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TECHNICAL REPORT 91-17

NAGRA THERMOCHEMICAL DATA BASE

I. CORE DATA

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ABSTRACT

A number of geochemical computer models are used within the Nagra programme to calculate speciation in aqueous solutions and the states of mineral-water equilibria. The thermochemical data bases accompanying these modelling programs do not contain identical data and so the programs may give different results. To minimize these differences, a thermochemical data base is being developed for use throughout the Nagra programme.

Nagra thermochemical data will be given in a series of reports, of which this is the first. This report descibes the structure and construction of the data set and includes data for core species and minerals. Core data are for aqueous species, minerals, and gases of elements commonly found in natural waters. The data are considered to be well established. Data for other elements will be included in supplemental report, and may be subject to more frequent change.

This report includes core data for water and its components (H_2O, O_2 and H_2), the halides (F^-, Cl^-, Br^- and I^-), sulphur (SO_4^{2-} and HS^-), nitrogen (NO_3^-, N_2 and NH_4^+), phosphate (PO_4^{3-}), borate ($B(HO)_3^0$), arsenic (AsO_4^{3-}) and As $(OH)_3^0$), carbon (CO_3^{2-}, C^0 and CH_4), the alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}), and the alkaline metals (Li^+, Na^+ and K^+).

ZUSAMMENFASSUNG

Innerhalb des Nagra-Programmes werden für die Berechnung der Speziation in wässriger Lösung und für die Berechnung von Löslichkeitslimiten verschiedene geochemische Computermodelle verwendet. Die diesen Modellen zugehörigen thermodynamischen Datenbasen enthalten teilweise voneinander abweichende Datensätze, die einzelnen Modelle werden deshalb im allgemeinen numerisch verschiedene Resultate liefern. Um solche Differenzen zu minimieren, wurde eine thermodynamische Datenbasis entwickelt, welche im gesamten Nagra-Programm Verwendung finden soll.

Nagra-spezifische thermodynamische Daten sollen in einer Reihe von Berichten publiziert werden, die vorliegende Arbeit ist die erste in dieser Reihe. Der Bericht beschreibt Struktur und Aufbau der Datensätze und enthält die Daten der sogenannten Core-Spezies und -Festphasen. Mit dem Prädikat "core" werden diejenigen Spezies, Minerale und Gase ausgezeichnet, welche hauptsächlich aus den in natürlichen Wässern gefundenen Elemente gebildet werden. Diese Core-Daten sind in weitem Umfeld anerkannt. Daten für andere Elemente werden in den nachfolgenden Berichten zusammengetragen. Diese Daten können in kürzeren zeitlichen Abständen angepasst werden.

Der vorliegende Bericht enthält Core-Daten für Wasser und seine Komponenten (H_2O, O_2 und H_2), Halogenide (F^-, Cl^-, Br^- und I^-), Schwefel (SO_4^{2-} und HS^-), Stickstoff (NO_3^-, N_2 und NH_4^+), Phosphat (PO_4^{3-}), Borat ($B(HO)_3^0$), Arsen (AsO_4^{3-}) und $As(OH)_3^0$), Kohlenstoff (CO_3^{2-}, C^0, und CH_4), Erdalkali-Metalle (Mg^{2+}, Ca^{2+}, Sr^{2+} und Ba^{2+}), und für Alkali-Metalle (Li^+, Na^+ und K^+).

RESUME

La Cédra utilise plusieurs modèles sur ordinateur pour le calcul des espèces chimiques en solution dans les systèmes eau-minéraux à l'équilibre. Les données thermochimiques de base utilisées pour les différents modèles étant différentes, les résultats livrés sont aussi différents. Pour produire des résultats cohérents, la Cédra est en train de développer sa propre base de données.

Les données thermochimiques de la Cédra seront publiées dans une série de rapports, dont celui-ci est le premier. Il décrit la structure et l'assemblage de la base de données. En plus, il comprend les espèces principales, les minéraux ainsi que les gaz des éléments les plus fréquents dans les eaux naturelles. Les données inclues dans ce rapport sont bien établies. Sujettes à de modifications plus fréquentes, les données relatives à d'autres éléments seront publiées dans des rapports complémentaires.

Le présent rapport contient les données fondamentales pour l'eau et ses éléments constitutifs (H_2O, O_2 et H_2), les halogènes (F^-, Cl^-, Br^- et I^-), le soufre (SO_4^{2-} et HS^-), l'azote (NO_3^-, N_2 et NH_4^+), le phospate (PO_4^{3-}), le borate ($B(HO)_3^0$) l'arsenic (AsO_4^{3-}) et $As(OH)_3^0$), le carbone (CO_3^{2-}, C^0 et CH_4), les métaux alcalino-terreux (Mg^{2+}, Ca^{2+}, Sr^{2+} et Ba^{2+}) et les métaux alcalins (Li^+, Na^+ et K^+).

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1   INTRODUCTION

Geochemical models are used in the Nagra programme to support performance assessment, for the interpretation of field hydrochemical data, and for the design and interpretation of laboratory experimental studies. Several geochemical computer programs are used for this modelling. PHREEQE (PARKHURST *et al.* 1985) is used by some investigators at the Paul Scherrer Institut (PSI) and by other Nagra contractors, and is included in RIPP2 (YUSAF & HAMILTON 1990a, b, and c), a program used internally at Nagra. MINEQL (WESTALL *et al.* 1976; SCHWEINGRUBER 1982) is used by other investigators at PSI. EQ3/EQ6 (WOLERY 1983; WOLERY *et al.* 1990) is used in the Departments of Mineralogy and Petrology and of Geology at Bern University.

Two types of data are required for geochemical models. The first describes the system of interest and includes temperature, water chemistry, identity of active minerals, *etc.* The second type is thermochemical data and includes descriptions of reactions among aqueous species, solids, and gases, the equilibrium constants for these reactions as functions of temperature, and formulations for calculating the thermodynamic activity coefficients of aqueous species. Different geochemical models should give virtually identical results for a given system when each is used with an equivalent thermodynamic data base (NORDSTROM *et al.* 1979; INTERA ENVIRONMENTAL CONSULTANTS 1983).

Thermodynamic data bases are supplied with most geochemical modelling programs and frequently are improved and expanded by those using the programs. This leads to differences among the data used for the various programs which, in turn, leads to different results when different programs are used to model the same system.

To minimize differences among the results of geochemical modelling performed for Nagra, it has been decided to standardize the thermochemical data used throughout the programme. Two types of data are distinguished. Core data are those for well-known aqueous species, minerals, and gases of elements commonly found in significant quantities in natural waters. Almost all the ionic strength of most solutions will comprise core species, and core species will also be the most important complexing ligands in most solutions. Because of the importance of core data, every attempt will be made to select only the best values. To assure comparability of the results of modelling undertaken over a period of time, the values for core data will not be changed for at least five years.

The second type of Nagra thermochemical data is supplemental data. These are for less well-known species, minerals, and gases, and are intended for specific types of modelling problems. Supplemental data sets will include species and minerals of such auxiliary elements as silicon (Si), aluminum (Al), iron (Fe), manganese (Mn), and other elements generally present in low concentrations in natural waters. They will also include the actinides and other elements of interest for safety assessment calculations, aqueous species and solids of importance at high pH values, as well as minerals important in the understanding of certain natural analogues. Supplemental data will be subject to more frequent change than will the core data.

Data on mineral and gas solubility and on the behaviour of dissolved entities are used for the type of geochemical modelling carried out within the Nagra programme. Equilibrium constants for the dissolution or formation of minerals and gases are required. Solution data requirements are determined by the conceptual model of solution behaviour that is embodied in the geochemical programs used. Most of the programs used on Nagra problems embody the ion-association model of solution behaviour (GARRELS & CHRIST 1965; WHITFIELD 1979; NORDSTROM & MUNOZ 1985). This model is appropriate for waters of ionic strengths up to at least that of sea water (c. 0.7 molal). It requires stability constants for the formation of associated ion pairs or complexes in solution, and parameters for the equation describing the activity coefficients of dissolved species. These data are included in this data set.

2   DATA BASE CONTENTS

Several computer programs modelling the thermodynamic behaviour of solutions are used to study water-rock interactions in Nagra projects. These programs require descriptions of the reactions to be modelled and equilibrium constants (K) for these reactions at the temperatures of interest. Thermochemical data bases for these programs include reaction stoichiometry, logK values for a standard temperature (25°C), and data to calculate logK values at other temperatures.

LogK values may be determined experimentally or calculated from more basic thermodynamic properties of the constituents of the reactions. Data sets may also include different forms of the reactions for the formation of a given mineral or aqueous species. Thus, logK values frequently cannot be compared directly among several data bases. The Nagra thermochemical data set includes values for the thermodynamic properties of the aqueous species, minerals, and gases it contains, as well as logK values for reactions among them. The logK values are required for the modelling programs. The thermodynamic properties can be used to compare this data set with other compilations.

Extensive calculations are needed to maintain consistency among the thermodynamic properties of chemical entities and the characteristics of reactions among them. To speed the calculations and assure consistency among its contents, the Nagra data base has been developed and maintained using the thermochemical data base management program PMATCH (PEARSON & AVIS 1989). Much of the description given below of the equations relating various thermodynamic properties to the values of reaction equilibrium constants follows the documentation for that program.

This section reviews the basic thermodynamic data types and equations by which they are related, in order to clarify the connections among the various quantities given in the data base. It also includes a description of the activity coefficient expressions used in the Nagra geochemical codes, and concludes with a description of the structure of the Nagra thermochemical data base.

2.1   Thermodynamic Quantities and Equilibrium Constants

Thermodynamics of individual entities are tabulated using standard state properties of formation including:

$$\Delta_f G^0 \; : \; \text{Gibbs energy of formation} \; (J \; mol^{-1})$$

$$\Delta_f H^0 \; : \; \text{Enthalpy of formation} \; (J \; mol^{-1})$$

$$\Delta_f S^0 \; : \; \text{Entropy of formation from the elements or,}$$

$$S^0 \qquad : \; \text{Absolute entropy} \; (J \; K^{-1} \; mol^{-1})$$

$$\Delta_f Cp^0 : \; \text{Heat capacity of formation from the elements or,}$$

$$Cp^0 \qquad : \; \text{Heat capacity} \; (J \; mol^{-1})$$

The standard state for thermodynamic properties used here is 25°C (298.15 K) and 1 bar (0.1 MPa). R, the gas constant, is taken as 8.31448 $(J \; K^{-1} \; mol^{-1})$.

Some gas data are given at 1 atm (0.101325 MPa) in their original sources. The entropy values of gases are sensitive to pressure and were converted from 1 atm to 1 bar using equations given by WAGMAN *et al.* (1982, p. 2-23):

$$S^0{}_{bar} - S^0{}_{atm} = R \; \ln \; (1.01325/1.0) = 0.1094 \; J \; K^{-1} \; mol^{-1}$$

The properties of a reaction are calculated from the standard state properties of its reactants and products as follows:

$$\Delta_r X = \Sigma_f X_{products} - \Sigma_f X_{reactants} \tag{2-1}$$

where X represents the thermodynamic property. The subscript f signifies that the properties are those of the formation of the substance. The subscript r signifies that the property is that of the reaction, as used in the following section.

2.2   Temperature Dependence of Equilibrium Constants

Equation 2-2 has been adopted as the equation relating logK values to temperature in the Nagra thermochemical data set.

$$logK(T) = A + BT + \frac{C}{T} + Dlog(T) + \frac{E}{T^2} \qquad (2\text{-}2)$$

In this equation, $\log K(T)$ is the base 10 logarithm of the equilibrium constant K at the temperature T and $A, B, C, D,$ and E are constants. This equation is convenient for calculations and is consistent with the presentation of a considerable body of thermodynamic data of geochemical significance.

The form of this equation results from choosing the equation of MAIER & KELLEY (1932) to express the variation of the heat capacity at constant pressure, C_p, with absolute temperature, T. This equation has been adopted by a number of other authors including LEWIS & RANDALL (1961, Equation 6.13), and HELGESON et al. (1978, Equation 19). The Maier-Kelley equation is written:

$$C_p = a + bT - cT^{-2} \qquad (2\text{-}3)$$

Note that in the equation used by LEWIS & RANDALL (1961), the coefficient c is positive rather than negative, as it is in the original paper of MAIER & KELLEY (1932), and in HELGESON et al. (1978).

Equations 2-4 through 2-10 show the relations between Equation 2-2 and such other thermodynamic properties of a reaction as $\Delta_r G^0$, $\Delta_r H^0$, $\Delta_r S^0, \Delta_r Cp^0$ and the coefficients $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ of the heat capacity equation. In these equations, $\ln 10$ is the natural logarithm of 10, ≈ 2.303.

$$\Delta_r G = -RT \ln K$$

$$= - R \ln 10 \left(AT + BT^2 + C + \frac{D}{\ln 10} (T \ln T) + \frac{E}{T} \right) \qquad (2\text{-}4)$$

$$\Delta_r H = RT^2 \left(\frac{d \ln K}{dT} \right)$$

$$= R \ln 10 \left(BT^2 - C + \frac{DT}{\ln 10} - \frac{2E}{T} \right)$$

(2-5)

$$\Delta_r S = - \frac{d\Delta_r G^0}{dT}$$

$$= R \ln 10 \left(A + 2BT + \frac{D}{\ln 10}(1 + \ln T) - \frac{E}{T^2} \right)$$

(2-6)

$$\Delta_r Cp = \frac{d\Delta_r H^0}{dT}$$

$$= R \ln 10 \left(2BT + \frac{D}{\ln 10} + \frac{2E}{T^2} \right)$$

(2-7)

$$\Delta_r a = R D$$

(2-8)

$$\Delta_r b = 2 R \ln 10 B$$

(2-9)

$$\Delta_r c = -2 R \ln 10 E$$

(2-10)

If sufficient experimental data are available to define all five coefficients A through E of Equation 2-2, the values for the Gibbs energy, enthalpy, entropy, heat capacity, and all three coefficients a through c of the heat capacity expression, can be found using Equations 2-4 through 2-10.

It is also necessary to be able to calculate values of the coefficients A through E of Equation 2-2 from the thermodynamic properties of the reaction calculated by

equations of the form of 2-1. This is done using the properties of the constituents of the reaction at the standard state, designated below by the superscript 0, and the following equations.

If the coefficients $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ of the heat capacity equation are available, the coefficients B, D, and E of Equation 2-2 are calculated using Equations 2-8, 2-9, and 2-10.

The coefficient C is calculated using $\Delta_r H^0$ and the standard temperature T^0:

$$C = B(T^0)^2 + \frac{DT^0}{\ln 10} - \frac{2E}{T^0} - \frac{\Delta_r H^0}{R \ln 10} \qquad (2\text{-}11)$$

or

$$C = \frac{\left(\Delta_r a T^0 + \frac{\Delta_r b}{2} (T^0)^2 + \frac{\Delta_r c}{T^0} - \Delta_r H^0 \right)}{R \ln 10} \qquad (2\text{-}12)$$

A is calculated from ΔS_r^0, and the standard temperature:

$$A = \frac{\Delta S_r^0}{R \ln 10} - 2BT^0 - \frac{D}{\ln 10} (1 + \ln T^0) + \frac{E}{(T^0)^2} \qquad (2\text{-}13)$$

or

$$A = \frac{\left(\Delta_r S^0 - \Delta_r a (1 + \ln T^0) - \Delta_r b T^0 - \frac{\Delta_r c}{2(T^0)^2} \right)}{R \ln 10} \qquad (2\text{-}14)$$

In some sources of data, $\Delta_r G^0$ may be given rather than either $\Delta_r H^0$ or ΔS_r^0. If this is the case, the missing value can be found using:

$$\Delta_r G^0 = \Delta_r H^0 - T^0 \Delta_r S^0 \qquad (2\text{-}15)$$

If $logK(T^0)$ is given, $\Delta_r G^0$ is calculated using Equation 2-4.

If $\Delta_r Cp$ is known only at the standard temperature, it is assumed to be constant with temperature. In this case, $\Delta_r Cp^0 = \Delta_r a$ and $\Delta_r b = \Delta_r c = 0$, so that:

$$D = \frac{\Delta_r Cp^0}{R} \qquad (2\text{-}16)$$

$$B = E = 0 \qquad (2\text{-}17)$$

$$C = \frac{\left(\Delta_r Cp^0\, T^0 - \Delta_r H^0\right)}{R \ln 10}$$

$$A = \frac{\left(\Delta_r S^0 - \Delta_r C_p^0\, (1 + \ln T^0)\right)}{R \ln 10} \qquad (2\text{-}18)$$

and the expression for $logK(T)$ has the form:

$$logK(T) = A + \frac{C}{T} + D\,log(T) \qquad (2\text{-}19)$$

This expression is also in common use in geochemistry (e.g., LANGMUIR & MEL-CHIOR, 1985).

For some reactions, $\Delta_r Cp^0$ will not be known and it must be assumed that $\Delta_r H$ is constant with temperature. Then:

$$B = D = E = 0 \qquad (2\text{-}20)$$

$$C = - \frac{\Delta_r H^0}{R \ln 10}$$

$$A = \frac{\Delta S_r^0}{R \ln 10} \qquad (2\text{-}21)$$

and the equation for *logK(T)* becomes:

$$logK(T) = \frac{\left(\Delta_r S^0 - \dfrac{\Delta_r H^0}{T}\right)}{R \ln 10} \tag{2-22}$$

Equation 2-22 is equivalent to the integrated van't Hoff equation often used to calculate *logK* at temperatures other than the reference temperature from values of *logK(T^0)* and $\Delta_r H^0$ at the reference temperature. This equivalence is shown as follows:

From Equation 2-15, at the standard temperature T^0,

$$\Delta_r S^0 = \frac{\Delta_r H^0}{T^0} - \frac{\Delta_r G^0}{T^0} = \frac{\Delta_r H^0}{T^0} + R \ln 10 \, logK(T^0)$$

Substituting for $\Delta_r S^0$ in Equation 2-22 and rearranging,

$$logK(T) = logK(T^0) - \frac{\Delta_r H^0}{R \ln 10}\left(\frac{1}{T} - \frac{1}{T^0}\right) \tag{2-23}$$

Equation 2-23 is the integrated van't Hoff equation as used in PHREEQE and other geochemical programs.

