C}^{-1}$
3	$-0.6557892(10^{-5})$	$\text{\AA}/^\circ\text{C}^2$	$0.1268348(10^{-4})$	$^\circ\text{C}^{-2}$

(49)–(52) also is limited to $\rho \geq 0.35 \text{ g/cm}^3$; this restriction reflects the corresponding limit of experimentally-based supercritical dissociation constants for NaCl (Oelkers and Helgeson, 1988), from which Shock and others (1992) retrieved the values of g that they fit to Equations (49)–(52).

For monatomic ions whose crystallographic radius, $r_{x,j}$, is known, r_{e,j,P_r,T_r} in Equation (48) can be obtained from

$$r_{e,j,P_r,T_r} = r_{x,j} + |Z_j|k_{Z_\pm}, \quad (53)$$

where k_{Z_\pm} is a constant equal to 0 \AA for anions and 0.94 \AA for cations (Helgeson and Kirkham, 1976; Helgeson, Kirkham, and Flowers, 1991; Tanger and Helgeson, 1988). For both monatomic and polyatomic ionic species whose standard molal entropy at the reference pressure and temperature is known, values for r_{e,j,P_r,T_r} can be obtained from the empirical correlation equation given by Shock and Helgeson (1988):

$$r_{e,j,P_r,T_r} = \frac{Z_j^2(\eta Y_{P_r,T_r} - 100)}{S_{j,P_r,T_r}^\circ - 71.5|Z_j|}. \quad (54)$$

Combining Equations (46)–(48) and (53) for charged aqueous species together with $r_{x,H^+} = 2.142 \text{ \AA}$ (Helgeson and Kirkham, 1976) leads to

$$\omega_j = \eta \left\{ \frac{Z_j^2}{r_{e,j}} - \frac{Z_j}{3.082 + g} \right\}, \quad (55)$$

which at P_r and T_r , where $g = 0$ (Tanger and Helgeson, 1988; Shock and others, 1992), can be written as

$$r_{e,j,P_r,T_r} = Z_j^2 \left(\frac{\omega_{j,P_r,T_r}}{\eta} + \frac{Z_j}{3.082} \right)^{-1}. \quad (56)$$

In practice, r_{e,j,P_r,T_r} of the j th charged aqueous solute species is obtained from $r_{x,j}$ or S_{j,P_r,T_r}° data using Equation (53) or (54), and converted into the corresponding ω_{j,P_r,T_r} value (which is stored in the thermodynamic database) using Equation (56). During SUPCRT92 execution, Equation (56) again is used to retrieve r_{e,j,P_r,T_r} from the archived ω_{j,P_r,T_r} .

For the j th neutral aqueous solute species, $\omega_{j,P,T} = \omega_{j,P_r,T_r}$ (Shock, Helgeson, and Sverjensky, 1989; Shock and Helgeson, 1990; Shock and others, 1992), which is consistent with $r_{e,j,P,T} = r_{e,j,P_r,T_r}$. [Strictly speaking, Shock, Helgeson, and Sverjensky (1989), Shock and Helgeson (1990), and Shock and others (1992) refer to the P/T -independence of the

effective Born coefficient ($\omega_{e,j}$) of the j th neutral aqueous solute species, which is given by (Helgeson, Kirkham, and Flowers, 1981) $\omega_{e,j} = (\eta Z_{e,j})/r_{e,j}$, where $Z_{e,j}$ represents the effective charge of this species.] Because the formal charge of neutral solutes is zero, Equations (47), (48), and (53)–(56) cannot be used directly to determine r_{e,j,P_r,T_r} or ω_{j,P_r,T_r} for these species. Nevertheless, if S_{j,P_r,T_r}° for a given neutral solute is known, then ω_{j,P_r,T_r} can be estimated using the empirical correlation equations proposed by Shock, Helgeson, and Sverjensky (1989). For neutral aqueous solute species that correspond to noble or diatomic gases, the correlation is

$$\omega_{j,P_r,T_r} = -1514.4S_{j,P_r,T_r}^\circ; \quad (57)$$

for polyatomic and polar neutral species, the correlation is

$$\omega_{j,P_r,T_r} = -1514.4S_{j,P_r,T_r}^\circ + 0.34(10^5). \quad (58)$$

Equations (57) and (58) can be used together with Equation (45), the equality $\omega_{j,P,T} = \omega_{j,P_r,T_r}$, and the equations given next to calculate the standard molal thermodynamic properties of neutral aqueous solute species.

Other standard molal thermodynamic properties. The apparent standard molal Gibbs free energy and enthalpy of formation of the j th aqueous solute species and the corresponding standard molal entropy can be calculated as a function of temperature and pressure from Equations (1) and (2), together with (Tanger and Helgeson, 1988)

$$\begin{aligned} G_{j,P,T}^\circ - G_{j,P_r,T_r}^\circ = & -S_{j,P_r,T_r}^\circ(T - T_r) \\ & - c_{1,j} \left[T \ln \left(\frac{T}{T_r} \right) - T - T_r \right] \\ & + a_{1,j}(P - P_r) + a_{2,j} \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \\ & - c_{2,j} \left\{ \left[\left(\frac{1}{T - \Theta} \right) - \left(\frac{1}{T_r - \Theta} \right) \right] \right. \\ & \times \left[\frac{\Theta - T}{\Theta} \right] - \frac{T}{\Theta^2} \ln \left[\frac{T_r(T - \Theta)}{T(T_r - \Theta)} \right] \left. \right\} \\ & + \left(\frac{1}{T - \Theta} \right) \left[a_{3,j}(P - P_r) + a_{4,j} \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right] \\ & - \omega_j(Z + 1) + \omega_{j,P_r,T_r}(Z_{P_r,T_r} + 1) \\ & + \omega_{j,P_r,T_r} Y_{P_r,T_r}(T - T_r), \end{aligned} \quad (59)$$

$$\begin{aligned}
 H_{j,P,T}^\circ - H_{j,P_r,T_r}^\circ &= -c_{1,j}(T - T_r) - c_{2,j} \\
 &\times \left[\left(\frac{1}{T - \Theta} \right) - \left(\frac{1}{T_r - \Theta} \right) \right] \\
 &+ a_{1,j}(P - P_r) + a_{2,j} \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \\
 &+ \left[\frac{2T - \Theta}{(T - \Theta)^2} \right] \left[a_{3,j}(P - P_r) + a_{4,j} \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right] \\
 &- \omega_j(Z + 1) + \omega_j TY + T(Z + 1) \left(\frac{\partial \omega_j}{\partial T} \right)_P \\
 &+ \omega_{j,P_r,T_r}(Z_{P_r,T_r} + 1) - \omega_{j,P_r,T_r} T_r Y_{P_r,T_r}, \quad (60)
 \end{aligned}$$

and

$$\begin{aligned}
 S_{j,P,T}^\circ &= S_{j,P_r,T_r}^\circ + c_{1,j} \ln \left(\frac{T}{T_r} \right) - \frac{c_{2,j}}{\Theta} \\
 &\times \left\{ \left[\frac{1}{T - \Theta} \right] - \left[\frac{1}{T_r - \Theta} \right] \right. \\
 &\left. + \frac{1}{\Theta} \ln \left[\frac{T_r(T - \Theta)}{T(T_r - \Theta)} \right] \right\} \\
 &+ \left(\frac{1}{T - \Theta} \right)^2 \left[a_{3,j}(P - P_r) \right. \\
 &\left. + a_{4,j} \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right] + \omega_j Y + (Z + 1) \\
 &\times \left(\frac{\partial \omega_j}{\partial T} \right)_P - \omega_{j,P_r,T_r} Y_{P_r,T_r}. \quad (61)
 \end{aligned}$$

The standard molal isobaric heat capacity of the *j*th aqueous solute species can be obtained from

$$\begin{aligned}
 C_{P_j,P,T} &= c_{1,j} + \frac{c_{2,j}}{(T - \Theta)^2} - \left[\frac{2T}{(T - \Theta)^3} \right] \\
 &\times \left[a_{3,j}(P - P_r) + a_{4,j} \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right] \\
 &+ \omega_j TX + 2TY \left(\frac{\partial \omega_j}{\partial T} \right)_P \\
 &+ T(Z + 1) \left(\frac{\partial^2 \omega_j}{\partial T^2} \right)_P, \quad (62)
 \end{aligned}$$

where *Y* and *X* denote the solvent Born functions defined by Equations (34) and (35), the $c_{1, \dots, 2,j}$ stand for *P/T*-independent adjustable regression parameters unique to the *j*th aqueous solute species, and the requisite partial derivatives of the conventional Born coefficient of this species consistent with Equation (55) are given by

$$\left(\frac{\partial \omega_j}{\partial P} \right)_T = -\eta \left\{ \frac{|Z_j|^3}{r_{e,j}^2} - \frac{Z_j}{(3.082 + g)^2} \right\} \left(\frac{\partial g}{\partial P} \right)_T, \quad (63)$$

Table 3. Adjustable regression coefficients $a_{f,i}$ used in Equations (52) and (74)–(76); modified from Shock and others (1992, table 4)

<i>i</i>	$a_{f,i}$	units
1	0.3666666(10 ²)	°C ⁻¹⁶
2	-0.1504956(10 ⁻⁹)	Å/bar ³
3	0.5017997(10 ⁻¹³)	Å/bar ⁴

$$\left(\frac{\partial \omega_j}{\partial T} \right)_P = -\eta \left\{ \frac{|Z_j|^3}{r_{e,j}^2} - \frac{Z_j}{(3.082 + g)^2} \right\} \left(\frac{\partial g}{\partial T} \right)_P, \quad (64)$$

and

$$\begin{aligned}
 \left(\frac{\partial^2 \omega_j}{\partial T^2} \right)_P &= 2\eta \left\{ \frac{Z_j^4}{r_{e,j}^3} - \frac{Z_j}{(3.082 + g)^3} \right\} \left(\frac{\partial g}{\partial T} \right)_P^2 \\
 &- \eta \left\{ \frac{|Z_j|^3}{r_{e,j}^2} - \frac{Z_j}{(3.082 + g)^2} \right\} \left(\frac{\partial^2 g}{\partial T^2} \right)_P, \quad (65)
 \end{aligned}$$

where the corresponding partial derivatives of the solvent function *g* consistent with Equations (49) are given by (Shock and others, 1992)

$$\left(\frac{\partial g}{\partial P} \right)_T = -b_g \rho \beta g (1 - \rho)^{-1} - \left(\frac{\partial f}{\partial P} \right)_T, \quad (66)$$

$$\begin{aligned}
 \left(\frac{\partial g}{\partial T} \right)_P &= \frac{g}{a_g} \left(\frac{\partial a_g}{\partial T} \right)_P \\
 &+ a_g \left(\frac{\partial (g/a_g)}{\partial T} \right)_P - \left(\frac{\partial f}{\partial T} \right)_P, \quad (67)
 \end{aligned}$$

and

$$\begin{aligned}
 \left(\frac{\partial^2 g}{\partial T^2} \right)_P &= \frac{g}{a_g} \left(\frac{\partial^2 a_g}{\partial T^2} \right)_P + 2 \left(\frac{\partial a_g}{\partial T} \right)_P \left(\frac{\partial (g/a_g)}{\partial T} \right)_P \\
 &+ a_g \left\{ b_g \rho \alpha \left(\frac{\partial (g/a_g)}{\partial T} \right)_P + (1 - \rho)^{b_g - 1} \right. \\
 &\times \left[\rho \alpha \left(\frac{\partial b_g}{\partial T} \right)_P - b_g \rho \alpha^2 + b_g \rho \left(\frac{\partial \alpha}{\partial T} \right)_P \right] \\
 &+ \ln(1 - \rho) \frac{g}{a_g} \left(\frac{\partial^2 b_g}{\partial T^2} \right)_P + \left(\frac{\partial b_g}{\partial T} \right)_P \\
 &\times \left[\ln(1 - \rho) \left(\frac{\partial (g/a_g)}{\partial T} \right)_P \right] \\
 &\left. + \rho \alpha (1 - \rho)^{b_g - 1} \right\} - \left(\frac{\partial^2 f}{\partial T^2} \right)_P, \quad (68)
 \end{aligned}$$

where

$$\begin{aligned}
 \left(\frac{\partial (g/a_g)}{\partial T} \right)_P &= b_g \rho \alpha (1 - \rho)^{b_g - 1} \\
 &+ \ln(1 - \rho) \frac{g}{a_g} \left(\frac{\partial b_g}{\partial T} \right)_P, \quad (69)
 \end{aligned}$$

$$\left(\frac{\partial a_g}{\partial T} \right)_P = a_{g,2} + 2a_{g,3} T, \quad (70)$$

$$\left(\frac{\partial b_g}{\partial T} \right)_P = b_{g,2} + 2b_{g,3} T, \quad (71)$$

$$\left(\frac{\partial^2 a_g}{\partial T^2} \right)_P = 2a_{g,3}, \quad (72)$$

$$\left(\frac{\partial^2 b_g}{\partial T^2} \right)_P = 2b_{g,3}, \quad (73)$$

$$\begin{aligned}
 \left(\frac{\partial f}{\partial P} \right)_T &= - \left[\left(\frac{T - 155}{300} \right)^{4.8} + a_{r,1} \left(\frac{T - 155}{300} \right)^{16} \right] \\
 &\times [3a_{r,2}(1000 - P)^2 + 4a_{r,3}(1000 - P)^3], \quad (74)
 \end{aligned}$$

$$\left(\frac{\partial f}{\partial T}\right)_p = \left[0.016 \left(\frac{T-155}{300}\right)^{3.8} + \frac{16a_{f,1}}{300} \left(\frac{T-155}{300}\right)^{15} \right] \times [a_{f,2}(1000-P)^3 + a_{f,3}(1000-P)^4], \quad (75)$$

and

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_p = \left[\frac{0.0608}{300} \left(\frac{T-155}{300}\right)^{2.8} + \frac{a_{f,1}}{375} \left(\frac{T-155}{300}\right)^{14} \right] \times [a_{f,2}(1000-P)^3 + a_{f,3}(1000-P)^4]. \quad (76)$$

Inventory of aqueous solute species and their associated data in the thermodynamic database. Calculation of the apparent standard molal Gibbs free energy and enthalpy of formation and the standard molal entropy, heat capacity, and volume of the *j*th aqueous

solute species using Equations (1), (2), and (45)–(76) requires values for $\Delta G_{f,j}^\circ$, $\Delta H_{f,j}^\circ$, $S_{j,P,T}^\circ$, $a_{1\dots 4,j}$, $c_{1\dots 2,j}$, $\omega_{j,P,T}$, and Z_j . These data are available currently for the 294 aqueous species other than H₂O listed alphabetically in Tables 4 and 5. The compilation includes a large number of the aqueous ions and electrolytes (Tanger and Helgeson, 1988; Shock and Helgeson, 1988), inorganic neutral species (Shock, Helgeson, and Sverjensky, 1989), organic species (Shock and Helgeson, 1990), and inorganic and organic metal complexes (Sverjensky, Shock, and Helgeson, 1992) that occur within natural aqueous solutions in a wide variety of geologic settings.

Table 4. Alphabetized listing of 294 aqueous species (excluding H₂O) that are contained in SPURNS92.DAT thermodynamic database. Chemical formulae for 86 aqueous organic species are provided in Table 5

SPECIES	SPECIES	SPECIES	SPECIES
1-BUTANAMINE,AQ	B(OH)3,aq	ETHYNE,AQ	Hg+2
1-BUTANOL,AQ	BENZENE,AQ	Er+3	Hg2+2
1-BUTENE,AQ	BF4-	Eu+2	Ho+3
1-BUTYNE,AQ	BO2-	Eu+3	I-
1-HEPTANAMINE,AQ	BUTANOATE,AQ	F-	I3-
1-HEPTANOL,AQ	BUTANOIC-ACID,AQ	FORMATE,AQ	IO-
1-HEPTENE,AQ	Ba(CO3),aq	FORMIC-ACID,AQ	IO3-
1-HEPTYNE,AQ	Ba+2	Fe(CH3COO)+	IO4-
1-HEXANAMINE,AQ	BaCl+	Fe(CH3COO)2,aq	ISOLEUCINE,AQ
1-HEXANOL,AQ	BaF+	Fe+2	In+3
1-HEXENE,AQ	Be+2	Fe+3	K+
1-HEXYNE,AQ	BeO2-2	FeCl+	KBr,aq
1-OCTANAMINE,AQ	Br-	FeCl2,aq	KCl,aq
1-OCTANOL,AQ	Br3-	GLUTAMIC-ACID,AQ	KHSO4,aq
1-OCTENE,AQ	BrO-	GLUTAMINE,AQ	KI,aq
1-OCTYNE,AQ	BrO3-	GLYCINE,AQ	KSO4-
1-PENTANAMINE,AQ	BrO4-	Ga+3	Kr,aq
1-PENTANOL,AQ	CN-	Gd+3	LEUCINE,AQ
1-PENTENE,AQ	CO2,aq	H+	La+3
1-PENTYNE,AQ	CO3-2	H2,aq	Li+
1-PROPANAMINE,AQ	Ca(CO3),aq	H2AsO3-	LiCl,aq
1-PROPANOL,AQ	Ca(HCO3)+	H2AsO4-	Lu+3
1-PROPENE,AQ	Ca+2	H2P2O7-2	METHANAMINE,AQ
1-PROPYNE,AQ	CaCl+	H2PO4-	METHANE,AQ
2-BUTANONE,AQ	CaCl2,aq	H2S,aq	METHANOL,AQ
2-HEPTANONE,AQ	CaF+	H2VO4-	METHIONINE,AQ
2-HEXANONE,AQ	CaSO4,aq	H3P2O7-	Mg(CO3),aq
2-OCTANONE,AQ	Cd+2	H3PO4,aq	Mg(HCO3)+
2-PENTANONE,AQ	Ce+3	HA#O4-2	Mg+2
A-AMINOBUTYRIC,AQ	Cl-	HCO3-	MgCl+
ACETATE,AQ	ClO-	HCrO4-	MgF+
ACETIC-ACID,AQ	ClO2-	HEPTANOATE,AQ	Mn+2
ACETONE,AQ	ClO3-	HEPTANOIC-ACID,AQ	MnCl+
ALANINE,AQ	ClO4-	HEXANOATE,AQ	MnO4-
ASPARAGINE,AQ	Co+2	HEXANOIC-ACID,AQ	MnO4-2
ASPARTIC-ACID,AQ	Co+3	HF,aq	MnSO4,aq
Ag(CO3)-	Cr2O7-2	HF2-	MoO4-2
Ag(CO3)2-3	CrO4-2	HNO3,aq	N-BUTANE,AQ
Ag+	Cs+	HO2-	N-BUTYLBENZENE,AQ
Ag+2	CsBr,aq	HPO4-2	N-HEPTANE,AQ
AgCl,aq	CsCl,aq	HS-	N-HEPTYLBENZENE,AQ
AgCl2-	CsI,aq	HSO3-	N-HEXANE,AQ
AgCl3-2	Cu+	HSO4-	N-HEXYLBENZENE,AQ
AgCl4-3	Cu+2	HSO5-	N-OCTANE,AQ
AgNO3,aq	Dy+3	HSe-	N-OCTYLBENZENE,AQ
Al(OH)+2	ETHANAMINE,AQ	HSeO3-	N-PENTANE,AQ
Al+3	ETHANE,AQ	HSeO4-	N-PENTYLBENZENE,AQ
Ar,aq	ETHANOL,AQ	HSiO3-	N-PROPYLBENZENE,AQ
Au+	ETHYLENE,AQ	HVO4-2	N2,aq
Au+3	ETHYLENE,AQ	He,aq	NH3,aq

continued opposite

Table 4—continued

SPECIES	SPECIES	SPECIES	SPECIES
NH4+	Pb(CH3COO)+	S4-2	Tl+
NO2-	Pb(CH3COO)2,aq	S4O6-2	Tl+3
NO3-	Pb+2	S5-2	Tm+3
Na+	PbCl+	S5O6-2	VALINE,AQ
NaBr,aq	PbCl2,aq	SERINE,AQ	VO+2
NaCl,aq	PbCl3-	SO2,aq	VO2+
NaF,aq	PbCl4-2	SO3-2	WO4-2
NaHSiO3,aq	Pd+2	SO4-2	Xe,aq
NaI,aq	Pr+3	Sc+3	Y+3
Nd+3	Ra+2	SeO3-2	Yb+2
Ne,aq	Rb+	SeO4-2	Yb+3
Ni+2	RbBr,aq	SiF6-2	Zn(CH3COO)+
NiCl+	RbCl,aq	SiO2,aq	Zn(CH3COO)2,aq
O2,aq	RbF,aq	Sm+2	Zn(CH3COO)3-
OCTANOATE,AQ	RbI,aq	Sm+3	Zn+2
OCTANOIC-ACID,AQ	ReO4-	Sn+2	ZnCl+
OH-	Rn,aq	Sr(CO3),aq	ZnCl2,aq
PENTANOATE,AQ	S2-2	Sr+2	ZnCl3-
PENTANOIC-ACID,AQ	S2O3-2	SrCl+	ZnCl4-2
PHENOL,AQ	S2O4-2	SrF+	
PHENYLALANINE,AQ	S2O5-2	THREONINE,AQ	
PO4-3	S2O6-2	TOLUENE,AQ	
PROPANE,AQ	S2O8-2	TRYPTOPHAN,AQ	
PROPANOATE,AQ	S3-2	TYROSINE,AQ	
PROPANOIC-ACID,AQ	S3O6-2	Tb+3	

Thermodynamic properties of minerals and gases

The apparent standard molal and standard molal properties of minerals and gases are calculated in SUPCRT92 using equations and data given by Helgeson and others (1978). These equations and data can be used for pressures from 1 to 10,000 bar and temperatures from 25°C to a maximum corresponding to that of the Maier-Kelly (1932) heat capacity coefficients for the specified mineral or gas. Predictive extrapolation of property values to conditions beyond these limits is governed by *caveat emptor*.

