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The CSIRO - SGTE - THERMODATA package
for thermodynamic computations at BMR

- * Overview: Geochemical applications
- * BMR extensions of database and species index
- * Installation at BMR

Christoph A. Heinrich
June 1987

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Acknowledgments

Brian Harrold has made all the software changes that were required to make THERMODATA run on the BMR-DG mainframe computer, and he wrote the conversion program SOLCONV with which the bulk of the new thermodynamic data file for aqueous species were derived. I am most grateful to Brian for his great help, and I admire the efficiency, enthusiasm and good humour with which he completed a difficult task (which wasn't made easier by some mistakes of mine). Both Brian and I would like to thank Liz Anderson, John Brown, Dave Downie and Rod Ryburn for their support. I would also like to acknowledge the support of John Walshe during the early stage of this work, when THERMODATA was set up at ANU.

I am very grateful to Mark Reed for his advice, for several programs, and particularly for his SOLTHERM data file, which is the result of months or years of thermodynamic data compilation. I would finally like to thank Alan Turnbull and Michael Wadsley for their friendly and expert help with the installation and use of THERMODATA over the last two years, first at ANU and then at BMR. I am grateful for the numerous program options they added during this time, to extend and facilitate the application of THERMODATA to geochemical problems.

I would like to thank Neville Higgins, Dick Henley and Subhash Jaireth for their comments on this manuscript.

Overview: Purpose and application of THERMODATA

Thermodynamic equilibrium calculations provide a powerful tool to develop and test new ideas about geochemical controls of ore mineral deposition. The CSIRO-SGTE THERMODATA program package has recently been established on BMR's Data General mainframe computer, and its thermodynamic database has been extended to a large number of compounds commonly occurring in hydrothermal ore fluids. The programs can be used for ore genesis and other geochemical research at BMR and, on request, by guests from universities and the mineral exploration industry.

What is THERMODATA?

Equilibrium thermodynamics provides a theoretical framework to quantify the stability of a chemical compound with regard to external conditions such as temperature, pressure, and its chemical environment. The CSIRO-SGTE THERMODATA is a general-purpose computer program package designed for the application of this theory to a wide variety of chemical problems. The package has been developed over the last ten years by A.G.Turnbull and M.W.Wadsley at CSIRO's Division of Mineral Chemistry in Port Melbourne. It has originally been used for industrial-chemical investigations such as the optimization of metallurgical processes. However, its generality and a number of recent extensions have made it equally valuable for ore genesis studies and other geochemical and petrological applications.

THERMODATA consists of two main parts:

(a) An extensive **databank of basic stability data** for a large number of organic and inorganic solid, liquid, gaseous and aqueous species. This databank comprises several data files, which include a number of large international compilations (e.g. the JANAF tables), a critical compilation of literature data by CSIRO, and some data for ionic species in supercritical aqueous solutions from Helgeson (University of California, Berkeley). A data file for ions and complexes in subcritical aqueous solutions at elevated temperature has been added at BMR, based on experimental data from the recent literature and a compilation by M.H.Reed (University of Oregon).

(b) Eight programs driven by a high-level command language to perform a wide range of functions based on this and any additional data supplied by the user. Applications range from simple tabulations like the solubility constant for a mineral dissolution reaction, through plotting of stability diagrams, to the quantitative prediction of mass transfer during step-wise equilibration of a hydrothermal fluid with a rock. The programs most commonly used in geochemistry will be briefly described below. In addition, the package includes a program for vapour pressure calculations based on a databank of gas properties, a program for the analysis of the energy efficiency of industrial chemical processes, and a program for the storage and retrieval of literature references to the sources of information in the databank.

The programs can be run either interactively, or in batch mode from commands typed into a job file. Most of the programs include options for graphic output. Tektronix or Hewlett-Packard format plot files are currently transferred from the mainframe computer through a communications network to an IBM-PC/XT clone microcomputer, where they can be viewed on screen or plotted on a HP pen plotter.

Function of the main programs

The program **FILER** is used to search and sort basic stability data for species in the databank, to perform least-squares fitting of additional data provided by the user, and to store new data in the data bank or a temporary user data file.

Program **REACT** calculates a wide choice of thermodynamic properties of individual compounds, or of any particular reaction. Conversely, **REACT** can be used to calculate, and regress as a function of temperature, any basic stability data for one species from an experimentally calibrated equilibrium reaction. This option has been extensively applied to published equilibrium constant data from high-temperature solubility studies, to establish the datafile **GIBBMRAQU** for high-temperature aqueous species.

Program **ESTIMA** offers a range of methods by which unavailable thermodynamic data can be estimated. For example, methods based on corresponding-state correlations can be used to extrapolate low-temperature stability data for an aqueous species to higher temperatures, where no experimental data may be available.

Program **SYSTEM** allows calculation of predominance phase diagrams with a choice of axes including any combination of temperature, pressure, and activities or fugacities of species or species ratios.

Figure 1 exemplifies the structure of the THERMODATA command language, in a job producing the predominance diagram shown in Figure 2. This example makes use of the LIGAND option of the program SYSTEM, to depict the effect of the changing state of the predominant 'ligand component', sulfur (H_2S , HS^- , etc.; dashed boundaries) on the solubility contour of the 'main area component', gold (Au insoluble outside, $\text{Au}(\text{HS})_2^-$ about 10 ppb or higher inside the solid triangle).

Definition of additional species of fixed activity under the AREAS/AXES heading permit calculations of predominance diagrams where, for example, pH of a fluid is constrained by equilibrium with wall rock minerals such as feldspar + muscovite + quartz.

Figure 1. (next page) An example of the command language of THERMODATA. The commands in the center column were used to calculate and plot the activity diagram shown in Fig.2 with the program SYSTEM. The language is based on command modules which are headed by a 'directive' name such as DIAGRAM, followed by option and parameter specifications, and terminated by a blank line. Some directive information is subdivided, e.g. AXES, LIGANDS and AREAS are subdirectives of the directive DIAGRAM (indented).

System definition	DIAGRAM AXES H2 (G) H E-1 (AQ) H2 O LIGANDS H2 S (AQ) H S <-> (AQ) H S O4 <-> (AQ) S O4 <2-> (AQ) AREAS AU AU H2 S2 E (AQ)	(axis species and species with fixed activity throughout diagram, e.g. H2O) (sulfur speciation affects speciation .. of .. main area component, gold, due to complexation)
List of all species to be considered		
Number of independent chemical components	COMPONENTS 1 1	(1 area component, Au, 1 ligand component, S)
Definition of fixed activity values	ACTIVITY 1., 1., 1. 1., .001, .001, .001, .001 1. .5E-7	(axis species) (ligand species) (main area species)
Collection of stability data for species	FILE GIBBMRAQU CPDMRLDAT	(aqueous complexes) (solids, elements)
Definition of external conditions	TEMPERATURE 573.15 PRESSURE 86.0	(Kelvin; 300 degC) (default; Psat)
Calculation Configuration of phase diagram	AXES ABSCISSA PH H E-1 (AQ) ORDINATE LOGP -1. H2 (G) LIMITS ABSCISSA 4., 10. ORDINATE -1. 5. AREAS	
Preparation of graphics output for screen or pen plotter	PLOT HEWLETT AREAS LABEL IDENTIFIER	(various commands for beautifying plot; omitted here)