Figure 2.1 illustrates the variation of *logK* values with temperature using these equations. When values for all parameters in Equation 2-2 are available, the lines marked Full Equation result. If the value of $\Delta_r Cp$ does not vary with temperature, *logK(T)* is calculated using Equation 2-19. Note that differences between *logK(T)* calculated with $\Delta_r Cp$ constant and those calculated using the full Equation 2-2 are less than 0.1 even at 100°C. When $\Delta_r H$ is held constant and the integrated van't Hoff equation, 2-23, is used, *logK(T)* values begin to differ by more than 0.1 from those from the full equation at 50 to 60°C. The assumption that *logK(T)* is invariant with temperature is useful only within a few degrees of 25°C.
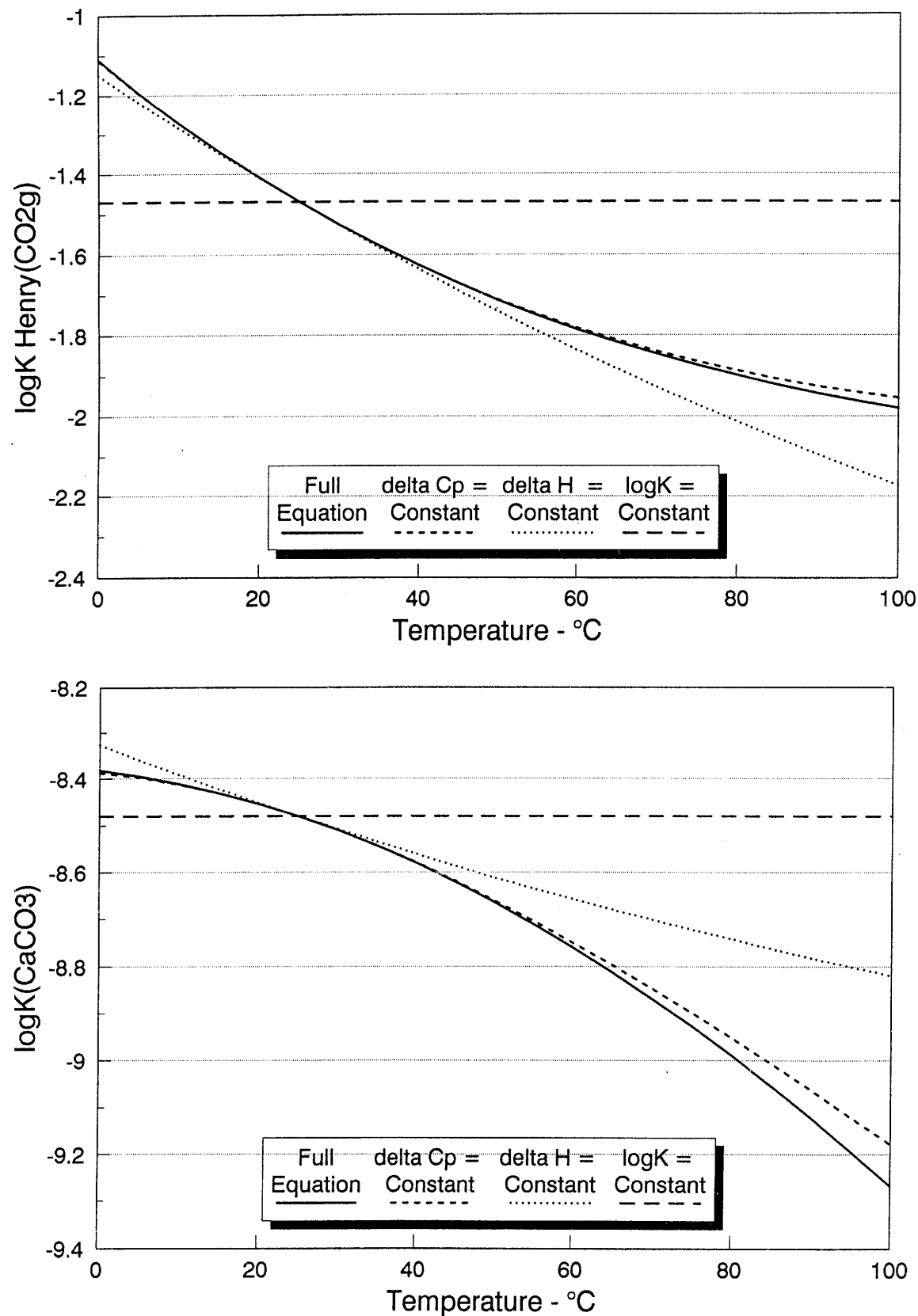
Figure 2.1:   Variation of logK with temperature for $CO_{2(g)}$ solubility (upper) and

calcite dissolution (lower) using different expressions for logK(T).

Variations of pressure as well as of temperature may change the equilibrium constant of a reaction from its value at standard conditions. For a constant temperature, this change is given by:

$$\frac{d\log K}{dP} = \frac{-\Delta_r V^0}{R\,T\,\ln 10} \qquad (2\text{-}24)$$

where $\Delta_r V^0$ is the volume change accompanying the reaction. $\Delta_r V^0$ is related to V^0, the partial molar volumes of the reactant and product species i, by an equation similar to Equation 2-1 for the other thermodynamic properties of the reaction:

$$\Delta_r V = \Sigma V_{products} - \Sigma V_{reactants} \qquad (2\text{-}25)$$

If it is assumed that $\Delta_r V^0$ does not vary with pressure, the value of $\log K$ at a pressure P can be found using the equation:

$$\log K(P) = \log K(P^0) - \frac{\Delta_r V^0}{R\,T\,\ln 10}(P - P^0) \qquad (2\text{-}26)$$

where P^0 is the standard pressure.

EQ3/EQ6 is the only geochemical modelling program used for a significant amount of Nagra work which includes the effects of pressure variation on equilibrium constants. Values for $\Delta_r V^0$ are not included in the Nagra thermochemical data base.

2.3   Activity Coefficients

To calculate the behaviour of aqueous solutions requires not only equilibrium constants for reactions among aqueous species, minerals, and gases, but also activity coefficients for dissolved species. The geochemical programs supporting Nagra work use different expressions to calculate activity coefficients. This section describes these equations, compares their results, and recommends parameter values.

The Nagra thermodynamic base, like the geochemical modelling programs with which it is to be used, is intended for solutions of low to moderate ionic strength for which the ion-association model is appropriate. In this model, activity coefficients are used with molal concentrations of free ions to calculate activities. In models intended for use with more concentrated solutions, such as the ion-interaction model of Pitzer, activity coefficients are used with the total concentration of a species to calculate ion activity. Activity coefficients for ion-interaction models are generally smaller than those appropriate for ion-association models.

Different expressions are used to calculate the activities of charged and uncharged dissolved species. Therefore, these types of species are described in separate sections. Complete discussions of activity coefficients can be found in a number of publications; those of WHITFIELD (1979) and NORDSTROM & MUNOZ (1985) are particularly recommended.

2.3.1   Activity coefficients of charged species

The geochemical modelling programs to be supported by this data base calculate activity coefficients using the extended Debye-Hückel equation or similar equations. The extended Debye-Hückel equation is written:

$$\log \gamma_i = - \frac{A \, z_i^2 \, I^{0.5}}{1 + B \, a_i^o \, I^{0.5}} \tag{2-27}$$

In this equation, γ_i is the activity coefficient of i and z_i is its charge. A and B are parameters of the solvent and vary with temperature. Values for A and B are calculated within the modelling programs and are given for several temperatures by NORDSTROM & MUNOZ (1985, Table 7-3). At 25°C, $A = 0.510$ and $B = 0.328$.

a_i^0 is known as the ion-size parameter or effective diameter of i. Values of this parameter for a number of ions were given by KIELLAND (1937) and are repeated in a number of publications (e.g. WHITFIELD 1979, Table 24; NORDSTROM & MUNOZ 1985, Table 7-4). These values are adopted for the Nagra data base for use with the extended Debye-Hückel equation.

I is the ionic strength of the solution:

$$I = \frac{1}{2} \Sigma \, m_j \, z_j{}^2 \tag{2-28}$$

where m_j is the molality $(mol \; j/kg \; H_2O)$, z_j is the charge of the jth species, and the sum is over all dissolved species.

The molal concentration scale is used in most geochemical modelling programs, because calculations involving solution mixing, or the addition or loss of solutes, are most conveniently made per unit mass of solvent. However, analytical data are commonly reported per unit volume of solution using molar concentrations. When examining older data, particularly, for possible use for geochemical modelling, it is important to ascertain the concentration unit used.

The extended Debye-Hückel equation is precise only in relatively dilute solutions, so several expanded versions have been developed and are used in PHREEQE and EQ3/EQ6 to accommodate more concentrated solutions. These are of the form:

$$\log \gamma_i = - \frac{A \, z_i^2 \, I^{0.5}}{1 + B \, a_i \, I^{0.5}} + b_i \, I \tag{2-29}$$

The parameters in this equation are the same as in the extended Debye-Hückel equation, except for a_i and b_i, which are evaluated differently in the two programs.

The equation in PHREEQE is that proposed by TRUESDELL & JONES (1974), and is referred to as the Truesdell-Jones equation (NORDSTROM & MUNOZ 1985) or the WATEQ equation (PARKHURST et al. 1985; PARKHURST 1990). Values of a_i and b_i are determined for each ion by fitting the equation to measured activities of pure salt solutions. PARKHURST (1990) has recently fit the WATEQ Debye-Hückel equation to a number of salt solutions and determined the a_i and b_i values given in Table 2.1. These values are adopted in the Nagra thermochemical data set for use with the WATEQ Debye-Hückel equation.

Table 2.1:   **Values of WATEQ Debye-Hückel parameters for various ions as determined by PARKHURST (1990, Table I)**

ION	aw	bw	ION	aw	bw	ION	aw	bw
Al+3	6.65	0.19	Fe+2	5.08	0.16	Pb+2	4.80	0.01
Ba+2	4.55	0.09	K+	3.71	0.01	Sr+2	5.48	0.11
Ca+2	4.86	0.15	Li+	4.76	0.20	Zn+2	4.87	0.24
Cd+2	5.80	0.10	Mg+2	5.46	0.22	Cl-	3.71	0.01
Co+2	6.17	0.22	Mn+2	7.04	0.22	ClO4-	5.30	0.08
Cs+	1.81	0.01	Na+	4.32	0.06	F-	3.46	0.08
Cu+2	5.24	0.21	Ni+2	5.51	0.22	SO4-2	5.31	-0.07

In EQ3/EQ6, Equation 2-29 is the Bdot equation of HELGESON (1969), (WOLERY *et al.* 1990). In this equation, a_i is a_i^o of the extended Debye-Hückel equation, and b_i is Bdot, which is a function only of temperature and equals 0.041 at 25°C., 0.0435 at 50°C., and 0.046 at 100°C. (HELGESON 1969, Table 2). EQ3/EQ6 uses the KIELLAND (1937) values of a_i^o, and calculates Bdot values as a function of temperature.

The Davies equation is also widely used to calculate activity coefficients. This equation is written:

$$\log \gamma_i = -A \, z_i^2 \left(\frac{I^{0.5}}{1 + I^{0.5}} - C_D \, I \right) \qquad (2\text{-}30)$$

C_D is usually assigned the value 0.2 or 0.3 (STUMM & MORGAN 1981, Table 3.3), and the remaining parameters are the same as in previous equations. The only ion-specific parameter in this equation is the charge of the ion, so the equation is often used for uncommon ions for which neither the ion-size parameter, a_i^0, nor the WATEQ parameters a_i and b_i are available. The Davies equation, with C_D = 0.2, is used to calculate activity coefficients in MINEQL, and there is an option for its use in PHREEQE with C_D = 0.3.
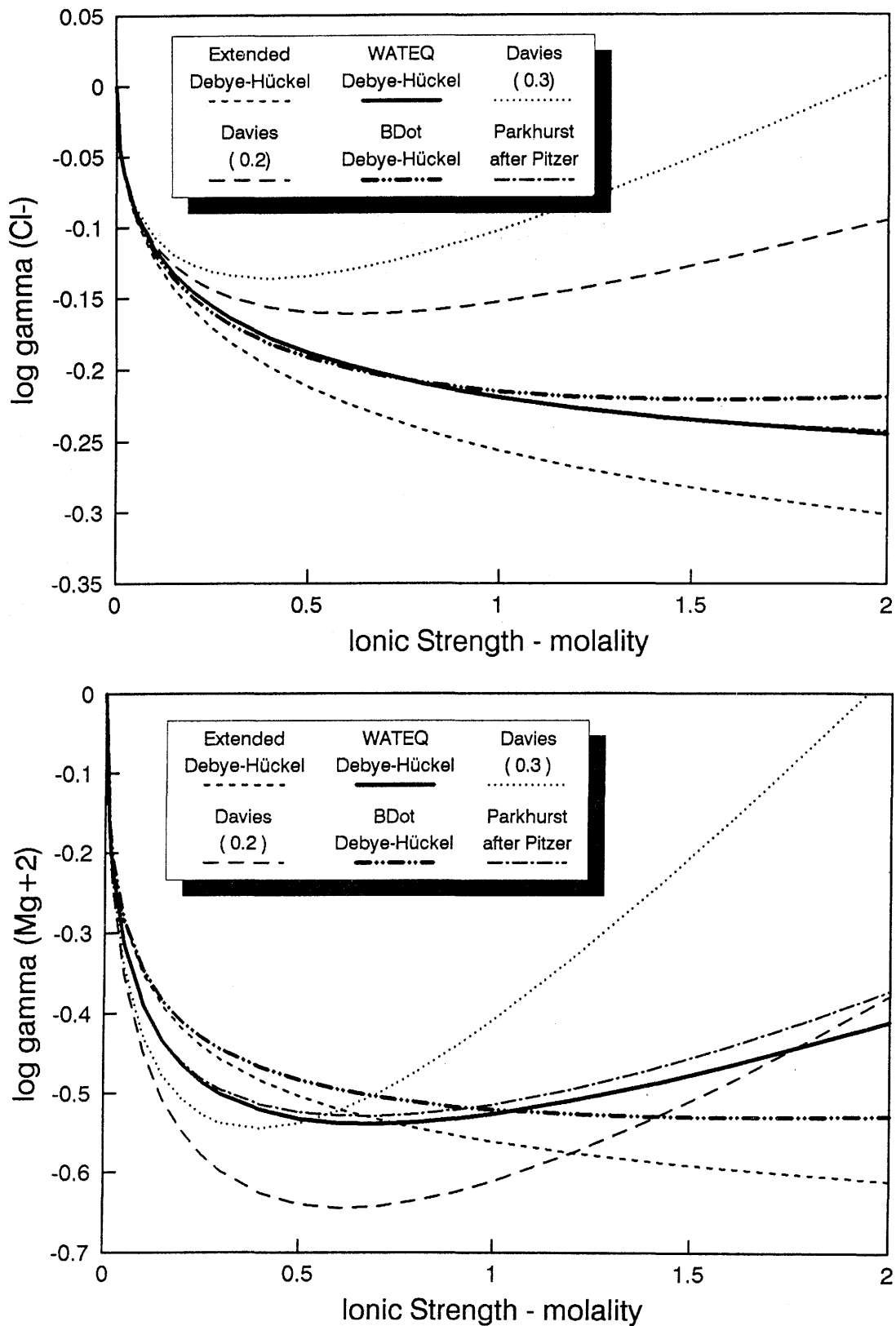
Figure 2.2: Variations of the activity coefficients for Cl⁻ (upper) and Mg⁺² (lower) calculated using various equations

Figure 2.2 shows the activity coefficients ($\log \gamma_i$) calculated using various equations at ionic strengths from 0 to 2 molal. Curves are shown for the extended WATEQ and Bdot Debye-Hückel expressions, and for the Davies equation with C_D equal to 0.2 and 0.3. There is also a curve based on Pitzer's equation for activity coefficients with parameter values fit by PARKHURST (1990, Table II). This curve best represents the experimental data.

As the upper figures shows, for Cl⁻ there is good agreement between the Pitzer, WATEQ, and Bdot equations at all ionic strengths. The extended Debye-Hückel also agrees reasonably well, but the Davies equation with either C_D value deviates greatly except at very low ionic strengths. For Mg^{+2}, the Pitzer and WATEQ equations also agree well, but the Bdot and extended Debye-Hückel equations give lower values at higher ionic strengths. The Davies equation with $C_D = 0.3$ begins to deviate significantly at about 1 m, and with $C_D = 0.2$ differs most from the others at about 0.5 m. In general, it appears that the WATEQ Debye-Hückel equation should be used where data for it are available, followed in order of declining preference by the Bdot and extended Debye-Hückel equations, and the Davies equation.

2.3.2. Activity coefficients of neutral species

A number of expressions are used to describe the activity coefficients of dissolved neutral species. GARRELS & CHRIST (1965) and HELGESON (1969) propose:

$$\log \gamma = c_0 I \tag{2-31}$$

This equation is used in PHREEQE with $c_0 = 0.1$ for all neutral species at all temperatures.