Equation of state and the standard molal volume. The equation of state for minerals can be expressed as

$$V_{P,T}^{\circ} = V_{P_r,T_r}^{\circ} + \sum_{i=1}^{\phi_{PT}} \Delta V_{i_t}^{\circ}, \quad (77)$$

where V° designates the standard molal volume of the specified mineral at the subscripted pressure and temperature, and $\Delta V_{i_t}^{\circ}$ represents the change in standard molal volume associated with the i th of the ϕ_{PT} solid/solid phase transitions (t) that occur along the straightline P - T path from P_r, T_r to P, T . Within the present computational framework, the only first-order phase transitions that can be considered are those for which the Clapeyron slope, $(\partial P/\partial T)_t$, is positive. Provision for lambda transitions also has been incorporated, which accounts for the thermodynamic effects of substitutional order/disorder in albite, dolomite, K-feldspar, and epidote (Helgeson and others, 1978).

Although Equation (77) is consistent with $(\partial V^{\circ}/\partial T)_P = (\partial V^{\circ}/\partial P)_T = 0$, these approximations do not cause serious departures from reality with regard to predicting stability relations of most minerals

through the range of P - T conditions which occur in the Earth's crust (Helgeson and others, 1978). Notable exceptions are quartz and coesite; for these species, the thermodynamic consequences of $(\partial V^{\circ}/\partial T)_P \neq 0$ are accounted for explicitly in SUPCRT92 by appropriate incorporation of Equations (109), (111), (114), and (115) from Helgeson and others (1978). Equation (77) also can be used for gases ($\phi_{PT} = 0$), where the adopted standard state convention is consistent with $V_{P,T}^{\circ} = V_{P_r,T_r}^{\circ} = 0$.

Other standard molal thermodynamic properties. The apparent standard molal Gibbs free energy and enthalpy of formation of a mineral or gas and the corresponding standard molal entropy can be calculated as a function of pressure and temperature from Equations (1), (2), and (77), together with (Helgeson and others, 1978)

$$\begin{aligned} G_{P,T}^{\circ} - G_{P_r,T_r}^{\circ} = & -S_{P_r,T_r}^{\circ}(T - T_r) \\ & + \sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_{i+1}} C_{P_r,i}^{\circ} dT \\ & - T \sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_{i+1}} C_{P_r,i}^{\circ} d \ln T \\ & + \int_{P_r}^P V_{P_r,T}^{\circ} dP - \sum_{i=1}^{\phi_P} \int_{P_{i,T}}^P \Delta V_{i_t}^{\circ} dP \\ & - \sum_{i=1}^{\phi_T} \frac{\Delta H_{i_t}^{\circ}}{T_i} (T - T_i), \end{aligned} \quad (78)$$

$$\begin{aligned} H_{P,T}^{\circ} - H_{P_r,T_r}^{\circ} = & \sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_{i+1}} C_{P_r,i}^{\circ} dT \\ & + \int_{P_r}^P V_{P_r,T}^{\circ} dP - \sum_{i=1}^{\phi_P} \int_{P_{i,T}}^P \Delta V_{i_t}^{\circ} dP + \sum_{i=1}^{\phi_T} \Delta H_{i_t}^{\circ}, \end{aligned} \quad (79)$$

and

$$S_{P_r, T}^\circ - S_{P_r, T_r}^\circ = \sum_{i=1}^{1+\phi_T} \int_{T_i}^{T_{i+1}} C_{P_r, i}^\circ d \ln T + \sum_{i=1}^{\phi_T} \frac{\Delta H_{T_i}^\circ}{T_i}, \quad (80)$$

where ϕ_T ($=0$ for gases) stands for the number of phase transitions from P_r, T_r to P_r, T ; $T_1 = T_r$; $T_{i>1} = \min(T_i, T_{i-1}, P_r)$; ϕ_P ($=0$ for gases) denotes the number of phase transitions from P_r, T to P, T ; $P_{i, T}$ represents the pressure of the i th phase transition at T , where $P_r < P_{i, T} < P$; $\Delta H_{T_i}^\circ$ designates the change in standard molal enthalpy associated with the i th phase transition; and $C_{P_r, i}^\circ$ can be obtained from the Maier-Kelly (1932) power function

$$C_{P_r, i}^\circ = a_i + b_i T + c_i T^{-2}, \quad (81)$$

where a_i , b_i , and c_i correspond to adjustable regression coefficients that are unique to the specified

mineral or gas from T_i to T_{i+1} . Note that in Equations (78)–(80), nonzero values for the terms summed for ϕ_T and ϕ_P are restricted to minerals that have undergone a phase transition from P_r, T_r to P_r, T and P_r, T to P, T , respectively.

Substitution of Equation (81) into Equations (78)–(80) leads to (Helgeson and others, 1978)

$$G_{P_r, T}^\circ - G_{P_r, T_r}^\circ = -S_{P_r, T_r}^\circ (T - T_r) + \sum_{i=1}^{1+\phi_T} a_i [T_{i+1} - T_i - T_{i+1} \ln(T_{i+1}/T_i)] + \sum_{i=1}^{1+\phi_T} \left\{ \frac{(-c_i - b_i T_{i+1} T_i^2)(T_{i+1} - T_i)^2}{2T_{i+1} T_i^2} \right\} + V_{P_r, T}^\circ (P - P_r) - \sum_{i=1}^{\phi_P} \int_{P_{i, T}}^P \Delta V_{T_i}^\circ dP - \sum_{i=1}^{\phi_T} \frac{\Delta H_{T_i}^\circ}{T_i} (T - T_i), \quad (82)$$

Table 5. Alphabetized listing of 86 aqueous organic species that are contained in SPURNS92.DAT thermodynamic database together with their chemical formulae

SPECIES	FORMULA	SPECIES	FORMULA
1-BUTANAMINE,AQ	C4H9NH2	ETHYLENE,AQ	C2H4
1-BUTANOL,AQ	C4H9OH	ETHYNE,AQ	C2H2
1-BUTENE,AQ	C4H8	FORMATE,AQ	HCOO-
1-BUTYNE,AQ	C4H6	FORMIC-ACID,AQ	HCOOH
1-HEPTANAMINE,AQ	C7H15NH2	GLUTAMIC-ACID,AQ	C5H9NO4
1-HEPTANOL,AQ	C7H15OH	GLUTAMINE,AQ	C5H10N2O3
1-HEPTENE,AQ	C7H14	GLYCINE,AQ	C2H5NO2
1-HEPTYNE,AQ	C7H12	HEPTANOATE,AQ	C6H13COO-
1-HEXANAMINE,AQ	C6H13NH2	HEPTANOIC-ACID,AQ	C6H13COOH
1-HEXANOL,AQ	C6H13OH	HEXANOATE,AQ	C5H11COO-
1-HEXENE,AQ	C6H12	HEXANOIC-ACID,AQ	C5H11COOH
1-HEXYNE,AQ	C6H10	ISOLEUCINE,AQ	C6H13NO2
1-OCTANAMINE,AQ	C8H17NH2	LEUCINE,AQ	C6H13NO2
1-OCTANOL,AQ	C8H17OH	METHANAMINE,AQ	CH3NH2
1-OCTENE,AQ	C8H16	METHANE,AQ	CH4
1-OCTYNE,AQ	C8H14	METHANOL,AQ	CH3OH
1-PENTANAMINE,AQ	C5H11NH2	METHIONINE,AQ	C5H11NO2S
1-PENTANOL,AQ	C5H11OH	N-BUTANE,AQ	C4H10
1-PENTENE,AQ	C5H10	N-BUTYL BENZENE,AQ	C6H5C4H9
1-PENTYNE,AQ	C5H8	N-HEPTANE,AQ	C7H16
1-PROPANAMINE,AQ	C3H7NH2	N-HEPTYL BENZENE,AQ	C6H5C7H15
1-PROPANOL,AQ	C3H7OH	N-HEXANE,AQ	C6H14
1-PROPENE,AQ	C3H6	N-HEXYL BENZENE,AQ	C6H5C6H13
1-PROPYNE,AQ	C3H4	N-OCTANE,AQ	C8H18
2-BUTANONE,AQ	C4H8O	N-OCTYL BENZENE,AQ	C6H5C8H17
2-HEPTANONE,AQ	C7H14O	N-PENTANE,AQ	C5H12
2-HEXANONE,AQ	C6H12O	N-PENTYL BENZENE,AQ	C6H5C5H11
2-OCTANONE,AQ	C8H16O	N-PROPYL BENZENE,AQ	C6H5C3H7
2-PENTANONE,AQ	C5H10O	OCTANOATE,AQ	C7H15COO-
A-AMINOBUTYRIC,AQ	C4H9NO2	OCTANOIC-ACID,AQ	C7H15COOH
ACETATE,AQ	CH3COO-	PENTANOATE,AQ	C4H9COO-
ACETIC-ACID,AQ	CH3COOH	PENTANOIC-ACID,AQ	C4H9COOH
ACETONE,AQ	C3H6O	PHENOL,AQ	C6H5OH
ALANINE,AQ	C3H7NO2	PHENYLALANINE,AQ	C9H11NO2
ASPARAGINE,AQ	C4H8N2O3	PROPANE,AQ	C3H8
ASPARTIC-ACID,AQ	C4H7NO4	PROPANOATE,AQ	C2H5COO-
BENZENE,AQ	C6H6	PROPANOIC-ACID,AQ	C2H5COOH
BUTANOATE,AQ	C3H7COO-	SERINE,AQ	C3H7NO3
BUTANOIC-ACID,AQ	C3H7COOH	THREONINE,AQ	C4H9NO3
ETHANAMINE,AQ	C2H5NH2	TOLUENE,AQ	C6H5CH3
ETHANE,AQ	C2H6	TRYPTOPHAN,AQ	C11H12N2O2
ETHANOL,AQ	C2H5OH	TYROSINE,AQ	C9H11NO3
ETHYLBENZENE,AQ	C6H5C2H5	VALINE,AQ	C5H11NO2

$$\begin{aligned}
 H_{P,T}^\circ - H_{P_r,T_r}^\circ &= \sum_{i=1}^{1+\phi_T} \left\{ a_i(T_{i+1} - T_i) \right. \\
 &+ \frac{b_i}{2}(T_{i+1}^2 - T_i^2) - c_i \left(\frac{1}{T_{i+1}} - \frac{1}{T_i} \right) \left. \right\} \\
 &+ V_{P_r,T_r}^\circ (P - P_r) - \sum_{i=1}^{\phi_P} \int_{P_{i,T}}^P \Delta V_{i,T}^\circ dP \\
 &+ \sum_{i=1}^{\phi_T} \Delta H_{i,T}^\circ,
 \end{aligned} \tag{83}$$

and

$$\begin{aligned}
 S_{P,T}^\circ - S_{P_r,T_r}^\circ &= \sum_{i=1}^{1+\phi_T} \left\{ a_i \ln(T_{i+1}/T_i) \right. \\
 &+ b_i(T_{i+1} - T_i) - \frac{c_i}{2} \left(\frac{1}{T_{i+1}^2} - \frac{1}{T_i^2} \right) \left. \right\} \\
 &+ \sum_{i=1}^{\phi_T} \frac{\Delta H_{i,T}^\circ}{T_i}.
 \end{aligned} \tag{84}$$

Although Equations (77)–(84) are general in the sense that values for ϕ_T and ϕ_P are unrestricted, minerals

in the SUPCRT92 database are characterized by $\phi_T \leq 3$ and $\phi_P \leq 2$.

Inventory of minerals and gases and their associated data in the thermodynamic database. Calculation of the apparent standard molal Gibbs free energy and enthalpy of formation and the standard molal entropy, heat capacity, and volume of a given mineral using Equations (1), (2), (77), and (81)–(84) requires values for ΔG_f° , ΔH_f° , S_{P_r,T_r}° , V_{P_r,T_r}° , $a_1 \dots 1 + \phi_N$, $b_1 \dots 1 + \phi_N$, $c_1 \dots 1 + \phi_N$, $\Delta H_{1 \dots \phi_N}^\circ$, $T_{1 \dots \phi_N, P_r}$, and $(\partial P / \partial T)_{1 \dots \phi_N}$ for the mineral, where ϕ_N designates the number of phase transitions. These values are available currently for the 179 minerals listed alphabetically in Table 6. The majority of these data were taken from Helgeson and others (1978), although certain parameters for some of the species were obtained elsewhere (Kelly, 1960; Pankratz, 1970; Pankratz and King, 1970; Robie, Hemingway, and Fisher, 1979; Wagman and others, 1982; Bowers and Helgeson, 1983; Jackson and Helgeson, 1985; Helgeson, 1985). The composite data set includes a

Table 6. Alphabetized listing of 179 minerals that are contained in SPRONS92.DAT thermodynamic database. Minerals for which ΔG_f° and ΔH_f° are unavailable in SPRONS92.DAT are given in boldface

SPECIES	FORMULA	SPECIES	FORMULA
ACANTHITE ^a	Ag ₂ S	CHRYSOTILE	Mg ₃ Si ₂ O ₅ (OH) ₄
AEGERINE ^b	NaFe ₃ (SiO ₃) ₂	CINNABAR	HgS
AKERMANITE	Ca ₂ MgSi ₂ O ₇	CLINOCHLORE,14A	Mg ₅ Al(AlSi ₃)O ₁₀ (OH) ₈
ALABANDITE	MnS	CLINOCHLORE,7A ^a	Mg ₅ Al(AlSi ₃)O ₁₀ (OH) ₈
ALBITE ^a	Na(AlSi ₃)O ₈	CLINOZOISITE	Ca ₂ Al ₃ Si ₃ O ₁₂ (OH)
ALBITE,HIGH ^a	NaAlSi ₃ O ₈	COESITE ^a	SiO ₂
ALBITE,LOW	Na(AlSi ₃)O ₈	COPPER,NATIVE	Cu
ALMANDINE ^a	Fe ₃ Al ₂ Si ₃ O ₁₂	CORDIERITE	Mg ₂ Al ₃ (AlSi ₅)O ₁₈
ALUNITE	KAl ₃ (OH) ₆ (SO ₄) ₂	CORDIERITE,HYDROUS	Mg ₂ Al ₃ (AlSi ₅)O ₁₈ *H ₂ O
AMESITE,14A ^a	Mg ₄ Al ₂ (Al ₂ Si ₂)O ₁₀ (OH) ₈	CORUNDUM	Al ₂ O ₃
AMESITE,7A	Mg ₂ Al(AlSi) ₅ O ₅ (OH) ₄	COVELLITE	CuS
AMORPHOUS-SILICA	SiO ₂ *NH ₂ O	CRISTOBALITE ^a	SiO ₂
ANALCIME	NaAlSi ₂ O ₆ *H ₂ O	CRISTOBALITE,ALPHA	SiO ₂
ANALCIME,DEHYDRATED	NaAlSi ₂ O ₆	CRISTOBALITE,BETA	SiO ₂
ANDALUSITE	Al ₂ SiO ₅	CRONSTEDTITE,7A ^b	Fe ₂ Fe(FeSi) ₅ O ₅ (OH) ₄
ANDRADITE	Ca ₃ Fe ₂ Si ₃ O ₁₂	CUMMINGTONITE	Mg ₇ Si ₈ O ₂₂ (OH) ₂
ANGLESITE	PbSO ₄	CUPRITE	Cu ₂ O
ANHYDRITE	CaSO ₄	DAPHNITE,14A	Fe ₅ Al(AlSi ₃)O ₁₀ (OH) ₈
ANNITE	KFe ₃ (AlSi ₃)O ₁₀ (OH) ₂	DAPHNITE,7A ^a	Fe ₅ Al(AlSi ₃)O ₁₀ (OH) ₈
ANORTHITE	Ca(Al ₂ Si ₂)O ₈	DIASPORE	AlO(OH)
ANTHOPHYLLITE ^b	Mg ₇ Si ₈ O ₂₂ (OH) ₂	DICKITE	Al ₂ Si ₂ O ₅ (OH) ₄
ANTIGORITE ^a	Mg ₄ Si ₃ O ₈ Si ₄ O ₈ (OH) ₆	DIOPSIDE	CaMg(SiO ₃) ₂
ARAGONITE	CaCO ₃	DOLOMITE	CaMg(CO ₃) ₂
ARTINITE	Mg ₂ (OH) ₂ (CO ₃)*3H ₂ O	DOLOMITE,DISORDERED	CaMg(CO ₃) ₂
AZURITE	Cu ₃ (OH) ₂ (CO ₃) ₂	DOLOMITE,ORDERED	CaMg(CO ₃) ₂
BARITE	BaSO ₄	EDENITE ^a	Na(Ca ₂ Mg ₅)(AlSi ₇)O ₂₂ (OH) ₂
BERNDTITE	SnS ₂	ENSTATITE ^b	MgSiO ₃
BOEHMITE	AlO(OH)	EPIDOTE	Ca ₂ FeAl ₂ Si ₃ O ₁₂ (OH)
BORNITE ^b	Cu ₅ FeS ₄	EPIDOTE,ORDERED	Ca ₂ FeAl ₂ Si ₃ O ₁₂ (OH)
BROMELLITE	BeO	EPISTILBITE ^a	Ca(Al ₂ Si ₆)O ₁₆ *6H ₂ O
BRUCITE	Mg(OH) ₂	FAYALITE	Fe ₂ SiO ₄
BUNSENITE ^b	NiO	FERROEDENITE ^a	Na(Ca ₂ Fe ₅)(AlSi ₇)O ₂₂ (OH) ₂
CA-AL-PYROXENE	CaAl(AlSi) ₆	FERROGEDRITE ^b	(Fe ₅ Al ₂)(Al ₂ Si ₆)O ₂₂ (OH) ₂
CALCITE	CaCO ₃	FERROPARGASITE	Na(Ca ₂ Fe ₄ Al)(Al ₂ Si ₆)O ₂₂ (OH) ₂
CASSITERITE	SnO ₂	FERROSILITE ^a	FeSiO ₃
CELADONITE	K(MgAl)Si ₄ O ₁₀ (OH) ₂	FERROTREMOLITE	(Ca ₂ Fe ₅)Si ₈ O ₂₂ (OH) ₂
CELESTINE	SrSO ₄	FERROUS-OXIDE	FeO
CERUSSITE	PbCO ₃	FLUOREDENITE ^a	Na(Ca ₂ Mg ₅)(AlSi ₇)O ₂₂ (F) ₂
CHABAZITE	Ca(Al ₂ Si ₄)O ₁₂ *6H ₂ O	FLUORITE	CaF ₂
CHALCEDONY	SiO ₂	FLUORPHLOGOPITE	KMg ₃ (AlSi ₃)O ₁₀ (F) ₂
CHALCOCITE ^b	Cu ₂ S	FLUORTREMOLITE	(Ca ₂ Mg ₅)Si ₈ O ₂₂ (F) ₂
CHALCOPYRITE ^b	Cu ₅ FeS ₂	FORSTERITE	Mg ₂ SiO ₄
CHAMOSITE,7A	Fe ₂ Al(AlSi) ₅ O ₅ (OH) ₄	GALENA	PbS
CHLORARGYRITE	AgCl	GEHLENITE	Ca ₂ (Al ₂ Si) ₇ O ₇
CHLORITOID	FeAl ₂ SiO ₅ (OH) ₂	GIBBSITE	Al(OH) ₃

^aMineral that undergoes one phase transition.

^bMineral that undergoes two phase transitions.