10ppb Au in 300C solution with .001m S(tot)

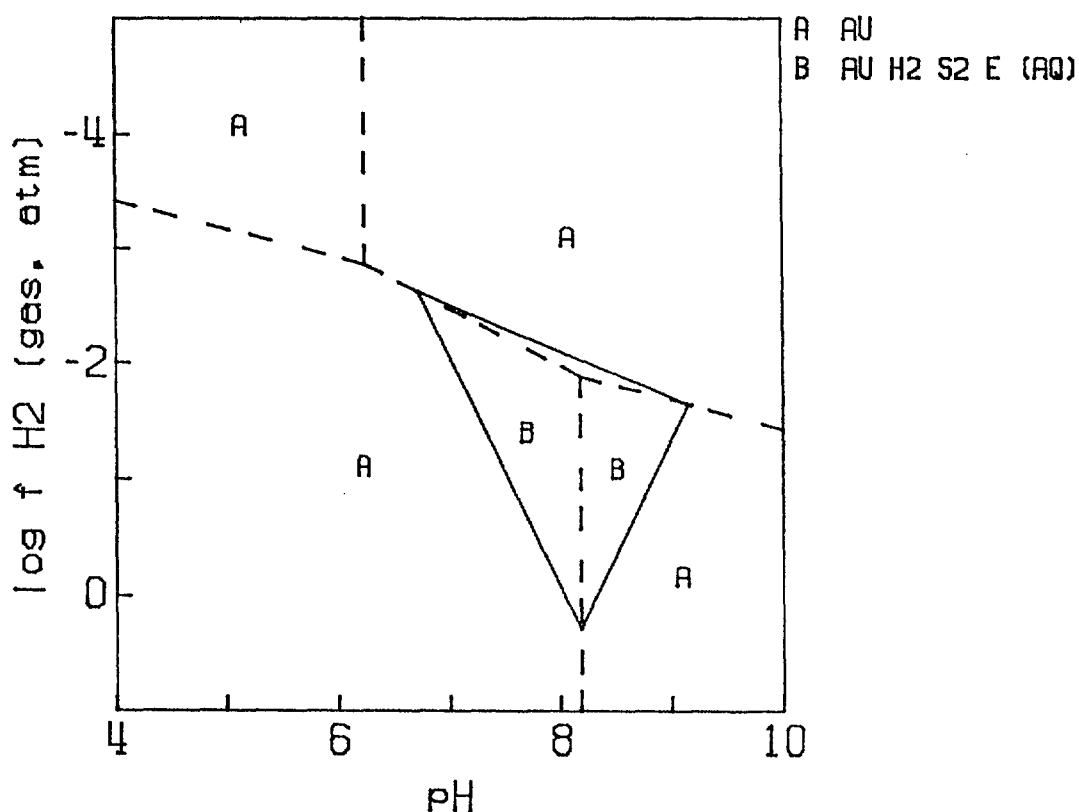


Figure 2. pH vs. redox diagram calculated with the program SYSTEM using the commands of Fig.1. The diagram shows the stability (predominance) field of dissolved gold at $a(\text{Au}(\text{HS})_2^-) \geq 5 \cdot 10^{-7}$ (≈ 10 ppm; inside the triangular 'main area' B). At constant total sulfur in solution, the stability of the sulfur-bearing gold complex depends on the speciation of sulfur, which is marked by the dashed 'ligand predominance areas' of HSO_4^- , SO_4^{2-} , HS^- and H_2S (unlabelled, in clockwise order).

Program CHEMIX calculates the state of equilibrium of a system of given bulk composition, which may include many phases containing up to 100 chemical species. For example, CHEMIX can be used to compute the change in composition of a hydrothermal fluid during equilibration with a wall rock, and the amounts of ore minerals precipitated, wall rock minerals consumed, and gangue or alteration minerals produced during this process. A variety of options for iterative calculations are available that can be used to satisfy additional constraints on a system (e.g. a constant total heat content, to predict the chemical effects of adiabatic boiling). Iterations can also be used to investigate the effect of variation of one parameter (e.g. temperature, or input composition) upon the equilibrium state of the system.

The commands explained in Figure 3 were used in a simple model for the progressive reaction of a gold-rich fluid with a graphitic or a magnetite-rich rock (Fig.4), in order to compare the efficiency of two possible ore depositing mechanisms in metamorphic gold vein deposits (Slate-belt and Archean greenstone belt deposits).

The program CHEMIX allows for non-ideal mixing properties of solution phases. The directive GAMMA offers a choice of currently 24 different activity models, i.e. functions relating the activity of species to the composition of non-ideal mixed phases. Models include virial coefficients for gases, Margules solutions for solids and melts, and the Debye-Hückel and Pitzer models for aqueous solutions. Required species-parameters must be supplied by the user but can be stored on separate data files.

Figure 3. (next page) A simple CHEMIX job to model the stepwise equilibration (titration) of a fluid with a graphitic rock. The commands produce the full-line portion of the plot shown in Fig.4 (below). The input fluid composition (directive INMOLE) has been obtained with a preceding CHEMIX calculation to obtain a gold-saturated fluid with the maximum possible gold concentration, i.e. a fluid initially buffered at the triple junction in field B of Fig.2.

System definition	SYSTEM GAS H2 O (G); C O2 (G); C H4 (G)
List of all phases and all contained species to be considered	AQUEOUS H2 O; C O2 (AQ); C H4 (AQ) H C O3 <-> (AQ); C O3 <2-> (aq); H2 S (AQ) H S E (aq); S O4 E2 (AQ); H S O4 E (AQ) NA E-1 (AQ); O H E (AQ); H E-1 (AQ) AU H2 S2 E (AQ)
	SINGLE AU; C
Definition of bulk composition of system: Input moles of species	INSPECIES ALL INMOLE .2757E-03 .1802E-09 .4260E-15 55.50 .6327E-06 .7190E-12 .3671E-06 .3276E-11 .3292E-01 .3251E-01 .3286E-01 .3891E-03 .7165E-03 .6680E-08 .6587E-03 0.00 0.00
Collection of stability data for species	FILE GIBBMRAQU CPDMRLDAT
Characterization of mixing properties of all non-ideal mixed phases (parameters omitted)	GAMMA AQUEOUS DEBYE-HUCKEL
Definition of external conditions	TEMPERATURE 573.15 PRESSURE 86.0
Calculation of selected solute concentrations, varying in response .. to .. varying input (titration) of graphite	STEP MOLALITY AQUEOUS AU H2 S2 E (AQ) H S <-> (AQ) H2 S (AQ) S O4 <2-> (AQ) C H4 (AQ) VARY INMOLE STEPSIZE .01 .001 .1 SINGLE C EQUILIBRATE
Preparation of graphics (omitted)	PLOT ...