In EQ3/EQ6, following HELGESON (1969), the activity coefficients of all neutral species are taken as equal to those of dissolved CO_2. These are calculated using the expression:

$$\log \gamma = c_1 \, T + c_2 \, T^2 + c_3 \, T^3 + c_4 \, T^4 \qquad\qquad (2\text{-}32)$$

where the coefficients c_i are temperature dependent and are given in the program. It is also an option in EQ3/EQ6 to calculate neutral species activity coefficients using the simple expression of the previous paragraph with c_0 equal to the Bdot parameter and so, also, a function of temperature.
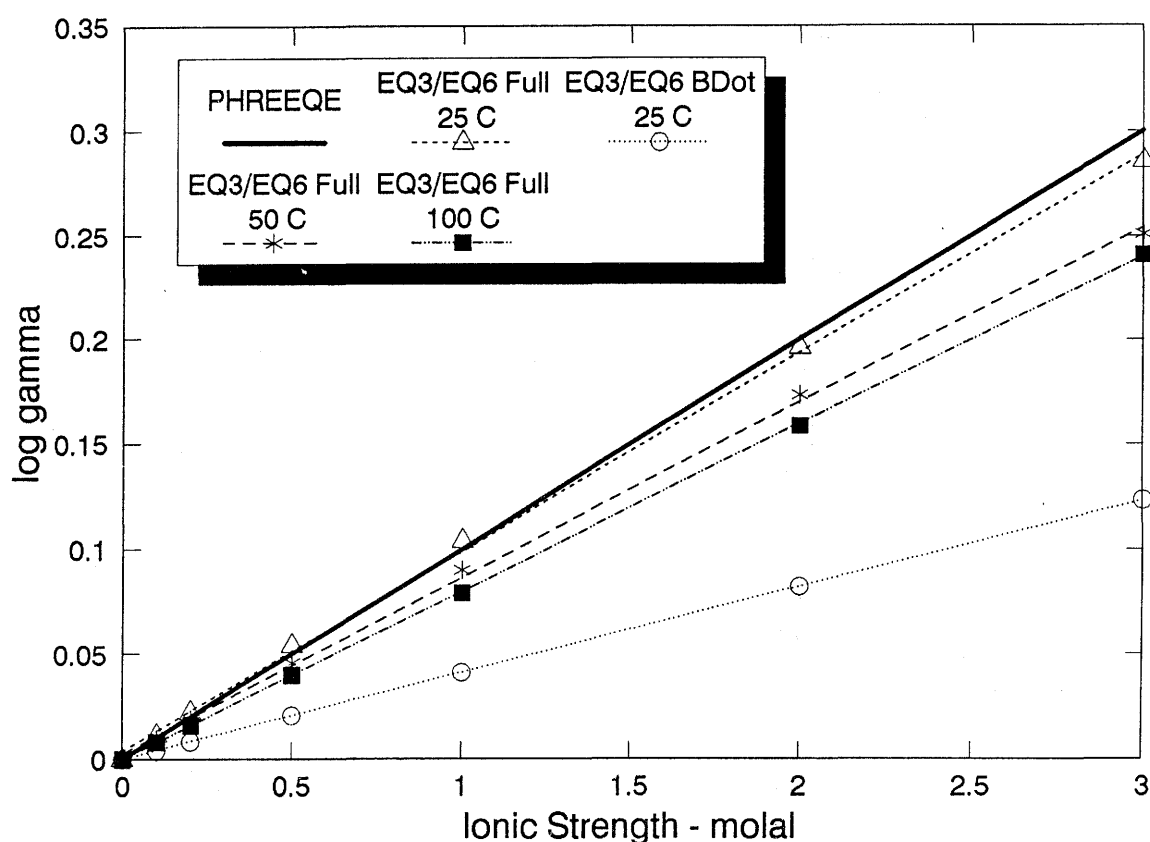
Figure 2.3:   Comparison of activity coefficients of neutral solutes calculated using equations of PHREEQE and EQ3\EQ6.

In MINEQL, activity coefficients for neutral species are set equal to one.

Figure 2.3 compares activity coefficients calculated using several procedures. At 25°C, the simple PHREEQE expression and the power series of EQ3/EQ6 give virtually the same results, while the Bdot option of EQ3/EQ6 results in far lower values. Even at 50°C and 100°C, the agreement between the PHREEQE and the

EQ3/EQ6 equations is close enough that adopting the simple PHREEQE expression will lead to only negligible differences in the results of modelling.

2.4 Description of Redox Conditions

Two conventions are commonly used to describe the redox state of solutions and to make calculations involving redox reactions.

The first of these, which is used in PHREEQE and MINEQL, writes redox reactions in terms of the electron (e^-) and describes solutions using the electron activity, α_{e^-}, as *pe*

$$pe = -\log(\alpha_{e^-}) \tag{2-33}$$

or as *Eh*

$$Eh = pe \left(\frac{T \ln 10 \; R}{F} \right) \tag{2-34}$$

In the latter equation, F is the Faraday constant, which equals 96,484.6 $J \; V^{-1} \; mol^{-1}$. Thus,

$$Eh \; (V) = pe \; T(K) \; 1.984 \cdot 10^{-4} \tag{2-35}$$

At 25°C,

$$Eh \; (V) = pe \; 5.916 \cdot 10^{-2} \tag{2-36}$$

The second convention, which is used in EQ3/EQ6, writes redox reactions using $O_{2(g)}$, and describes the redox state of solutions using oxygen fugacity $f_{O_{2(g)}}$.

The reactions given with the Nagra thermochemical data base are written using the electron. These reactions can be rewritten in terms of $O_{2(g)}$ by adding the reaction

$$2H_2O - 4H^+ - 4e^- = O_{2(g)} \qquad\qquad (2\text{-}37)$$
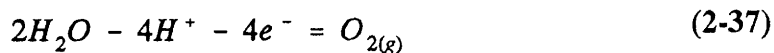
to eliminate electrons. Thermodynamic data for this reaction are given in Section 4.2.1.

In modelling reactions, PHREEQE solves for redox state using an equation describing the conservation of electrons (PARKHURST *et al.* 1985, p. 9). Use of this equation requires that a property termed the operational valence (OPV) be assigned to each entity in the data base. For entities which have no constituents participating in redox reactions, the OPV is zero. Thus, for Na^+, Cl^-, and halite (NaCl), the OPV is zero. For entities participating in redox reactions, the OPV is the formal valence of the elements being oxidized or reduced. For example, for Fe^{+2}, OPV equals $+2$, and for Fe^{+3}, OPV equals $+3$. For CO_3^{-2}, which contains carbon in the $+4$ state, OPV equals $+4$, while for methane CH_4, OPV equals -4. The OPV of a compound is the sum of the OPVs of its constituents. Thus, for siderite $FeCO_3$, OPV equals $+6$.

2.5   Data Base Structure

The data base includes information on aqueous species, minerals and other solids, and gases. Two types of aqueous species are distinguished: **master species** and **product species**.

All reactions are written in terms of a group of aqueous species known as master species (or basis species in the literature on EQ3/EQ6). When modelling analysed waters or defining laboratory solutions, the analysed total concentrations of dissolved substances are usually input to the geochemical program, which then calculates the model composition of the solution in terms of both master and product species concentrations. The data base includes the thermodynamic properties of formation of master species as well as their charge, OPV, and parameters for the Debye-Hückel and WATEQ Debye-Hückel equations for activity coefficients.

Product species are formed in solution by reaction among master species. The data base describes the stoichiometry of these reactions, and gives their equilibrium constants as functions of temperature by giving as many as are available of the parameters A through E in Equation 2-2. The data base also includes the charge, OPV and activity coefficient parameters for each species as well as its thermody-

namic properties of formation. The latter are consistent with the coefficients given for the *logK(T)* equation and the properties of formation of the master species, according to the equations in Section 2.2.

Minerals and gases are also formed by reactions among master species. The data base includes the same information for them as for product species, except that no charge or activity coefficient parameters are required.

There are several considerations in the choice of master species. First, there must be at least one master species for each element to be included in the data base. Second, if the element of interest can undergo redox reactions, it must be decided whether the data base is to support modelled redox reactions as if they were always at equilibrium (**redox coupled** with respect to the element) or as if they do not maintain redox equilibrium (**redox decoupled** with respect to the element).

If an element is considered redox coupled, only a single master species is chosen. Other redox states of the element are written as product species, and their concentrations are calculated based on the redox potential of the solution.

If the element is considered redox decoupled, a master species must be chosen for each redox state of the element. In this case, a redox potential for the solution can be calculated if measured concentrations of elements in different redox states are available.

Compilations of thermodynamic and aqueous reaction data (*e.g.* SMITH & MARTELL 1976, 1989; MARTELL & SMITH 1982; GRENTHE *et al.* 1990) commonly include a very large number of aqueous species, all of which could be included in a data base as product species. Many of these are likely to occur in significant concentrations only in solutions of concentrations or redox states outside the range of conditions for which the data base is to be used. Thus, to keep data bases to manageable sizes and to minimize the computer size and running time required for modelling programs, only product species likely to be present under the conditions of interest are included. The reasons for choosing the specific master and product species included in the Nagra thermochemical data base are given in Chapter 4 for the core data and in the respective reports on the supplemental data.

Mineral and gas data are provided for information about possible controls on solution compositions. Unlike product species, they are not all included in the

model of the aqueous solution, solved by the geochemical program. Thus, the inclusion of large lists of minerals and gases in thermodynamic data bases does not significantly increase the computer size and time required for geochemical modelling. Data on many minerals give the user the opportunity to test a water for saturation with respect to many possible phases, or to choose from among many solids and gases to set the composition of the solution being modelled.

3   SOURCES OF THERMOCHEMICAL DATA

Thermodynamic data from a number of sources were used in compiling this core data set. Some of these sources, together with additional sources, will also be used in compiling the supplemental data sets for additional elements. This section lists and briefly describes the sources of core data. It is not meant to be an exhaustive catalogue of general sources of thermochemical data.

Two types of data compilations were used and are described separately. The first comprises compilations of the thermodynamic properties of elements, aqueous species, solids, and gases. The second comprises existing data bases for aqueous solution models. Commonly, these contain reactions and equilibrium constants, rather than the thermodynamic properties of individual entities. Some of these data bases are those now in use in various Nagra programmes, and others are those used in other nuclear waste programmes.

3.1   Compilations of Thermodynamic Properties

Several compilations of the thermochemical properties of formation of elements, aqueous species, gases, and solids were used. These included the CODATA tables (GARVIN et al. 1987; COX et al. 1989), the auxiliary data selected as part of the NEA compilation of uranium data (GRENTHE et al. 1990) and tables issued by the US National Institute of Science and Technology (NIST, formerly National Bureau of Standards, NBS) (WAGMAN et al. 1982).

The CODATA tables include relatively few entities, but contain very carefully selected, internally consistent data. Thus, when thermochemical properties are required for the core data, CODATA values were chosen when available. The NEA compilation also uses CODATA values whenever possible, so values for the same entity in the two data bases are always identical. The NIST tables are more complete than the CODATA or NEA compilations, but are older. Thermochemical properties were taken from the NIST tables only if they were not available in the other two compilations.

For the most part, these compilations were used as the sources of the thermochemical properties of the master species. Properties of the product species, minerals, and gases were derived from reactions and their equilibrium constants selected from the data bases described in the next section. In a few cases, it was

necessary to calculate equilibrium constants from thermodynamic properties of formation. When this was done, the properties of all constituents of the reaction used for the calculation were taken from the same compilation to ensure consistency.

3.2   Data Bases Compiled for Geochemical Solution Modelling

The data bases used by geochemical modelling programs generally include the stoichiometry of the reactions to be modelled and the thermodynamic properties of those reactions. The data bases for different codes may write a reaction leading to a given aqueous species, mineral, or gas in different forms. Each will have different properties of reaction, and so different data bases cannot generally be directly compared. To make comparison possible, properties of formation of the product species were calculated from the properties of the reactions and the properties of formation of the reactants as described in Chapter 2. If the same properties of formation are used for the master species in different data sets, the properties of formation of aqueous species, minerals, and gases can be directly compared.

Data for the reactions included in the Nagra core data set were selected after consideration and comparison among data bases now used in the Nagra programme, data bases and other compilations used widely outside the Nagra programme, and the results of a few particularly important experimental studies.

3.2.1   Data bases now used by Nagra

These data bases include equilibrium constants for reactions and are not all written with the same redox species. They required conversion to a common basis before their contents could be directly compared.

- NTB 86-19
  This data base is in PHREEQE format. It includes only common anions, cations and neutral species, and minerals and gases. It was used in developing the hydrochemically consistent set of ground-water chemistry data from the samples from the Nagra deep boreholes (PEARSON *et al.* 1989).

- **MINEQL-PSI**

  This is a very large data base, founded on the SCHWEINGRUBER (1983) data set used in calculations for Gewähr, and further described by WAN-NER (1986). It includes organic ligands and elements important in radioactive waste disposal. For many entities, only 25°C data are given; the remainder have $\Delta_r H^0$ values. The data are in MINEQL format, but have been converted to PHREEQE format. MINEQL reactions are written without water, because it is assumed that the program will be used only in such dilute solutions that the thermodynamic activity of water, α_{H_2O}, is virtually one. In converting MINEQL to PHREEQE data, it has been necessary to manually add H_2O to the reactions.

- **EQ3/EQ6**

  This is also a very large data base including data for dissolved species, minerals, and gases. The data are given as equilibrium constants at discrete temperatures, but many reactions have only 25°C, or 0, 25, and 60°C values. They are in EQ3/EQ6 format, and redox reactions are written in terms of $O_{2(g)}$. This data base is used at Uni-Bern with EQ3/EQ6, and with the models of reactive transport developed there.

3.2.2   Other compilations and code data bases

Several compilations of data for aqueous solution modelling, and data bases from other geochemical modelling programs widely used outside the Nagra group were also considered. These include:

- **NORDSTROM et al. (1990)**

  This is a compilation of data on relatively few elements, with their important aqueous species and minerals. It was assembled by Nordstrom and a large group of his colleagues, and represents what the authors consider to be the best set of thermodynamic data which is presently available for the elements it includes. The data are frequently identical with NTB 86-19 data.

- SOLMINEQ.88 (KHARAKA *et al.* 1989)

  This is a very large data base of interest because it includes many mineral data, as well as many organic anions commonly found in natural waters. Although this program has a large data set, its reactions are hard-programed, rather than embedded in user-defined matrices, as they are in the geochemical programs used by Nagra. Thus, SOLMINEQ.88 data require manual conversion before use or comparison with other sources.

- HATCHES: (CROSS & EWART *in press*)

  This is a large data base in PHREEQE format assembled for use in nuclear waste studies. The quality and internal consistency of the data included are unknown, and the data base was not examined during core data selection.

- MINTEQA2 (ALLISON *et al.* 1990)

  This large data base is widely used in U. S. hazardous waste studies. It may contain metals data unavailable elsewhere and be useful in developing supplemental data bases. It was not examined for core data selection.

- PHRQPITZ (PLUMMER *et al.* 1988)

  This is the version of PHREEQE which uses Pitzer equations for activity coefficients and, therefore, includes only a few aqueous complexes. However, its mineral data represent a consistent set of data on minerals of importance to water chemistry, and were consulted in developing the core data.

3.2.3   Special studies

Data were also taken from selected publications on individual elements and groups of elements. The publications are discussed in the sections on data selection in Chapter 4. Reports of this type consulted in preparing the core data set were principally those of Plummer, Busenberg, and colleagues on the solution behaviour and minerals of the alkaline earth elements and carbonate species.

4   CORE DATA

4.1   General Criteria

Core data, once established, will be fixed for the next phase of Nagra studies, a period of about five years. This will eliminate the need for recalculations because of data base changes, and will permit comparison of calculations made at different stages in the programme. The core data include principally well-known reactions, so it is unlikely significantly different new data will be proposed during this period.

The elements chosen for inclusion in the core data make up the majority of the solids dissolved in most natural waters, or are important complexing ligands. A few additional elements of well-known chemical behaviour are also included. In accordance with CODATA and NIST practice, the elements are discussed in their standard order of arrangement. Because this may not be a familiar arrangement, it is shown in Figure 4.1.
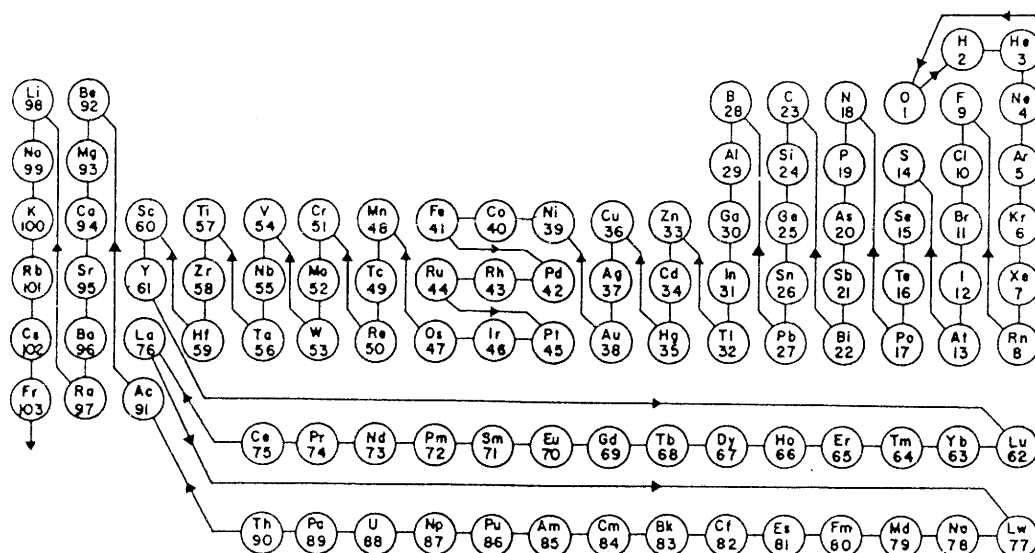
Figure 4.1:   Standard order of arrangement of the elements (COX *et al.* 1989, p. 3).

4.1.1   Elements and Master Species

Each element in the data base requires at least one master species. If the element is to be modelled as if reactions do not take place among its redox states (redox decoupled), one master species is required for each redox state.

The master species are those dominant in neutral to slightly alkaline waters. The selections are based on the Eh-pH diagrams given by BROOKINS (1988), POUR-BAIX (1974), and STUMM & MORGAN (1981), and the hydrolysis data of BAES & MESMER (1976).

The data required for each master species comprise its charge, redox state, and activity coefficient parameters. For comparing existing thermodynamic data bases for aqueous modelling, values for the thermodynamic properties of formation of master species are also useful.

The master species for the core data set and their thermodynamic properties of formation are listed in Appendix Table A1, together with their molar masses, operational valences (OPV), and activity coefficient parameters. The rationale for the selection of these species is discussed in the following sections of this chapter.