Table 6—continued

SPECIES	FORMULA	SPECIES	FORMULA
GLAUCOPHANE	$\text{Na}_2(\text{Mg}_3\text{Al}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$	PD-OXYANNITE ^c	$\text{KFe}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})\text{O}$
GOLD,NATIVE	Au	PERICLASE	MgO
GRAPHITE	C	PHILLIPSITE,CA*	$\text{Ca}(\text{Al}_2\text{Si}_5)\text{O}_{14}\cdot 5\text{H}_2\text{O}$
GREENALITE	$\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$	PHILLIPSITE,K*	$\text{K}_2(\text{Al}_2\text{Si}_5)\text{O}_{14}\cdot 5\text{H}_2\text{O}$
GROSSULAR	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	PHILLIPSITE,NA*	$\text{Na}_2(\text{Al}_2\text{Si}_5)\text{O}_{14}\cdot 5\text{H}_2\text{O}$
GRUNERITE	$\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	PHLOGOPITE	$\text{KMg}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$
HALITE	NaCl	POTASSIUM-OXIDE	K ₂ O
HALLOYSITE	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	PREHNITE*	$\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$
HASTINGSITE ^b	$\text{Na}(\text{Ca}_2\text{Fe}_4\text{Fe})(\text{Al}_2\text{Si}_6)\text{O}_{22}(\text{OH})_2$	PYRITE	FeS ₂
HEDENBERGITE	$\text{CaFe}(\text{SiO}_3)_2$	PYROPE*	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
HEMATITE ^b	Fe ₂ O ₃	PYROPHYLLITE	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$
HERZENBERGITE ^a	SnS	PYRRHOTITE ^b	FeS
HEULANDITE ^c	$\text{Ca}(\text{Al}_2\text{Si}_7)\text{O}_{18}\cdot 6\text{H}_2\text{O}$	QUARTZ*	SiO ₂
HUNTITE	$\text{CaMg}_3(\text{CO}_3)_4$	QUICKSILVER*	Hg
HYDROMAGNESITE	$\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4\cdot 4\text{H}_2\text{O}$	RHODOCHROSITE	MnCO ₃
IRON ^c	Fe	RICHTERITE	$\text{Na}_2(\text{CaMg}_5)\text{Si}_8\text{O}_{22}(\text{OH})_2$
JADEITE	$\text{NaAl}(\text{SiO}_3)_2$	RIEBECKITE ^b	$\text{Na}_2(\text{Fe}_3\text{Fe}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$
K-FELDSPAR	$\text{K}(\text{AlSi}_3)\text{O}_8$	ROMARCHITE	SnO
KALSILITE*	$\text{K}(\text{AlSi})\text{O}_4$	RUTILE	TiO ₂
KAOLINITE	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	SANIDINE,HIGH	$\text{K}(\text{AlSi}_3)\text{O}_8$
KYANITE	Al_2SiO_5	SEPIOLITE	$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2(\text{H}_2\text{O})_2\cdot 4\text{H}_2\text{O}$
LARNITE ^b	Ca_2SiO_4	SIDERITE	FeCO ₃
LAUMONTITE	$\text{Ca}(\text{Al}_2\text{Si}_4)\text{O}_{12}\cdot 4\text{H}_2\text{O}$	SILLIMANITE	Al_2SiO_5
LAWSONITE*	$\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2\cdot 2\text{H}_2\text{O}$	SILVER,NATIVE	Ag
LEONHARDITE	$\text{Ca}_2(\text{Al}_4\text{Si}_8)\text{O}_{24}\cdot 7\text{H}_2\text{O}$	SMITHSONITE	ZnCO ₃
LIME	CaO	SODIUM-OXIDE	Na ₂ O
MAGNESIOHASTINGSITE ^b	$\text{Na}(\text{Ca}_2\text{Mg}_4\text{Fe})(\text{Al}_2\text{Si}_6)\text{O}_{22}(\text{OH})_2$	SPESSARTINE*	$\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
MAGNESIORIEBECKITE ^b	$\text{Na}_2(\text{Mg}_3\text{Fe}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$	SPHALERITE	ZnS
MAGNESITE	MgCO ₃	SPINEL	MgAl_2O_4
MAGNETITE*	Fe ₃ O ₄	STAUROLITE	$\text{Fe}_2\text{Al}_9\text{Si}_4\text{O}_{23}(\text{OH})$
MALACHITE	$\text{Cu}_2(\text{OH})_2(\text{CO}_3)$	STILBITE*	$\text{NaCa}_2(\text{Al}_5\text{Si}_13)\text{O}_{36}\cdot 14\text{H}_2\text{O}$
MANGANOSITE	MnO	STRONTIANITE	SrCO ₃
MARGARITE*	$\text{CaAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$	SYLVITE	KCl
MERWINITE	$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$	TALC	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
METACINNABAR	HgS	TENORITE	CuO
MICROCLINE,MAXIMUM	$\text{K}(\text{AlSi}_3)\text{O}_8$	TIN,NATIVE*	Sn
MINNESOTAITE	$\text{Fe}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	TITANITE	CaTiSiO_5
MONTICELLITE	CaMgSiO_4	TREMOLITE	$(\text{Ca}_2\text{Mg}_6)\text{Si}_8\text{O}_{22}(\text{OH})_2$
MUSCOVITE	$\text{KA}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$	WAIRAKITE	$\text{Ca}(\text{Al}_2\text{Si}_4)\text{O}_{12}\cdot 2\text{H}_2\text{O}$
NATROLITE*	$\text{Na}_2(\text{Al}_2\text{Si}_3)\text{O}_{10}\cdot 2\text{H}_2\text{O}$	WITHERITE	BaCO ₃
NEPHELINE	$\text{Na}(\text{AlSi})\text{O}_4$	WOLLASTONITE	CaSiO ₃
NESQUEHONITE*	$\text{MgCO}_3\cdot 3\text{H}_2\text{O}$	WURTZITE	ZnS
NICKEL*	Ni	ZINCITE	ZnO
PARAGONITE	$\text{NaAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$	ZOISITE	$\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$
PARGASITE	$\text{Na}(\text{Ca}_2\text{Mg}_4\text{Al})(\text{Al}_2\text{Si}_6)\text{O}_{22}(\text{OH})_2$		

^aMineral that undergoes one phase transition.

^bMineral that undergoes two phase transitions.

^cMineral that undergoes three phase transitions.

large number of the oxides, silicates, carbonates, sulfides, and sulfates that constitute abundant rock-forming minerals in the Earth's crust.

Description of the thermodynamic behavior of gases using Equations (1), (2), and (77)–(84) requires values of the same properties as those noted for minerals. These data are available currently for the 16 gases listed alphabetically in Table 7.

Thermodynamic properties of reactions among minerals, gases, and aqueous species

For any reaction among i minerals and gases (excluding H₂O), j aqueous solute species, and H₂O, the change in apparent standard molal Gibbs free energy or enthalpy of formation can be expressed as

$$\Delta \Xi_{P,T}^\circ = \sum_{i=1}^i v_i \Delta \Xi_{i,P,T}^\circ + \sum_{j=1}^j v_j \Delta \Xi_{j,P,T}^\circ + v_{\text{H}_2\text{O}} \Delta \Xi_{\text{H}_2\text{O},P,T}^\circ \quad (85)$$

and the corresponding change in the standard molal entropy, heat capacity, or volume can be written as

$$\Delta \Xi_{P,T}^\circ = \sum_{i=1}^i v_i \Xi_{i,P,T}^\circ + \sum_{j=1}^j v_j \Xi_{j,P,T}^\circ + v_{\text{H}_2\text{O}} \Xi_{\text{H}_2\text{O},P,T}^\circ \quad (86)$$

where v_i , v_j , and $v_{\text{H}_2\text{O}}$ refer to the stoichiometric reaction coefficient of the subscripted species. Values for $\Delta G_{P,T}^\circ$, $\Delta H_{P,T}^\circ$, $\Delta S_{P,T}^\circ$, $\Delta C_{P,T}^\circ$, and $\Delta V_{P,T}^\circ$ of reaction can be obtained from Equations (85) and (86) by combining appropriate statements of the preceding equations. For example, the specific statement of Equation (85) representing $\Delta G_{P,T}^\circ$ of reaction can be evaluated using Equation (1) together with Equation (82) for minerals and gases, Equations (8), (12), (32), (36), (40)–(44), and (46)–(59) for aqueous solute species, and Equations (7), (22), and (27) for H₂O. The logarithm of the corresponding equilibrium constant ($K_{P,T}$) can be expressed as

$$\log K_{P,T} = \frac{-\Delta G_{P,T}^\circ}{\ln(10)RT} \quad (87)$$

where R stands for the gas constant (1.9872 cal mol⁻¹ K⁻¹).

Table 7. Alphabetized listing of 16 gases that are contained in SPRONS92.DAT thermodynamic database. Note that gases, unlike minerals, are specified in SUPCRT92 reactions by their chemical formulae

GAS	FORMULA	GAS	FORMULA
AMMONIA	NH _{3,g}	NEON	Ne _g
ARGON	Ar _g	NITROGEN	N _{2,g}
CARBON-DIOXIDE	CO _{2,g}	OXYGEN	O _{2,g}
HELIUM	He _g	RADON	Rn _g
HYDROGEN	H _{2,g}	STEAM	H ₂ O _g
HYDROGEN-SULFIDE	H ₂ S _g	SULFUR	S _{2,g}
KRYPTON	Kr _g	SULFUR-DIOXIDE	SO _{2,g}
METHANE	CH _{4,g}	XENON	Xe _g

THE SUPCRT92 SOFTWARE PACKAGE

The SUPCRT92 software package facilitates practical application of the equations and data described here to define equilibrium constraints on geochemical processes in diverse geologic systems. The package consists of three interactive programs, MPRONS92, CPRONS92, and SUPCRT92, and a thermodynamic database, SPRONS92.DAT. The flow of information between the user, database, and programs is schematically illustrated in Figure 4. In this section, we describe the contents and format of the thermodynamic database and the input and output specifications, limitations, and successful operation of the programs. Before moving on to these specifics, however, several general comments regarding the package are in order.

First, regarding robustness: note that SUPCRT92, MPRONS92, and CPRONS92 do not embody fail-safe error-checking capabilities with regard to user-input blunders. Hence, although the software will recover successfully from many common input gremlins, others will on occasion cause abnormal program termination. Where relevant, these possibilities are discussed in the Appendices that present generic interactive sessions with the programs, but nowhere at great length.

Second, regarding portability: every effort has been made to ensure conformance of the SUPCRT92 package to ANSI 77 FORTRAN standard. As a result, relatively trouble-free compilation, library linkage, and execution of the codes is anticipated across a wide variety of operating systems and hardware environments. The package was developed originally within the VAX/VMS environment; subsequently, it has been ported readily to several UNIX-based systems (e.g. the Alliant FX/80 and SUN workstations and SPARCstations), DOS-based Personal Computers (e.g. the IBM PC AT), and Apple Macintosh systems (e.g. the SE/30 and II[si,ci,fx]). Hence, although unforeseen incompatibilities may occur in some instances, such nuances typically should require but minor remedial efforts.

Third, regarding storage requirements: the executable versions of SUPCRT92, MPRONS92, and CPRONS92 together with the thermodynamic database in sequential- and direct-access format occupy roughly 0.85 Mbyte of disk space. The standard installation procedure is summarized in Appendix 1.

Fourth, with regard to verifying the accuracy of SUPCRT92 calculations: in order to verify that SUPCRT92 is operating correctly (i.e. that the program accurately represents the equations it encodes, which is not to be confused with the separate issue of verifying the accuracy with which these equations represent experimental data), one should execute the program for each of the sample input files provided on the distribution disk, and ensure uniform conformance of the calculated output files with their disk counterparts.

In many situations, such verification also can be accomplished by comparison with published values of the standard molal thermodynamic properties of

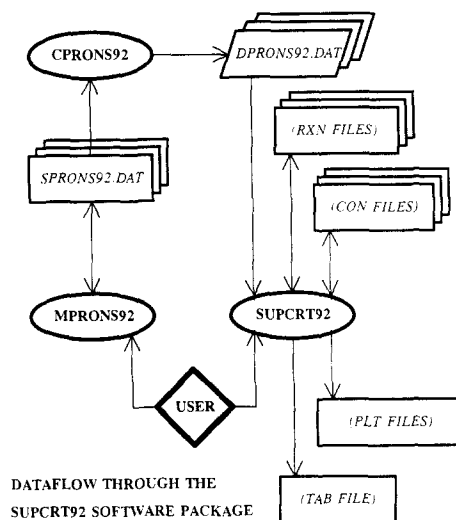


Figure 4. Schematic diagram depicting dataflow through SUPCRT92 software package. Ovals designate interactive software, rectangles represent sequential-access ASCII files, rhombs denote direct-access files, and diamond signifies operator. Where file libraries are represented graphically, specified name refers to default file—except where given parenthetically, in which situation all contained files are created by operator during interactive sessions with SUPCRT92. Arrows direct flow of information. First, one has option of creating modified version of default or other existing thermodynamic database using MPRONS92, which if exercised must be followed by pipe through CPRONS92 in order to generate its direct-access equivalent, which is read by SUPCRT92. Operator then directs SUPCRT92 calculations by specifying direct-access datafile together with RXN and CON files, which can be read from existing libraries or generated interactively. Calculated results are written to TAB file and, optionally, to PLT files which facilitate their graphical depiction.

specific species. All thermodynamic properties of H_2O that can be calculated using SUPCRT92 have been tabulated by Johnson and Norton (1991) for conditions within and near the H_2O critical region (pressures from 200 to 450 bar and temperatures from 350 to 475°C). At 25°C and 1 bar, the analogous properties for minerals and gases have been tabulated by Helgeson and others (1978), and those for aqueous species other than H_2O are given by Tanger and Helgeson (1988), Shock and Helgeson (1988, 1990), Shock, Helgeson, and Sverjensky (1989), and Sverjensky, Shock, and Helgeson (1992).

Note that values of V_{j,P_r,T_r}° and C_{P_j,P_r,T_r}° for the j th aqueous solute species calculated using SUPCRT92 and those tabulated by Tanger and Helgeson (1988) and Shock and Helgeson (1988, 1990) differ slightly owing to the use of different equations to calculate the dielectric constant and Born functions of H_2O . These differences in V_{j,P_r,T_r}° and C_{P_j,P_r,T_r}° values are proportional in magnitude to $|Z_j|$, but are small

even for trivalent cations such as Al^{3+} , where use of the Johnson–Norton (1991) dielectric equation (SUPCRT92) leads to $V_{Al^{3+},P_r,T_r}^\circ = -45.3 \text{ cm}^3/\text{mol}$ and $C_{P_{Al^{3+}},P_r,T_r}^\circ = -31.8 \text{ cal mol}^{-1} \text{ K}^{-1}$, whereas use of the Helgeson–Kirkham (1974a) expression (Shock and Helgeson, 1988) leads to $V_{Al^{3+},P_r,T_r}^\circ = -44.4 \text{ cm}^3/\text{mol}$ and $C_{P_{Al^{3+}},P_r,T_r}^\circ = -32.5 \text{ cal mol}^{-1} \text{ K}^{-1}$.

Fifth, regarding inconveniences associated with the static storage allocation scheme of FORTRAN: this unfortunate feature of the language necessitates pre-compilation assignment of array dimensions to values that certain applications undoubtedly will render insufficient. Anticipating this eventuality, the most susceptible array-dimensioning variables in the SUPCRT92 package and their current values are summarized in Table 8. These values are exclusively assigned using PARAMETER statements; hence, it is a simple matter to increment these variables as necessary. Note that if certain of these variables are incremented (or decremented), it also is necessary to modify the DATA statements that initialize

Table 8. Summary of array-dimensioning variables in SUPCRT92 software package. Relevant program, current value, and brief description is given for each variable. Values given are for general distribution (D) versions of code modules SUP92[D,PC].F, REAC92[D,PC].F, and REP92[D,PC].F. For PC versions, $MAXINC = MAXISO = MAXODD = 21$ and $MAXRXN = 10$; all other variables have same values in both D and PC versions. All value assignments are accomplished using PARAMETER statements; hence, these values can be incremented readily as needed. If certain of these variables are modified, one also must revise initialization of dependent array variables in several DATA statements (see text). *S92*, *M92*, and *C92* are abbreviations for SUPCRT92, MPRONS92, and CPRONS92

PGM	VARIABLE	VALUE	DESCRIPTION
<i>S92</i>	<i>IABC</i>	3	number of Maier–Kelly heat capacity coefficients for a specific phase of a given mineral
	<i>MAXBAD</i>	10	maximum number of unrecognized species in a reaction that will be displayed to the user during an interactive session
	<i>MAXAQS</i>	10	maximum number of aqueous species other than H_2O in a given reaction
	<i>MAXGAS</i>	10	maximum number of gases in a given reaction
	<i>MAXINC</i>	75	maximum number of increments in the second independent state property in the <i>CON</i> file ($\geq MAXODD$)
	<i>MAXISO</i>	21	maximum number of isopleths in the <i>CON</i> file
	<i>MAXLEN</i>	20	maximum length in characters of all species names
	<i>MAXMIN</i>	10	maximum number of minerals in a given reaction
	<i>MAXMK</i>	4	maximum number of sets of heat capacity coefficients for a given mineral (equivalent to $MAXTRN + 1$)
	<i>MAXODD</i>	75	maximum number of state–condition coordinates separated by nonuniform increments in the <i>CON</i> file ($\leq MAXINC$)
	<i>MAXRXN</i>	50	maximum number of reactions in the <i>RXN</i> file
	<i>MAXTRN</i>	3	maximum number of phase transitions for a given mineral
	<i>MAXTRY</i>	5	maximum number of repeated prompts to obtain the filename for the thermodynamic database
<i>M92</i>	<i>MAXAQ</i>	500	maximum number of aqueous species in the input or output <i>SPRONS92.DAT</i> database
	<i>MAXCHG</i>	100	maximum number of species of a given type that can be added, modified, or deleted during a single session
	<i>MAXMG</i>	200	maximum number of minerals that undergo a specific number of phase transitions or gases in the input or output <i>SPRONS92.DAT</i> database
	<i>NTPLUS</i>	4	maximum number of sets of heat capacity coefficients for a given mineral (equivalent to $MAXTRN + 1$)
<i>C92</i>	<i>NTPLUS</i>	4	maximum number of sets of heat capacity coefficients for a given mineral (equivalent to $MAXTRN + 1$)

dependent array variables. Specifically, if *MAXINC* or *MAXISO* are revised, one also must update the appropriate DATA statements in BLOCK DATA *consts* of program module SUP92[D,PC] (the program modules are described next) that initialize all variables contained in COMMON BLOCKS *H2Ogrd* and *badtd*. Similarly, if *MAXMIN* is revised, one also must modify the appropriate DATA statements in SUBROUTINES *rununi* and *runodd* (also located in program module SUP92[D,PC]) that initialize variables *TPDdum* and *ptdumb*.

And finally, regarding input and output filenames: note that the names of the input and output files described next—SPRONS92.DAT, DPRONS92.DAT, CON, RXN, TAB and PLT—are generic. The actual user-specified names must be 20 characters or less in length, but are otherwise unrestricted.

SPRONS92.DAT: the thermodynamic database

SPRONS92.DAT [PRONS is an acronym for PRO(perties of) N(atural) S(ubstances) attributed to E. L. Shock; the prefix S refers to the sequential-access format of this ASCII file] contains the standard molal thermodynamic data at 25°C, 1 bar and *P/T*-independent coefficients and parameters that are needed to calculate the standard molal thermodynamic properties of each aqueous species, mineral, and gas listed in Tables 4–7 as a function of temperature and pressure using the equations as described. The file also lists all references from which these thermodynamic data, coefficients, and parameters were obtained.

Minerals that do and do not undergo phase transitions, gases, and aqueous species other than H₂O are each distinguished by the unique set of coefficients and parameters used to calculate their standard molal thermodynamic properties as a function of temperature and pressure. Hence, the organization of data within the individual "species block" for each of these species types is unique, but uniform for all individual members of a given type. In SPRONS92.DAT, six species types are differentiated: minerals that do not

undergo phase transitions, minerals that undergo from one to three phase transitions, gases, and aqueous species other than H₂O. The organization of data in SPRONS92.DAT for each of the 16 gases listed in Table 7 and the 127 minerals listed in Table 6 that do not undergo phase transition is summarized in Table 9; the analogous data structure for the 52 minerals listed in Table 6 that undergo one or more phase transitions is summarized in Table 10; and the corresponding species-block format for the 294 aqueous solute species listed in Table 4 is summarized in Table 11.

At present, SPRONS92.DAT cannot accommodate data for more than three phase transitions of a given mineral (see *MAXTRN*, Table 8). Moreover, SUPCRT92 is not configured presently to facilitate calculation of the standard molal thermodynamic properties of minerals beyond a fourth phase transition, although the necessary modifications are straightforward.