Progressive rock reaction of Au-fluid

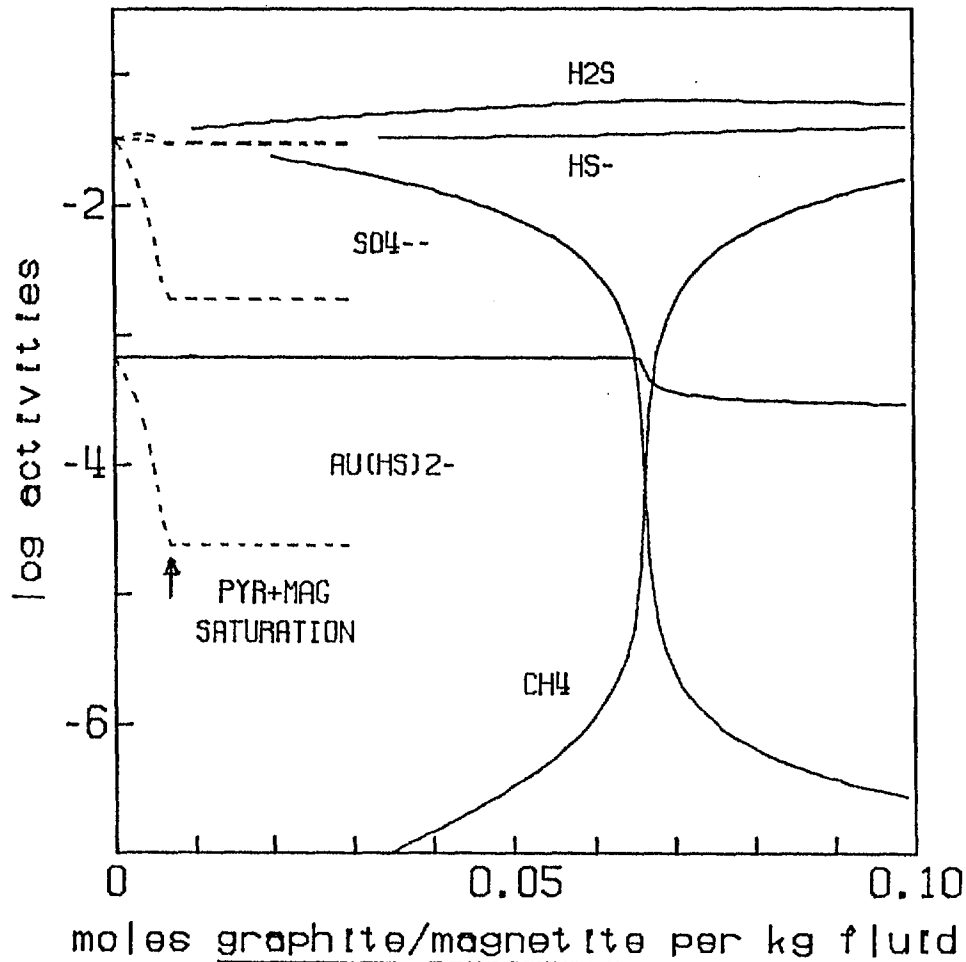


Figure 4. CHEMIX plot showing predicted change in fluid composition of a gold-rich solution during progressive reaction with a graphitic rock (solid lines; commands from Fig.3), or a magnetite-rich rock (dashed lines). Note precipitation of 45% of the dissolved gold after reaction of 1kg of fluid with 0.07 moles of graphite due to the drop in redox state of the fluid (increase of CH_4 in solution). By contrast, reaction of the same fluid with a magnetite-rich rock provides a more 'efficient' gold precipitation mechanism, that will deposit more than 99% of the gold after reaction with a much smaller amount of magnetite. This is due to the combined effects of reduction and de-sulfidation of the fluid, leading to conversion of magnetite to pyrite.

Limitations, and recent extensions of programs and data base

The application of the THERMODATA programs is primarily limited by the availability of basic stability data for species or chemical systems under the P-T conditions of interest, and secondly by the functional relationships and/or the parameters required to express activity - compositions relationships for particular mixed phases.

Basic stability data (Free energy data). The original data bank has a good coverage of inorganic gaseous species and solids including most simple minerals, and a fair coverage of organic and low-temperature aqueous species. However it is limited with regard to more complex minerals such as end-members of geologically important solid solutions, and the absence of specific volume data makes computation of high-pressure (e.g. metamorphic) equilibria somewhat cumbersome.

The databank contains few data for aqueous complexes at elevated temperature. There is an increasing amount of high-temperature equilibrium data for aqueous systems available in the literature, even though many geologically important systems remain poorly characterized (e.g. Fe-Cl-O-H). Over the last 12 months much of the more recent data available for subcritical solutions have been critically evaluated, fitted and collected in a new data file GIBBMRAQU. A sequential method of evaluation (rather than a simultaneous solution) has been used to build up this data file. As a basis, data for elements, gaseous and solid species were accepted from the file CPDMRLDAT of the THERMODATA data bank, and data for simple aqueous species to 300°C were then adapted from a critical compilation by Cobble et al. (1982; NTIS Report EPRI-NP-2400) and recent experimental data. Using similar principles, the databank SOLTHERM of Reed (University of Oregon) was converted to a reference state that is internally consistent with CPDMRLDAT. The combined GIBBMRAQU file now includes data for 175 aqueous species of geochemical interest, over the temperature range of 25 to at least 300°C.

Activity coefficient models. Even if stability data are available for pure species, applications may be limited by the availability of activity - composition relationships for components in mixed phases. In many cases basic experimental data are unavailable to obtain, for example, the interaction parameters required to apply the Pitzer model for concentrated electrolyte solutions to hydrothermal brines, so that the less accurate Extended Debye-Huckel approximation must be used. In other cases available experimental data may be not readily

expressed in terms of the activity coefficient models offered by program CHEMIX, so that a new program module must be written. Such an extension is currently underway, to include activity coefficients for neutral species such as CO_2 in high-temperature saline fluids.

Recent geological applications, and future potential

The THERMODATA programs have been used in several recent studies of **hydrothermal ore formation**, for example the estimation of the high-temperature stability of aqueous arsenic species and the possible role of arsenopyrite in the formation of tin deposits (Econ.Geol. 81/3, 1986). CHEMIX is currently used to quantify the efficiency of various ore precipitating mechanisms in granite-related Sn-W systems, and to investigate possible chemical controls on the genesis and localization of hydrothermal copper ores at Mount Isa.

The Pitzer solution model of CHEMIX has been successfully used in the evaluation of saline groundwaters as a potential tool in **hydrogeochemical exploration** (A.Giblin, CSIRO).

In future, THERMODATA will be extended for the quantitative interpretation of **fluid inclusion data**. Preliminary studies have been directed at the thermodynamic stability of hydrocarbons recently found in fluid inclusions from hydrothermal ore deposits (BMR Research Newsletter, 6, 1987). However, full coverage of the non-ideality of the relevant chemical systems at high pressure and temperature will require new program modules for activity coefficient models to be added.