Table 4.1 gives the thermodynamic properties of species and elements required to calculate the properties of the master species in both the core and some of the supplemental data sets. The table also includes thermodynamic properties of additional aqueous species, minerals, and gases that were taken from the same sources as the data on their component master species, and are useful for developing or checking reaction data.

The sources of the data chosen are indicated in the tables. These are principally the CODATA, NIST, and NEA compilations. Generally, CODATA values were used if available. The selection of individual species and their data is discussed in the remaining sections of this chapter.

When only enthalpy and entropy values are available, as from the CODATA compilation, Gibbs energies of formation values are calculated using:

$$\Delta_f G^0 = \Delta_f H^0 - T^0 \Delta_f S^0 \qquad\qquad (4\text{-}1)$$

where $\Delta_f S^0$ is the entropy of formation of the species from its elements rather than its absolute entropy. For neutral species

$$\Delta_f S^0 = S^0 - \Sigma S^0 \text{ (elements)}$$

and for charged species

$$\Delta_f S^0 = S^0 - \Sigma S^0 \text{ (elements)} + (n/2)\ S^0(H_{2(g)}) \qquad \text{(4-2)}$$

in which n is the charge (WAGMAN *et al.* 1982, p. 2-22). Similarly, the values for heat capacity, and of the coefficients *a, b,* and *c* of the heat capacity equation, are for formation from the elements.

The NIST tables include $\Delta_f G^0$ and Cp^0 values for many species, as well as $\Delta_f H^0$ and S^0 values, for a pressure of 1 bar. The compilers of the NIST tables point out that in some cases the "best" values of $\Delta_f G^0$ and $\Delta_f H^0$ are based on measurements of different properties than are the "best" values of S^0 so that the three values given in their tables may violate Equation 4-1 (WAGMAN *et al.* 1982, p. 2-16). When NIST thermodynamic properties are used, the values of $\Delta_f G^0$ and $\Delta_f H^0$ included in Table 4.1 are those in the NIST tables, and values of $\Delta_f S^0$ were calculated from them using Equation 4-1. Thus, the $\Delta_f S^0$ values in Table 4.1 may not be identical with values calculated from S^0 values given in the NIST compilation.

Table 4.1: Thermodynamic properties of formation of master species and their elements, and of selected other aqueous species, minerals and gases. (Page 1 of 2)

Std. No.	Name	Type	Redox State	Cha-rge	dfH0 kJ/mol	dfG0 kJ/mol	S0 J/mol-K	dfS0 (elem) J/mol-K	Cp0 J/mol-K	dfCp0 (elem) J/mol-K
1	O2(g)	Gas		0	0	0 a	205.152 bd	0	29.378 b	0
	O2(aq)	M		0	-12.06	16.52 i	109.29 i	-95.86	229.16 i	199.78
2	H2(g)	Gas		0	0	0 a	130.680 bd	0	28.836 b	0
	H2(aq)	M		0	-4.04	17.73 i	57.66 i	-73.02	173.03 i	144.19
	H+	M	H(I)	1	0	0 a	a	0	a	0
	e-	M		-1	0	0 a	a	0	a	0
	H2O	M		0	-285.830	-237.140 bd	69.950 bd	-163.306	75.351 b	31.826
	OH-	S		-1	-230.015	-157.220 bd	-10.9 bd	-244.156	-148.5 c	-192.025
9	F2(g)			0	0	0 a	202.791 bd	0	31.30 bc	0
	F-	M	F(-I)	-1	-335.35	-281.52 bd	-13.8 bcd	-180.5	-106.7 c	-136.8
	HF(aq)	S	F(-I)	0	-323.15	-299.68 d	88.00 d	-78.74		
	HF2-	S	F(-I)	-1	-655.50	-583.71 d	92.68 d	-240.79		
10	Cl2(g)			0	0	0 a	223.081 bd	0	33.91 c	0
	Cl-	M	Cl(-I)	-1	-167.080	-131.22 bd	56.60 bd	-120.28	-136.4 c	-167.8
11	Br2(l)			0	0	0 a	152.21 bcd	0	75.69 c	0
	Br-	M	Br(-I)	-1	-121.41	-103.85 bd	82.55 bd	-58.90	-141.8 c	-194.1
12	I2(cr)			0	0	0 a	116.14 bcd	0	54.438 c	0
	I-	M	I(-I)	-1	-56.78	-51.72 bd	106.45 bd	-16.96		
14	S(cr)	Sulphur	S(0)	0	0	0 a	32.054 bd	0	22.64 c	0
	SO4-2	M	S(VI)	-2	-909.34	-744.00 bd	18.50 bd	-554.54	-293 c	-403
	HSO4-	P	S(VI)	-1	-886.9	-755.3 bd	131.7 bd	-441.3	-84 c	-194
	H2S(g)	Gas	S(-II)	0	-20.6	-33.4 bd	205.81 bd	43.08	34.25 b	-17.23
	H2S(aq)	P	S(-II)	0	-38.6	-27.6 bd	126 bd	-37		
	HS-	M	S(-II)	-1	-16.3	12.24 bd	67 bd	-95.734		
	S-2	P	S(-II)	-2						
18	N2(g)	Gas	N(0)	0	0	0 a	191.609 bcd	0	29.124 bc	0
	N2(aq)	M	N(0)	0	-10.44	18.19 i	95.58 i	-96.03	250.19 i	221.07
	NO3-	M	N(V)	-1	-206.85	-110.79 bd	146.70 bd	-322.17	-86.6 c	-159.6
	NH4+	M	N(-III)	1	-133.26	-79.40 bd	111.17 bd	-180.65	79.9 c	22.1
	NH3(aq)	S	N(-III)	0	-81.17	-26.7 d	109.04 d	-182.78		
19	P(cr)		P(0)	0	0	0 a	41.09 bc	0	23.84 c	0
	PO4-3	S	P(V)	-3	-1284.4	-1025.49 d	-220.97 d	-868.38		
	HPO4-2	M	P(V)	-2	-1299.0	-1095.99 bd	-33.5 bd	-680.91		
	H2PO4-	S	P(V)	-1	-1302.6	-1137.15 bd	92.5 bd	-554.91		
	H3PO4	S	P(V)	0	-1294.12	-1149.37 d	161.91 d	-485.50		
20	As(cr)	Arsenic	As(0)	0	0	0 a	35.1 c	0	24.62 c	0
	AsO4-3	S	As(V)	-3	-888.14	-648.41 cd	-162.8 cd	-804.1		
	HAsO4-2	M	As(V)	-2	-906.34	-714.60 cd	-1.7 cd	-643.1		
	H2AsO4-	S	As(V)	-1	-909.56	-753.17 cd	117 cd	-524.5		
	H3AsO4	S	As(V)	0	-902.5	-766.0 cd	184 cd	-457.8		
	As(OH)4-	S	As(III)	-1	-1000.69	-824.24 c	180.4 c	-591.8		
	As(OH)3	M	As(III)	0	-742.2	-639.80 c	195.0 c	-343.5		
23	C(cr)	Graphite	C(0)	0	0	0 a	5.74 bcd	0	8.517 bc	0
	CO3-2	S	C(IV)	-2	-675.23	-527.90 bd	-50.0 bd	-494.15		
	HCO3-	M	C(IV)	-1	-689.93	-586.85 bd	98.4 bd	-345.75		
	CO2(aq)	S	C(IV)	0	-413.26	-385.97 bd	119.36 bd	-91.53		
	CO2(g)	Gas	C(IV)	0	-393.51	-394.37 bcd	213.78 bd	2.88	37.13 bc	-0.76
	CH4(g)	Gas	C(-IV)	0	-74.81	-50.72 c	186.264 c	-80.798	35.309 c	-30.866
	CH4(aq)	M	C(-IV)	0	-88.61	-34.42 j	85.346 j	-181.754	185.12 j	176.60

Table 4.1: **Thermodynamic properties of formation of master species and their elements, and of selected other aqueous species, minerals and gases. (Page 2 of 2)**

Std. No.	Name	Type	Redox State	Charge	dfHO kJ/mol		dfGO kJ/mol		SO J/mol-K		dfSO (elem) J/mol-K	CpO J/mol-K		dfCpO (elem) J/mol-K
28	B(cr)		B(0)		0		0	a	5.90	bcd	0	11.09	bc	0
	B(OH)3(aq)	M	B(III)	0	-1072.8		-969.30	bd	162.4	bd	-347.1			
	B(OH)4-	S	B(III)	-1	-1344.03		-1153.15	c	102.6	c	-640.2			
93	Mg(cr)		Mg(0)		0		0		32.67	bc	0	24.87	bc	0
	Mg+2	M	Mg(II)	2	-467.0		-455.4	b	-137	b	-39.0			
94	Ca(cr)		Ca(0)		0		0	a	41.588	b	0	25.929	b	0
	Ca+2	M	Ca(II)	2	-543.0		-552.807	b	-56.2	b	32.89	-281.38	b	-278.47
	Ca(OH)+	S	Ca(II)	1			-717.0	b						
	Ca(OH)2	Portlandite	Ca(II)		-985.16		-897.498	b	83.4	b	-294.02	87.488	b	3.35
	CaF2	Fluorite	Ca(II)		-1228.004		-1175.57	b	68.514	b	-175.86	67.042	b	9.81
	CaSO4	Anhydrite	Ca(II)		-1434.508		-1321.98	b	106.525	b	-377.42	99.66	b	-7.67
	CaSO40	S	Ca(II)	0	-1448.95		-1310.76	b	20.454	b	-463.49			
	CaSO4.2H2O	Gypsum	Ca(II)		-2022.92		-1797.361	b	193.93	b	-756.53	186.02	b	-8.35
	CaCO3	Calcite	Ca(II)		-1207.586		-1129.07	b	91.71	b	-263.34	83.472	b	4.96
	CaCO3	Aragonite	Ca(II)		-1207.776		-1128.15	b	87.99	b	-267.07	82.32	b	3.81
	CaCO30	S	Ca(II)	0	-1203.03		-1098.91	b	5.836	b	-349.22			
	CaHCO3+	S	Ca(II)	1	-1216.00		-1145.74	b	119.4	b	-235.65			
95	Sr(cr)		Sr(0)		0		0	a	55.7	ed	0			0
	Sr+2	M	Sr(II)	2	-550.90		-563.83	ed	-31.5	ed	43.4			
	SrCO3	Strontianite	Sr(II)		-1225.77		-1144.73	e	97.2	e	-271.8			
	SrCO3	S	Sr(II)	0	-1204.30		-1107.82	e	45.4	e	-323.6			
	SrHCO3+	S	Sr(II)	1	-1215.56		-1157.52	e	174.4	e	-194.7			
96	Ba(cr)		Ba(0)		0		0	a	62.42	fd	0			0
	Ba+2	M	Ba(II)	2	-532.5		-555.36	fd	8.4	fd	76.7			
	BaCO3	Witherite	Ba(II)		-1210.85		-1132.21	f	112.13	f	-263.8			
	BaCO3	S	Ba(II)	0	-1222.6		-1067.85	f	-143.3	f	-519.0			
	BaHCO3+	S	Ba(II)	1	-1245.7		-1136.68	f	10.0	f	-365.7			
98	Li(cr)		Li(0)		0		0	a	29.12	bcd	0	24.86	b	0
	Li+	M	Li(I)	1	-278.47		-292.92	bd	12.24	bd	48.46			
99	Na(cr)		Na(0)		0		0	a	51.3	bcd	0	28.23	bc	0
	Na+	M	Na(I)	1	-240.34		-261.95	bd	58.45	bcd	72.49			
100	K(cr)		K(0)		0		0	a	64.68	bd	0	29.6	b	0
	K+	M	K(I)	1	-252.14		-282.51	bd	101.2	bd	101.86			

a: By Convention
b: CODATA (GARVIN et al. 1987; COX et al. 1989)
c: NIST (WAGMAN et al. 1982)
d: NEA (GRENTHE et al. 1990)
e: BUSENBERG et al. (1984)
f: BUSENBERG & PLUMMER (1986)
i: From CODATA values for gases and solubility data of Table 4.2.
j: From NIST values for gases and solubility data of Table 4.2.

A final draft version edition of the NEA uranium data base became available (GRENTHE *et al.* 1990) as this report was being prepared. It includes data on a number of non-uranium auxiliary species which are also included in the core data set. The NEA uses CODATA values when available, but includes data on species not in the CODATA compilation as well.

Properties of formation of the ions Sr^{+2} and Ba^{+2} are not given by CODATA, and the values in the NIST tables have been superseded. The data of BUSENBERG *et al.* (1984) for Sr^{+2} and BUSENBERG & PLUMMER (1986) for Ba^{+2} are used.

Table 4.2:   Gas solubilities with temperature. Except as noted, coefficients were derived from those given by WHITFIELD (1979, Appendix Table 8) and are valid from 0 to 65-70°C.

GAS	Solubility at 298.15 K (mol/kg) log Kh		A	C/T	D log T	B T	E/T^2
O_2	1.28E-03	-2.894	-6.096651E+01	3.376712E+03	1.839764E+01	4.101333E-03	
H_2	7.84E-04	-3.106	-7.645288E+01	3.037284E+03	2.631231E+01	-6.533214E-03	
N_2	6.51E-04	-3.186	-6.990691E+01	3.662355E+03	2.155827E+01	3.663863E-03	
CH_4	1.39E-03	-2.856	-7.806599E+01	3.957200E+03	2.503828E+01	-6.229365E-05	
H_2S	1.03E-01	-0.988	-6.319920E+01	3.572772E+03	2.023095E+01	5.620051E-04	
CO_2	3.39E-02	-1.470	-6.767946E+01	3.796457E+03	2.166933E+01	-4.788560E-04	
CO_2*	3.40E-02	-1.468	1.083865E+02	-6.919530E+03	-4.045154E+01	1.985076E-02	6.693650E+05

Coefficients for CO_2* from PLUMMER AND BUSENBERG (1982), valid from 0 to 250°C

Several dissolved gases, $O_{2(aq)}$, $H_{2(aq)}$, $N_{2(aq)}$, and $CH_{4(aq)}$, are included among the master species. No CODATA thermodynamic properties are available for these dissolved gases, and only limited data appear in the NIST compilation. However, there are excellent and complete CODATA values for $O_{2(g)}$, $H_{2(g)}$, and $N_{2(g)}$, and NIST data on $CH_{4(g)}$, and gas solubilities are well known. The solubilities used here are based on equations given by WHITFIELD (1979, Appendix Table 8), which are valid for a temperature range from 0 to between 65 and 70°C. These solubilities are given in Table 4.2. They were used with the relationships given in Section 2.2.1 and CODATA or NIST values for the thermodynamic properties of

the gases (Table 4.1) to calculate the properties of the aqueous master species $O_{2(aq)}$, $H_{2(aq)}$, $N_{2(aq)}$, and $CH_{4(aq)}$.

For the purpose of relating differences in $\Delta_f G^0$ values from various sources with logK values of reactions derived from them, it is convenient to recall that at 298.15 K:

$$\Delta_r G^0 = -5.708 \, logK$$

4.1.2   Solute species, minerals, and gases

The remainder of this chapter discusses the solute species, minerals, and gases in the core data base, including the reasons for their selection and for the choice of data for them. The discussion begins with the fundamental master species H_2O, H^+ and e^- and the elements H_2 and O_2. Species associated in solution (ion pairs or complexes), minerals, and gases are generally grouped by anion.

4.2   Oxygen, hydrogen, the electron, and water

Water and species representing its component elements hydrogen and oxygen are fundamental to modelling aqueous solutions. If it is intended to model only very dilute solutions, one can assume that the activity of water, α_{H2O}, equals one, and water can be left out of the model equations solved. This procedure is followed in the MINEQL code. Other geochemical programs explicitly model the activity of water, so it is included in the core data set. Properties of the solute species, minerals, and gases of this group are given in Table A2.

4.2.1   Master species: H^+, e^-, or $O_{2(g)}$, H_2O, $O_{2(aq)}$, and $H_{2(aq)}$

The properties of these and the other master species are given in Table A1 and were selected based on the following considerations.

The master species for hydrogen is H^+. By convention, all its thermodynamic properties are zero.

$H_{2(aq)}$ and $O_{2(aq)}$ are useful when interpreting dissolved gas analyses, and they are included in the core data set. Their thermodynamic properties of formation were

calculated from the CODATA values for $O_{2(g)}$ and $H_{2(g)}$ and the gas solubilities in Table 4.2, as described in Section 4.1.1.

The master species associated with redox reactions could be either the electron, e^-, or oxygen, $O_{2(g)}$. For the core data set, the electron has been chosen. Like H^+, all its thermodynamic properties are zero by convention.

In Section 2.4, it was pointed out that the reaction:

$$2H_2O - 4H^+ - 4e^- = O_{2(g)}$$
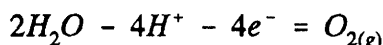
can be used to convert between redox reactions written in terms of the electron and those written using $O_{2(g)}$. Based on the data in Table 4.1, the properties of this reaction are:

$$logK(25) = -83.092$$
$$\Delta_r G^0 = 474.28 \; kJ \; mol^{-1}$$
$$\Delta_r H^0 = 571.66 \; kJ \; mol^{-1}$$
$$\Delta_r Cp^0 = -63.65 \; J \; mol^{-1} \; K^{-1}$$

From these values and the equations of Section 2.2, the equation for the equilibrium constant of the conversion reaction is:

$$logK(T) = 39.32895 - \frac{30851.71}{T} - 7.655715 \; log(T).$$

4.2.2 Oxide and hydroxide solute species, minerals, and gases

Reactions and properties of oxide and hydroxide aqueous species, minerals, and gases are shown in Appendix Table A2.

The aqueous species include the OH^- ion and OH^- ion pairs with the alkali and alkaline earth metals. Oxide and hydroxide minerals of these elements are also included in Table A2.

The thermodynamic data on the reactions forming these species and minerals were taken from the compilation of NORDSTROM *et al.* (1990). Properties of formation of OH⁻, $CaOH^+_{(aq)}$, and portlandite $Ca(OH)_2$ are included in the CODATA compilations and are shown in Table A2. As the table shows, the CODATA values agree well with values calculated from the reaction data chosen.