MPRONS92: a program for modifying the thermodynamic database

MPRONS92 [MPRONS is an acronym for M(odify) PRONS] is an interactive program that facilitates user-specified modification of the SPRONS92.DAT thermodynamic database. MPRONS92 reads SPRONS92.DAT or any other database generated by MPRONS92, queries the user for additions, deletions, or modifications to be made to this database, executes the requested set of updates, then generates a new thermodynamic database that incorporates the specified changes. If the set of user-specified updates includes modification of species names or addition of new species, MPRONS92 will automatically realphabetize the affected class of species. A generic interactive session with MPRONS92 is given in Appendix 2.

Because the ASCII character set is somewhat system-dependent, the alphabetization of species whose names contain digits, hyphens, underscores, commas, or other nonalphabetic characters can be expected to differ slightly across diverse computing environments.

Table 9. Generic species block for gases and minerals that do not undergo phase transitions. Abbreviations: VAR (variable), FMT (FORTRAN 77 format), *abbrev* (abbreviation), *scform* (structural chemical formula), *ecform* (elemental chemical formula), *ref* (literature reference: an integer that refers to citation index given at top of SPRONS92.DAT), and *date* (date last revised). Units: ΔG_f° and ΔH_f° (cal/mol), $S_{P,T}^\circ$ (cal mol⁻¹ K⁻¹), $V_{P,T}^\circ$ (cm³/mol), a (cal mol⁻¹ K⁻¹), b (cal mol⁻¹ K⁻²), c (cal K mol⁻¹), and T_{max} (K). Where values for ΔG_f° and ΔH_f° are unavailable, default null value of 999999 is inserted; note that these null values are not used in SUPCRT92 calculations

LINE	VAR	VAR	VAR	VAR	FMT
1	<i>name</i>	<i>scform</i>			1x,a20,a30
2	<i>abbrev</i>	<i>ecform</i>			1x,a15,5x,a40
3	<i>ref</i>	<i>date</i>			1x,a5,15x,a9
4	ΔG_f°	ΔH_f°	$S_{P,T}^\circ$	$V_{P,T}^\circ$	4x,2(2x,f12.1),2(2x,f8.3)
5	$a(10^0)$	$b(10^3)$	$c(10^{-5})$		4x,3(2x,f12.6)
6	T_{max}	[for <i>a</i> , <i>b</i> , and <i>c</i>]			8x,f7.2

Table 10. Generic species block for minerals that undergo phase transitions. Abbreviations: VAR (variable), FMT (FORTRAN 77 format), *abbrev* (abbreviation), *scform* (structural chemical formula), *ecform* (elemental chemical formula), *ref* (literature reference: an integer that refers to citation index given at top of SPRONS92.DAT), and *date* (date last revised). Units: ΔG_f° , ΔH_f° , and ΔH_i° (cal/mol), $S_{P,T}^\circ$ (cal mol⁻¹ K⁻¹), $V_{P,T}^\circ$ and ΔV_i° (cm³/mol), $a_{[i,n]}$ (cal mol⁻¹ K⁻¹), $b_{[i,n]}$ (cal mol⁻¹ K⁻²), $c_{[i,n]}$ (cal K mol⁻¹), $T_{max,n}$ and $T_{i,P}$ (K), and $(\partial P/\partial T)_i$ (bar/K). Line 5 is repeated $n-1$ times, once for each of $n-1$ (≤ 3) phase transitions specified mineral undergoes. Where values of ΔG_f° , ΔH_f° , ΔH_i° , ΔV_i° , and $(\partial P/\partial T)_i$ are unavailable, default null value of 999999 is inserted; note that these null values are not used in SUPCRT92 calculations

LINE	VAR	VAR	VAR	VAR	FMT
1	<i>name</i>	<i>scform</i>			2x,a20,a30
2	<i>abbrev</i>	<i>ecform</i>			2x,a15,5x,a40
3	<i>ref</i>	<i>date</i>			2x,a5,15x,a9
4	ΔG_f°	ΔH_f°	$S_{P,T}^\circ$	$V_{P,T}^\circ$	4x,2(2x,f12.1),2(2x,f8.3)
5	$a_i(10^0)$	$b_i(10^3)$	$c_i(10^{-5})$	$T_{i,P}$	4x,3(2x,f12.6),2x,f7.2,
	ΔH_i°	ΔV_i°	$(\partial P/\partial T)_i$		2x,f8.1,2(2x,f10.3)
6	$a_n(10^0)$	$b_n(10^3)$	$c_n(10^{-5})$		4x,3(2x,f12.6)
7	$T_{maz,n}$	[for a_n , b_n , and c_n]			8x,f7.2

CPRONS92: a program for converting the thermodynamic database into direct-access format

CPRONS92 [CPRONS is an acronym for C(onvert) PRONS (from sequential-access format to direct-access format)] is an interactive program that reads SPRONS92.DAT or any other sequential-access thermodynamic database generated by MPRONS92 and writes its direct-access equivalent, generically referred to as the DPRONS92.DAT file. SUPCRT92 is designed to read data from the DPRONS92.DAT file, rather than from SPRONS-92.DAT, because the direct-access format facilitates significantly improved run-time efficiency. A generic session with CPRONS92 is given in Appendix 3.

SUPCRT92: a program for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions

SUPCRT92 is an interactive program that reads or facilitates user-generation of two input files, CON and RXN; reads data from the user-specified DPRONS92.DAT thermodynamic database; calculates the standard molal thermodynamic properties

of each reaction specified in the RXN file over the range of state conditions given in the CON file using the equations as described; writes the calculated reaction properties to an output TAB file; and optionally writes these calculated properties to a series of output PLT files that facilitate their graphical depiction.

Subprogram modules. The SUPCRT92.F source code is divided into four subprogram units: SUP92[D,PC].F, REAC92[D,PC].F, H2O92D.F, and REP92[D,PC].F. This division follows from the single-purposeness of the individual modules, as described here.

SUP92[D,PC].F: a program module that reads input data from the user-generated CON and RXN files, reads requisite data from the user-specified DPRONS92.DAT thermodynamic database, pipes these aggregate data through subroutine REAC92, and interfaces the calculated reaction properties with module REP92[D,PC].

REAC92[D,PC].F: a subprogram module that contains subroutine REAC92 and other auxiliary routines that calculate the apparent standard

Table 11. Generic species block for aqueous species other than H₂O. Abbreviations: VAR (variable), FMT (FORTRAN 77 format), *abbrev* (abbreviation), *scform* (structural chemical formula), *ecform* (elemental chemical formula), *ref* (literature reference: integer that refers to citation index given at top of SPRONS92.DAT), and *date* (date last revised). Units: ΔG_f° and ΔH_f° (cal/mol), $S_{P,T}^\circ$ (cal mol⁻¹ K⁻¹), a_1 (cal mol⁻¹ bar⁻¹), a_2 (cal/mol), a_3 (cal K mol⁻¹ bar⁻¹), a_4 (cal K mol⁻¹), c_1 (cal mol⁻¹ K⁻¹), c_2 (cal K mol⁻¹), $\omega_{P,T}$ (cal/mol), and *charge* is dimensionless. When values for specific properties of given species (e.g. $a_{1...4}$ for HNO₃, aq) are unavailable, default null value of 999 is inserted; note that these null values are not used in SUPCRT92 calculations

LINE	VAR	VAR	VAR	VAR	FMT
1	<i>name</i>	<i>scform</i>			2x,a20,a30
2	<i>abbrev</i>	<i>ecform</i>			6x,a15,5x,a40
3	<i>ref</i>	<i>date</i>			6x,a5,15x,a9
4	ΔG_f°	ΔH_f°	$S_{P,T}^\circ$		4x,2(2x,f10.0),4x,f8.3
5	$a_1(10^1)$	$a_2(10^{-2})$	$a_3(10^0)$	$a_4(10^{-4})$	4x,4(2x,f8.4,2x)
6	$c_1(10^0)$	$c_2(10^{-4})$	$\omega_{P,T}(10^{-5})$	<i>charge</i>	4x,3(2x,f8.4,2x),9x,f3.0

molal Gibbs free energy and enthalpy and the associated standard molal entropy, heat capacity, and volume of reactions among minerals, gases, and aqueous species as a function of temperature and pressure.

H2O92D.F: a subprogram module that contains subroutine H2O92 and other auxiliary routines that calculate the dependent state, electrostatic, and standard molal thermodynamic properties of H₂O as a function of the specified independent state conditions.

REP92[D,PC].F: a subprogram module that contains subroutine REPORT and other auxiliary routines that write the TAB file, which lists all relevant data from DPRONS92.DAT together with the calculated standard molal thermodynamic properties of each reaction, and the PLT files, which contain only the calculated properties in a format suitable for two-dimensional plotting.

The PC versions of these modules are appropriate for use within the restricted accessible-memory environment (typically less than 640 kbyte) of standard-configuration DOS-based Personal Computers. These modules differ from the corresponding general-distribution (D) versions only in the values assigned to certain of the PARAMETER variables summarized in Table 8.

Input specifications. SUPCRT92 requires two input files: the CON file, which specifies reaction-independent parameters such as the set of temperatures, pressures, and H₂O densities for which dependent reaction properties are to be calculated, and the RXN file, which specifies the set of chemical reactions to be considered. The reactions and reaction-independent data are contained on separate files to facilitate the specification of common state-condition grids for use with many different suites of reactions. Both the CON and RXN files can be generated during an interactive session with SUPCRT92 by appropriate response to query sequences; alternatively, CON and RXN files created and saved during previous sessions can be used.

Because certain reaction-independent options written to the CON file are mutually exclusive, the sequence of program queries is somewhat response-dependent. The complete range of query/response sequences, augmented with suggestions regarding user strategy, is summarized in Appendix 4.

The CON file: SUPCRT92 is flexible with regard to the nature of independent state conditions that can be specified in the CON file. The standard molal thermodynamic properties of reactions can be calculated along the liquid side of the H₂O vaporization boundary by specifying either T or P ; in the single-phase regions of H₂O by specifying either T or P , or T and H₂O density; or, using the univariant curve option (see next), by specifying either T and $\log K$, or P and $\log K$. In addition, the range of state conditions

over which calculations are to be performed can be specified as an orthogonal grid of uniform increments or a set of conditions that are related by unequal increments; the latter option is useful in the context of calculations associated with experimental data. Alternatively, one of three default ranges can be selected: (1) from 0 to 350°C at 50°C increments along the liquid side of H₂O vaporization boundary, (2) from 0 to 1000°C at 100°C increments and from 500 to 5000 bar at 500 bar increments across the single-phase regions of H₂O, or (3) along the eight-element grid used by the EQ3/6 software package (Wolery, 1979, 1983; Wolery and others, 1990): 0, 25, and 60°C at 1.013 bar, and 100, 150, 200, 250, and 300°C along the liquid side of the H₂O vaporization boundary.

In the context of SUPCRT92 calculations along the H₂O vaporization boundary, note that for $T < 99.6324^\circ\text{C}$ (where the vaporization pressure is 1 bar), the pressure is set to 1 bar instead of the actual vaporization pressure, which is less than 1 bar. If the *actual* vaporization pressure at $T < 99.6324^\circ\text{C}$ is desired, this can be accomplished by specifying the nonuniform increment option. Also note that the metastable specification of 0°C always is replaced with 0.01°C, the temperature at the H₂O triple point.

During an interactive SUPCRT92 session, one selects among the preceding options for the CON file by responding to a sequence of queries; these responses set the relevant program variables, which themselves are not of importance to the user. Nevertheless, a generic summary of these variables is provided at the top of each CON file, primarily for the convenience of those who prefer their local screen editor over interactive question-and-answer sessions. As described in Table 12, parameter values specified on the first line of the CON file dictate the nature of parameters contained on the following lines; hence, the contents of the file are variable. The complete range of generic CON files is summarized in Table 13. In addition, the two CON files that are generated by following the specific examples presented in Appendix 4 are given in Appendix 5.

Several limitations apply to the range of state conditions that can be specified on the CON file. Each of these results from the required static dimensioning of FORTRAN arrays as noted. For orthogonal grids of uniform increments within the single-phase regions of H₂O, the maximum number of state-condition isopleths that can be specified is 21 (see *MAXISO*, Table 8); the associated maximum number of increments in the second independent state variable (e.g. temperature) is 75 (see *MAXINC* in Table 8). For a range of uniform increments along the H₂O vaporization boundary, the maximum number of such increments is again 75 (see *MAXINC* in Table 8); for a set of conditions separated by nonuniform increments, the maximum number of such coordinates that can be specified is also 75 (see *MAXODD* in Table 8).

Table 12. Variation in independent state variables that can be specified on the CON file as function of parameters *isat*, *iopt*, and *iplot*, which are given on first line of file. *Isat* determines phase region of H₂O, *iopt* defines which are to be independent variables, and *iplot* specifies order in which calculations are performed. In a given cell of this table, first state property listed represents isopleth and second refers to incremental variable along that isopleth. For example, if *isat* is set to zero and *iopt* to two, then for each isobar in specified set (defined by *isofmin*, *max,inc*] in Table 13), calculations will be carried out and tabulated as a function of temperature across requested range (*v2fmin*, *max,inc*] in Table 13).

ISAT	IOPT		IPLLOT
—	1	2	—
0	ρ, T	P, T	1
0	T, ρ	T, P	2
1	T	P	3

The RXN file: the RXN file specifies the suite of reactions among minerals, gases, and aqueous species whose standard molal thermodynamic properties are to be calculated by SUPCRT92 over the range of conditions specified on the CON file. To generate the RXN file during an interactive session with SUPCRT92, one specifies for each reaction a descriptive title and the species stoichiometry, using the names for minerals, gases, and aqueous species that are given in the SPRON92.DAT thermodynamic database. To specify the stable phase of H₂O in a given reaction, one enters exactly that "H2O", which is *not* included in SPRONS92.DAT (H₂O is unique in

this regard; data used to compute its properties are contained in subroutine H2O92, which also performs the property calculations, as discussed previously). To specify *metastable* steam, enter "H2O, g", data for which is included in SPRONS92.DAT. The foregoing specifications set the appropriate program variables, the details of which are transparent to the user. However, a generic summary of these variables is included at the top of each RXN file, again for the convenience of those who prefer screen editors over interactive sessions. This summary is presented and described in Table 14. In addition, the two RXN files that are generated by following the specific examples presented in Appendix 4 are given in Appendix 6.

As can be seen in Table 14, the first line of the RXN file specifies whether the reactions that follow contain one or more aqueous species. Because the calculation of H₂O properties—which is required for any reaction involving an aqueous species—dominates the overall execution time of any SUPCRT92 run, and because many reactions containing aqueous species usually are included in a single RXN file, these H₂O properties are calculated but once across the range of state conditions defined on the CON file, then stored for use in all dependent reactions. This approach leads to a significant reduction in execution time that in balance far outweighs the additional overhead in storage costs. Hence, if one desires to calculate the standard molal thermodynamic properties of a number of reactions that contain aqueous species, the composite execution time is dramatically smaller if these reactions are specified on a single RXN file, as opposed to a suite of files. This is particularly true in situations where the property calculations are to be carried out across a large number of state-condition coordinates.

Table 13. Five different types of CON files. Values of parameters specified on first line (see Table 12) determine which variables are given on following lines. *Isotfmin*, *max*, and *inc*] and *oddv1(i)* correspond to state-condition isopleths; *v2fmin*, *max*, and *inc*] and *oddv2(i)* refer to second independent (incremental) state variable; and *Kfmin*, *max*, and *inc*] denote minimum, maximum, and incremental values of log *K*. When *univar* and *noninc* are set to zero, calculations are performed across orthogonal grids of uniform increments along liquid side of H₂O vaporization boundary (type A) or in single-phase regions of H₂O (type B); when *noninc* is nonzero, analogous calculations are carried out for sets of coordinates separated by unequal increments (types C and D); when *univar* is set to one, dependent state variable is calculated as function of independent state property and log *K* (type E). Note that all variables are read in free format.

TYPE	H ₂ O REGION	INCR	VARIABLES
A	VAPORIZATION BOUNDARY	EVEN	Line 1 (free format): <i>isat</i> , <i>iopt</i> , <i>iplot</i> , <i>univar</i> , <i>noninc</i> Line 2 (free format): <i>isomin</i> , <i>isomax</i> , <i>isoinc</i>
B	SINGLE-PHASE REGIONS	EVEN	Line 1 (free format): <i>isat</i> , <i>iopt</i> , <i>iplot</i> , <i>univar</i> , <i>noninc</i> Line 2 (free format): <i>isomin</i> , <i>isomax</i> , <i>isoinc</i> Line 3 (free format): <i>v2min</i> , <i>v2max</i> , <i>v2inc</i>
C	VAPORIZATION BOUNDARY	ODD	Line 1 (free format): <i>isat</i> , <i>iopt</i> , <i>iplot</i> , <i>univar</i> , <i>noninc</i> Lines <i>i=2..1+noninc</i> (free format): <i>oddv1(i-1)</i>
D	SINGLE-PHASE REGIONS	ODD	Line 1 (free format): <i>isat</i> , <i>iopt</i> , <i>iplot</i> , <i>univar</i> , <i>noninc</i> Lines <i>i=2..1+noninc</i> (free format): <i>oddv1(i-1)</i> , <i>oddv2(i-1)</i>
E	SINGLE-PHASE REGIONS (UNIVARIANT CURVE OPTION)	EVEN	Line 1 (free format): <i>isat</i> , <i>iopt</i> , <i>iplot</i> , <i>univar</i> , <i>noninc</i> Line 2 (free format): <i>isomin</i> , <i>isomax</i> , <i>isoinc</i> Line 3 (free format): <i>Kmin</i> , <i>Kmax</i> , <i>Kinc</i> Line 4 (free format): <i>v2min</i> , <i>v2max</i>

Table 14. Generic summary of variables contained on the RXN file. *Nreac* defines number of reactions described; *iwet* specifies whether any of these reactions do (value of one) or do not (values of zero) contain aqueous species. Each reaction block includes descriptive title, line specifying number of minerals (*nm*), aqueous species other than H₂O (*na*), and gases (*ng*) in reaction, whether H₂O is (*nw* set to one) or is not (*nw* set to zero) present, and reaction coefficient (*coeff*), common *name*, and structural chemical *formula* of each species, where prefixes *m*, *a*, and *g* refer to minerals, aqueous species, and gases. When present, H₂O concludes reaction stoichiometry

VARIABLES	FORMAT
Line 1: <i>nreac, iwet</i>	(free format)
Line 2: [blank]	(free format)
Line 3: <i>descriptive title</i>	(a80)
Line 4: <i>nm, na, ng, nw</i>	(free format)
<i>nm</i> Lines: <i>coeff mname mform</i>	(1x,f9.3,2x,a20,2x,a30)
<i>ng</i> Lines: <i>coeff aname aform</i>	(1x,f9.3,2x,a20,2x,a30)
<i>na</i> Lines: <i>coeff gname gform</i>	(1x,f9.3,2x,a20,2x,a30)
(1 Line: <i>coeff H2O H2O</i>)	(1x,f9.3,2x,a20,2x,a30)
** each of the <i>nreac</i> reaction blocks	
** contains $3+nm+ng+na+nw$ lines	

The reactions specified in the RXN file are subject to several limitations. First, of all the species in each reaction must be present in the DPRONS92.DAT thermodynamic database being used during the current SUPCRT92 run; it follows that the name used to reference each species in the RXN file must be *identical* to its name in the DPRONS92.DAT database. For the unmodified SPRONS92.DAT, these names are given in Tables 4–7. There also are restrictions regarding the number of species that can be included in a single reaction and the number of reactions that can be included in a single RXN file. Specifically, each reaction must include ≤ 10 minerals, ≤ 10 gases, and ≤ 10 aqueous species other than H₂O (see *MAXMIN*, *MAXGAS*, and *MAXAQS* in Table 8); each RXN file must include ≤ 50 such reactions (see *MAXRXN* in Table 8). Finally, note that SUPCRT92 does not check the reactions specified on the RXN file for mass or electrical balance; this responsibility is left to the user. Because the program does not perform these balance checks, the standard molal thermodynamic properties of an individual mineral, gas, or aqueous species can be obtained by specifying a reaction containing only that mineral, gas, or aqueous species with a reaction coefficient of one.

Output specifications. Given appropriate CON and RXN files, SUPCRT92 produces an output TAB file that summarizes the calculated standard molal thermodynamic properties of all reactions included in the RXN file over a range of conditions specified on the CON file. (Note that if the RXN file is built interactively during SUPCRT92 execution, a throw-away file named *zero.dat* also will be produced. This file contains one line whose only visible character is the numeral 0.) Optionally, a series of PLT files can

be generated that facilitate graphical depiction of these calculated reaction properties.