Margules mixing models have been proposed in the recent theoretical literature to represent activity coefficient in silicate melts. CHEMIX includes several Margules activity models, and could therefore be adapted to quantitatively model **igneous processes** such as partial melting or melt - crystal fractionation, in order to study their role in the evolution of ore-forming plutons or diamondiferous magmas.

Practical considerations for new users

The elements of the THERMODATA command language are well documented in a series of manuals by Turnbull and Wadsley (1987). The same information and a number of example jobs are available as on-line help on the computer. The following documentation describes the features and limitations of the GIBBMRAQU data file, the function of the program SOLCONV that was written to create part of this file from the data of M.Reed, and changes to the THERMODATA code that were required to install the programs on the Data General computer.

This documentation should enable a new user with a basic understanding of thermodynamics to familiarize himself with the THERMODATA language. Experience has shown, however, that this may involve a substantial time investment, and occasionally some initial frustration. Depending on interest a limited amount of service will therefore be provided to solve smaller jobs. Generally however, a collaborative approach to new applications is envisaged, at least for the near future. This should increase the chance of detection of any errors that may still be present in the programs and in the data bank, particularly the GIBBMRAQU file. In addition such an approach allows sharing the results of often time-consuming literature searches between users, provided that any additional data is fitted in a manner consistent with the existing data bank.

Databank extensions 'GIBBMRAQU' and 'GIBBMRSOL'

Summary - Important hints and warnings

The original CSIRO-SGTE-THERMODATA package, Version V, includes a number of large data files containing stability data for chemical species in a variety of formats (see Turnbull and Wadsley, 1987, 'Introduction' and 'Databank Index'). The present chapter describes the methods by which additional data has been built up to supplement the existing data bank for applications to hydrothermal geochemistry. This has some important consequences for the correct use of the data files GIBBMRAQU (aqueous species to 300°C) and GIBBMRSOL (minerals to 300°C).

1. Combination of data files and search sequence

GIBBMRAQU and GIBBMRSOL were built up to be internally consistent with the databank file CPDMRLDAT. In the FILE directive, data search from GIBBMRAQU and GIBBMRSOL **must always be followed** (not preceded!) by a search of CPDMRLDAT for reference element data, e.g.

FILE
GIBBMRAQU
GIBBMRSOL
CPDMRLDAT

Any combination, in the same job, of mineral data from GIBBMRSOL with mineral data from any other sources, including CPDMRLDAT, should be avoided or checked very carefully for internal consistency.

2. Extrapolation of data to higher temperature

Data sets from GIBBMRAQU with a full 6-parameter free energy function ($A \neq B \neq C \neq D \neq E \neq F \neq 0.0000$) and a stated temperature range 298.15 to 573.15K **must never be extended** beyond about 325°C (600K).

Data sets from GIBBMRSOL must not be extended at all beyond the stated range 298.15 to 623.15.

An understanding of the method and sequence of data buildup of GIBBMRAQU, as described in the next section, is essential

* if data for additional species needs to be fitted in a consistent manner (especially for later inclusion in the data file);

* and particularly, if new and better data for species with an existing entry in the database need to be inserted.

Build-up of GIBBMRAQU for high-temperature aqueous species

The data file GIBBMRAQU contains parameters for the temperature-function of the Gibbs free energy of formation from elements for simple and complex aqueous species. Standard state is the hypothetical ideal 1 molal solution in liquid water, at the pressure of the vapour saturation curve. The temperature range is generally from 25°C to 300 or 350°C.

The parameters of the free energy function were obtained by fitting tabulated equilibrium constants or free energies for reactions (including formation reactions from elements) using the THIRDLAW method of program REACT. This procedure, which was automated in a separate program SOLCONV to convert and include the data file SOLTHERM (see below), ensures internal consistency of added data with the reference state of existing data at any stage of data buildup. A method of sequential data build-up has been used, rather than one of simultaneous solution (cf. Wagman et al., 1982, p.2-14).

All files relevant to the following sequence of steps are kept in a subdirectory CHRIS.PEG:THERMO:BMRDATA, and subdirectories thereof.

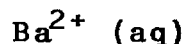
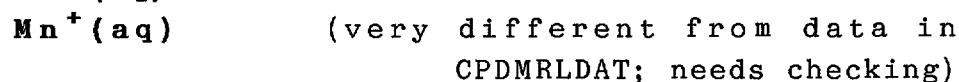
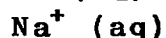
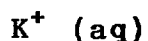
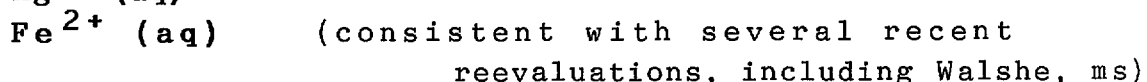
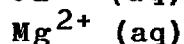
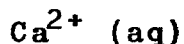
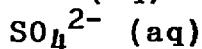
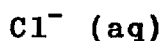
1. Since the databank file CPDMRLDAT contains by far the largest number of species of geological interest, it was accepted as the base reference for all elements, gases, and simple minerals such as oxides and sulfides. However none of these species were refitted and included in GIBBMRAQU. CPDMRLDAT must therefore always be searched after GIBBMRAQU for reference element data

2. The free energy of formation of $H^+(aq)$ is set to 0.0 at all temperatures, following the convention used by CPDMRLDAT.

3. A single-range refit for liquid H_2O was based on the data from CPDMRLDAT up to 300°C, an extension to 350°C along the liquid/vapour curve based on fugacity data given by Helgeson et al., 1974, Table 31), and a further extension to 600°C along a P-T curve of constant density $d = d(350^\circ C) = 1.74 \text{ g/cm}^3$ based on the fugacities tabulated by Burnham et al. (1969). The isochoric extension into the supercritical range has only been used for some semiquantitative applications but not for any of the following fitting.

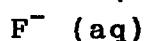
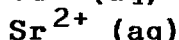
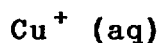
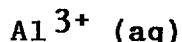
4. Data for $CO_2(aq)$, $H_2S(aq)$, and $CH_4(aq)$ were fitted to Henry constant data by Drummond (1981).

5. HCO_3^- (aq) and HS^- (aq) were fitted to pK values tabulated by Cobble et al. (1981). Tabulated free energies of formation from the same source were used for the following species:



6. Zn^{2+} (aq) from CPDMRLDAT (25°C) and Bourcier (1983; 100-350°C)

7. The following species were taken from CPDMRLDATA and refitted to the GIBBMRAQU format, generally using 3 fit parameters.



The re-fit was mainly needed for convenient conversion of the data file SOLTHERM by the program SOLCONV (see step 8. below).

In all datasets obtained in steps 4, 5, 6 and 7, care was taken not to overfit the data, and generally a 3-parameter fit (corresponding to a constant partial molal heat capacity) was sufficient to represent the free energy of formation within a few hundred cal/mol or less.

8. The following steps were taken to complete a **subsidiary data file GIBREED.FMT**, which is required by program SOLCONV to convert the data file **SOLTHERM** to an elemental reference state.