Table A2 also includes reactions by which one can calculate the oxidation potential, *pe*, and the partial pressures of $O_{2(g)}$ and $H_{2(g)}$ from the dissolved concentrations of $O_{2(aq)}$ and $H_{2(aq)}$, or set concentrations from defined partial pressures.

4.3　　　Halides:　Fluorine, chlorine, bromine, and iodine

4.3.1　　　Master species:　F⁻, Cl⁻, Br⁻, and I⁻

Species with charges of minus one dominate the aqueous solutions of all halide elements, and were chosen as the master species. The reference states for fluorine and chlorine are the gases $F_{2(g)}$ and $Cl_{2(g)}$, for bromine, the liquid $Br_{2(l)}$, and for iodine, the solid $I_{2(cr)}$. CODATA values of $\Delta_f H^0$ and S^0 are available for all four aqueous ions and reference species, and are given in Tables A1 and 4.1. The Cp^0 values given for F⁻, Cl⁻, and Br⁻ are from the NIST tables. The NIST values of S^0 for these species agreed with the CODATA values within 0.1 J K⁻¹ mol⁻¹.

4.3.2　　　Halide solute species

Reactions and properties of halide aqueous species and minerals are given in Appendix Table A3.

The only hydrolysis products of halide ions which are of sufficient strength to be included in this data base are HF^0 and HF_2^-. The thermodynamic data for these species are taken from the NEA compilation. The remaining species are F⁻ and Cl⁻ ion pairs, the data for which are from NORDSTROM *et al.* (1990). These authors also include data on HF^0 and HF_2^-. The NEA values for HF^0 agree with those calculated from the data of NORDSTROM *et al.* (1990), but the values for HF_2^- differ by the equivalent of 0.12 in logK.

The mineral fluorite, CaF_2, is common in aqueous systems, and may influence ground-water chemistry. In spite of the ubiquity and simple chemistry of this mineral, values for its thermodynamic properties differ widely. Values given by CODATA, NORDSTROM *et al.* (1990, Table I) and the data bases for MINEQL-PSI and EQ3/EQ6 differ by as much as 0.55 in logK. Fluorite is not included in the core data.

4.4   Sulphur

Redox processes are important in the sulphur system. Sulphate, S(VI), is stable under oxidizing conditions and sulphide, S(-II), under reducing conditions. Under intermediate conditions, elemental sulphur, S(0), has a small range of stability, and it is included as a mineral species in the core data base. Various other species including sulphites, S(IV), and thiosulphates, $S_2O_3^{-2}$, S(II), may occur metastably. These species are not included in the core data set, but their properties are given in the NIST compilation and they are among the NEA auxiliary data. They could easily be added to one of the supplemental Nagra data sets.

4.4.1   Master species: SO_4^{-2} and HS^-

SO_4^{-2} is the dominant S(VI) species and is the master species for this redox state. The enthalpy and entropy of this species and the Gibbs energy derived from them are CODATA values. Entropy differences between the CODATA and NIST compilations are 0.2 and 1.5 J mol^{-1} K^{-1}, respectively, for $S^0_{(cr)}$ and SO_4^{-2}. Thus, the $\Delta_f Cp^0$ value shown in Tables 4.1 and A1, which is based on the NIST Cp^0 values, should be used with caution.

$H_2S_{(aq)}$ is the dominant S(-II) species below pH *c.* 7 and HS^- at higher pH values. HS^- is the master species for the S(-II) species, and $H_2S_{(aq)}$ is included as a product species. Enthalpy and entropy data for both species are CODATA values. None of the compilations include Cp^0 values for any aqueous S(-II) species. However, CODATA gives a full set of values for $H_2S_{(g)}$ and from these and the gas solubilities in Table 4.2, data on $H_2S_{(aq)}$ could be calculated.

If only one master species is used for the element sulphur, SO_4^{-2} should be chosen. Forms containing reduced sulphur then become product species, and their activities and concentrations are calculated by the geochemical model from the SO_4^{-2} concentration and redox potential given. Redox reactions connecting the sulphur

master species are listed below, with thermodynamic data derived from those in Table 4.1 and Appendix Table A1.

$$SO_4^{-2} + 8H^+ + 6e^- - 4H_2O = S^0_{(cr, \; rhombic)}$$
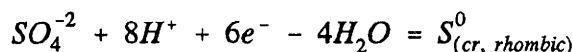
$$logK(25) = 35.838$$
$$\Delta_r G^0 = -204.56 \; kJ \; mol^{-1}$$
$$\Delta_r H^0 = -233.98 \; kJ \; mol^{-1}$$
$$\Delta_r Cp^0 = 530 \; J \; mol^{-1} \; K^{-1}$$

$$logK(T) = -190.6790 + \frac{20480.66}{T} + 63.78207 \; log(T)$$

$$SO_4^{-2} + 9H^+ + 8e^- - 4H_2O = HS^-$$
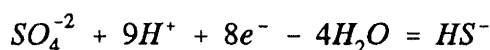
$$logK(25) = 33.694$$
$$\Delta_r G^0 = -192.32 \; kJ \; mol^{-1}$$
$$\Delta_r H^0 = -250.28 \; kJ \; mol^{-1}$$
$$\Delta_r Cp^0 = 530 \; J \; mol^{-1} \; K^{-1}$$

$$logK(T) = -195.6791 + \frac{21332.08}{T} + 63.78207 \; log(T)$$

4.4.2   Sulphate solute species and minerals

Reactions and properties of SO_4^{-2} aqueous species are given in Table A4. The only SO_4^{-2} hydrolysis species included in the core data is HSO_4^- which prevails below pH c. 2. The remaining aqueous species are SO_4^{-2} and HSO_4^- ion pairs with the alkali and alkaline earth metals. The data on these reactions are from NORDSTROM et al. (1990). CODATA properties for HSO_4^- and $CaSO_4^0$ are also available. There is good agreement between CODATA $\Delta_f G^0$ values and those calculated from the reaction data, but the $\Delta_f H^0$ values agree less well.

Table A4 also includes alkaline earth sulphate minerals. The CODATA compilation includes data on the $CaSO_4$ minerals, gypsum, and anhydrite. Again, there

is good agreement between the CODATA and calculated $\Delta_f G^0$ values, but less agreement in the pairs of $\Delta_f H^0$ values.

4.4.3   Reduced sulphur solute species and minerals

Reactions and properties of reduced sulphur aqueous species and minerals are given in Table A4. Sulphide, S(-II), hydrolysis products are $H_2S_{(aq)}$, HS^- and S^{-2}. HS^- is the master species, and $H_2S_{(aq)}$ is included as an additional aqueous species.

The $\Delta_f G^0$ and $\Delta_f S^0$ values for $H_2S_{(aq)}$ are from CODATA. The logK(25) value resulting from this choice agrees well with the value used in NTB 86-19 (PEARSON et al. 1989), but there is strong disagreement between the two $\Delta_f H^0$ values.

The S^{-2} species is important because it is used in mineral reactions. It will be included in a supplemental data base, but is not present in the core data because there is considerable uncertainty about its stability. Historically, values of logK in the range of -13 to -14 have been used for the reaction

$$HS^- \rightarrow S^{-2} + H^+$$
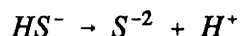
With this range of values, S^{-2} would be the dominant S(II) species at pH values above 13 or 14. Based on recent experimental data, the NEA data base accepts a logK value of -19 ± 2 for HS^- dissociation (GRENTHE et al. 1990, Section VI. 2.1.1). If this value is accepted into the Nagra data base, it will be important to review the data for all sulphide minerals for consistency with it.

$S^0_{(aq)}$ has a small field of stability, and S-polymers may also be important in interpreting Pt-electrode measurements (NORDSTROM & PUIGDOMENECH 1986). Data for these species will also be included in a supplemental data set.

Table A4 also includes elemental sulphur (rhombic) as a mineral, as well as three reactions with which to calculate oxidation potentials corresponding to analysed concentrations of sulphur species. The first of these couples is the S(VI)/S(-II) couple and the others are S(VI)/S(0) and S(0)/S(-II) couples, respectively. Reactions for the latter couples assume that the activity of solid sulphur is one.

4.5   Nitrogen

Redox processes are as important to the chemistry of nitrogen as they are to sulphur chemistry. The dominant oxidation states in natural waters are N(V), nitrate, N(III), ammonia and amines, and N(0), nitrogen gas. N(III), nitrite, is an important consideration in water supply problems, but it is not included in this data set because it is never the dominant nitrogen species (STUMM & MORGAN 1981, Figure 7.8).

4.5.1   Master species: NO_3^-, $N_{2(aq)}$, and NH_4^+

NO_3^-, nitrate, is the dominant N(V) species at all pH values and is a master species in the core data set. N_2 is the dominant N(0) species at all pH values with $N_{2(aq)}$ as its master species. $N_{2(g)}$ is included in the data set as a gas. NH_4^+ is the major N(-III) species below pH $c.$ 9, and is the master species for that oxidation state.

Enthalpy and entropy values for NO_3^- and NH_4^+ in Tables 4.1 and A1 are from CODATA. CODATA and NIST entropy values for NO_3^- and NH_4^+ differ by 0.3 and 2 J K^{-1} mol^{-1}, respectively. Thus, the $\Delta_f Cp^0$ values in Tables 4.1 and A1, which are based on NIST Cp^0 values, should be used with caution. The properties of $N_{2(aq)}$ were derived from CODATA values for $N_{2(g)}$ and the solubility of that gas, as described in Section 4.1.1.

If only one master species is used for the element nitrogen, NO_3^- is commonly chosen, although $N_{2(aq)}$ is stable at the redox state of most groundwaters. Forms containing reduced nitrogen then become product species and their activities and concentrations are calculated by the geochemical model from the NO_3^- concentration and redox potential given. Redox reactions connecting the nitrogen master species are listed below, with thermodynamic data derived from that in Table 4.1.

$$2NO_3^- + 12H^+ + 10e^- - 6H_2O = N_{2(aq)}$$
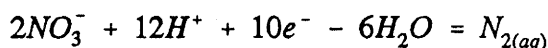
$$logK(25) = 207.267$$
$$\Delta_r G^0 = -1183.07 \; kJ \; mol^{-1}$$
$$\Delta_r H^0 = -1311.72 \; kJ \; mol^{-1}$$
$$\Delta_r a_{Cp} = 689.40$$
$$\Delta_r b_{Cp} = 0.1403$$

$$logK(T) = -265.9060 + 0.00366386 \; T + \frac{79579.16}{T} + 87.91702 \; log(T)$$
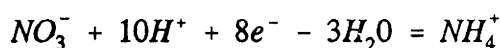
$$NO_3^- + 10H^+ + 8e^- - 3H_2O = NH_4^+$$
$$logK(25) = 119.138$$
$$\Delta_r G^0 = -680.03 \; kJ \; mol^{-1}$$
$$\Delta_r H^0 = -783.90 \; kJ \; mol^{-1}$$
$$\Delta_r Cp^0 = 277.2 \; Jmol^{-1} \; K^{-1}$$
$$logK(T) = -115.1679 + \frac{45263.37}{T} + 33.33745 \; log(T)$$

4.5.2   Nitrogen solute species and gases

Nitrogen reactions and gas are shown in Table A4. The only aqueous species included, in addition to the master species, is $NH_{3(aq)}$, which is the dominant N(-III) species at pH values greater than c. 9.

$N_{2(g)}$ is included in Table A4, as are reactions for calculating redox potentials corresponding to analysed concentrations of nitrogen in various redox states. The couples included are $NO_3^-/N_{2(aq)}$, $N_{2(aq)}/NH_4^+$, and NO_3^-/NH_4^+.

4.6   Phosphate, borate, and arsenic

Phosphorus occurs in the P(V) state as phosphate (PO_4^{-3}) under conditions found in natural waters, and boron as the B(III) state as borate ($B(OH)_3^0$). Arsenic can be present both in the As(V) state as arsenate (AsO_4^{-3}), and in the As(III) state as arsenite ($As(OH)_3^0$). The solution chemistry of As(V) species closely resembles that of P(V) species, and the chemistry of As(III) species resembles that of B(III)

species, so it is convenient to discuss the three elements together. The As(0) state also occurs as native arsenic.

4.6.1   Master species: HPO_4^{-2}, $HAsO_4^{-2}$, $As(OH)_3^0$, and $B(OH)_3^0$

Data on these species are given in Tables 4.1 and A1.

Each of the four hydrolysis products of phosphate (PO_4^{-3}) dominates within some pH range between 0 and 14. HPO_4^{-2}, which dominates between 7 and 12, is the master species. The other species, $H_3PO_4^0$, $H_2PO_4^{-1}$ and PO_4^{-3}, are included in the core data set as product species.

Enthalpy and entropy data for the master species HPO_4^{-2}, and the product species $H_2PO_4^-$, are CODATA values. The NEA auxiliary data include values for the other product species $H_3PO_4^0$ and PO_4^{-3}. The NIST compilation includes no heat capacity data for phosphate species.

The master species for boron is boric acid, $B(OH)_3$, which prevails under neutral and acidic conditions. The properties of this species in Tables 4.1 and A1 are from CODATA.

Arsenic occurs in three oxidation states in natural aqueous solutions. The most oxidized form, As(V), arsenate, AsO_4^{-3}, is analogous to phosphate and hydrolyses to arsenic acid. All four arsenate hydrolysis species are dominant at some range between pH 0 and 14. $HAsO_4^{-2}$ dominates between pH 7 and 11, and is the master species. The other three species are included in the core data set as product species.

The speciation of arsenious arsenic, As(III), is not treated consistently in the existing data sets examined. SOLMINEQ.88 and the NTB 86-19 data set include arsenious acid (H_3AsO_3) and some of its dissociation products, data for which are included in the NIST compilation. MINEQL-PSI includes the species AsO_2^- and $HAsO_2$, which also appear in the NIST compilation. According to BAES & MESMER (1976, Section 16.1), As(III) is analogous to boron, and the species actually present are $As(OH)_3^0$ at pH values below c. 9 and $As(OH)_4^-$ at higher pH values. These species are included in the EQ3/EQ6 data set and have been chosen for the new core data set. $As(OH)_3^0$ is the master species. Its thermodynamic properties of formation are those of H_3AsO_3 as given in the NIST compilation.

$As^0_{(cr)}$ is stable under certain redox conditions at all pH values when sulphur concentrations are very low. It is included as a mineral.

If only one master species is used for the element arsenic, $HAsO_4^{-2}$ should be chosen. The redox reaction connecting the arsenic master species follows, with thermodynamic data derived from those in Table 4.1.

$$HAsO_4^{-2} + 4H^+ + 2e^- - H_2O = As(OH)_3^0$$
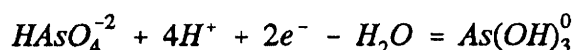
$$logK(25) = 28.441$$
$$\Delta_r G^0 = -162.34 \ kJ \ mol^{-1}$$
$$\Delta_r H^0 = -121.69 \ kJ \ mol^{-1}$$
$$\Delta_r Cp^0 = 31.83 \ J \ mol^{-1} \ K^{-1}$$

$$logK(T) = -4.012500 + \frac{6852.07}{T} + 3.827857 \ log(T)$$

4.6.2   Phosphate and borate solute species

Properties and reactions of dissolved phosphate and borate species are given in Appendix Table A5.

BAES & MESMER (1976, Section 6.1) discuss borate hydrolysis. At dissolved boron concentrations below 0.05 m, the only important aqueous species are $B(OH)_3^0$ and $B(OH)_4^-$. $B(OH)_3^0$ dominates at pH values below c. 9 and is the master species, while $B(OH)_4^-$ is included as a product species. The logK of formation of the species is taken as the mean of expressions 1 and 2 given by BAES & MESMER (1976, Table 6.2). The NIST compilation also includes $\Delta_f G^0$ and $\Delta_f H^0$ data for $B(OH)_4^-$ (= BO_2^{-2} + 2 H_2O). The NIST and calculated $\Delta_f G^0$ values agree within the equivalent of 0.1 logK units.

Phosphoric acid, H_3PO_4, and all three of its hydrolysis products $H_2PO_4^-$, HPO_4^{-2}, and PO_4^{-3} are included in the core data. HPO_4^{-2} is the master species. The logK and $\Delta_r H^0$ values for the reactions by which the other species are formed are those adopted by the NEA. These logK values are within 0.03 units of the values given by BAES & MESMER (1976, Table 16.1) in their discussion of the comparative behaviour of phosphoric and arsenic acids.

Phosphate species are strong complexing ligands with a number of cations, and a number of phosphate complexes will be present in the supplemental data sets.

4.6.3   Arsenic solute species and mineral

Data on arsenic species and one mineral are given in Table A5.

The behaviour of As(V), arsenate, is analogous to that of phosphate. Thus, the core data includes arsenic acid, H_3AsO_4, and its three hydrolysis products. The NIST values for $\Delta_f G^0$ and $\Delta_f H^0$ of the species are used. These values are also accepted by the NEA. The logK values for the reactions among these species calculated from the NIST data agree within 0.2 units with those given by BAES & MESMER (1976, Table 16.1).

Arsenic (III) is similar to borate in that its dissolved species at low concentrations are $As(OH)_3^0$ and $As(OH)_4^-$. Both species are included in the core data with $As(OH)_3^0$ as the master species, and data taken from the NIST compilation. The values used for $As(OH)_4^-$ equal those for $AsO_2^- + 2H_2O$. The logK and $\Delta_r H^0$ values for the hydrolysis of $As(OH)_3^0$ to $As(OH)_4^-$ agree with those given by BAES & MESMER (1976, Section 16.1) within 0.06 units and 0.2 kJ mol^{-1}, respectively.

Native arsenic, As(0), is included as a mineral. Its properties of formation equal zero by convention.

Table A5 also includes two reactions by which formal oxidation potentials can be calculated from measured arsenic concentrations. The first is based on the concentrations of As(V) and As(III). The second is based on a specified As(V) concentration and the presence of solid As of activity 1.