The TAB file: a brief section at the top of the TAB file provides a summary of the associated input and output file names and contents. Then, for each reaction specified on the RXN file, the TAB file reiterates the descriptive title and species stoichiometry, lists all data contained on the DPRONS92.DAT thermodynamic database for each species in the reaction, and tabulates the standard molal properties of the reaction calculated at 25°C and 1 bar as well as across the range of conditions specified on the CON file. These properties include the equilibrium constant, the apparent standard molal Gibbs free energy and enthalpy of formation, and the standard molal enthalpy, heat capacity, and volume of reaction. Note that the usual set of reference-state properties is incomplete for some species; these unknown property values are distinguished on the TAB file by the appearance of blank spaces where the known value would otherwise be given. When one or more species in a reaction is characterized by incomplete reference-state data, SUPCRT92 assigns temporary values of zero as necessary to facilitate calculations, and so informs the user by printing

CAUTION: INCOMPLETE DATA

FOR ONE OR MORE SPECIES

just above the tabulated reaction properties.

The number of significant figures provided for a given property is limited to a value commensurate with the present uncertainty limits on the equations. However, graphical representation of property calculations typically requires additional precision beyond these limits. This is one reason why the series of PLT files can be produced optionally; on these files (see

next), all properties are tabulated to seven significant figures.

Unlike the CON and RXN files, the TAB file does not list the cryptic names for program variables followed by their values; rather, the data and calculated properties are listed in an easy-to-read format under headings that are familiar to the geochemist. The best way to familiarize oneself with the TAB file is to peruse the two files generated by following the specific examples discussed in Appendix 4; these are given in Appendix 7. Interpretation of these example files is facilitated by reference to the following paragraphs, which discuss how SUPCRT92 handles state-condition limits of the calculations, mineral-phase transitions, and univariant equilibria.

The range of conditions over which the standard molal thermodynamic properties of a given reaction can be calculated using SUPCRT92 is determined by the species involved in the reaction and the restrictions noted previously on the equations used to represent the thermodynamic behavior of minerals, gases, and aqueous species. In general, the thermodynamic properties of reactions that involve only minerals, gases, and H₂O can be calculated over a range of T - P - ρ conditions which exceeds that for reactions that contain neutral aqueous species other than H₂O, which in turn exceeds that for reactions that include charged aqueous species. When SUPCRT92 encounters a T - P - ρ coordinate that lies beyond some calculational limit of one or more species in the current reaction, an appropriate warning message or explanatory comment is written to the TAB file. The warning messages are just that: calculated properties are written to both the TAB and PLT files. In contrast, the explanatory comments are written in lieu of the reaction properties in the exact location on the TAB and PLT files where the properties would otherwise be given. The specific conditions that give rise to these necessarily terse messages and comments for different types of reactions are described next.

Reactions containing H₂O: in the single-phase regions of H₂O, it may be convenient to define uniform-increment, orthogonal T - P or T - ρ grids whose dimensions encompass a small number of coordinates that fall beyond the stability limits of fluid H₂O. When faced with grids of this type, SUPCRT92 will perform and report calculations for each coordinate lying within the boundaries of fluid H₂O stability, but skip calculations for the outlying coordinates, making note of their exclusion on the TAB file. This feature facilitates calculations across T - P or T - ρ grids that partially overlap the stability regions for ice phases as well as T - ρ grids that intersect the liquid-vapor dome; these situations would otherwise require a patchwork of CON files. As an example, recall the default T - P grid which extends from 500 to 5000 bar and 0 to 1000°C. In this situation, the entire grid falls within the limits of fluid H₂O stability except for the 5000 bar, 0°C coordinate,

which lies within the stability region of ice V. In response to this and other encroachments into the ice fields, the standard molal thermodynamic properties of reactions involving H₂O or other aqueous species will be replaced on the TAB file with the following message:

BEYOND RANGE OF APPLICABILITY
OF H₂O EQUATION OF STATE

When SUPCRT92 encounters metastable T - ρ grid locations within the liquid-vapor dome, the program cannot calculate the standard molal thermodynamic properties of *any* reaction (not just those that contain aqueous species); hence, the message

T, DH₂O FALLS WITHIN
LIQ-VAPT-DH₂O DOME

is printed in lieu of reaction properties.

For T - P - ρ conditions that fall between the limits of the equation of state for H₂O developed by Haar, Gallagher, and Kell (1984) and those of the H₂O dielectric equation given by Johnson and Norton (1991), the standard molal thermodynamic properties of reactions among minerals, gases, and H₂O can be calculated. However, the corresponding calculations for reactions that involve aqueous species other than H₂O cannot be carried out, as described next.

Reactions containing aqueous species other than H₂O: the T - P - ρ region where the standard molal thermodynamic properties of aqueous species other than H₂O can be calculated using the equations described here is restricted to that of the dielectric equation for H₂O, and in the situation of charged ions and complexes, further confined to that of the solvent function g . When SUPCRT92 encounters conditions falling beyond either of these limits in the context of a reaction that involves aqueous species other than H₂O, the program writes one of the two explanatory comments in place of—or in addition to—the standard molal thermodynamic properties of the reaction.

If the current reaction contains only *neutral* aqueous solute species, then all of its standard molal properties will be calculated and reported to 5000 bar and 1000°C *except* where H₂O density is greater than 1.10 g/cm³ or less than 0.05 g/cm³ (Fig. 2), in which situation SUPCRT92 will report

BEYOND VALIDITY RANGE OF MINERAL
OR AQUEOUS SPECIES EQNS

instead of the usual property values. More specifically, this "validity range" refers to that of the equations used to calculate the dielectric constant and Born functions of H₂O (Johnson and Norton, 1991).

If the current reaction contains *charged* aqueous species, the range of conditions over which the preceding message is reported expands to H₂O densities < 0.35 g/cm³, and also includes temperatures between

350 and 400°C when $P < 500$ bar (region 3 of Fig. 3). Moreover, within the additional region defined by H_2O densities > 0.35 , $P < 1000$ bar, and $T > 350^\circ C$, uncertainties in partial derivatives of the solvent function g restrict calculations to those of the apparent standard molal Gibbs free energy and the equilibrium constant (region 2 of Fig. 3). As a result, when SUPCRT92 encounters conditions within this region, this program reports

DELTA G ONLY

(CHARGED AQUEOUS SPECIES),

in place of the apparent standard molal enthalpy and the standard molal entropy, heat capacity, and volume of reaction that otherwise would be tabulated.

Reactions containing minerals and gases: there are no absolute restrictions, in terms of bounding temperatures or pressures, on the calculation of the standard molal thermodynamic properties of minerals and gases using SUPCRT92. However, as noted, one is strongly advised to regard such calculations as provisional extrapolations for pressures greater than 10,000 bar and temperatures beyond the maximum limit of Maier-Kelly (1932) heat capacity coefficients. These temperature maxima are listed on the TAB file for each mineral and gas that occurs in each reaction specified on the RXN file. To further ensure appreciation of these limits, for each reaction that includes one or more mineral or gas, SUPCRT92 responds to the first pressure it encounters above 10,000 bar by reporting

CAUTION: BEYOND P LIMIT OF

APPROXIMATIONS IN MIN/GAS EQNS.

In analogous response to the first temperature it encounters beyond the maximum limit of the Maier-Kelly (1932) coefficients for one or more mineral, SUPCRT92 reports

CAUTION: BEYOND T LIMIT OF CP

COEFFS FOR A MINERAL OR GAS.

In both instances, property values then are calculated and reported to both the TAB and PLT files. Note that these warnings are given but once; hence, the presumption is made that temperatures and pressures are given in ascending order in the CON file.

For reactions that contain minerals which undergo phase transitions, the tabulated standard molal thermodynamic properties of reaction are interleaved with messages that indicate the precise locations of these transitions, which cause discontinuities in computed reaction properties. Mineral phase-transition boundaries represent a different type of equation limit than those discussed previously for the expressions used to calculate the thermodynamic properties of H_2O and other aqueous species. Beyond a phase transition, the equations themselves remain the same (except for the activation of

transition-dependent terms); only the Maier-Kelly coefficients, characteristic of the stable phase, change. However, these transition-dependent terms and coefficient changes impose discontinuities into computed standard molal thermodynamic properties. Because these discontinuities are subtle in some reactions, information regarding the exact location of phase transitions may be useful in unraveling the source of such discontinuities. For this reason, when consecutive elements of an orthogonal T - P or T - ρ grid specified in the CON file bridge one or more mineral phase transitions, SUPCRT92 reports the intervening T - P - ρ location where the transitions occur between the rows of reaction properties calculated at the bridging conditions. In addition, for each bridging coordinate that lies within $\pm 25^\circ C$ of a phase transition, the standard molal isobaric heat capacity of this reaction, which otherwise would be reported, is replaced with "TRANSITION". This substitution reflects the relatively large uncertainties associated with predicting heat capacity in the immediate vicinity of a phase transition (Helgeson and others, 1978).

Note that the locations of mineral phase transitions cannot be reported by SUPCRT92 when CON files containing T - P or T - ρ conditions separated by nonuniform increments are used, because such data need not be arranged in uniformly ascending order. Another instance where SUPCRT92 cannot report phase transition data is when univariant curves are being calculated, as described next.

The univariant curve option: the univariant curve option can be used to locate $T(\log K, P)$ or $P(\log K, T)$ for any reaction. In SUPCRT92, these calculations are performed using the golden-section search algorithm (e.g. Miller, 1984), which in theory and practice is foolproof when applied to well-posed problems; that is those for which a unique solution in fact does exist. In the present application, for example, location of $T(\log K, P)$ within an initial search range $T_1 \dots T_2$ ($T_1 < T_2$), well-posed problems satisfy the following conditions: (1) $T(\log K, P)$ does in fact exist, where $T_1 \leq T \leq T_2$, (2) this temperature is unique, (3) $\log K(T)_p$ describes a strictly (3a) unimodal and (3b) continuous function, and (4) appropriate values for the maximum number of iterations performed during the golden-section search and the tolerance level for success have been encoded in the software. If one assumes (4), problems that additionally satisfy (1)-(3b) will always be solved correctly, and the appropriate results printed to the TAB file. Note, however, that problems satisfying (1) but not necessarily (2) and (3) will on rare occasions return an accurate solution as well!

Moreover, seemingly well-posed problems, again rarely, will fail to return a solution; instead, SUPCRT92 prints a message indicating this failure. Given that conditions (1)-(3a) usually can be ensured with relative ease, the hidden difficulty may lie in subtle failure to satisfy (3b). The discontinuity may

reflect an overlooked mineral-phase transition, or even an extremely minute break in the apparent standard molal Gibbs free energy of an aqueous species along the critical-region boundary that separates application of the H₂O equation of state given by Haar, Gallagher, and Kell (1984) and that developed by Levelt Sengers and others (1983). However, virtually all such situations are resolved readily by judicious refinement of the limits bounding the initial search range ($T_1 \dots T_2$, continuing the example cited here). In fact, failure to satisfy condition (1) is probably the general cause of failure to complete successfully the univariant calculation. For example, if one were to attempt calculation of $T(\log K = 0, P = 30,000 \text{ bar})$ for the quartz-coesite equilibrium for the range 350–400°C, SUPCRT92 would respond with

LOG K = 0.00 not found at P = 30000;

$$350 \leq T \leq 400$$

instead of printing the standard molal thermodynamic properties of this equilibrium, which at 30,000 bar occurs at approximately 900.841°C.

The PLT files: the PLT files contain the same calculated values that are tabulated on the TAB file, but in a format designed to facilitate their smooth interface with various commercial graphics software. Two different suites of files can be generated: those of so-called "generic" format, and those of KaleidaGraph™ format. The first of these is generic in the sense that—following minor editorial modification—the files can be interfaced with almost any two-dimensional graphics utility; however, prior to such modification they cannot be interfaced directly with any specific graphics package. This approach facilitates use of the generic PLT files with a wide variety of graphics software, rather than restricting this use to a particular package. Of course, the ability to generate files that can be interfaced directly with specific graphics software also is advantageous. As a beginning step in that direction, one has the option of generating PLT files in KaleidaGraph™ format. These files can be read directly into KaleidaGraph™, a versatile graphics application developed for Macintosh systems by Abelbeck Software (distributed by Synergy Software, Inc.).

Generic PLT files: if the generic format is selected, a separate PLT file will be generated for each thermodynamic property calculated; each of these files includes data for all of the reactions specified on the RXN file. With the exception of PLT files that contain the P – T projections of univariant equilibria (see next), the naming convention for these files is *prefix.[k,g,h,s,c,v]xy*, where *prefix* represents a user-specified filename prefix (≤ 16 characters) and *k*, *g*, *h*, *s*, *c*, and *v* refer to the equilibrium constant, apparent standard molal Gibbs free energy and enthalpy, and standard molal entropy, heat capacity, and volume of reaction. Analogous files that contain calculated

values of the dependent state variable(s) also are produced. For calculations in the single-phase regions of H₂O, this dependent variable (either P or H₂O density) is reported to a file named *prefix.dxy*, where the first letter of the suffix is an abbreviation for "dependent variable". For calculations along the H₂O vaporization boundary or the default eight-element EQ3/6 grid, the two dependent variables (the density of vapor-saturated liquid H₂O together with either P or T), are written into files named *prefix.[d,2]xy*, where the "2" stands for "second dependent variable".

If the univariant curve option is selected, SUPCRT92 will generate a single PLT file that contains the P – T projections calculated for the range of $\log K$ values and set of chemical reactions that are specified on the CON and RXN files, respectively. The naming convention for this file is *prefix.uxy*, where the first letter of the suffix is an abbreviation for "univariant".

Each generic PLT file follows the same format. First, a brief section summarizing the associated input and output files is given (identical to that which occurs in the TAB file). Then, for each reaction, the following sequence is provided: (1) two lines that specify the reaction number and its descriptive title, (2) one line that specifies the current state-condition isopleth, increment, and calculated reaction property (or, in the case of univariant runs, the current $\log K$, state-condition isopleth, and calculated dependent state property), (3) a list of x – y coordinates along that isopleth ($\log K$ for univariant runs), where x refers to the state-condition increment (isopleth for univariant runs) and y denotes the reaction property (dependent state property for univariant runs)—both of which are provided to seven significant figures. Sequences (2) and (3) are repeated as necessary.

Two samples of generic-format PLT files are provided in Appendix 8. These were generated by following the two example SUPCRT92 runs discussed in Appendix 4.

The KaleidaGraph™ PLT files: if the KaleidaGraph™ format is selected, the suite of PLT files generated by SUPCRT92 subsequently can be read directly into standard KaleidaGraph™ data windows. Both the naming conventions for and the number of PLT files generated in this situation are different than if the generic option were selected; there also are additional restrictions, beyond those summarized in Table 8, on the number of reactions and state-condition isopleths that can be considered. Specifically, when the KaleidaGraph™ option is selected, SUPCRT92 can generate PLT files for a maximum of 10 reactions across a maximum of 11 isopleths per reaction.

Because FORTRAN writes output data sequentially row-by-row (each row being of character-length restricted by practical considerations) and KaleidaGraph™ plots data as column versus column(s) (of essentially unrestricted length), it is

necessary to buffer calculated reaction properties (internally within SUPCRT92) reaction-by-reaction before writing these data to the PLT files. In general, this increases the number of PLT files generated, requires modification of their naming conventions, and imposes the previously noted practical restrictions on the number of reactions that can be processed and the number of isopleths that can be considered for each reaction.

For calculations in the single-phase regions of H₂O, the naming convention for KaleidaGraph™-format PLT files is *prefixR##. [d,k,g,h,s,c,v]xy*, where *prefix* (≤ 13 characters) is given by the user, *R##* stands for "reactions R01... \leq R10", and the first letter of the suffix (defined as previously) denotes the specific property grid contained on the file. Hence, for such calculations, the number of files generated is seven times the number of reactions being considered. For calculations along the H₂O vaporization boundary or the eight-element default EQ3/6 grid, the naming convention is *prefixR##.axy*, where the first letter of the suffix is an abbreviation for "all properties". In contrast to the generic PLT option, which produces eight PLT files for such calculations (and any number of reactions), the KaleidaGraph™ option generates *one* PLT file *per* reaction, which contains all thermodynamic properties, ordered by column.

If one has selected the univariant curve option, the naming convention is *prefixR##.uxy*, where the first letter of the suffix stands for "univariant", and the calculated *P-T* projections for each reaction are written to separate files.

Similar to their generic counterparts, each of the KaleidaGraph™ PLT files contains a banner section that summarizes the associated input and output files. Following this header, the format differs depending on the type of calculations reported. For calculations within the single-phase regions of H₂O, each of the eight PLT files for a given reaction tabulates its particular property such that the state-condition isopleths are indexed by column (reference values given in the first row), and the state-condition increments by row (reference values given in the first column). This also is the format used in the univariant PLT files, except that here the dependent state property is tabulated as a function of $\log K$ values (indexed by columns) and state-condition isopleths (indexed by rows). For calculations along the H₂O vaporization boundary or across the default EQ3/6 grid, the first column reports the independent state property, the second and third columns list the two dependent state properties, and columns four through nine give the thermodynamic properties.

Restrictions: generation and use of the PLT files, in either generic or KaleidaGraph™ format, are subject to two restrictions. First, these files can be produced only during runs where the CON file specifies an independent state-condition grid of uniform increments (the default eight-element EQ3/6

grid being the lone exception to this rule). This is because PLT files generated in association with sets of coordinates separated by unequal increments are not of general use because uniform ascending or descending order of such sets is not required.

Secondly, the *T-P-ρ* limits on the predictive equations that suppress tabulation of reaction properties on the TAB file similarly prohibit their inclusion on the PLT files (compare Appendices 7.1 and 8.1). Hence, for calculations along a state-condition isopleth that enters and then continues beyond a restricted region (e.g. region 3 of Fig. 3 for a reaction that contains charged aqueous species), the associated PLT files must be used with caution. Note that although nothing will be written to generic-format files while within this restricted region, zero entries (which must subsequently be replaced with blanks) will be tabulated in the KaleidaGraph™-format files.

CONCLUDING REMARKS

The recent equations and data encoded in the SUPCRT92 software package permit quantitative description of equilibrium constraints on geochemical processes in a wide variety of geologic settings. The package itself facilitates practical application of these recent advances to solve geochemical problems that involve bulk compositions and *P-T* conditions as varied as those associated with groundwater environments, diagenetic systems, hydrothermal ore deposits, and metamorphic terrains. Similar to their predecessors, however, the equations and data used in SUPCRT92 should be viewed as no more than the latest advancements in a perennial evolution. On the other hand, they also should be viewed as constituting no less than arguably the most comprehensive theoretical model currently available for describing and predicting the equilibrium thermodynamic behavior of minerals, gases, aqueous species, and reactions as a function of temperature and pressure. In addition, the software package itself offers several new computational schemes and operational features that facilitate significantly improved performance and versatility relative to its predecessors. Hence, SUPCRT92 represents an important benchmark that provides a rigorously tested and documented point of departure for future advances.

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- is networked to the target machine. If necessary, transfer the files to the target machine using local transfer procedures.
- (2) Create the object-code equivalents of SUP92D.F, REP92D.F, REAC92D.F, and H2O92D.f using the local F77 compiler, then combine these object codes with predefined F77 function libraries using the local linker to create an executable SUPCRT92.
 - (3) Compile and link CPRONS92.F to create an executable CPRONS92.
 - (4) Execute CPRONS92, specifying SPRONS92.DAT as the input sequential-access thermodynamic database and DPRONS92.DAT as its output direct-access equivalent. A generic interactive session with CPRONS92 is given in Appendix 3.
 - (5) Execute SUPCRT92 using the test library of input files provided on the disk and ensure agreement of the calculated output files with their disk counterparts; report any discrepancies to the authors. A generic interactive session with SUPCRT92 is provided in Appendix 4. This session can be used to generate the CON, RXN, TAB, and PLT files given in Appendices 5–8, which represent two problems selected from the test library.
 - (6) If modification of the standard-issue thermodynamic database (SPRONS92.DAT) is desired, compile and link MPRONS92.F to create an executable MPRONS92, which facilitates such modification. A generic interactive session with MPRONS92 is given in Appendix 2.

APPENDIX 2

Generic interactive session with MPRONS92

MPRONS92 is an interactive program that facilitates modification of the standard-issue thermodynamic database, SPRONS92.DAT. The program requires as input a sequential-access database (either SPRONS92.DAT or a derivative thereof generated during a previous MPRONS92 run) together with a set of directives that specify the species and data to be added, deleted, or modified. These directives are entered by the user in response to a sequence of program queries. Given appropriate input, MPRONS92 generates a new sequential-access database that incorporates all the requested changes. In the following generic MPRONS92 session, program queries are given in boldface except for the embedded program variables, which are distinguished by italics. During an actual session, these italicized variables are replaced by their current values, and the numbers that identify prompts below are not printed.