The data file SOLTHERM has been compiled by M.H.Reed (University of Oregon). It contains entries for the equilibrium constant $\log K(T)$ of reactions that relate a complex aqueous, gaseous or mineral species to an arbitrarily chosen set of 27 simple aqueous 'component species' (H^+ , H_2O , Cl^- , SO_4^{2-} , etc.). Accordingly, SOLTHERM expresses the stoichiometric composition of all complex aqueous species and minerals in terms of formation from these 'component species'.

To be used by the THERMODATA programs, the stability data

contained in SOLTHERM had to be recalculated to the ordinary reference state, i.e. free energy of formation from elements. This requires data for the free energy of formation from elements for the 27 'component species', which is collected in the data file GIBREED.FMT. This file was created with the standard 'GIB' format of THERMADATA/FILER and contains the component species data in the order defined by SOLTHERM.

Most of the component species data in GIBREED.FMT has been obtained in steps 2 through 7, above. The remaining species,



were obtained by REACT/THIRDLAW fitting of logK(T) values for QUARTZ, SILVER, GOLD, and MERCURY, respectively, of the SOLTHERM data file, accepting data for the solids from CPDMRLDATA and treating the 'component species' as unknowns. To maintain a standard format for possible later updates of SOLTHERM, dummy data for I⁻, Br⁻, As³⁺ and Sb³⁺ was added to GIBREED.FMT, but these elements are not used in our version of SOLTHERM.

9. Conversion of SOLTHERM data for aqueous complexes to the reference state of formation from elements, using a separate program SOLCONV.

The **program SOLCONV** was written by Brian Harrold (ANU Geology Department) and is documented in more detail in a file SOLCONV.DOC in the directory CHRIS.PEG:THERMO:BMRDATA. It performs the following main steps:

(i) Calculate free energy of formation of 27 'component species' at 25, 50, 100, 150, 200, 250, 300 and 350°C from parameters read from GIBREED.FMT

(ii) Read 3 lines from SOLTHERM containing data for first complex species.

(iii) Line 1 of (ii) defines the old composition vector (on the basis of 'component species'). Calculate the new stoichiometry vector (on elemental basis) by multiplication of the old vector with a matrix relating the 'component species' to elements.

(iv) From logK_R(25, 50, 100, ..., 300, (,350)°C), listed in line 2 of the SOLTHERM entry, calculate the free energy of formation of the species, DGF(T), based on stoichiometry (step iii) and the free energies of formation of the 'component species' (step (i) above).

(v) Estimate by non-linear least squares regression the 6 parameters A, B, ...F of the temperature function of the free energy of formation from elements:

$$DGF(T) = A + B*T + C*T*T + D*T*T*T + E/T + F*T*\ln T$$

For this regression Turnbull and Wadsley's subroutines FITDGR and MATINV (normally called by the THIRDLAW/REACT directive), were modified and inserted into SOLCONV.

(vi) Write results of (ii) and (v) into new file GIBSOLTHERM.ADD in a 'GIB' format readable by the ADD/FILER directive of THERMODATA. Go to (ii) to process next species.

10. Editing and splitting of the output file GIBSOLTHERM.ADD, and insertion of all aqueous species data into a new databank file GIBBMRAQU, using FILER.

First addition = GIBBMRAQU.AD1 = first 86 aqueous species from GIBSOLTHERM.ADD

Second addition = GIBBMRAQU.AD2 = remaining 55 aqueous species sets from GIBSOLTHERM.ADD

Third addition = GIBBMRAQU.AD3 = 'component species' from GIBREED.FMT, as derived in steps 1-8 above, excluding dummy data for I⁻, Br⁻, As³⁺, Sb³⁺.

Fourth addition = GIBBMRAQU.AD4 = additional species obtained in fit steps 1-8;
Plus species for which recent experimental data supersedes entries in SOLTHERM (e.g. HCl(aq), Au(HS)₂⁻);
Plus species for which no data is given in SOLTHERM (e.g. aqueous Sn species).

A more detailed record is kept in the documentation file README.DOC in CHRIS.PEG:THERMO:BMRDATA, where future updates and additions will be recorded.

Index to aqueous species in the GIBBMRAQU data file

ELEMENTS ARE IN ALPHABETIC ORDER
BOTH WITHIN AND BETWEEN FORMULAS

PHASE NUMBERS OF ANY ALLOTROPES
OTHER THAN THE MOST STABLE ONE
ARE GIVEN IN BRACKETS AFTER STATE

TOTAL NUMBER OF SUBSTANCES 175

DATE 11 - 7 - 87

SPECIES FORMULA	SPECIES NAME	T LIMIT
Ag <+>(aq)	silver ion aqu backfitted to soltherm ago, =mrl within 400cals	623
Ag Cl (aq)	agcl	573
Ag Cl2<->(aq)	agcl2-	573
Ag Cl3<2->(aq)	agcl3--	573
Ag Cl4<3->(aq)	agcl4---	573
Ag F (aq)	agf	573
Ag H S (aq)	aghs	573
Ag H2S2<->(aq)	ag(hs)2-	573
Ag O4S <->(aq)	agso4-	573
Ag2H2S3<2->(aq)	ag2h2s3=	573
Al <3+>(aq)	alumina ion aqu, refit to mrl, exact	623
Al F <2+>(aq)	alf++	573
Al F2<+>(aq)	alf2+	573
Al F3(aq)	alf3	573
Al F4<->(aq)	alf4-	573
Al F5<2->(aq)	alf5--	573
Al H O <2+>(aq)	aloh++	573
Al H2O2<+>(aq)	al(oh)2+	573
Al H4O4<->(aq)	al(oh)4-	573
Al O4S <+>(aq)	also4+	573
Al O8S2<->(aq)	also4)2-	573
Au <+>(aq)	au+	573
Au <3+>(aq)	au+++	573

GIBBMRAQU

SPECIES FORMULA	SPECIES NAME	T LIMIT
Au Cl ₂ <->(aq)	gold dichloride complex aqu backfitted to soltherm	623
Au Cl ₄ <->(aq)	aucl ₄ -	573
Au H ₂ S ₂ <->(aq)	shenberger	623
Au H ₂ S ₂ <->(aq,1)	au(hs) ₂ - (soltherm)	573
Au ₂ H ₂ S ₃ <2->(aq)	au ₂ h ₂ s ₃ =	573
Ba <2+>(aq)	barium ion aqu cobble et al 1981	623
Ba Cl <+>(aq)	bacl ₄ +	573
Ba Cl ₂ (aq)	bacl ₂	573
Ba F <+>(aq)	baf ₄ +	573
Ba H O <+>(aq)	baoh ₄ +	573
C H Mg O ₃ <+>(aq)	mghco ₃ +	623
C H Na O ₃ (aq)	nahco ₃	623
C H O ₃ <->(aq)	bicarbonate ion aqueous, pk cobble et al. 81 p.4-24; drummond for co ₂	673
C H O ₃ Sr <+>(aq)	srhco ₃ +	623
C H O ₃ Zn <+>(aq)	znhco ₃ +	623
C H ₂ O ₃ (aq)	h ₂ co ₃	573
C H ₄ (aq)	drummond	673
C Mg O ₃ (aq)	mgco ₃	623
C Mn O ₃ (aq)	mnco ₃	623
C Na O ₃ <->(aq)	naco ₃ -	623
C O ₂ (aq)	drummond	673
C O ₃ <2->(aq)	co ₃ --	623
C O ₃ Pb (aq)	pbco ₃	573
C O ₃ Sr (aq)	srco ₃	623
Ca <2+>(aq)	calcium ion aqu, cobble et al. 81;	573
Ca C H O ₃ <+>(aq)	cahco ₃ +	623
Ca C O ₃ (aq)	caco ₃	623
Ca Cl <+>(aq)	cacl ₄ +	623
Ca Cl ₂ (aq)	cacl ₂	623
Ca F <+>(aq)	caf ₄ +	573
Ca H O <+>(aq)	caoh ₄ +	573
Ca O ₄ S (aq)	caso ₄	573
Cl <->(aq)	chloride ion aqueous mrl refit within 25cal; deviation coblle 100cal	623
Cl Cu <+>(aq)	cuc ₄ +	573
Cl Cu (aq)	cuc ₄	573
Cl Fe <+>(aq)	fecl ₄ +	573