4.7   Carbon

Redox processes are important in the carbon system. C(IV) is stable under oxidizing conditions and occurs as $CO_{2(g)}$, or as carbonate, CO_3^{-2}, minerals, and aqueous species. The most reduced form of carbon is C(-IV), represented by methane, CH_4. C(0) is also common and is represented by carbohydrates, CH_2O, and elemental carbon, as graphite or diamond. Petroleum hydrocarbons and organic molecules may include carbon in almost any formal oxidation state between

(IV) and (-IV). The core data set will include only carbonate species, graphite, and methane. Many organic ligands of possible importance as complexing agents are included in the MINEQL-PSI, HATCHES and SOLMINEQ.88 data bases, and could be assembled into a Nagra supplemental data base.

4.7.1   Master species: HCO_3^- and $CH_{4(aq)}$

$C(IV)$ occurs as gaseous CO_2, or as carbonate (CO_3^{-2}) or one of its hydrolysis products. HCO_3^- is the dominant aqueous carbonate species at pH values between c. 6 and 10, and is chosen as the master species. The other carbonate hydrolysis products, CO_3^- and $CO_{2(aq)}$ (= H_2CO_3 - H_2O), are included as product species. CO_2 is also included as a gas.

CODATA recommends a more complete and precise set of thermodynamic properties of formation for $CO_{2(g)}$ than it does for HCO_3^-, the master species chosen for carbonate. To maintain the high precision of the CODATA $CO_{2(g)}$ data in the core data set, values for the properties of formation of HCO_3^- given in Table 4.1 and used in the core data were calculated from the CODATA $CO_{2(g)}$ values and the equations representing equilibria among dissolved carbonate species given by PLUMMER & BUSENBERG (1982) and used for the core data, as described in the following section.

Under reducing conditions $C(-IV)$ is important. $CH_{4(aq)}$ is the master species and gaseous $CH_{4(g)}$ is also included. Thermodynamic properties for these species are given in the NIST compilation. For $CO_{2(g)}$, the CODATA and NIST $\Delta_f H^0$ values are identical, and the S^0 values differ by only 0.04 J mol^{-1} K^{-1}.

Elemental carbon, C^0, graphite, is included as a mineral. The absolute entropy of this substance is the same in both the CODATA and NIST compilations.

Carbon also occurs in a number of intermediate valence states in organic compounds found in natural waters. No organic species are included in the core data set. Because of their importance as complexing ligands, they could well be included in one of the supplemental data bases for the Nagra programme.

If only one master species is to be used for the element carbon, HCO_3^- should be chosen. Reactions relating the carbon master species are listed below, together with thermodynamic data derived from those in Tables 4.1 and A1.

$$HCO_3^- + 5H^+ + 4e^- - 3H_2O = C^0$$
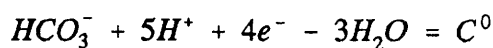
$$logK(25) = 21.820$$
$$\Delta_r G^0 = -124.54 \ kJ \ mol^{-1}$$
$$\Delta_r H^0 = -167.27 \ kJ \ mol^{-1}$$
$$\Delta_r a_{C_p} = -653.8$$
$$\Delta_r b_{C_p} = 1.5725$$
$$\Delta_r c_{C_p} = -3.888E+07$$

$$logK(T) = 208.1775 + 0.04106888 \ T + \frac{4606.129}{T} - 78.63525 \ log(T) + \frac{1015549.9}{T^2}$$

$$HCO_3^- + 9H^+ + 8e^- - 3H_2O = CH_{4(aq)}$$
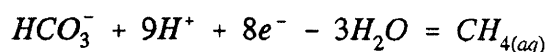
$$logK(25) = 27.849$$
$$\Delta_r G^0 = -158.96 \ kJ \ mol^{-1}$$
$$\Delta_r H^0 = -255.88 \ kJ \ mol^{-1}$$
$$\Delta_r a_{C_p} = -476.5$$
$$\Delta_r b_{C_p} = 1.5701$$
$$\Delta_r c_{C_p} = -3.888E+07$$

$$logK(T) = 136.6894 + 0.04100659 \ T + \frac{2778.061}{T} - 57.30937 \ log(T) + \frac{1015549.9}{T^2}$$

4.7.2   Carbonate solute species, minerals, and gases

Reactions and properties of carbonate aqueous species, minerals, and gases are listed in Table A6.

PLUMMER & BUSENBERG (1982) critically evaluated experimental data on the system $CaCO_3$-H_2O between 0 and 90°C. Equations they developed describing equilibrium among dissolved carbonate species and the solubility of $CaCO_3$ minerals calcite and aragonite are widely used (*e.g.* PARKHURST *et al.* 1985; NORDSTROM *et al.* 1990), and are adopted for the core data.   BUSENBERG *et al.* (1984) and BUSENBERG & PLUMMER (1986) describe their continuing work on carbonate solution and minerals including Sr^{+2} and Ba^{+2}. The solution

species and mineral data from these sources are also adopted for the core data set. Data for the Ca-, Sr- and Ba-carbonate species and minerals, as well as for the Mg-carbonate species, are given as equations for logK(T) and are valid between 0 to 10 and 80 to 90°C.

NORDSTROM et al. (1990) include the data just described in their compilation, and also include logK(25) data and $\Delta_r H^0$ values for additional solution species and minerals. These data are also included in the core data set and shown in Table A6.

Table 4.1, the thermodynamic constants of formation of the carbonate species and minerals were calculated. These values can be compared with data included in the CODATA and other critical compilations which were given in Table 4.1 and are repeated in Table A6. In all but a few cases, the core data are within the uncertainties assigned to the critically evaluated values. The exceptions are the $BaHCO_3^+$ and $BaCO_3^0$ values which disagree by such large amounts as to suggest an error in their calculation in the original BUSENBERG & PLUMMER (1986) article. There is also an unexplained difference of about 6 kJ/mol for the $\Delta_f H^0$ of $CaHCO_3^+$ given in the CODATA compilation (GARVIN et al. 1987).

Carbonate and, to a lesser extent, bicarbonate, form complexes with many cations. A number of these complexes will be given in the supplemental data bases.

4.7.3   Reduced carbon solute species, minerals, and gases

The reduced carbon entities included in the data base are C(-IV) as dissolved and gaseous methane, $CH_{4(aq)}$ and $CH_{4(g)}$, and C^0 as the mineral graphite.

Graphite is the standard state for elemental carbon, so its properties of formation are zero by convention.

The thermodynamic properties of formation of $CH_{4(g)}$ are those given in the NIST compilation. The properties of the master species, $CH_{4(aq)}$, are derived from those of the gas and the solubility data of Table 4.2, as described in Section 4.1.1.

One reaction is also included in Table A6 from which the formal oxidation potentials can be calculated corresponding to analysed concentrations of C(IV) and C(-IV).

4.8   Alkaline earth metals: Magnesium, calcium, strontium, and barium

Alkaline earth elements occur in solution as the divalent cations Mg^{+2}, Ca^{+2}, Sr^{+2}, and Ba^+. Their properties of formation are given in Table 4.1. Those for Mg^{+2} and Ca^{+2} are from CODATA, while those for Sr^{+2} and Ba^{+2} are from BUSENBERG et al. (1984) and BUSENBERG & PLUMMER (1986).

These elements form a number of aqueous complexes and minerals, which are important in geochemical modelling, and are given in the core data base. These include hydroxides, carbonates, and sulphates. Phosphate and arsenate complexes and minerals are also stable, and may be important under certain circumstances. However, their properties are not well enough known to include them in the core data.

4.9   Alkali metals: Lithium, sodium, and potassium

The alkali metals occur in solution as the monovalent cations Li^+, Na^+, and K^+. Their properties are given in Table 4.1 and are from CODATA. Alkali metals form important complexes with carbonate and sulphate which are included in the core data. All solids formed by alkali metals with anions included in the core data are highly soluble. Thus, none are included in the core data.

5   SUMMARY

Geochemical modelling within the Nagra programme is done by several groups using different computer models and a number of thermochemical data bases. To achieve consistency among the results of modelling by different groups, a Nagra thermochemical data base is being prepared to be used by all groups. The Nagra core data base will include data for fundamental aqueous species, minerals. Supplemental data bases for aqueous species, minerals, and gases with less well-known thermodynamic properties, or which are required for special purpose modelling, will also be prepared. Data in the supplemental data bases will be subject to more frequent change.

This report provides the core Nagra thermochemical data. These data include the properties of formation and of reaction for important aqueous species, minerals, and gases, as well as parameters useful for the calculation of activity coefficients and redox reactions for each species. Core data are given for the elements oxygen, hydrogen, the halides, sulphur, nitrogen, phosphorous, arsenic, boron, and carbon. The rationale for the selection of the individual data items is discussed, as is the interrelationship of the various thermodynamic properties which were used in assuring that the data given are internally consistent.

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APPENDIX: Nagra Core Thermochemical Data

The Nagra core data are given in the following six tables.

Table A1 contains data for the master species. There is one line of data and at least one line of text for each species. The line of data contains:

Master species name, Formula Weight and Change

OPV: Operational Valence (see Section 2.4)

DH a: Debye-Hückel parameter a_i or a_i^0

DH b: Debye-Hückel parameter b_i or zero

$\Delta_f G^0$: Gibbs energy of formation (kJ mol^{-1})

$\Delta_f H^0$: Enthalpy of formation (kJ mol^{-1})

$\Delta_f S^0$: Entropy of formation (J K^{-1} mol^{-1})

$\Delta_f Cp_a^0$, $\Delta_f Cp_b^0$, $\Delta_f Cp_c^0$: Coefficients a, b, and c of the Maier-Kelley heat capacity equation (see Section 2.2)

The line(s) of text give the sources for the data. The citations are as they appear in the reference section of the report, except:

CODATA (1987): GARVIN *et al.* 1987
CODATA (1989): COX *et al.* 1989
NEA (1990): GRENTHE *et al.* 1990
NIST (1982): WAGMAN *et al.* 1982

Tables A2 through A6 contain the reaction data for aqueous product species, minerals, and gases, and reactions with which Pe values can be calculated from measured concentrations of oxidized and reduced species. There are three lines of data and at least one line of text for each entity.

The first line begins with the name of the product species, mineral, gas, or redox couple, and continues with the association reaction for the entity. The second line includes thermodynamic and other properties of the entity and its association reaction. Many of the properties given in this line are the same as for the master species, but the following additional properties also appear:

$\Delta_f Cp^0$: Heat capacity of formation at 25 °C

$\Delta_r H^0$: Enthalpy of reaction at 25 °C

$\Delta_r Cp^0$: Heat capacity of reaction at 25 °C

$logK(25)$: logK of reaction at 25 °C.

The third line of data contains the five parameters A through E of Equation 2-2 for logK as a function of temperature.

Following the numerical data, there are one to three lines of text. The last line or two gives the sources of the data chosen for the reaction. For some entities, there is an additional first line of text that gives values for properties of the entity from sources of high quality data other than the source chosen. Comparing these values with the numerical data for the entity indicates the level of consistency of the core data set with other widely accepted thermodynamic data sets.

As an example, consider the product species CO_3^{-2}, the first species in Table A6. The next-to-last line of text shows that the values chosen for the core data set were the coefficients of the logK equation given by PLUMMER & BUSENBERG (1982), which are the same values given by NORDSTROM et al. (1990). The last line indicates that the values chosen for the Debye-Hückel parameters a_i and b_i are also from PLUMMER & BUSENBERG (1982). The first line of text provides the information that the $\Delta_f G^0$ and $\Delta_f H^0$ values given by COX et al. (1989) are -527.90 and -675.23 kJ mol^{-1}, respectively. For comparison, the values of these properties in the core data set given in the second line of data are -527.919 and -675.314 kj mol^{-1}, respectively.

Table A1:   Properties of master species. (Page 1 of 3)

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
H+	1.0074	1.0	0.00	9.00	0.00	0.000	0.000	0.000	0.000	0.000000E+00	0.000000E+00

fX: = 0.0 by convention
DHA: WHITFIELD (1979) Tab 24.

E-	0.0005	-1.0	-1.00	0.00	0.00	0.000	0.000	0.000	0.000	0.000000E+00	0.000000E+00

fX: = 0.0 by convention

H2O	18.0153	0.0	0.00	0.00	0.00	-237.140	-285.830	-163.307	31.826	0.000000E+00	0.000000E+00

fX: CODATA (1989)

O2(AQ)	31.9988	0.0	4.00	0.00	0.00	16.521	-12.059	-95.858	152.964	1.570351E-01	0.000000E+00

fX: from CODATA (1989) values for O2(g), and WHITFIELD (1979) solubility data

H2(AQ)	2.0159	0.0	2.00	0.00	0.00	17.726	-4.039	-73.000	218.769	-2.501489E-01	0.000000E+00

fX: from CODATA (1989) values for H2(g), and WHITFIELD (1979) solubility data

F-	18.9989	-1.0	0.00	3.46	0.08	-281.520	-335.350	-180.547	-136.800	0.000000E+00	0.000000E+00

fG, fH: CODATA (1987, 1989); fCp: NIST (1982)
DHA, DHB: PARKHURST (1990) Tab. I.

CL-	35.4535	-1.0	0.00	3.71	0.01	-131.220	-167.080	-120.275	-167.800	0.000000E+00	0.000000E+00

fG, fH: CODATA (1989); fCp: NIST (1982)
DHA, DHB: PARKHURST (1990) Tab. I.

BR-	79.9040	-1.0	0.00	3.00	0.00	-103.850	-121.410	-58.897	-194.100	0.000000E+00	0.000000E+00

fG, fH: CODATA (1987, 1989); fCp: NIST (1982)
DHA: WHITFIELD (1979) Tab. 24.

I-	126.9050	-1.0	0.00	3.00	0.00	-51.720	-56.780	-16.971	0.000	0.000000E+00	0.000000E+00

fG, fH: CODATA (1989); fCp: NIST (1982)
DHA: WHITFIELD (1979) Tab. 24.

SO4-2	96.0590	-2.0	6.00	5.31	-0.07	-744.000	-909.340	-554.553	-403.000	0.000000E+00	0.000000E+00

fG, fH: CODATA (1989); fCp: NIST (1982)
DHA, DHB: PARKHURST (1990) Tab. I.

HS-	33.0680	-1.0	-2.00	3.50	0.00	12.240	-16.300	-95.724	0.000	0.000000E+00	0.000000E+00

fG, fH: CODATA (1989)
DHA: WHITFIELD (1979) Tab. 24.

NO3-	62.0054	-1.0	5.00	3.00	0.00	-110.790	-206.850	-322.187	-159.600	0.000000E+00	0.000000E+00

fG, fH: CODATA (1989); fCp: NIST (1982)
DHA: WHITFIELD (1979) Tab. 24.

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
NH4+	18.0379	1.0	-3.00	2.50	0.00	-79.400	-133.260	-180.647	22.100	0.000000E+00	0.000000E+00

fG, fH: CODATA (1989); fCp: NIST (1982)
DHA: WHITFIELD (1979) Tab. 24.

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
N2(AQ)	28.0134	0.0	0.00	0.00	0.00	18.188	-10.437	-96.009	179.242	1.402849E-01	0.000000E+00

fX: from CODATA (1989) values for N2(g), and WHITFIELD (1979) solubility data

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
HPO4-2	95.9804	-2.0	0.00	4.00	0.00	-1095.990	-1299.000	-680.899	0.000	0.000000E+00	0.000000E+00

fG, fH: CODATA (1989)
DHA: WHITFIELD (1979) Tab. 24.

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
HASO4-2	139.9272	-2.0	5.00	4.00	0.00	-714.600	-906.340	-643.099	0.000	0.000000E+00	0.000000E+00

fG, fH: NIST (1982); NEA (1990)
DHA: est. equal HPO4-2

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
AS(OH)3	125.9438	0.0	3.00	0.00	0.00	-639.800	-742.200	-343.451	0.000	0.000000E+00	0.000000E+00

fG, fH: NIST (1982)

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
HCO3-	60.0094	-1.0	4.00	5.40	0.00	-586.875	-690.215	-346.604	749.276	-1.572479E+00	3.888421E+07

CODATA (1989): dfH0 = -689.93, dfS0 = -345.75
fG, fH, fCp: from values for CO2(g) from CODATA (1989), and values for logK(h) and logK(1)
        from PLUMMER & BUSENBERG (1982).
DHA, DHB: PLUMMER & BUSENBERG (1982).

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
CH4(AQ)	16.0432	0.0	-4.00	0.00	0.00	-34.416	-88.607	-181.758	177.310	-2.385011E-03	0.000000E+00

fX: from NIST (1982) values for CH4(g), and WHITFIELD (1979) solubility data

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
B(OH)3	61.8320	0.0	0.00	0.00	0.00	-969.300	-1072.800	-347.141	0.000	0.000000E+00	0.000000E+00

fG, fH: NIST (1982); CODATA (1989)

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
MG+2	24.3040	2.0	0.00	5.46	0.22	-455.400	-467.000	-38.907	0.000	0.000000E+00	0.000000E+00

fG, fH: CODATA (1989).
DHA, DHB: PARKHURST (1990) Tab. I.

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
CA+2	40.0800	2.0	0.00	4.86	0.15	-552.807	-543.000	32.893	-278.470	0.000000E+00	0.000000E+00

fx0: CODATA (1987 1989)
DHA, DHB: PARKHURST (1990) Tab. I.

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
SR+2	87.6200	2.0	0.00	5.48	0.11	-563.830	-550.900	43.367	0.000	0.000000E+00	0.000000E+00

fG, fH: BUSENBERG et al. (1984)
DHA, DHB: PARKHURST (1990) Tab. I.

	Formula Weight	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$
BA+2	137.3400	2.0	0.00	4.55	0.09	-555.360	-532.500	76.673	0.000	0.000000E+00	0.000000E+00

fG, fH: BUSENBERG & PLUMMER (1986)
DHA, DHB: PARKHURST (1990) Tab. I.

LI+	6.9390	1.0	0.00	4.76	0.20	-292.920	-278.470	48.466	0.000	0.000000E+00	0.000000E+00

fG, fH: CODATA (1989).
DHA, DHB: PARKHURST (1990) Tab. I.

NA+	22.9892	1.0	0.00	4.32	0.06	-261.950	-240.340	72.480	0.000	0.000000E+00	0.000000E+00

fG, fH: CODATA (1989).
DHA, DHB: PARKHURST (1990) Tab. I.