1.0 specify name of an EXISTING sequential-access THERMODYNAMIC DATABASE:

Enter the appropriate filename. If the specified file exists in the present directory, proceed to 1.2; if it does not, proceed to 1.1. (*Note:* specification of an existing file other than SPRONS92.DAT or one of its MPRONS92-generated derivatives will result in abnormal program termination.)

1.1 nonexistent file or invalid specifications . . . try again

If the preceding query was 1.0, then the specified file could not be located in the present directory; if it was 1.2, then the specified file already exists in this directory and your system does not permit file overwrites. Return to the preceding query.

1.2 specify name of a NEW sequential-access THERMODYNAMIC DATABASE:

Enter the appropriate filename. If the specified file does not exist already in the present directory, proceed to 2.0.

APPENDIX 1

Installation of the SUPCRT92 Package

As footnoted on the title page, the complete SUPCRT92 software package is available on a 5.25" 1.2 Mbyte DOS disk which can be obtained at no cost from the Laboratory of Theoretical Geochemistry. This disk contains all source codes, the standard-issue thermodynamic database, and a library of sample input and output files. Also included is the readme.doc file, which describes the contents of the distribution disk, including the test library, and discusses the following installation procedure in greater detail (especially with regard to installation on DOC-based Personal Computers and Apple Macintosh systems). This procedure, which facilitates assembly of SUPCRT92, CPRONS92, and MPRONS92 in executable form, is intimately familiar to those who work with computer environments routinely; *readers lacking this logistic experience are urged to consult their local experts.*

- (1) Download all files from the distribution disk to any appropriate local machine; that is one which is equipped with a 5.25" 1.2 Mbyte DOS disk drive and

If the specified file does exist already, proceed to 2.0 if your computing environment permits file overwrites, or to 1.1 if it does not.

2.0 Would you like to ADD, DELETE, or MODIFY any species type? (y/n)

Species type refers, sequentially, to minerals having zero, one, two, and three phase transitions, gases, and aqueous species. If you respond in the affirmative, proceed to 2.1. If you respond in the negative, the current value of *species type* will be incremented and query 2.0 repeated, until this current value is "aqueous species", in which case MPRONS92 will transfer all aqueous species data and then terminate.

2.1 specify number of species to ADD:

Enter the appropriate number. If the specified value, *n-add*, is zero, proceed to 2.3; otherwise, proceed to 2.2.

2.2 specify *n-add* species names; one per line:

Enter the list of species to be added, and proceed to 2.3.

2.3 specify number of species to DELETE:

Enter the appropriate number. If the specified value, *n-del*, is zero, proceed to 2.5; otherwise, proceed to 2.4.

2.4 specify *n-del* species names; one per line:

Enter the list of species to be deleted, and proceed to 2.5. (Note: if *n* of the *n-del* species to be deleted do not exist in the present database, you will ultimately be informed "n of the species to be deleted were not found".)

2.5 specify number of species to MODIFY:

Enter the appropriate number. If the specified value, *n-mod*, is non-zero, proceed to 2.6. If zero is specified but species are to be added, proceed to 2.8. If zero is specified and no species are to be added, the current value of *species type* will be incremented and query 2.0 repeated, unless this current value is "aqueous species", in which instance MPRONS92 will transfer all aqueous species data and then terminate.

2.6 specify *n-mod* species names; one per line:

Enter the list of species to be modified, and proceed to 2.7. (Note: if *n* of the *n-mod* species to be modified do not exist in the present database, you will ultimately be informed "n of the species to be modified were not found".)

2.7 modify data for name

name: *name*

Would you like to update this value? (y/n)

If you respond in the affirmative, you will be queried for a new name. Additional prompts then will be issued that specify the current value of each data field for *name*, and offer opportunity to revise this value. After the update is complete: if more species of the current *species type* are to be modified, *name* is incremented and prompt 2.7 repeated; if no more species of this type are to be modified but such species are to be added, proceed to 2.8; if no more species of this type are to be modified or added, the current *species type* will be incremented and query 2.0 repeated, unless this current value is "aqueous species", in which instance MPRONS92 will transfer all aqueous species data and then terminate.

2.8 specify requisite data for name

abbreviation [e.g., Qtz]:

Enter the appropriate abbreviation. Additional prompts then will be issued requesting values for each data field of *name* characteristic of the current *species type*. After the new species entry is complete: if more species of the current type are to be added, *name* is incremented and

query 2.8 repeated; if no more species of this type are to be added, the current value of *species type* will be incremented and query 2.0 repeated, unless this current value is "aqueous species", in which case MPRONS92 will transfer all aqueous species data and then terminate.

APPENDIX 3

Generic Interactive Session with CPRONS92

CPRONS92 is a interactive program that reads SPRONS92.DAT or any of its MPRONS92-generated derivatives and writes the direct-access equivalent, DPRONS92.DAT, which is subsequently read by SUPCRT92. In the following generic CPRONS92 session, program queries are given in boldface except for the embedded program variables, which are distinguished by italics. During an actual session, these italicized variables are replaced by their current *values*, and the numbers that identify prompts below are not printed.

1.0 specify name of INPUT sequential-access

THERMODYNAMIC DATABASE:

Enter the appropriate filename. If the specified file exists in the present directory, proceed to 1.2; if it does not, proceed to 1.1. (Note: specification of an existing file other than SPRONS92.DAT or one of its MPRONS92-generated derivatives will result in abnormal program termination.)

1.1 nonexistent file or invalid specifications . . . try again

If the preceding query was 1.0, then the specified file could not be located in the present directory; if it was 1.2, then the specified file already exists in this directory and your system does not permit file overwrites. Return to the preceding query.

1.2 specify name of OUTPUT direct-access

THERMODYNAMIC DATABASE:

Enter the appropriate filename. If the specified file does not already exist in the present directory, proceed to 2.0. If the specified file does already exist, proceed to 2.0 if your computing environment permits file overwrites, or to 1.1 if it does not.

2.0 starting min1 transfer

starting min2 transfer

starting min3 transfer

starting min4 transfer

starting gas transfer

starting aqueous species transfer

These messages report progression through the transfer process. When the system prompt returns, program execution is completed.

APPENDIX 4

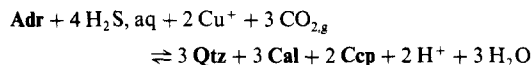
Generic Interactive Session with SUPCRT92

SUPCRT92 is an interactive program that facilitates calculation of the standard molal thermodynamic properties of reactions among minerals, gases, and aqueous species as a function of temperature and pressure. Input specifications for SUPCRT92 are contained on three separate files: (1) the supporting thermodynamic database (the default file is DPRONS92.DAT), (2) the CON file, which specifies reaction-independent data such as choice of independent state properties and their range of values (several default CON files are available), and (3) the RXN file, which specifies the suite of reactions whose thermodynamic properties are to be calculated. During an interactive session, one specifies a filename for the thermodynamic database to be used. For the CON and RXN files, one can either

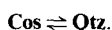
specify all requisite data through response to a sequence of program queries, or request use of CON and RXN files created and saved during previous runs. Given appropriate input, SUPCRT92 produces an output TAB file that lists all calculated reaction properties and other relevant information; optionally, a suite of PLT files that facilitate graphical depiction of the calculations can be generated.

Because certain reaction-independent options are mutually exclusive, the sequence of program queries is somewhat response dependent. The following generic interactive session presents the entire range of query/response sequences. Warnings and suggestions regarding strategy are provided where appropriate. Note that program queries are given in boldface except for the embedded program variables, which are distinguished by italics. During an actual session, these italicized variables are replaced by their current values, and the numbers that identify prompts are not printed.

Although the following interactive session with SUPCRT92 is fully generic, two specific example runs also are included. The first, referred to as the skarn example, illustrates use of the default P - T grid to calculate the standard molal thermodynamic properties of the reaction



for a wide range of pressure and temperature. This reaction includes all types of species present in the thermodynamic database: minerals that do (quartz [Qtz] and chalcopyrite [Cep]) and do not (andradite [Adr] and calcite [Cal]) undergo phase transitions, a gas, H_2O , and charged and neutral aqueous species other than H_2O . To run the skarn example, follow the sequence of enumerated prompts earmarked by the S superscripts. The CON, RXN, TAB, and PLT files generated by this run are given in Appendices 5.1, 6.1, 7.1, and 8.1. The second run, referred to as the quartz-coesite example, demonstrates use of SUPCRT92 to calculate the P - T projection of the univariant quartz-coesite (Qtz-Cos) transition, which is defined by the reaction



To run this example, follow the sequence identified by the Q superscripts. The CON, RXN, TAB and PLT files generated by this run are given in Appendices 5.2, 6.2, 7.2, and 8.2.

1.0^{S,Q} would you like to use the default thermodynamic database? (y/n)

Enter "y[es]" or "n[o]". An affirmative response—as is appropriate for the skarn and quartz-coesite examples—requests use of DPRONS92.DAT. If this file exists in the present directory, proceed to 2.0; if it does not, proceed to 1.2. A negative response permits use of a customized database generated previously using MPRONS92; proceed to 1.1.

1.1 specify filename for thermodynamic database:

Enter the appropriate filename. If the specified file exists in the present directory, proceed to 2.0; if it does not, proceed to 1.2. (*Note:* specification of an existing file other than SPRONS92.DAT or one of its MPRONS92-generated derivatives will result in abnormal program termination.)

**1.2 nonexistent file or invalid specifications... try again
Cannot find filename
enter correct filename:**

Filename corresponds to the thermodynamic database requested (in response to query 1.0 or 1.1), which could not be located in the present directory. Enter the correct filename. If a recognized file is specified, pro-

ceed to 2.0; if not, query 1.2 will be repeated up to four times. After five failures to specify a recognized file, proceed to 1.3.

**1.3 I am tired of looking for this file;
please do the legwork yourself!
Bye for now...
FORTRAN STOP**

As indicated, the program terminates.

2.0^{S,Q} choose file option for specifying reaction-independent parameters:

- 1 = select one of three default files**
- 2 = select an existing nondefault file**
- 3 = build a new file**

Specifying "1"—as is appropriate for the skarn example (unless one wishes to examine the sequence of queries associated with building a new CON file, in which instance the default P - T grid also can be constructed explicitly by specifying "3" and responding appropriately to the following prompts)—requests default settings for all reaction-independent parameters; proceed to 2.1. Specifying "2" requests use of an existing nondefault CON file; proceed to 2.2. Specifying "3"—as is appropriate for the quartz-coesite example (unless anxious to obtain calculated results, in which case specify "2" and at prompt 2.2 enter *qcgett.con*)—requests construction of a new CON file; proceed to 2.3.

2.1^S specify solvent phase region:

- 1 = one-phase region**
- 2 = liq-vap saturation curve**
- 3 = EQ3/6 one-phase/sat curve**

Specifying "1"—as is appropriate for the skarn example—requests that reaction properties be calculated over the default P - T grid: from 0 to 1000°C at 50°C increments and from 500 to 5000 bar at 500 bar increments; specifying "2" requests such calculations over the default grid along the H_2O vaporization boundary: from 0 to 350°C at 25°C increments; specifying "3" requests such calculations across the eight-element grid used by EQ3/6 software package (Wolery, 1979, 1983): 0.01, 25, and 60°C at 1.01322 bar and 100, 150, 200, 250, and 300°C along the H_2O vaporization boundary. Proceed to 3.0.

2.2 specify file name:

Enter the appropriate file name. If the specified file exists in the present directory, proceed to 3.0; if it does not, you will be informed "nonexistent file or invalid specifications... try again" and query 2.2 will be repeated.

2.3^S specify solvent phase region:

- 1 = one-phase region**
- 2 = liq-vap saturation curve**

Specifying "1"—as is appropriate for the quartz-coesite example—requests that reaction properties be calculated within the single-phase regions of H_2O ; proceed to 2.4. Specifying "2" requests that such calculations be performed along the liquid branch of the H_2O vaporization boundary; proceed to 2.5.

2.4^Q specify independent state variables:

- 1 = temperature (degC), density[H2O] (g/cc)**
- 2 = temperature (degC), pressure (bars)**

Specifying "1" requests that temperature and density define the independent state variables for subsequent calculation of reaction properties; proceed to 2.6. Specifying "2"—as is appropriate for the quartz-coesite example—requests that such calculations be performed in the context of temperature and pressure as independent state properties; proceed to 2.7.

2.5 specify independent liq-vap saturation variable:**1 = temperature (degC)****2 = pressure (bars)**

Specifying "1" requests temperature as the independent state variable on the H₂O vaporization boundary for subsequent calculation of reaction properties; specifying "2" requests that such calculations be performed in the context of pressure as the independent state property. Proceed to 2.9.

2.6 specify tabulation option:**1 = calculate isochoric(t) tables****2 = calculate isothermal(d) tables**

Specifying "1" requests that reaction properties be tabulated as a function of temperature for each isochore; specifying "2" requests that these properties be tabulated as a function of density along each isotherm. Proceed to 2.9.

2.7^o would you like to use the univariant curve option;**i.e., calculate T(logK,P) or P(logK,T)? (y/n)**

An affirmative response—as is appropriate for the quartz-coesite example—defines equilibrium constants together with temperature or pressure as the independent variables; proceed to 2.10. A negative response requests that temperature and pressure be the independent variables; proceed to 2.8.

2.8 specify tabulation option:**1 = calculate isobaric (t) tables****2 = calculate isothermal (p) tables**

Specifying "1" requests that reaction properties be tabulated as a function of temperature for each isobar; specifying "2" requests that these properties be tabulated as a function of pressure along each isotherm. Proceed to 2.9.

2.9 specify table-increment option:**1 = calculate tables having uniform increments****2 = calculate tables having unequal increments**

Specifying "1" indicates that reaction properties are to be calculated at uniform increments along an orthogonal grid of independent state-condition coordinates: if this run involves the H₂O vaporization boundary, proceed to 2.11; otherwise, proceed to 2.12. Specifying "2" requests that such properties are to be calculated for a set of independent state-condition coordinates related by unequal increments: if this run involves the H₂O vaporization boundary, proceed to 2.17; otherwise, proceed to 2.18.

2.10^o specify univariant calculation option:**1 = calculate T(logK,isobars)****2 = calculate P(logK,isotherms)**

Specifying "1"—as is appropriate for the quartz-coesite example—requests log *K* and pressure as independent variables; specifying "2" requests log *K* and temperature as independent variables. Proceed to 2.14.

2.11 specify independent state property**min, max, increment**

The value of *independent state property* (TEMP(degC) or PRES(bars)) reflects your response to query 2.5. Enter the desired **min**, **max**, and **increment (inc)** trio. If $ninc (= [\max - \min]/inc)$ is not an integer, proceed to 2.21; if $ninc + 1$ exceeds the array-dimension limit that defines the maximum number of coordinates that can be considered in a single run (see Table 8), proceed to 2.22; otherwise, proceed to 2.17.

2.12 specify independent state-condition isopleths:**min, max, increment:**

The value of *independent state-condition isopleths* (ISOCHORES(g/cc), ISOTHERMS(degC), or ISOBARS(bars)) reflects your response to query 2.[6,8].

Enter the desired **min**, **max**, and **increment (inc)** trio. If $ninc (= [\max - \min]/inc)$ is not an integer, proceed to 2.21; if $ninc + 1$ exceeds the array-dimension limit that defines the maximum number of coordinates that can be considered in a single run (see Table 8), proceed to 2.22; otherwise, proceed to 2.13.

2.13 specify independent state-condition increment range**min, max, increment:**

The value of *independent state-condition increment* (DH2O(g/cc), TEMP(degC), or PRES(bars)) reflects your response to query 2.[6,8]. Enter the desired **min**, **max**, and **increment (inc)** trio. If $ninc (= [\max - \min]/inc)$ is not an integer, proceed to 2.21; if $ninc + 1$ exceeds the array-dimension limit that defines the maximum number of coordinates that can be considered in a single run (see Table 8), proceed to 2.23; otherwise, proceed to 2.19.

2.14^o specify independent state-condition isopleths:**min, max, increment**

The value of *independent isopleths* (ISOBARS(bars) or ISOTHERMS(degC)) reflects your response to query 2.10. Enter the desired **min**, **max**, and **increment (inc)** trio—for the quartz-coesite example, enter "25000, 35000,2500". If $ninc (= [\max - \min]/inc)$ is not an integer, proceed to 2.21; if $ninc + 1$ exceeds the array-dimension limit that defines the maximum number of coordinates that can be considered in a single run (see Table 8), proceed to 2.22; otherwise, proceed to 2.15.

2.15^o specify logK range:**Kmin, Kmax, Kincrement**

Enter the desired log *K* range—for the quartz-coesite example, enter "0,0,0". Proceed to 2.16.

2.16^o specify bounding independent state condition range:**min, max**

The values of *independent state condition* (TEMP(degC) or PRES(bars)) and *min, max* (Tmin, Tmax; or Pmin, Pmax) reflects your response to query 2.10. Enter the desired search range—for the quartz-coesite example, enter "350,1400". Proceed to 2.19 (*Note*: successful application of SUPCRT92 to calculate the *P-T* projections of univariant equilibria hinges critically on specification of an appropriate bounding range for the *independent state condition*. Criteria used to define such ranges are discussed previously.)

2.17 specify liq-vap saturation state property values;**one per line, concluding with a zero:**

The value of *state property* (TEMP(degC) or PRES(bars)) reflects your response to query 2.5. After concluding the list as indicated or entering the maximum number of coordinates that can be considered in a single run (Table 8), proceed to 2.19.

2.18 specify independent state conditions[s] values;**one pair per line, concluding with 0,0:**

The value of *independent state condition* [TEMP(degC), DH2O(g/cc); DH2O(g,cc), TEMP(degC); TEMP(degC), PRES(bars); or PRES(bars), TEMP(degC)] reflects your response to queries 2.[4,6,8]. After concluding the list as indicated or entering the maximum number of coordinates that can be considered in a single run (see Table 8), proceed to 2.19.

2.19^o would you like to save these reaction-independent parameters to a file? (y/n)

If you respond in the affirmative—which is appropriate for the quartz-coesite example—proceed to 2.20; otherwise, proceed to 3.0.