GIBBMRAQU

SPECIES FORMULA	SPECIES NAME	T LIMIT
C1 Fe <2+>(aq)	fecl++	573
C1 H (aq)	ruaya	623
C1 H ₄ O ₄ Sn <->(aq)	pabalan	623
C1 Hg <+>(aq)	hgcl+	573
C1 Hg H O (aq)	hgcl _{oh}	573
C1 K (aq)	kcl	573
C1 Mg <+>(aq)	mgcl+	623
C1 Na (aq)	nacl	623
C1 Pb <+>(aq)	pbcl+	573
C1 Sn <+>(aq)	pabalan	623
C1 Zn <+>(aq)	zncl+	623
C12Cu <->(aq)	cuc12-	573
C12Cu (aq)	cuc12	573
C12Fe <+>(aq)	fec12+	573
C12Fe (aq)	fec12	573
C12H ₂ O ₂ Sn (aq)	pabalan	623
C12H ₄ O ₄ Sn<2->(aq)	pabalan	623
C12Hg (aq)	hgcl2	573
C12Pb (aq)	pbcl2	573
C12Sn (aq)	pabalan	623
C12Zn (aq)	zncl2	623
C13Cu <->(aq)	cuc13-	573
C13Cu <2->(aq)	cuc13--	573
C13Fe (aq)	fec13	573
C13Hg <->(aq)	hgcl3-	573
C13Pb <->(aq)	pbcl3-	573
C13Sn <->(aq)	pabalan	623
C13Zn <->(aq)	zncl3-	623
C14Cu <2->(aq)	cuc14--	573
C14Fe <->(aq)	fec14-	573
C14Hg <2->(aq)	mercury tetrachloride complex aqu backfitted to soltherm hg	623
C14Pb <2->(aq)	pbcl4--	573
C14Sn <2->(aq)	pabalan	623
C14Zn <2->(aq)	zncl4--	623
Cu <+>(aq)	cuprous ion aqu mrl exact refit	623
Cu <2+>(aq)	cu++	573
Cu F <+>(aq)	cuf+	573
Cu H O <+>(aq)	cuoh+	573
Cu H ₂ S ₂ <->(aq)	cu(hs)2-	573
Cu H ₄ S ₃ <->(aq)	cuh ₄ s ₃ -a	573
Cu H ₄ S ₃ <->(aq,1)	cuh ₄ s ₃ -b	573
Cu O ₄ S (aq)	cuso ₄	573

GIBBMRAQU

SPECIES FORMULA	SPECIES NAME	T LIMIT
F <->(aq)	fluorine ion aqu mrl refit	623
F H (aq)	hf	573
F Hg <+>(aq)	hgf+	573
F Mg <+>(aq)	mgf+	573
F Na (aq)	naf	573
F Pb <+>(aq)	pbf+	573
F Sr <+>(aq)	srf+	573
F Zn <+>(aq)	znf+	573
F2H <->(aq)	hf2-	573
Fe <2+>(aq)	ferrous ion aqueous cobble et al. 81)	573
Fe <3+>(aq)	fe+++	573
Fe F <+>(aq)	fef+	573
Fe F <2+>(aq)	fef++	573
Fe F2<+>(aq)	fef2+	573
Fe F3(aq)	fef3	623
Fe H O <+>(aq)	feoh+	623
Fe H2O2(aq)	fe(oh)2	623
Fe H3O3<->(aq)	fe(oh)3-	623
Fe H3O3(aq)	fe(oh)3	623
Fe H4O4<->(aq)	fe(oh)4-	623
Fe O4S <+>(aq)	feso4+	573
Fe O4S (aq)	feso4	573
H <+>(aq)	hydrogen ion aqueous	873
H K O (aq)	baes-mesmer frank	623
H K O4S (aq)	khso4	573
H Mg O <+>(aq)	mgoh+	573
H Mn O <+>(aq)	mnoh+	573
H Na O (aq)	naoh	573
H Na S (aq)	nahs	623
H O <->(aq)	oh-	623
H O Sr <+>(aq)	sroh+	623
H O Zn <+>(aq)	znoh+	623
H O4S <->(aq)	bisulfate ion aqueous refit mrl = cobble = cubiciotti	573
H S <->(aq)	bisulfide aqueous, pk cubiciotti; h2s drummond	673
H2(aq)	h2 aq.	573
H2O	water liquid mrl(25-300;1/v); bhd(350-600 rho=1.74)	873
H2O S Zn (aq)	znoh(hs)	623
H2O2Zn (aq)	znoh2	573

		GIBBMRAQU
SPECIES FORMULA	SPECIES NAME	T LIMIT
H2O4Si <2->(aq)	h2sio4--	623
H2Pb S2(aq)	pb(hs)2	573
H2S (aq)	hydrogen sulfide aqueous, drummond	673
H2S2Zn (aq)	zn(hs)2	623
H3O3Zn <->(aq)	znoh3-	573
H3O4Si <->(aq)	h3sio4-	573
H3Pb S3<->(aq)	pb(hs)3-	573
H3S3Zn <->(aq)	zn(hs)3-	623
H4O4Zn <2->(aq)	znoh4--	573
H4Pb S3(aq)	pbh4s3	573
H4S4Zn <2->(aq)	zn(hs)4=	623
H5O5Sn <->(aq)	pabalan	623
Hg <2+>(aq)	hg++	573
Hg H O <+>(aq)	hgoh+	573
Hg H2O2(aq)	hg(oh)2	573
Hg H3S3<->(aq)	hg(hs)3-	573
Hg H4S3(aq)	hgh4s3	573
Hg S2<2->(aq)	hgs2--	573
Hg2<2+>(aq)	hg2++	573
K <+>(aq)	potassium ion aqu cobble etal. 81 within 200cals	623
K O4S <->(aq)	kso4-	573
Mg <2+>(aq)	magnesium ion aqu, cobble et al. 81; dont extrapolate	573
Mg O4S (aq)	mgso4	573
Mn <2+>(aq)	manganese ion aqu cobble et al.1981; very different from mrl	573
Mn O4S (aq)	mnso4	573
Na <+>(aq)	sodium ion aqu cobble et al.81 within 150cals	623
Na O4S <->(aq)	nasO4-	573
O2(aq)	o2 aq.	573
O2Si (aq)	silica aq, backfit to reed's quartz	623
O4S <2->(aq)	sulfate ion aqu cobble refit within 200cals	623
O4S Zn (aq)	znso4	573
O4Sr S (aq)	srso4	623