K+	39.0978	1.0	0.00	3.71	0.01	-282.510	-252.140	101.861	0.000	0.000000E+00	0.000000E+00

fG, fH: CODATA (1989)
DHA, DHB: PARKHURST (1990) Tab. I.

Table A2: Reactions of oxide and hydroxide aqueous species, minerals, and gases (Page 1 of 2)

Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cp^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$	$\Delta_r H^0$	$\Delta_r Cp^0$	logK(25)
logK(T):	A		B		C		D		E				

PRODUCT SPECIES

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OH-             1.000  H2O       -1.000  H+
    -1.0   0.00  10.65   0.21  -157.232  -229.926  -243.816  -179.117    881.918 -1.941183E+00  4.287081E+07   55.904  -210.943  -14.000
          -2.839710E+02 -5.069842E-02  1.332300E+04  1.022445E+02 -1.119669E+06
             CODATA (1989): dfG0 = -157.220, dfH0 = -230.02; NIST (1982): dfCp0 = -177.09
             LGK Coef: NORDSTROM et al. (1990)
             DHA, DHB: PARKHURST (1990)


LIOH0           1.000  LI+       1.000  H2O       -1.000  H+
     0.0   0.00   0.00   0.00  -452.204  -564.300  -375.971    31.826     31.826  0.000000E+00  0.000000E+00    0.000     0.000  -13.640
          -1.364000E+01  0.000000E+00  0.000000E+00  0.000000E+00 -0.000000E+00
             NORDSTROM et al. (1990)


NAOH0           1.000  NA+       1.000  H2O       -1.000  H+
     0.0   0.00   0.00   0.00  -418.152  -526.170  -362.295    31.826     31.826  0.000000E+00  0.000000E+00    0.000     0.000  -14.180
          -1.418000E+01  0.000000E+00  0.000000E+00  0.000000E+00 -0.000000E+00
             NORDSTROM et al. (1990)


KOH0            1.000  K+        1.000  H2O       -1.000  H+
     0.0   0.00   0.00   0.00  -437.114     0.000     0.000     0.000      0.000  0.000000E+00  0.000000E+00    0.000     0.000  -14.460
          -1.446000E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
             NORDSTROM et al. (1990)


CAOH+           1.000  CA+2      1.000  H2O       -1.000  H+
     1.0   0.00   0.00   0.00  -717.000     0.000     0.000     0.000      0.000  0.000000E+00  0.000000E+00    0.000     0.000  -12.780
          -1.278000E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
             CODATA (1987): dfG0 = -717.0
             NORDSTROM et al. (1990)


MGOH+           1.000  MG+2      1.000  H2O       -1.000  H+
     1.0   0.00   0.00   0.00  -627.242     0.000     0.000     0.000      0.000  0.000000E+00  0.000000E+00    0.000     0.000  -11.440
          -1.144000E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
             NORDSTROM et al. (1990)


SROH+           1.000  SR+2      1.000  H2O       -1.000  H+
     1.0   0.00   0.00   0.00  -725.112     0.000     0.000     0.000      0.000  0.000000E+00  0.000000E+00    0.000     0.000  -13.290
          -1.329000E+01  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
             NORDSTROM et al. (1990)
```

	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cp^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$	$\Delta_r H^0$	$\Delta_r Cp^0$	logK(25)
logK(T):	A		B		C		D		E					

BAOH+ 1.000 BA+2 1.000 H2O -1.000 H+
1.0 0.00 0.00 0.00 -715.615 0.000 0.000 0.000 0.000 0.000000E+00 0.000000E+00 0.000 0.000 -13.470
-1.347000E+01 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00
NORDSTROM et al. (1990)

MINERALS AND GASES

PORTLANDITE 1.000 CA+2 2.000 H2O -2.000 H+
0.00 -896.947 -984.956 -295.185 -214.818 -214.818 0.000000E+00 0.000000E+00 129.704 0.000 -22.800
-7.643067E-02 0.000000E+00 -6.775032E+03 0.000000E+00 -0.000000E+00
CODATA (1987, 1989): fG0 = -897.498; fH0 = -985.16 kJ/mol
NORDSTROM et al. (1990)

BRUCITE 1.000 MG+2 2.000 H2O -2.000 H+
0.00 -833.559 -925.274 -307.613 63.652 63.652 0.000000E+00 0.000000E+00 113.386 0.000 -16.840
3.024798E+00 0.000000E+00 -5.922689E+03 0.000000E+00 -0.000000E+00
NORDSTROM et al. (1990)

PE:H+/H2(AQ) 1.000 H+ -0.500 H2(AQ)
1.00 0.000 0.000 0.000 0.000 0.000 0.000000E+00 0.000000E+00 -2.019 72.094 -1.553
-3.822643E+01 -3.266605E-03 1.518633E+03 1.315617E+01 -0.000000E+00
GF, HF = 0.0 by convention

PE:O2(AQ)/H2O 0.250 O2(AQ) 1.000 H+ -0.500 H2O
1.00 0.000 0.000 0.000 0.000 0.000 0.000000E+00 0.000000E+00 -139.900 -34.033 21.497
5.409404E+00 -1.025333E-03 6.868753E+03 -2.685490E+00 -0.000000E+00
GF, HF = 0.0 by convention

O2(G) 1.000 O2(AQ)
4.00 0.000 0.000 0.001 0.000 0.000 6.735534E-09 0.000000E+00 12.059 -199.784 2.894
6.096651E+01 -4.101330E-03 -3.376712E+03 -1.839764E+01 0.000000E+00
CODATA (1989): fX0 = 0.0
LGK Coef derived from equations in WHITFIELD (1979, App Tab 8)

H2(G) 1.000 H2(AQ)
-2.00 -0.000 0.000 0.003 0.000 0.000 1.307609E-08 0.000000E+00 4.039 -144.187 3.106
7.645288E+01 6.533210E-03 -3.037284E+03 -2.631230E+01 0.000000E+00
CODATA (1989): fX0 = 0.0
LGK Coef derived from equations in WHITFIELD (1979, App Tab 8)

Table A3:   Reactions of halide aqueous species

	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cp^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$	$\Delta_r H^0$	$\Delta_r Cp^0$	logK(25)
logK(T):	A		B		C		D		E					

PRODUCT SPECIES

NAF0   1.000 NA+   1.000 F-
  0.0   0.00   0.00   0.00 -542.100   0.000   0.000   0.000   0.000 0.000000E+00 0.000000E+00   0.000   0.000   -0.240
       -2.400000E-01 0.000000E+00 0.000000E+00 0.000000E+00   0.000000E+00
       NORDSTROM et al. (1990)

HF0   1.000 H+   1.000 F-
  0.0   0.00   0.00   0.00 -299.700 -323.150   -75.652 -136.800   0.000 0.000000E+00 0.000000E+00   12.200   0.000   3.185
       5.322442E+00 0.000000E+00 -6.372617E+02 0.000000E+00   0.000000E+00
       NORDSTROM et al. (1990): logK(25) = 3.18, dfH0 = 13.30
       fG, fH: NEA (1990)

HF2-   1.000 H+   2.000 F-
 -1.0   0.00   4.00   0.00 -583.700 -655.500 -240.818 -273.600   0.000 0.000000E+00 0.000000E+00   15.200   0.000   3.620
       6.282514E+00 0.000000E+00 -7.939654E+02 0.000000E+00 -0.000000E+00
       NORDSTROM et al. (1990): logK(25) = 3.76, drH0 = 19.0
       fG, fH: NEA (1990)

CAF+   1.000 CA+2   1.000 F-
  1.0   0.00   0.00   0.00 -839.692 -861.112   -71.841 -415.270 -415.270 0.000000E+00 0.000000E+00   17.238   0.000   0.940
       3.960036E+00 0.000000E+00 -9.004236E+02 0.000000E+00 -0.000000E+00
       NORDSTROM et al. (1990)

MGF+   1.000 MG+2   1.000 F-
  1.0   0.00   4.00   0.00 -747.308 -788.961 -139.704 -136.800 -136.800 0.000000E+00 0.000000E+00   13.389   0.000   1.820
       4.165659E+00 0.000000E+00 -6.993582E+02 0.000000E+00 -0.000000E+00
       NORDSTROM et al. (1990)

Table A4: Reactions of sulphur- and nitrogen-bearing aqueous species, minerals, and gases (Page 1 of 3)

| | Charge | OPV | DH a | DH b | Δ_fG^0 | Δ_fH^0 | Δ_fS^0 | Δ_fCp^0 | Δ_fCpa^0 | Δ_fCpb^0 | Δ_fCpc^0 | Δ_rH^0 | Δ_rCp^0 | logK(25) |
| | logK(T): | A | | B | | C | | D | | E | | | | |

PRODUCT SPECIES

HSO4-   1.000 H+   1.000 SO4-2
-1.0   6.00   4.00   0.00 -755.346 -893.212 -462.406 -163.769 -237.663 2.478435E-01 0.000000E+00   16.128   239.231   1.988
      -5.688900E+01 6.473000E-03 2.307900E+03 1.988580E+01 0.000000E+00
      CODATA (1989): dfG0 = -755.3, dfH0 = -886.9
      DHA: WHITFIELD (1979 Tab 24)
      LGK Coef: NORDSTROM et al. (1990)

LISO4-   1.000 LI+   1.000 SO4-2
-1.0   6.00   4.00   0.00 -1040.573   0.000   0.000   0.000   0.000 0.000000E+00 0.000000E+00   0.000   0.000   0.640
       6.400000E-01 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00
      NORDSTROM et al. (1990)

NASO4-   1.000 NA+   1.000 SO4-2
-1.0   6.00   4.00   0.00 -1009.946 -1144.994 -452.955 -403.000 -403.000 0.000000E+00 0.000000E+00   4.686   0.000   0.700
       1.520981E+00 0.000000E+00 -2.447754E+02 0.000000E+00 -0.000000E+00
      NORDSTROM et al. (1990)

KSO4-   1.000 K+   1.000 SO4-2
-1.0   6.00   4.00   0.00 -1031.362 -1152.066 -404.844 -403.000 -403.000 0.000000E+00 0.000000E+00   9.414   0.000   0.850
       2.499291E+00 0.000000E+00 -4.917362E+02 0.000000E+00 -0.000000E+00
      NORDSTROM et al. (1990)

CASO40   1.000 CA+2   1.000 SO4-2
 0.0   6.00   0.00   0.00 -1309.935 -1445.436 -454.473 -681.470 -681.470 0.000000E+00 0.000000E+00   6.904   0.000   2.300
       3.509480E+00 0.000000E+00 -3.606066E+02 0.000000E+00 -0.000000E+00
      CODATA (1987); dfG0 = -1310.76, dfG0 = -1448.95
      NORDSTROM et al. (1990)

MGSO40   1.000 MG+2   1.000 SO4-2
 0.0   6.00   0.00   0.00 -1212.928 -1357.303 -484.236 -403.000 -403.000 0.000000E+00 0.000000E+00   19.037   0.000   2.370
       5.705234E+00 0.000000E+00 -9.943999E+02 0.000000E+00 -0.000000E+00
      NORDSTROM et al. (1990)

SRSO40   1.000 SR+2   1.000 SO4-2
 0.0   6.00   0.00   0.00 -1320.901 -1451.537 -438.156 -403.000 -403.000 0.000000E+00 0.000000E+00   8.703   0.000   2.290
       3.814678E+00 0.000000E+00 -4.545828E+02 0.000000E+00 -0.000000E+00
      NORDSTROM et al. (1990)

	Charge	OPV	DH a	DH b	$\Delta_f G^0$	$\Delta_f H^0$	$\Delta_f S^0$	$\Delta_f Cp^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$	$\Delta_r H^0$	$\Delta_r Cp^0$	logK(25)
logK(T):	A		B		C		D		E					

BASO40   1.000 BA+2   1.000 SO4-2
```
 0.0   6.00   0.00   0.00 -1314.771    0.000    0.000    0.000    0.000  0.000000E+00  0.000000E+00    0.000    0.000    2.700
       2.700000E+00  0.000000E+00  0.000000E+00  0.000000E+00  0.000000E+00
       NORDSTROM et al. (1990)
```

H2S(AQ)   1.000 HS-   1.000 H+
```
 0.0  -2.00   0.00   0.00   -27.600  -38.600  -36.894    0.000    0.000  0.000000E+00  0.000000E+00  -22.300    0.000    6.980
       3.072931E+00  0.000000E+00  1.164831E+03  0.000000E+00 -0.000000E+00
       fG, fH: CODATA (1989)
```

NH3(AQ)   1.000 NH4+   -1.000 H+
```
 0.0  -3.00   0.00   0.00   -26.659  -81.148 -182.758   22.100   22.100  0.000000E+00  0.000000E+00   52.112    0.000   -9.240
      -1.102563E-01  0.000000E+00 -2.722033E+03  0.000000E+00 -0.000000E+00
       NEA (1990):  dfG0 = -26.7, dfH0 = -81.17
       logK(25), drH0: NEA (1990).
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                          MINERALS AND GASES
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GYPSUM   1.000 CA+2   1.000 SO4-2   2.000 H2O
```
       6.00                -1797.234 -2023.546 -759.052 -409.439 -409.439  0.000000E+00  0.000000E+00    0.454  208.379    4.581
      -6.824010E+01  0.000000E+00  3.221510E+03  2.506270E+01  0.000000E+00
       CODATA (1987); dfG0 = -1797.36, dfH0 = -2022.92
       LogK Coef: NORDSTROM et al. (1990)
```

ANHYDRITE   1.000 CA+2   1.000 SO4-2
```
       6.00                -1321.679 -1445.184 -414.239 -100.840 -100.840  0.000000E+00  0.000000E+00    7.156  580.630    4.357
      -1.975200E+02  0.000000E+00  8.668800E+03  6.983500E+01  0.000000E+00
       CODATA (1987): dfG0 = -1321.98, dfH0 = -1434.51
       LogK Coef: NORDSTROM et al. (1990)
```

CELESTITE   1.000 SR+2   1.000 SO4-2
```
       6.00                -1345.684 -1455.901 -369.670   17.408-45602.583  9.442377E+01 -1.552750E+09    4.339  420.408    6.632
       1.480596E+04  2.466092E+00 -7.569685E+05 -5.436359E+03  4.055360E+07
       LogK Coef: NORDSTROM et al. (1990)
```

BARITE   1.000 BA+2   1.000 SO4-2
```
       6.00                -1356.270 -1468.414 -376.133    1.034    1.034  0.000000E+00  0.000000E+00  -26.574  404.034    9.970
      -1.360350E+02  0.000000E+00  7.680410E+03  4.859500E+01  0.000000E+00
       LogK Coef: NORDSTROM et al. (1990)
```

Charge	OPV	DH a		DH b		$\Delta_f G^0$		$\Delta_f H^0$		$\Delta_f S^0$		$\Delta_f Cp^0$	$\Delta_f Cpa^0$	$\Delta_f Cpb^0$	$\Delta_f Cpc^0$	$\Delta_r H^0$	$\Delta_r Cp^0$	logK(25)
logK(T):		A		B		C		D		E								

SULPHUR(RHOMB)   1.000 HS-   -1.000 H+   -1.000 E-
        0.00   0.000   0.000   0.000   0.000   0.000 0.000000E+00 0.000000E+00   16.300   0.000   2.144
        5.000082E+00 0.000000E+00 -8.514234E+02 0.000000E+00 -0.000000E+00
        dfG0 and dfH0 = 0.0 by convention

PE:SO4-2/HS-   0.125 HS-   0.500 H2O   -0.125 SO4-2   -1.125 H+
        1.00   0.000   0.000   0.000   0.000   0.000 0.000000E+00 0.000000E+00   31.285   -66.288   -4.212
        2.445989E+01 0.000000E+00 -2.666510E+03 -7.972758E+00 -0.000000E+00
        dfG0 and dfH0 of e- = 0.0 by convention.

PE:SO4-2/S0   0.667 H2O   -0.167 SO4-2   -1.333 H+
        1.00   0.000   0.000   0.000   0.000   0.000 0.000000E+00 0.000000E+00   38.976   -88.398   -5.970
        3.178423E+01 0.000000E+00 -3.412583E+03 -1.063209E+01 -0.000000E+00
        Assumes S0 activity = 1.
        dfG0 and dfH0 of e- = 0.0 by convention.

PE:S0/HS-   0.500 HS-   -0.500 H+
        1.00   0.000   0.000   0.000   0.000   0.000 0.000000E+00 0.000000E+00   8.150   0.000   1.072
        2.500041E+00 0.000000E+00 -4.257117E+02 0.000000E+00 -0.000000E+00
        Assumes S0 activity = 1.
        dfG0 and dfH0 of e- = 0.0 by convention.

PE:NO3-/NH4+   0.125 NH4+   0.375 H2O   -0.125 NO3-   -1.250 H+
        1.00   0.000   0.000   0.000   0.000   0.000 0.000000E+00 0.000000E+00   97.987   -34.647   -14.892
        1.439590E+01 0.000000E+00 -5.657922E+03 -4.167182E+00 -0.000000E+00
        dfG0 and dfH0 of e- = 0.0 by convention.

PE:NO3-/N2(AQ)   0.100 N2(AQ)   0.600 H2O   -0.200 NO3-   -1.200 H+
        1.00   0.000   0.000   0.000   0.000   0.000 0.000000E+00 0.000000E+00   131.172   -73.122   -20.727
        2.659060E+01 -3.663860E-04 -7.957916E+03 -8.291702E+00 -0.000000E+00
        dfG0 and dfH0 of e- = 0.0 by convention.

PE:N2(AQ)/NH4+   0.333 NH4+   -0.167 N2(AQ)   -1.333 H+
        1.00   0.000   0.000   0.000   0.000   0.000 0.000000E+00 0.000000E+00   42.676   29.486   -5.168
       -5.931499E+00 6.107655E-04 -1.824232E+03 2.707826E+00 -0.000000E+00
        dfG0 and dfH0 of e- = 0.0 by convention.