2.20^o specify filename:

Enter an appropriate filename. If the specified file does not already exist in the present directory, proceed to 3.0. If the specified file does already exist, proceed

- to 3.0 if your computing environment permits file overwrites; if it does not, you will be informed “**nonexistent file or invalid specifications... try again**”, and query 2.20 will be repeated.
- 2.21 Ill-defined min,max,increment trio**
Revise specifications.
 Return to the previous query.
- 2.22 Number of specified isopleths (*n*) exceeds MAXISO (MAXISO).**
Revise specifications.
 Return to the previous query.
- 2.23 Number of specified increments (*n*) exceeds MAXINC (MAXINC).**
Revise specifications.
 Return to the previous query.
- 3.0^{S,Q} choose file option for specifying reactions**
1 = use an existing reaction file
2 = build a new reaction file:
 Specifying “1” requests use of an existing reaction file; proceed to 3.1. Specifying “2”—as is appropriate for the skarn and quartz-coesite examples (unless anxious to obtain calculated results, in which situation specify “1” and at prompt 3.1 enter *skarn.rxn* or *qc.rxn*)—facilitates construction of a new reaction file; proceed to 3.2.
- 3.1 specify name of reaction file:**
 Enter the appropriate filename. If the specified file exists in the present directory, proceed to 4.0; if it does not, you will be informed “**nonexistent file or invalid specifications... try again**”, and query 3.1 will be repeated.
- 3.2^{S,Q} specify number of reactions to be processed:**
 Respond as indicated—enter “1” for the skarn and quartz-coesite examples; proceed to 3.3.
- 3.3^{S,Q} input title (≤80 characters) for reaction *i-reac* of *n-reac*:**
N-reac and *ireac* (= 1 . . *n-reac*) represent the final and current reaction, respectively.
 Enter an appropriate title; proceed to 3.4.
- 3.4^{S,Q} enter [coeff species] pairs, separated by blanks, one pair per line, for reaction *i-reac* (conclude with [0])**
 Enter the desired reaction in the manner indicated. *Note that all species must be identified using the precise name given in the thermodynamic database.*
 For the skarn example, enter
- ```
-1 ANDRADITE
-4 H2S,aq
-2 Cu+
-3 CO2,g
3 QUARTZ
3 CALCITE
2 CHALCOPYRITE
2 H+
3 H2O
0
```
- For the quartz-coesite example, enter
- ```
-1 QUARTZ
1 COESITE
0
```
- If, while entering the reaction, you accidentally type a line that cannot possibly define a [coeff species] pair—for example *-w QUARTZ*—proceed immediately to 3.5. After you have entered the entire reaction: if all species in the reaction exist in the thermodynamic database being used, proceed to 3.7; if one or more of these species do not exist in this database—for example you inadvertently mistyped QUARTZ as QUARTX—proceed to 3.6.
- 3.5 ill-defined [coeff species] pair; try again**
 Enter the revised [coeff species] pair—for example *-1 QUARTZ*—followed by the rest of the reaction. After you have entered the entire reaction: if all species in the reaction exist in the thermodynamic database being used, proceed to 3.7; if one or more of these species do not exist in this database—for example you inadvertently mistyped QUARTZ as QUARTX—proceed to 3.6.
- 3.6^{S,Q} the following species were not found in database *dbname***
QUARTX
input new [coeff species] pairs to replace these incorrect entries (conclude with [0])
Dbname is the name of the thermodynamic database being used during this run. Reenter [coeff species] pairs for the unrecognized species only (“3 QUARTZ” for the skarn example or “-1 QUARTZ” for the quartz-coesite example); *do not retype the entire reaction*. After the reaction stoichiometry has been limited to recognized species, proceed to 3.7.
- 3.7^{S,Q} reaction *i-reac* stoichiometry:**
 For the skarn example:
- ```
-1.000 ANDRADITE Ca3Fe2Si3O12
-3.000 CARBON-DIOXIDE CO2,g
-4.000 H2S,aq H2S(0)
-2.000 Cu+ Cu(+)
 3.000 CALCITE CaCO3
 2.000 CHALCOPYRITE CuFeS2
 3.000 QUARTZ SiO2
 2.000 H+ H(+)
 3.000 H2O H2O
```
- For the quartz-coesite example:
- ```
-1.000 QUARTZ          SiO2
 1.000 COESITE         SiO2
```
- is this correct? (y/n)**
 If your response is negative, return to 3.4; if affirmative—as is appropriate for the skarn and quartz-coesite examples—the program increments the current value of *i-reac* and returns to 3.3, unless the incremented value exceeds *n-reac*, in which situation proceed to 3.8.
- 3.8^{S,Q} would you like to save these reactions to a file? (y/n)**
 If your response is affirmative—as is appropriate for the skarn and quartz-coesite examples—proceed to 3.9; otherwise, proceed to 4.0.
- 3.9^{S,Q} specify file name:**
 Enter an appropriate file name. If the specified file does not already exist in the present directory, proceed to 4.0. If the specified file does exist already, proceed to 4.0 if your computing environment permits file overwrites; if it does not, you will be informed “**nonexistent file or invalid specifications... try again**”, and query 3.9 will be repeated.
- 4.0^{S,Q} specify name for tabulated output file:**
 Enter an appropriate file name. If the specified file does not exist already in the present directory (or your system permits file overwrites), proceed to 4.1 unless you specified the *unequal-increment table option* (query 2.9), in which instance proceed to 5.0. If the specified file does exist already and your system does not permit

overwrites, you will be informed "nonexistent file or invalid specifications . . . try again", and query 4.0 will be repeated.

4.1 specify option for x-y plot files:

logK, G, H, S, Cp, and V of reaction:

1 = do not generate plot files

2 = generate plot files in generic format

3 = generate plot files in KaleidaGraph format

Specifying "1" requests that x-y plot files not be generated; proceed to 5.0. Specifying "2" requests that "generic"-format x-y plot files be generated; with minor post-execution editing, these files may be interfaced with a variety of two-dimensional graphics packages. If you specify "2" and this run involves calculation of univariant equilibria, proceed 4.2; if it does not, proceed to 4.3. Specifying "3" requests that "KaleidaGraph"-format x-y plot files be generated; these may be interfaced directly with the KaleidaGraph graphics package on Apple Macintosh systems. If you specify "3" and this run involves calculation of univariant equilibria, proceed to 4.4; if it involves calculations along the H₂O vaporization boundary, proceed to 4.5; if it involves calculations within the single-phase regions of H₂O, proceed to 4.6.

4.2^s specify prefix for name of the x-y plot file

suffix will be ".uxy"

Enter an appropriate prefix; only the first 16 characters of this prefix will be used. If the specified file does not exist already in the present directory (or your system permits file overwrites), proceed to 5.0. If the file does exist already and your system does not permit overwrites, you will be informed "nonexistent file or invalid specifications . . . try again", and query 4.2 will be repeated.

4.3^s specify prefix for names of x-y plot files

suffix will be ".[d,[2],k,g,h,s,c,v]xy"

Enter an appropriate prefix; only the first 16 characters of this prefix will be used. If each of the specified files does not exist already in the present directory (or your system permits file overwrites), proceed to 5.0. If one or more of these files does exist already and your system does not permit overwrites, you will be informed "nonexistent file or invalid specifications . . . try again", and query 4.3 will be repeated.

4.4^s specify prefix for names of x-y plot files

suffix will be "R# #.uxy"

"R# #" refers to the sequence "R01" . . . "R[n-reac]". Enter an appropriate prefix; only the first 13 characters of this prefix will be used. If each of the specified files

does not exist already in the present directory (or your system permits file overwrites), proceed to 5.0. If one or more of these files does exist already and your system does not permit overwrites, you will be informed "nonexistent file or invalid specifications . . . try again", and query 4.4 will be repeated.

4.5^s specify prefix for names of x-y plot files

suffix will be "R# #.axy"

"R# #" refers to the sequence "R01" . . . "R[n-reac]". Enter an appropriate prefix; only the first 13 characters of this prefix will be used. If each of the specified files does not exist already in the present directory (or your system permits file overwrites), proceed to 5.0. If one or more of these files does exist already and your system does not permit overwrites, you will be informed "nonexistent file or invalid specifications . . . try again", and query 4.5 will be repeated.

4.6^s specify prefix for names of x-y plot files

suffix will be "R# #.[d,[2],k,g,h,s,c,v]xy"

"R# #" refers to the sequence "R01" . . . "R[n-reac]". Enter an appropriate prefix; only the first 13 characters of this prefix will be used. If each of the specified files does not exist already in the present directory (or your system permits file overwrites), proceed to 5.0. If one or more of these files does exist already and your system does not permit overwrites, you will be informed "nonexistent file or invalid specifications . . . try again", and query 4.6 will be repeated.

5.0^{s,q} execution in progress . . .

No response required; this message simply indicates that the requested calculations are underway. The following messages report progression through these calculations. If one or more of the specified reactions contains H₂O or aqueous species—as in the situation of the skarn example, proceed to 5.1; otherwise—as in the situation of the quartz-coesite example, proceed to 5.2.

5.1^s calculating H₂O properties . . .

Proceed to 5.2.

5.2^{s,q} calculating properties for reaction i-reac of n-reac . . .

This message is repeated for i-reac = 1 . . . n-reac. Afterwards, proceed to 5.3.

5.3^{s,q} . . . execution completed.

If the preceding session is executed for the skarn or quartz-coesite examples, the CON, RXN, TAB, and PLT files generated should be identical—other than differences in descriptive reaction titles and filenames—to those given in Appendices 5-8.

APPENDIX 5

Example CON Files

5.1. The Skarn example

The CON file generated by following the skarn example during the interactive session with SUPCRT92 (Appendix 4). (Because the default P-T grid was used in this example, no CON file actually was generated during this session. However, the file illustrated, which can be generated easily by the interested reader, contains the identical parameter and variable settings that define the default P-T grid.) The associated RXN, TAB, and PLT files are contained in Appendices 6.1, 7.1, and 8.1.

```

Line 1 (free format): isat, iopt, iplot, univar, noninc
Line 2 (free format): isomin, isomax, isoinc
Line 3 (free format): v2min, v2max, v2inc
*****
      0      2      1      0      0
500.000000000000      5000.000000000000      500.000000000000
0.0000000000000000      1000.000000000000      100.000000000000

```


5.2. The quartz-coesite example

The CON file generated by following the quartz-coesite example during the interactive session with SUPCRT92 (Appendix 4). The associated RXN, TAB, and PLT files are contained in Appendices 6.2, 7.2, and 8.2.

```

Line 1 (free format): isat, iopt, iplot, univar, noninc
Line 2 (free format): isomin, isomax, isoinc
Line 3 (free format): Kmin, Kmax, Kinc
Line 4 (free format): v2min, v2max
  0  2  1  1  0
25000.000000000000      35000.000000000000      2500.000000000000
0.0000000000000000      0.0000000000000000      0.0000000000000000
350.00000000000000      1400.000000000000

```

APPENDIX 6

Example RXN Files

6.1. The Skarn example

The RXN file generated by following the skarn example during the interactive session with SUPCRT92 (Appendix 4). The associated CON, TAB, and PLT files are given in Appendices 5.1, 7.1, and 8.1.

```

Line 1: nreac, iwet          (free format)
Line 2: [blank]             (free format)
Line 3: descriptive title   (a80)
Line 4: nm, na, ng, nw      (free format)
nm Lines: coeff mname mform (1x,f9.3,2x,a20,2x,a30)
ng Lines: coeff aname aform (1x,f9.3,2x,a20,2x,a30)
na Lines: coeff gname gform (1x,f9.3,2x,a20,2x,a30)
[1 Line:  coeff H2O   H2O]  (1x,f9.3,2x,a20,2x,a30)

*** each of the nreac reaction blocks
*** contains 3+nm+ng+na+nw lines

*****

  1  1

skarn reaction
  4  3  1  1
-1.000 ANDRADITE          Ca3Fe2Si3O12
 3.000 QUARTZ             SiO2
 3.000 CALCITE            CaCO3
 2.000 CHALCOPYRITE      CuFeS2
-4.000 H2S,aq            H2S(0)
-2.000 Cu+                Cu(+)
 2.000 H+                  H(+)
-3.000 CO2,g             CARBON-DIOXIDE
 3.000 H2O                 H2O

```

6.2. The quartz-coesite example

The RXN file generated by following the quartz-coesite example during the interactive session with SUPCRT92 (Appendix 4). The associated CON, TAB, and RXN files are given in Appendices 5.2, 7.2, and 8.2.

```

Line 1: nreac, iwet          (free format)
Line 2: [blank]              (free format)
Line 3: descriptive title    (a80)
Line 4: nm, na, ng, nw      (free format)
nm Lines: coeff mname mform (1x,f9.3,2x,a20,2x,a30)
ng Lines: coeff aname aform (1x,f9.3,2x,a20,2x,a30)
na Lines: coeff gname gform (1x,f9.3,2x,a20,2x,a30)
[l Line:  coeff H2O  H2O]    (1x,f9.3,2x,a20,2x,a30)

*** each of the nreac reaction blocks
*** contains 3+nm+ng+na+nw lines

*****
1 0

quartz--coesite equilibrium
  2 0 0 0
  -1.000 COESITE          SiO2
   1.000 QUARTZ           SiO2

```

APPENDIX 7

Example TAB Files

7.1. The Skarn example

The TAB file generated by following the skarn example during the interactive session with SUPCRT92 (Appendix 4). The associated CON, RXN, and PLT files are found in Appendices 5.1, 6.1, and 8.1. Because the default P - T grid specified in the CON file extends from 0 to 1000°C and 500 to 5000 bar and the skarn reaction contains minerals that do and do not undergo phase transitions, charged and neutral aqueous species, a gas, and H₂O, this TAB file illustrates virtually every type of information that may appear on such a file cast in P - T coordinates.

7.2. The quartz-coesite example

The TAB file generated by following the quartz-coesite example during the interactive session with SUPCRT92 (Appendix 4). The associated CON, RXN, and PLT files are contained in Appendices 5.2, 6.2, and 8.2. Results tabulated on this file may be compared with those depicted graphically by Helgeson and others (1978, fig. 19).

Appendices 7.1-7.2 follow

```

***** SUPCRT92: input/output specifications for this run
      USER-SPECIFIED CON FILE containing
      T-P-D grid & option switches: file not saved
      USER-SPECIFIED RXN FILE containing
      chemical reactions: skarn.rxn
      THERMODYNAMIC DATABASE: dprons92.dat
      SUPCRT-GENERATED TAB FILE containing
      tabulated reaction properties (this file): skdefl.tab
      SUPCRT-GENERATED PLOT FILES containing
      reaction properties for x-y plots: skdefl.kxy      etc.

***** summary of option switches
      isat, iopt, iplot, univar, noninc:  0 2 1 0 0

***** summary of state conditions
      ISOBARS (bars) : min, max, increment:  500.0000 5000.0000 500.0000
      TEMP (degC) range: min, max, increment:   0.0000 1000.0000 100.0000

***** REACTION 1 ***** REACTION 1 *****
REACTION TITLE:
      skarn reaction

REACTION STOICHIOMETRY:

```

COEFF.	NAME	FORMULA
-1.000	ANDRADITE	Ca3Fe2Si3O12
-3.000	CARBON-DIOXIDE	CO2,g
-4.000	H2S,aq	H2S(0)
-2.000	Cu+	Cu(+)
3.000	QUARTZ	SiO2
3.000	CALCITE	CaCO3
2.000	CHALCOPYRITE	CuFeS2
2.000	H+	H(+)
3.000	H2O	H2O

STANDARD STATE PROPERTIES OF THE SPECIES AT 25 DEG C AND 1 BAR

..... MINERALS

NAME	DELTA G (cal/mol)	DELTA H (cal/mol)	S (cal/mol/K)	V (cc/mol)	Cp (cal/mol/K)
ANDRADITE	-1296819.	-1380345.	70.130	131.850	83.4
QUARTZ	-204646.	-217650.	9.880	22.688	10.6
CALCITE	-269880.	-288552.	22.150	36.934	19.6
CHALCOPYRITE	-44900.	-44453.	31.150	42.830	23.1

MAIER-KELLY COEFFICIENTS

PHASE TRANSITION DATA

NAME	a(10**0)	b(10**3)	c(10**5)	T limit (C)	Htr (cal/mol)	Vtr (cc/mol)	dPdttr (bar/K)
ANDRADITE	113.532	15.636	-30.889	826.85			
QUARTZ	11.220	8.200	-2.700	574.85	290.	0.372	38.500
post-transition 1	14.410	1.940	0.000	1726.85			
CALCITE	24.980	5.240	-6.200	926.85			
CHALCOPYRITE	20.790	12.800	-1.340	556.85	2405.		
post-transition 1	-141.400	210.000	0.000	656.85	0.		
post-transition 2	41.220	0.000	0.000	926.85			

..... GASES

NAME	DELTA G (cal/mol)	DELTA H (cal/mol)	S (cal/mol/K)	V (cc/mol)	Cp (cal/mol/K)
CO2,g	-94254.	-94051.	51.085	0.	8.9

MAIER-KELLY COEFFICIENTS

NAME	a(10**0)	b(10**3)	c(10**5)	T limit (C)
CO2,g	10.570	2.100	-2.060	2226.85

..... AQUEOUS SPECIES

NAME	DELTA G (cal/mol)	DELTA H (cal/mol)	S (cal/mol/K)	V (cc/mol)	Cp (cal/mol/K)

H2S,aq	-6673.	-9001.	30.000	35.0	42.8
Cu+	11950.	17132.	9.700	-8.1	13.7
H+	0.	0.	0.000	0.0	0.0
H2O	-56688.	-68317.	16.712	18.1	18.0

EQUATION-OF-STATE COEFFICIENTS

NAME	a1(10**1)	a2(10**2)	a3(10**0)	a4(10**4)	c1(10**0)	c2(10**4)	omega(10**5)
H2S,aq	6.5097	6.7724	5.9646	-3.0590	32.3000	4.7300	-0.1000
Cu+	0.7835	-5.8682	8.0565	-2.5364	17.2831	-0.2439	0.3351
H+	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

STANDARD STATE PROPERTIES OF THE REACTION AT 25 DEG C AND 1 BAR

PRES (bars)	TEMP (degC)	DH2O (g/cc)	LOG K	DELTA G (cal)	DELTA H (cal)	DELTA S (cal/K)	DELTA V (cc)	DELTA Cp (cal/K)
1.000	25.000	0.997	74.084	-101068.	-148224.	-154.3	63.3	-118.0

STANDARD STATE PROPERTIES OF THE REACTION AT ELEVATED TEMPERATURES AND PRESSURES

PRES (bars)	TEMP (degC)	DH2O (g/cc)	LOG K	DELTA G (cal)	DELTA H (cal)	DELTA S (cal/K)	DELTA V (cc)	DELTA Cp (cal/K)
500.000	0.000	1.024	83.189	-103974.	-142570.	-137.0	64.4	-234.9
500.000	100.000	0.980	51.487	-87909.	-154949.	-176.5	57.4	-91.8
500.000	200.000	0.897	31.958	-69188.	-163355.	-196.6	62.5	-78.3
500.000	300.000	0.777	18.597	-48772.	-171046.	-211.3	75.5	-79.3
500.000	400.000	0.578	8.563	-26374.	*** DELTA G ONLY (CHARGED AQUEOUS SPECIES) ***			
500.000	500.000	0.257	*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***					
500.000	587.811	0.170	PHASE TRANSITION #1 for QUARTZ					
500.000	556.850	0.190	PHASE TRANSITION #1 for CHALCOPYRITE					

500.000	0.164	600.000	0.164	*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***					
500.000	0.142	656.850	0.142	PHASE TRANSITION #2 for CHALCOPYRITE					
500.000	0.130	700.000	0.130	*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***					
500.000	0.110	800.000	0.110	*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***					
500.000	0.097	900.000	0.097	*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***					
500.000	0.087	1000.000	0.087	*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***					
1000.000	1.045	0.000	1.045	82.602	-103240.	-141088.	-134.3	58.8	-271.6
1000.000	1.000	100.000	1.000	51.087	-87227.	-154373.	-176.8	56.8	-94.6
1000.000	0.924	200.000	0.924	31.615	-68445.	-163037.	-197.5	61.8	-80.9
1000.000	0.823	300.000	0.823	18.269	-47912.	-170999.	-212.7	69.6	-81.5
1000.000	0.693	400.000	0.693	8.415	-25919.	-180218.	-227.5	67.0	-110.3
1000.000	0.528	500.000	0.528	0.625	-2213.	-195250.	-248.2	-19.1	-191.5
1000.000	0.434	556.850	0.434	PHASE TRANSITION #1 for CHALCOPYRITE					
1000.000	0.374	600.000	0.374	-5.879	23486.	-207241.	-282.9	-231.2	TRANSITION
1000.000	0.373	600.798	0.373	PHASE TRANSITION #1 for QUARTZ					
1000.000	0.315	656.850	0.315	PHASE TRANSITION #2 for CHALCOPYRITE					
1000.000	0.282	700.000	0.282	*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***					
1000.000	0.231	800.000	0.231	*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***					
1000.000	0.198	900.000	0.198	*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***					
1000.000	0.176	1000.000	0.176	*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***					
1500.000	1.064	0.000	1.064	82.061	-102564.	-140135.	-133.3	54.5	-287.6
1500.000	1.017	100.000	1.017	50.692	-86553.	-153846.	-177.2	56.1	-96.3
1500.000	0.946	200.000	0.946	31.275	-67711.	-162683.	-198.3	61.2	-82.7
1500.000	0.858	300.000	0.858	17.954	-47086.	-170689.	-213.6	68.6	-79.2

1500.000	400.000	0.751	8.136	-25060.	-178818.	-226.7	74.3	-84.5
1500.000	500.000	0.630	0.499	-1766.	-187907.	-239.3	65.3	-99.1
1500.000	556.850	0.559						
1500.000	600.000	0.508	-5.650	22575.	-194151.	-246.9	17.9	TRANSITION
1500.000	613.785	0.493						
1500.000	656.850	0.448						
1500.000	700.000	0.410	-10.665	47489.	-200263.	-253.4	-68.6	-73.7
1500.000	800.000	0.341						
1500.000	900.000	0.293						
1500.000	1000.000	0.259						
2000.000	0.000	1.081	81.558	-101935.	-139584.	-133.6	51.0	-287.9
2000.000	100.000	1.033	50.301	-85886.	-153358.	-177.7	55.5	-97.2
2000.000	200.000	0.966	30.939	-66983.	-162307.	-199.0	60.6	-84.0
2000.000	300.000	0.886	17.644	-46273.	-170401.	-214.5	67.5	-79.0
2000.000	400.000	0.793	7.847	-24168.	-178273.	-227.2	74.5	-78.7
2000.000	500.000	0.691	0.252	-891.	-186145.	-238.1	77.7	-79.0
2000.000	556.850	0.633						
2000.000	600.000	0.590	-5.801	23177.	-189654.	-242.4	70.2	-63.3
2000.000	626.772	0.564						
2000.000	656.850	0.537						
2000.000	700.000	0.500	-10.668	47504.	-193208.	-246.2	47.8	-56.5
2000.000	800.000	0.429	-14.738	72371.	-197946.	-250.8	13.4	-37.8
2000.000	900.000	0.374						
2000.000	900.000	0.374	-18.182	97598.	-200935.	-253.5	-19.7	-23.8