SPECIES FORMULA	SPECIES NAME	GIBBMRAQU T LIMIT
Pb <2+>(aq)	lead ion aqu mrl exact refit	623
S <2->(aq)	s--	573
Sr <2+>(aq)	strontium ion aqu mrl exact refit	623
Zn <2+>(aq)	zinc ion aqueous mrl(25); bourcier(100-350c)	623

Derivation and limitations of GIBBMRSOL for hydrothermal minerals

This file was created from the second part of the converted data file GIBSOLTHERM.ADD, which contains mineral and gas species data. It was obtained as a 'bonus' from the conversion of the aqueous data but its use is somewhat limited due to its indirect derivation history. It is considered as a temporary measure and will gradually be replaced by primary data.

The mineral data in the file SOLTHERM of M.Reed is based on the "Summary and critique of thermodynamic properties of minerals" published by Helgeson et al. (1978), which is the basis of the program SUPCRT (available at ANU Geology Department). The original compilation has an extended temperature range up to igneous/metamorphic conditions, but its conversion to SOLTHERM by M.Reed required a temperature limitation to 350°C, due to the special reference state of SOLTHERM. Our back-conversion to free energy of formation from elements is unsatisfactory, not only because of the artificial temperature limitation, but also because any errors in the free energy of the aqueous 'component species' are passed on to the mineral data.

For example, errors in the free energy of $\text{HS}^-(\text{aq})$ or $\text{SO}_4^{2-}(\text{aq})$ will affect the free energy of formation of oxides like hematite and magnetite, because the two sulfur species were chosen by Reed as the basis for expressing all redox reactions. However, the oxygen fugacity of a buffer pair hematite/magnetite will not be affected by that, provided that data for both minerals are taken from GIBBMRSOL.

GIBBMRSOL should be used with caution, and under no circumstance should data from GIBSOLTHERM be combined with mineral data from any other source, including CPDMRLDAT.

Before storing the mineral data in GIBBMRSOL, the entries for elemental phases COPPER, GOLD, MERCURY and GRAPHITE were removed, because they are redundant. The gaseous species from SOLTHERM were also omitted, after they were checked and found closely similar to the data in CPDMRLDAT up to at least 300°C. Polymorphs other than the most stable low-temperature phase were numbered (1), (2), etc. (see Index below).

Index to minerals in the GIBBMRSOL data file

Sequence is alphabetical according to mineral name
same as original SOLTHERM by M.Reed

PHASE NUMBERS OF ANY ALLOTROPE
OTHER THAN THE MOST STABLE ONE
ARE GIVEN IN BRACKETS AFTER STATE

TOTAL NUMBER OF SUBSTANCES 122

DATE 11 - 7 - 87

SPECIES FORMULA	SPECIES NAME	T LIMIT
Ag2S	acanthit	623
Ca2Mg 07Si2	akermani	623
Mn S	alabandi	623
Al Na 08Si3(1)	albit-hi	623
Al Na 08Si3	albit-lo	623
Al3H6K 014S2	alunite	623
Al H2Na 07 Si2	analcime	623
Al Na 06 Si2 (1)	anal-dhy	623
Al2O5Si	andalusi	623
Ca3Fe2012Si3	andradit	623
04 Pb S	anglesit	623
Ca 04S	anhydrit	623
Al Fe3H2K 012Si3	annite	623
Al2Ca 08Si2	anorthit	623
H2Mg7024Si8	anthophy	623
H3.876Mg309.188Si2.125	antigori	623
Ca C 03(1)	aragonit	623
C H8Mg208	artinite	623
C2Cu3H208	azurite	623
Ba 04S	barite	623
Al2.33H2Mg .165012Si3.67	beide-mg	623
Al H 02(1)	boehmite	623
Cu Fe .2S .8	bornit/5	623
H2Mg 02	brucite	623
Ca C 03	calcite	623
H1.5Mg1.2505S	camin625	598
H Mg1.505S	camin75	598
04Sr S	celestite	623
C 03Pb	cerussit	623

SPECIES FORMULA	SPECIES NAME	T LIMIT
02Si (2)	chalcedo	623
Cu ₂ S	chalcoci	623
Cu Fe S ₂	chalcopy	623
H ₄ Mg ₃ O ₉ Si ₂	chrysoti	623
Hg S	cinnabar	598
Hg S (1)	cinn-met	598
Al H ₄ Mg _{2.5} O ₉ Si _{1.5}	clcl14/2	623
Al Fe _{2.5} H ₄ O ₉ Si _{1.5}	dap14/2*	623
Al H ₄ Mg _{2.5} O ₉ Si _{1.5} (2)	cl14-o/2	623
Al ₂ H ₈ Mg ₅ O ₁₈ Si ₃ (1)	clchl7a	623
Al ₂ Fe ₅ H ₈ O ₁₈ Si ₃ (1)	daph7a*	623
Al ₃ Ca ₂ H O ₁₃ Si ₃	clinozoi	623
Al ₂ Ca ₂ Fe H O ₁₃ Si ₃ (1)	epid-ord	623
Al ₄ H ₂ Mg ₂₀ 19Si ₅	cord-hyd	623
Al ₄ Mg ₂₀ 18Si ₅	cord-anh	623
Al ₂ O ₃	corundum	623
Cu S	covellit	623
02Si (3)	cristoba	623
02Si (4)	cristo-a	623
02Si (5)	cristo-b	623
Cu ₂ O	cuprite	623
Al H O ₂	diaspore	623
Ca Mg O ₆ Si ₂	diopside	623
Ca Fe O ₆ Si ₂	hedenber	623
Ca C ₂ Mg O ₆	dolomite	623
Ca C ₂ Mg O ₆ (1)	dolo-ord	623
Ca C ₂ Mg O ₆ (2)	dolo-dis	623
Mg O ₃ Si	enstatit	623
Al ₂ Ca ₂ Fe H O ₁₃ Si ₃	epidote	623
Fe ₂ O ₄ Si	fayalite	623
Al K O ₈ Si ₃	feldsp-k	623
Fe O ₃ Si	ferrosil	623
Ca F ₂	fluorite	623
Mg ₂ O ₄ Si	forsteri	623
Pb S	galena	623
Al ₂ Ca ₂ O ₇ Si	gehlenit	623
Al H ₃ O ₃	gibbsite	623
Fe ₃ H ₄ O ₉ Si ₂	greenal*	623
Al ₂ Ca ₃ O ₁₂ Si ₃	grossula	623
Fe ₇ H ₂ O ₂₄ Si ₈	gruneri*	623
Ca H ₄ O ₆ S	gypsum	623
Cl Na	halite	623
Fe ₂ O ₃	hematite	623