N2(G)   1.000 N2(AQ)
        0.00   0.000   0.000   0.000   -0.000   -0.000 -9.728459E-08 0.000000E+00   10.437   -221.068   3.186
        6.990691E+01 -3.663863E-03 -3.662355E+03 -2.155827E+01 0.000000E+00
        CODATA (1989): fX0: 0.0
        LGK Coef derived from equations in WHITFIELD (1979, App Tab 8)

Table A5: Reactions of phosphorous-, arsenic-, and boron-bearing aqueous species, and minerals (Page 1 of 2)

| Charge | OPV | DH a | DH b | Δ_fG^0 | Δ_fH^0 | Δ_fS^0 | Δ_fCp^0 | Δ_fCpa^0 | Δ_fCpb^0 | Δ_fCpc^0 | Δ_rH^0 | Δ_rCp^0 | logK(25) |
| logK(T): | A | | B | | C | | D | | E | | | | |

PRODUCT SPECIES

PO4-3   1.000 HPO4-2   -1.000 H+
  -3.0   0.00   4.00   0.00 -1025.497 -1284.400 -868.364   0.000   0.000 0.000000E+00 0.000000E+00   14.600   0.000 -12.350
       -9.792144E+00 0.000000E+00 -7.626247E+02 0.000000E+00 -0.000000E+00
            DHA: WHITFIELD (1979, Tab 24)
            logK(25), drH0: NEA (1990)

H2PO4-   1.000 HPO4-2   1.000 H+
  -1.0   0.00   4.50   0.00 -1137.144 -1302.600 -554.942   0.000   0.000 0.000000E+00 0.000000E+00   -3.600   0.000   7.210
        6.579296E+00 0.000000E+00 1.880444E+02 0.000000E+00 -0.000000E+00
            CODATA (1989): dfG0 = -1137.15, dfH0 = -1302.6
            DHA: WHITFIELD (1979, Tab 24)
            logK(25), drH0: NEA (1990)

H3PO4   1.000 HPO4-2   2.000 H+
   0.0   0.00   0.00   0.00 -1149.359 -1294.100 -485.464   0.000   0.000 0.000000E+00 0.000000E+00   4.900   0.000   9.350
        1.020846E+01 0.000000E+00 -2.559494E+02 0.000000E+00 -0.000000E+00
            logK(25), drH0: NEA (1990)

B(OH)4-   1.000 B(OH)3   1.000 H2O   -1.000 H+
  -1.0   0.00   4.50   0.00 -1153.727 -1344.577 -640.116 -164.771   31.826 -6.593909E-01 0.000000E+00   14.053 -196.597   -9.235
        3.496000E+00 -1.722150E-02 -2.264920E+03 0.000000E+00 0.000000E+00
            NIST(1982): dfG0 = -1153.15, dfH0 = -1344.03
            DHA: estimated
            logK coef: BAES & MESMER(1976 Tab 6.2)

ASO4-3   1.000 HASO4-2   -1.000 H+
  -3.0   5.00   4.00   0.00 -648.410 -888.140 -804.058   0.000   0.000 0.000000E+00 0.000000E+00   18.200   0.000 -11.596
       -8.407637E+00 0.000000E+00 -9.506691E+02 0.000000E+00 -0.000000E+00
            DHA: estimated
            GF, HF: NIST(1982), NEA (1990)

H2ASO4-   1.000 HASO4-2   1.000 H+
  -1.0   5.00   4.50   0.00 -753.170 -909.560 -524.535   0.000   0.000 0.000000E+00 0.000000E+00   -3.220   0.000   6.757
        6.193164E+00 0.000000E+00 1.681953E+02 0.000000E+00 -0.000000E+00
            DHA: WHITFIELD (1979, Tab 24)
            GF, HF: NIST(1982), NEA (1990)

H3ASO4   1.000 HASO4-2   2.000 H+
   0.0   5.00   0.00   0.00 -766.000 -902.500 -457.823   0.000   0.000 0.000000E+00 0.000000E+00   3.840   0.000   9.005
        9.677805E+00 0.000000E+00 -2.005807E+02 0.000000E+00 -0.000000E+00
            GF, HF: NIST(1982), NEA (1990)

| | Charge | OPV | DH a | DH b | $\Delta_f G^0$ | $\Delta_f H^0$ | $\Delta_f S^0$ | $\Delta_f Cp^0$ | $\Delta_f Cpa^0$ | $\Delta_f Cpb^0$ | $\Delta_f Cpc^0$ | $\Delta_r H^0$ | $\Delta_r Cp^0$ | logK(25) |
| | logK(T): | A | | B | C | | D | | E | | | | | |

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AS(OH)4-             1.000  AS(OH)3    1.000  H2O        -1.000  H+
      -1.0   3.00    4.50    0.00   -824.240 -1000.690  -591.816     0.000     0.000  0.000000E+00  0.000000E+00   27.340   -31.826   -9.233
             6.691240E+00  0.000000E+00 -1.923743E+03 -3.827857E+00 -0.000000E+00
             DHA: estimated
             GF, HF: NIST(1982) (= AsO2- + 2 H2O)
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                              MINERALS AND GASES

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ARSENIC              1.000  HASO4-2    7.000  H+          5.000  E-       -4.000  H2O
       0.00                  0.000     0.000      0.000     0.000    0.000  0.000000E+00  0.000000E+00  -236.980   127.304   40.989
             -4.506589E+01  0.000000E+00  1.436115E+04  1.531143E+01 -0.000000E+00
             dfX0 = 0 by convention.


PE:AS(5)/AS(3)       0.500  AS(OH)3    0.500  H2O        -0.500  HASO4-2  -2.000  H+
       1.00                  0.000     0.000      0.000     0.000    0.000  0.000000E+00  0.000000E+00    60.845   -15.913  -14.221
             2.006250E+00  0.000000E+00 -3.426037E+03 -1.913929E+00 -0.000000E+00
             dfX0 of e- = 0 by convention


PE:AS(5)/AS(0)       0.800  H2O       -0.200  HASO4-2    -1.400  H+
       1.00                  0.000     0.000      0.000     0.000    0.000  0.000000E+00  0.000000E+00    47.396   -25.461   -8.198
             9.013179E+00  0.000000E+00 -2.872229E+03 -3.062286E+00 -0.000000E+00
             Assumes As(0) activity = 1.
             dfX0 of e- = 0 by convention
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Charge  OPV  DH a  DH b    ΔfG0      ΔfH0      ΔfS0      ΔfCp0     ΔfCpa0     ΔfCpb0         ΔfCpc0         ΔrH0     ΔrCp0    logK(25)
logK(T):    A           B             C             D              E


                        PRODUCT SPECIES


CO3-2              -1.000  H+        1.000  HCO3-
   -2.0   4.00   5.40   0.00  -527.919  -675.314  -494.367  -447.490   1072.916  -2.817957E+00   6.046815E+07    14.901   -290.506   -10.329
          -1.078871E+02  -3.252849E-02   5.151790E+03   3.892561E+01  -5.637139E+05
          CODATA (1989): dfG0 = -527.90, dfH0 = -675.23
          LGK Coef: PLUMMER & BUSENBERG (1982) = NORDSTROM et al. (1990)
          DHA: PLUMMER & BUSENBERG (1982)


CO2(AQ)            1.000  H+       -1.000  H2O        1.000  HCO3-
    0.0   4.00   0.00   0.00  -385.991  -413.494   -92.247    177.840   -337.087   7.600622E-01  -2.562920E+07    -9.109    366.649     6.352
          3.563094E+02   6.091964E-02  -2.183437E+04  -1.268339E+02   1.684915E+06
          CODATA (1989): dfG0 = -385.97, dfH0 = -413.26
          LGK Coef: PLUMMER & BUSENBERG (1982) = NORDSTROM et al. (1990)


CAHCO3+            1.000  CA+2       1.000  HCO3-
    1.0   4.00   4.00   0.00  -1145.993  -1221.952  -254.768  -843.732  -3509.937  1.040962E+01   3.888421E+07    11.263   -408.279     1.106
          1.209120E+03   3.129400E-01  -3.476505E+04  -4.787820E+02   0.000000E+00
          CODATA (1987): dfG0 = -1145.74, dfH0 = -1216.0
          LGK Coef: PLUMMER & BUSENBERG (1982) = NORDSTROM et al. (1990)


MGHCO3+            1.000  MG+2       1.000  HCO3-
    1.0   4.00   4.00   0.00  -1048.372  -1153.927  -354.032     16.977    923.236  -1.572479E+00   3.888421E+07     3.288    173.960     1.068
         -5.921500E+01   0.000000E+00   2.537455E+03   2.092298E+01   0.000000E+00
          LGK Coef: NORDSTROM et al. (1990)


SRHCO3+            1.000  SR+2       1.000  HCO3-
    1.0   4.00   4.00   0.00  -1157.467  -1215.814  -195.699     12.735    749.276  -1.003239E+00   3.888421E+07    25.301    169.719     1.185
         -3.248000E+00   1.486700E-02   0.000000E+00   0.000000E+00   0.000000E+00
          BUSENBERG et al. (1984): dfG0 = -1157.52, dfH0 = -1215.56
          LGK Coef: BUSENBERG et al. (1984) = NORDSTROM et al. (1990)


BAHCO3+            1.000  BA+2       1.000  HCO3-
    1.0   4.00   4.00   0.00  -1147.838  -1199.453  -173.117     -0.941    749.276  -1.049109E+00   3.888421E+07    23.262    156.043     0.982
         -3.093800E+00   1.366900E-02   0.000000E+00   0.000000E+00   0.000000E+00
          BUSENBERG & PLUMMER (1986): dfG0 = -1136.68, dfH0 = -1245.7 kJ/mol
          LGK Coef: BUSENBERG & PLUMMER (1986) = NORDSTROM et al. (1990)


NAHCO30            1.000  NA+        1.000  HCO3-
    0.0   4.00   0.00   0.00  -847.398     0.000      0.000      0.000      0.000   0.000000E+00   0.000000E+00     0.000      0.000    -0.250
         -2.500000E-01   0.000000E+00   0.000000E+00   0.000000E+00   0.000000E+00
          lgK(25): NORDSTROM et al. (1990)
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| | Charge | OPV | DH a | DH b | $\Delta_f G^0$ | $\Delta_f H^0$ | $\Delta_f S^0$ | $\Delta_f Cp^0$ | $\Delta_f Cpa^0$ | $\Delta_f Cpb^0$ | $\Delta_f Cpc^0$ | $\Delta_r H^0$ | $\Delta_r Cp^0$ | logK(25) |
| | logK(T): | A | | B | C | | D | | E | | | | | |

CACO30   1.000 CA+2   -1.000 H+   1.000 HCO3-
0.0   4.00   0.00   0.00 -1099.129 -1203.482 -350.004 -105.114   4833.688 -1.428331E+01 6.046815E+07   29.733   330.340   -7.105
-1.336619E+03 -3.319725E-01 4.066454E+04 5.247436E+02 -5.637139E+05
CODATA (1987): dfG0 = -1098.91, dfH0 = -1203.03
LGK Coef: PLUMMER & BUSENBERG (1982) = NORDSTROM et al. (1990)

MGCO30   1.000 MG+2   -1.000 H+   1.000 HCO3-
0.0   4.00   0.00   0.00 -1000.326 -1130.963 -438.158 -371.347   1072.916 -2.562570E+00 6.046815E+07   26.252   -214.363   -7.349
-1.068961E+02 -2.585849E-02 5.151790E+03 3.892561E+01 -5.637139E+05
LGK Coef: NORDSTROM et al. (1990)

SRCO30   1.000 SR+2   -1.000 H+   1.000 HCO3-
0.0   4.00   0.00   0.00 -1107.760 -1204.387 -324.088 -301.071   1072.916 -2.326864E+00 6.046815E+07   36.728   -144.087   -7.524
-1.089061E+02 -1.970249E-02 5.151790E+03 3.892561E+01 -5.637139E+05
BUSENBERG et al. (1984): dfG0 = -1107.82, dfH0 = -1204.30
LGK Coef: BUSENBERG et al. (1984) = NORDSTROM et al. (1990)

BACO30   1.000 BA+2   -1.000 H+   1.000 HCO3-
0.0   4.00   0.00   0.00 -1098.765 -1192.973 -315.973 -347.933   1072.916 -2.484040E+00 6.046815E+07   29.742   -190.949   -7.616
-1.077741E+02 -2.380749E-02 5.151790E+03 3.892561E+01 -5.637139E+05
BUSENBERG & PLUMMER (1986): dfG0 = -1067.85, dfH0 = -1222.6
LGK Coef: BUSENBERG & PLUMMER (1986) = NORDSTROM et al. (1990)

NACO3-   1.000 NA+   -1.000 H+   1.000 HCO3-
-1.0   4.00   4.00   0.00   -797.118 -878.375 -272.537 -447.490   1072.916 -2.817957E+00 6.046815E+07   52.180   -290.506   -9.059
-1.000859E+02 -3.252849E-02 3.204519E+03 3.892561E+01 -5.637139E+05
NORDSTROM et al. (1990)

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CALCITE   1.000 CA+2   -1.000 H+   1.000 HCO3-
4.00   -1129.128 -1208.705 -266.904 -430.870   199.182 1.683035E-01 6.046815E+07   24.510   4.584   -1.849
6.401940E+01 4.546451E-02 2.312471E+03 -3.266939E+01 -5.637139E+05
CODATA (1987): dfG0 = -1129.07, dfH0 = -1207.586, dfCp25 = 4.96
LGK Coef: PLUMMER & BUSENBERG (1982) = NORDSTROM et al. (1990)

ARAGONITE   1.000 CA+2   -1.000 H+   1.000 HCO3-
4.00   -1128.307 -1207.481 -265.549 -430.870   199.182 1.683035E-01 6.046815E+07   25.734   4.584   -1.993
6.409020E+01 4.546451E-02 2.248497E+03 -3.266939E+01 -5.637139E+05
CODATA (1987): dfG0 = -1128.15, dfH0 = -1207.776
LGK Coef: PLUMMER & BUSENBERG (1982) = NORDSTROM et al. (1990)

| | Charge | OPV | DH a | DH b | $\Delta_f G^0$ | $\Delta_f H^0$ | $\Delta_f S^0$ | $\Delta_f Cp^0$ | $\Delta_f Cpa^0$ | $\Delta_f Cpb^0$ | $\Delta_f Cpc^0$ | $\Delta_r H^0$ | $\Delta_r Cp^0$ | logK(25) |
| logK(T): | A | | B | | C | | D | | E | | | | | |

DOLO_ORD   1.000 CA+2   1.000 MG+2   -2.000 H+   2.000 HCO3-
8.00   -2161.593 -2321.148   -535.152 -1173.450   1867.361 -5.635913E+00   1.209363E+08   69.282   -581.013   -3.568
-1.917674E+02 -6.505698E-02   8.241352E+03   7.785122E+01 -1.127428E+06
NORDSTROM et al. (1990)

DOLO_DIS   1.000 CA+2   1.000 MG+2   -2.000 H+   2.000 HCO3-
8.00   -2158.453 -2314.228   -522.471 -1173.450   1867.361 -5.635913E+00   1.209363E+08   76.202   -581.013   -4.118
-1.911051E+02 -6.505698E-02   7.879873E+03   7.785122E+01 -1.127428E+06
NORDSTROM et al. (1990)

STRONTIANITE   1.000 SR+2   -1.000 H+   1.000 HCO3-
4.00   -1144.664 -1224.539   -267.903   22.987   1543.392 -2.817957E+00   6.046815E+07   16.576   179.970   -1.058
-2.629176E+02 -3.252849E-02   1.239138E+04   9.551199E+01 -5.637139E+05
BUSENBERG et al. (1984): dfG0 = -1144.73, dfH0 = -1225.77
LGK Coef: BUSENBERG et al. (1984) = NORDSTROM et al. (1990)

WITHERITE   1.000 BA+2   -1.000 H+   1.000 HCO3-
4.00   -1132.148 -1210.754   -263.646   136.369   3039.207 -7.454656E+00   6.046815E+07   11.961   293.353   -1.767
-7.155291E+02 -1.536265E-01   2.516304E+04   2.754204E+02 -5.637139E+05
BUSENBERG & PLUMMER (1986): dfG0 = -1132.21, dfH0 = -1210.85
LGK Coef: BUSENBERG & PLUMMER (1986) = NORDSTROM et al. (1990)

GRAPHITE   1.000 HCO3-   5.000 H+   4.000 E-   -3.000 H2O
0.00   0.000   0.000   0.000   0.000   0.000   0.000000E+00   0.000000E+00   -167.275   252.462   21.820
2.081775E+02   4.106888E-02 -4.606129E+03 -7.863525E+01   1.015550E+06
dfG0, dfH0 = 0 by convention

PE:HCO3/CH4(AQ)   0.125 HCO3-   1.125 H+   -0.125 CH4(AQ)   -0.375 H2O
1.00   0.000   0.000   0.000   0.000   0.000   0.000000E+00   0.000000E+00   -31.985   53.633   3.481
1.708618E+01   5.125824E-03   3.472576E+02 -7.163672E+00   1.269437E+05
dfG0, dfH0 = 0 by convention

CO2(G)   1.000 H+   -1.000 H2O   1.000 HCO3-
4.00   -394.370   -393.510   2.883   -0.760   -0.760   2.535693E-08 -2.917451E+00   10.875   188.050   7.820
2.479229E+02   4.106888E-02 -1.491484E+04 -8.638236E+01   1.015550E+06
CODATA (1987, 1989): dfG0 = -394.373, dfH0 = -393.51, dfCp25 = -0.760
LGK Coef: PLUMMER & BUSENBERG (1982) = NORDSTROM et al. (1990)

CH4(G)   1.000 CH4(AQ)
-4.00   -50.720   -74.810   -80.798   -30.866   -30.866   1.394603E-07   0.000000E+00   13.797   -207.465   2.856
7.806599E+01   6.229365E-05 -3.957200E+03 -2.503828E+01   0.000000E+00
NIST (1982): dfG0 = -50.72, dfH0 = -74.81, dfCp25 = -30.87
LGK Coef derived from equations in WHITFIELD (1979, App Tab 8)