*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***

*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***

*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***

PHASE TRANSITION #1 for CHALCOPYRITE

PHASE TRANSITION #1 for QUARTZ

PHASE TRANSITION #2 for CHALCOPYRITE

*** CAUTION: BEYOND T LIMIT OF CP COEFFS FOR A MINERAL OR GAS ***

*** BEYOND RANGE OF APPLICABILITY OF AQUEOUS SPECIES EQNS ***										
2000.000	1000.000	0.333								
2500.000	0.000	1.096	81.084	-101343.	-139346.	-134.9	48.1			-276.1
2500.000	100.000	1.048	49.915	-85226.	-152904.	-178.2	54.9			-97.3
2500.000	200.000	0.984	30.606	-66262.	-161916.	-199.7	60.0			-85.1
2500.000	300.000	0.910	17.339	-45473.	-170098.	-215.4	66.5			-79.4
2500.000	400.000	0.826	7.559	-23283.	-177913.	-228.0	73.6			-77.0
2500.000	500.000	0.736	-0.015	53.	-185443.	-238.4	79.6			-73.4
2500.000	556.850	0.685			PHASE TRANSITION #1 for CHALCOPYRITE					
2500.000	600.000	0.648	-6.034	24107.	-188126.	-241.7	82.5			-52.8
2500.000	639.759	0.614			PHASE TRANSITION #1 for QUARTZ					
2500.000	656.850	0.600			PHASE TRANSITION #2 for CHALCOPYRITE					
2500.000	700.000	0.566	-10.851	48317.	-190606.	-244.3	81.5			-48.4
2500.000	800.000	0.497	-14.861	72976.	-195032.	-248.7	76.1			-40.5
2500.000	900.000	0.442			*** CAUTION: BEYOND T LIMIT OF CP COEFFS FOR A MINERAL OR GAS ***					
2500.000	900.000	0.442	-18.260	98017.	-198889.	-252.1	73.1			-38.1
2500.000	1000.000	0.397	-21.181	123390.	-202940.	-255.4	77.6			-44.3
3000.000	0.000	1.109	80.636	-100783.	-139358.	-137.0	45.7			-254.8
3000.000	100.000	1.062	49.533	-84573.	-152477.	-178.9	54.4			-97.0
3000.000	200.000	1.001	30.276	-65548.	-161514.	-200.4	59.5			-85.8
3000.000	300.000	0.931	17.038	-44684.	-169775.	-216.2	65.5			-80.0
3000.000	400.000	0.854	7.276	-22411.	-177598.	-228.8	72.3			-76.6
3000.000	500.000	0.773	-0.283	1002.	-185033.	-239.1	79.0			-71.7
3000.000	556.850	0.727			PHASE TRANSITION #1 for CHALCOPYRITE					

3000.000	600.000	0.693	-6.286	25112.	-187481.	-242.1	85.0	-49.9	
3000.000	652.746	0.652		PHASE TRANSITION #1 for QUARTZ					
3000.000	656.850	0.649		PHASE TRANSITION #2 for CHALCOPYRITE					
3000.000	700.000	0.618	-11.085	49359.	-189646.	-244.4	90.9	-46.7	
3000.000	800.000	0.553	-15.075	74025.	-194127.	-248.8	95.5	-43.6	
3000.000	900.000	0.497	*** CAUTION: BEYOND T LIMIT OF CP COEFFS FOR A MINERAL OR GAS ***						
3000.000	900.000	0.497	-18.462	99102.	-198564.	-252.7	102.6	-46.2	
3000.000	1000.000	0.452	-21.385	124578.	-203567.	-256.8	113.6	-54.5	
3500.000	0.000	1.121	80.208	-100248.	-139573.	-139.7	43.7	-225.6	
3500.000	100.000	1.076	49.154	-83926.	-152073.	-179.5	53.8	-96.2	
3500.000	200.000	1.016	29.949	-64840.	-161106.	-201.0	59.0	-86.2	
3500.000	300.000	0.950	16.742	-43906.	-169430.	-217.0	64.7	-80.6	
3500.000	400.000	0.878	6.998	-21555.	-177285.	-229.6	71.1	-76.6	
3500.000	500.000	0.804	-0.548	1939.	-184710.	-239.9	77.8	-71.5	
3500.000	556.850	0.761	PHASE TRANSITION #1 for CHALCOPYRITE						
3500.000	600.000	0.730	-6.539	26127.	-187121.	-242.9	84.5	-49.5	
3500.000	665.733	0.683	PHASE TRANSITION #1 for QUARTZ						
3500.000	656.850	0.689	PHASE TRANSITION #2 for CHALCOPYRITE						
3500.000	700.000	0.660	-11.332	50459.	-189235.	-245.1	92.5	-47.4	
3500.000	800.000	0.598	-15.315	75203.	-193890.	-249.7	100.2	-46.4	
3500.000	900.000	0.544	*** CAUTION: BEYOND T LIMIT OF CP COEFFS FOR A MINERAL OR GAS ***						
3500.000	900.000	0.544	-18.700	100383.	-198691.	-253.9	109.7	-50.5	
3500.000	1000.000	0.499	-21.628	125996.	-204114.	-258.4	121.1	-58.4	
4000.000	0.000	1.132	79.799	-99737.	-139957.	-143.0	41.9	-189.6	

4000.000	100.000	1.088	48.779	-83286.	-151690.	-180.2	53.3	-95.1	
4000.000	200.000	1.030	29.625	-64137.	-160693.	-201.6	58.6	-86.4	
4000.000	300.000	0.967	16.449	-43138.	-169067.	-217.7	63.9	-81.1	
4000.000	400.000	0.900	6.724	-20712.	-176961.	-230.4	69.9	-76.9	
4000.000	500.000	0.830	-0.809	2860.	-184407.	-240.7	76.3	-71.7	
4000.000	556.850	0.791							
				PHASE TRANSITION #1 for CHALCOPYRITE					
4000.000	600.000	0.761	-6.790	27129.	-186848.	-243.7	83.1	-50.0	
4000.000	678.720	0.710							
				PHASE TRANSITION #1 for QUARTZ					
4000.000	656.850	0.724							
				PHASE TRANSITION #2 for CHALCOPYRITE					
4000.000	700.000	0.696	-11.579	51561.	-188987.	-246.0	91.6	TRANSITION	
4000.000	800.000	0.637	-15.559	76400.	-193812.	-250.7	99.7	-48.5	
4000.000	900.000	0.585							
				*** CAUTION: BEYOND T LIMIT OF CP COEFFS FOR A MINERAL OR GAS ***					
4000.000	900.000	0.585	-18.945	101694.	-198820.	-255.2	109.0	-52.3	
4000.000	1000.000	0.540	-21.875	127436.	-204360.	-259.7	119.0	-58.7	
4500.000	0.000	1.143	79.406	-99245.	-140482.	-146.7	40.4	-148.8	
4500.000	100.000	1.100	48.408	-82652.	-151325.	-180.9	52.8	-93.7	
4500.000	200.000	1.044	29.303	-63440.	-160277.	-202.2	58.1	-86.5	
4500.000	300.000	0.984	16.159	-42379.	-168686.	-218.3	63.2	-81.6	
4500.000	400.000	0.920	6.455	-19883.	-176622.	-231.1	68.8	-77.2	
4500.000	500.000	0.854	-1.064	3764.	-184099.	-241.5	74.9	-72.1	
4500.000	556.850	0.817							
				PHASE TRANSITION #1 for CHALCOPYRITE					
4500.000	600.000	0.789	-7.037	28113.	-186591.	-244.6	81.5	-50.7	
4500.000	691.707	0.733							
				PHASE TRANSITION #1 for QUARTZ					
4500.000	656.850	0.754							
				PHASE TRANSITION #2 for CHALCOPYRITE					

4500.000	700.000	0.728	-11.823	52645.	-188764.	-246.9	89.7	TRANSITION	
4500.000	800.000	0.671	-15.799	77579.	-193719.	-251.7	97.4	-49.7	
4500.000	900.000	0.621	*** CAUTION: BEYOND T LIMIT OF CP COEFFS FOR A MINERAL OR GAS ***						
4500.000	900.000	0.621	-19.184	102979.	-198815.	-256.3	105.8	-52.6	
4500.000	1000.000	0.576	-22.114	128829.	-204296.	-260.7	113.9	-57.1	
5000.000	0.000	*** BEYOND RANGE OF APPLICABILITY OF H2O EQUATION OF STATE **							
5000.000	100.000	1.111	48.039	-82023.	-150975.	-181.7	52.4	-92.0	
5000.000	200.000	1.056	28.983	-62748.	-159861.	-202.8	57.7	-86.4	
5000.000	300.000	0.999	15.873	-41628.	-168290.	-219.0	62.5	-82.1	
5000.000	400.000	0.938	6.190	-19067.	-176266.	-231.8	67.8	-77.5	
5000.000	500.000	0.876	-1.315	4651.	-183777.	-242.2	73.6	-72.5	
5000.000	556.850	0.841	PHASE TRANSITION #1 for CHALCOPYRITE						
5000.000	600.000	0.815	-7.278	29076.	-186320.	-245.4	79.8	-51.4	
5000.000	656.850	0.781	PHASE TRANSITION #2 for CHALCOPYRITE						
5000.000	700.000	0.756	-12.089	53829.	-190406.	-249.8	86.5	TRANSITION	
5000.000	704.694	0.753	PHASE TRANSITION #1 for QUARTZ						
5000.000	800.000	0.702	-16.033	78727.	-193557.	-252.6	94.7	-50.4	
5000.000	900.000	0.653	*** CAUTION: BEYOND T LIMIT OF CP COEFFS FOR A MINERAL OR GAS ***						
5000.000	900.000	0.653	-19.415	104220.	-198657.	-257.2	101.9	-51.9	
5000.000	1000.000	0.609	-22.342	130157.	-203967.	-261.5	108.4	-54.3	

**** SUPCRT92: input/output specifications for this run

USER-SPECIFIED CON FILE containing
T-P-D grid & option switches: qcgett.con

USER-SPECIFIED RXN FILE containing
chemical reactions: qc.rxn

THERMODYNAMIC DATABASE: dprons92.dat

SUPCRT-GENERATED TAB FILE containing
tabulated reaction properties (this file): qcgett.tab

SUPCRT-GENERATED PLT FILES containing
reaction properties for x-y plots: qcgett.uxy etc.

**** summary of option switches

isat, iopt, iplot, univar, noninc: 0 2 1 1 0

**** summary of state conditions

ISOBARS (bars) : min, max, increment: 25000.0000 35000.0000 2500.0000
TEMP (degC) range: min, max, increment: 350.0000 1400.0000 0.0000

***** REACTION 1 *****

REACTION TITLE:

quartz--coesite equilibrium

REACTION STOICHIOMETRY:

COEFF.	NAME	FORMULA
-1.000	COESITE	SiO2
1.000	QUARTZ	SiO2

STANDARD STATE PROPERTIES OF THE SPECIES AT 25 DEG C AND 1 BAR

..... MINERALS

NAME	DELTA G (cal/mol)	DELTA H (cal/mol)	S (cal/mol/K)	V (cc/mol)	Cp (cal/mol/K)
COESITE	-203541.	-216614.	9.650	20.641	10.4
QUARTZ	-204646.	-217650.	9.880	22.688	10.6

NAME	MAIER-KELLY COEFFICIENTS				PHASE TRANSITION DATA			
	a (10**0)	b (10**3)	c (10**5)	T limit (C)	Htr (cal/mol)	Vtr (cc/mol)	dEdTtr (bar/K)	
COESITE	11.000	8.200	-2.700	574.85				
post-transition 1	14.190	1.940	0.000	1726.85				
QUARTZ	11.220	8.200	-2.700	574.85	290.	0.372		38.500
post-transition 1	14.410	1.940	0.000	1726.85				
STANDARD STATE PROPERTIES OF THE REACTION AT 25 DEG C AND 1 BAR								
PRES (bars)	TEMP (degC)	DH20 (g/cc)	LOG K	DELTA G (cal)	DELTA H (cal)	DELTA S (cal/K)	DELTA V (cc)	DELTA Cp (cal/K)
1.000	25.000	0.000	0.810	-1105.	-1036.	0.2	2.0	0.2
STANDARD STATE PROPERTIES OF THE REACTION AT ELEVATED TEMPERATURES AND PRESSURES								
PRES (bars)	TEMP (degC)	DH20 (g/cc)	LOG K	DELTA G (cal)	DELTA H (cal)	DELTA S (cal/K)	DELTA V (cc)	DELTA Cp (cal/K)
25000.000	384.651	0.000						
25000.000	384.651	0.000	0.000	0.	266.	0.4	2.0	0.2
27500.000	659.673	0.000						
27500.000	659.673	0.000	0.000	0.	449.	0.5	2.0	0.2
30000.000	900.841	0.000						
30000.000	900.841	0.000	0.000	0.	624.	0.5	2.0	0.2
32500.000	1122.781	0.000						
32500.000	1122.781	0.000	0.000	0.	796.	0.6	2.0	0.2
35000.000	1331.746	0.000						
35000.000	1331.746	0.000	0.000	0.	964.	0.6	2.0	0.2

APPENDIX 8

Example PLT Files

8.1. The Skarn example

The PLT file for logk generated by following the skarn example during the interactive session with SUPCRT92 (Appendix 4). The associated CON, RXN, and TAB files are given in Appendices 5.1, 6.1, and 7.1.

```

***** SUPCRT92: input/output specifications for this run

      USER-SPECIFIED CON FILE containing
      T-P-D grid & option switches: file not saved

      USER-SPECIFIED RXN FILE containing
      chemical reactions: skarn.rxn

      THERMODYNAMIC DATABASE: dprons92.dat

      SUPCRT-GENERATED TAB FILE containing
      tabulated reaction properties: skdefl.tab

***** summary of option switches

      isat, iopt, iplot, univar, noninc:  0  2  1  0  0

***** summary of state conditions

      ISOBARS (bars) : min, max, increment:  500.0000  5000.0000  500.0000
      TEMP(degC) range: min, max, increment:    0.0000  1000.0000  100.0000

*****
REACTION 1
TITLE: skarn reaction

PRES (bars) = 500.0000 ; TEMP (degC), logK

0.0000000E+00  0.8318938E+02
0.1000000E+03  0.5148657E+02
0.2000000E+03  0.3195784E+02
0.3000000E+03  0.1859725E+02
0.4000000E+03  0.8562579E+01

PRES (bars) = 1000.0000 ; TEMP (degC), logK

0.0000000E+00  0.8260168E+02
0.1000000E+03  0.5108702E+02
0.2000000E+03  0.3161467E+02
0.3000000E+03  0.1826934E+02
0.4000000E+03  0.8414890E+01
0.5000000E+03  0.6254935E+00
0.6000000E+03 -0.5878577E+01

PRES (bars) = 1500.0000 ; TEMP (degC), logK

0.0000000E+00  0.8206100E+02
0.1000000E+03  0.5069201E+02
0.2000000E+03  0.3127526E+02
0.3000000E+03  0.1795423E+02
0.4000000E+03  0.8136037E+01
0.5000000E+03  0.4990846E+00
0.6000000E+03 -0.5650317E+01
0.7000000E+03 -0.1066498E+02

PRES (bars) = 2000.0000 ; TEMP (degC), logK

0.0000000E+00  0.8155750E+02
0.1000000E+03  0.5030137E+02
0.2000000E+03  0.3093922E+02
0.3000000E+03  0.1764413E+02

```

```

0.4000000E+03  0.7846569E+01
0.5000000E+03  0.2518584E+00
0.6000000E+03 -0.5801115E+01
0.7000000E+03 -0.1066822E+02
0.8000000E+03 -0.1473834E+02
0.9000000E+03 -0.1818154E+02

```

PRES (bars) = 2500.0000 ; TEMP (degC), logK

```

0.0000000E+00  0.8108413E+02
0.1000000E+03  0.4991494E+02
0.2000000E+03  0.3060632E+02
0.3000000E+03  0.1733897E+02
0.4000000E+03  0.7559095E+01
0.5000000E+03 -0.1503362E-01
0.6000000E+03 -0.6033799E+01
0.7000000E+03 -0.1085078E+02
0.8000000E+03 -0.1486140E+02
0.9000000E+03 -0.1825963E+02
0.1000000E+04 -0.2118084E+02

```

PRES (bars) = 3000.0000 ; TEMP (degC), logK

```

0.0000000E+00  0.8063570E+02
0.1000000E+03  0.4953252E+02
0.2000000E+03  0.3027635E+02
0.3000000E+03  0.1703834E+02
0.4000000E+03  0.7276096E+01
0.5000000E+03 -0.2833062E+00
0.6000000E+03 -0.6285514E+01
0.7000000E+03 -0.1108486E+02
0.8000000E+03 -0.1507510E+02
0.9000000E+03 -0.1846177E+02
0.1000000E+04 -0.2138476E+02

```

PRES (bars) = 3500.0000 ; TEMP (degC), logK

```

0.0000000E+00  0.8020831E+02
0.1000000E+03  0.4915394E+02
0.2000000E+03  0.2994917E+02
0.3000000E+03  0.1674179E+02
0.4000000E+03  0.6997953E+01
0.5000000E+03 -0.5482306E+00
0.6000000E+03 -0.6539446E+01
0.7000000E+03 -0.1133194E+02
0.8000000E+03 -0.1531497E+02
0.9000000E+03 -0.1870038E+02
0.1000000E+04 -0.2162826E+02

```

PRES (bars) = 4000.0000 ; TEMP (degC), logK

```

0.0000000E+00  0.7979904E+02
0.1000000E+03  0.4877900E+02
0.2000000E+03  0.2962466E+02
0.3000000E+03  0.1644895E+02
0.4000000E+03  0.6724487E+01
0.5000000E+03 -0.8085268E+00
0.6000000E+03 -0.6790337E+01
0.7000000E+03 -0.1157938E+02
0.8000000E+03 -0.1555880E+02
0.9000000E+03 -0.1894463E+02
0.1000000E+04 -0.2187541E+02

```

PRES (bars) = 4500.0000 ; TEMP (degC), logK

```
0.000000E+00 0.7940559E+02
0.100000E+03 0.4840753E+02
0.200000E+03 0.2930269E+02
0.300000E+03 0.1615949E+02
0.400000E+03 0.6455374E+01
0.500000E+03 -0.1063996E+01
0.600000E+03 -0.7036529E+01
0.700000E+03 -0.1182282E+02
0.800000E+03 -0.1579887E+02
0.900000E+03 -0.1918397E+02
0.100000E+04 -0.2211448E+02
```

PRES (bars) = 5000.0000 ; TEMP (degC), logK

```
0.100000E+03 0.4803939E+02
0.200000E+03 0.2898317E+02
0.300000E+03 0.1587311E+02
0.400000E+03 0.6190271E+01
0.500000E+03 -0.1314811E+01
0.600000E+03 -0.7277640E+01
0.700000E+03 -0.1208865E+02
0.800000E+03 -0.1603269E+02
0.900000E+03 -0.1941519E+02
0.100000E+04 -0.2234244E+02
```


8.2. The quartz-coesite example

The PLT file generated by following the quartz-coesite example during the interactive session with SUPCRT92 (Appendix 4). The associated CON, RXN, and TAB files are given in Appendices 5.2, 6.2, and 7.2.

```
***** SUPCRT92: input/output specifications for this run

      USER-SPECIFIED CON FILE containing
      T-P-D grid & option switches: qcgett.con

      USER-SPECIFIED RXN FILE containing
      chemical reactions: qc.rxn

      THERMODYNAMIC DATABASE: dprons92.dat

      SUPCRT-GENERATED TAB FILE containing
      tabulated reaction properties: qcgett.tab

***** summary of option switches

      isat, iopt, iplot, univar, noninc:  0  2  1  1  0

***** summary of state conditions

      ISOBARS (bars) : min, max, increment:  25000.0000  35000.0000  2500.0000
      TEMP (degC) range: min, max, increment:   350.0000  1400.0000   0.0000

*****

REACTION 1
TITLE: quartz--coesite equilibrium

LOG K =  0.00000E+00 ; PRES (bars), TEMP (degC) =

0.2500000E+05  0.3846509E+03
0.2750000E+05  0.6596733E+03
0.3000000E+05  0.9008411E+03
0.3250000E+05  0.1122781E+04
0.3500000E+05  0.1331746E+04
```