SPECIES FORMULA	SPECIES NAME	T LIMIT
Ca C ₄ Mg ₃ O ₁₂	huntite	623
Al _{2.3} H ₂ K .6Mg .25O ₁₂ Si _{3.5}	illite	623
Al Na O ₆ Si ₂	jadeite	623
Al K O ₄ Si	kalsilit	623
Al ₂ H ₄ O ₉ Si ₂	kaolinit	623
H ₈ Mg ₃ O ₁₅ Si ₄	kerolite	598
Al ₂ Ca H ₈ O ₁₆ Si ₄	laumonti	623
Ca O	lime	623
C Mg O ₃	magnesit	623
C ₄ H ₁₀ Mg ₅ O ₁₈	magn-hyd	623
Fe ₃ O ₄	magnetit	623
C Cu ₂ H ₂ O ₅	malachit	623
Mn O	manganos	623
Al ₄ Ca H ₂ O ₁₂ Si ₂	margarit	623
Ca ₃ Mg O ₈ Si ₂	merwinit	623
Al K O ₈ Si ₃ (1)	micr-max	623
Ca Mg O ₄ Si	monticel	623
Al ₃ H ₂ K O ₁₂ Si ₃	muscovit	623
Al ₃ H ₂ Na O ₁₂ Si ₃	paragoni	623
C H ₆ Mg O ₆	nesqueho	623
Al _{1.5} Ca H Mg ₂ Na .5O ₁₂ Si ₃	pargas/2	623
Al _{1.5} Ca Fe ₂ H Na .5O ₁₂ Si ₃	par/2fe*	623
Mg O	periclas	623
Al H ₂ K Mg ₃ O ₁₂ Si ₃	phlogopi	623
Al ₂ Ca ₂ H ₂ O ₁₂ Si ₃	prehnite	623
Fe S ₂	pyrite	623
Al ₂ H ₂ O ₁₂ Si ₄	pyrophyll	623
Al ₂ Ca O ₆ Si	px.ca-al	623
Fe S	pyrrhoti	623
C Mn O ₃	rhodochr	623
Mn O ₃ Si	rhodonit	623
Al K O ₈ Si ₃ (2)	sanid-hi	623
H ₁₄ Mg ₄ O ₂₃ Si ₆	sepiolit	623
C Fe O ₃	siderite	623
O ₂ Si (6)	silic-am	623
C O ₃ Zn	smithson	623
S Zn	sphaleri	623
Al ₂ Mg O ₄	spinel	623
C O ₃ Sr	strontia	623
Cl K	sylvite	623
H ₂ Mg ₃ O ₁₂ Si ₄	talc	623
Fe ₃ H ₂ O ₁₂ Si ₄	minneso*	623
Cu O	tenorite	623

SPECIES FORMULA	SPECIES NAME	GIBBMRSOL
		T LIMIT
Ca ₂ H ₂ Mg ₅ O ₂₄ Si ₈	tremolit	623
Ca ₂ Fe ₅ H ₂ O ₂₄ Si ₈	actinol*	623
Al ₂ Ca H ₄ O ₁₄ Si ₄	wairakit	623
Ba C O ₃	witherit	623
Ca O ₃ Si	wollasto	623
S Zn (1)	wurtzite	623
Al ₃ Ca ₂ H O ₁₃ Si ₃ (1)	zoisite	623

References to main data sources

(Only major compilations and sources used for 'component species' data are given)

Bourcier WL (1983) stabilities of chloride and bisulfide complexes of zinc in hydrothermal solutions. PhD Penn.State Univ.

Burnham CW, Holloway JR, Davis NF (1969) Thermodynamic properties of water to 1000°C and 10000 bars. Geol.Soc.Am.Spec.Pap. 132, 96pp.

Cobble JW, Murray RC, Turner PJ, Chen K (1982) High-temperature thermodynamic data for species in aqueous solutions. Nat.Tech.Inform. Service Rept. EPRI-NP-2400, 1-197.

Drummond SE (1981) Boiling and mixing of hydrothermal fluids: Chemical effects on mineral precipitation. Penn.State Univ. Ph.D. Thesis, 380 pp.

Helgeson HC, Delany JM, Nesbitt HW, Bird DK (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. Am.J.Sci. 281-A, 1-229.

Turnbull AG, Wadsley MW (1986) The CSIRO-SGTE THERMODATA system. Introduction; Databank index; FILER; ESTIMA; REACT; SYSTEM; CHEMIX; VAPOUR; EXERGY; 9 vols. CSIRO Div. Mineral Chemistry, Port Melbourne. [Copies located room 369 BMR].

Reed, MH (1982) Calculation of multicomponent chemical equilibria and reaction processes in systems involving minerals, gases and an aqueous phase. Geochim. Cosmochim.Ac. 46, 513-528 [Introduction to SOLTHERM data file].

Installation of THERMODATA

on the Data General MV20000 computer

Source code alterations in existing files

Installation of THERMODATA on the Data General MV20000 mainframe computer at BMR required a number of changes of the programs, which were originally written for a VAX/VMS computer. Some of the alterations of existing routines in the FORTRAN-77 source code were required because of the differences in the directory structure between the two operating systems. Some routines had to be added on the DG to allow file management in a similar way to the VAX operation (e.g. due to the absence of multiple file versions on DG). Some CLI commands were created and included in the description because they are helpful for future modification and re-compilation of the programs.

The following is a list of changes introduced and documented by B.Harrold.

1. Modification to string character ">" or "<".

Subroutines

ADDREF.F77
DISPLA.F77
EDITOR.F77
EXFAAA.F77
FREAD.F77
GETREF.F77
HEADER.F77
INFORM.F77
REFER.F77
SETKEY.F77
SPFORM.F77
VTABLE.F77

The FORTRAN compiler on the DG identifies '<' and '>' as delimiters for octal numbers, so these cannot be used as individual characters, even in the context of character strings. To prevent compilation errors, a simple change is necessary, thus :

```

>   is   changed to   <GT>
<
<LT>

```

2. HEADER.F77

Firstly, changes have been made to the open statement in line 32. The VAX requires the logical name DIRLOC to be defined as the data file OPTIONS.FMT. This instruction has been modified to open the file directly. This is valid because the searchlist includes the directory containing the options file OPTIONS.FMT.

```

C
C      READ OPTION FILE
C
      OPEN(UNIT=LR,FILE='DIRLOC',STATUS='OLD',
&      IOSTAT=IOS,ACCESS='SEQUENTIAL')
-----
amended to
-----
C
C      READ OPTION FILE
C
      OPEN(UNIT=LR,FILE='OPTIONS.FMT',STATUS='OLD',
&      IOSTAT=IOS,ACCESS='SEQUENTIAL')

```

Secondly, since the output file is already open (cf ASSIO.F77), line 67 (OPEN statement) is commented out. In addition to this, the logical name for IO to the terminal is ':PER' and hence a change is made from 'TT:' to ':PER' on line 70

```

C
C      OPEN INPUT & OUTPUT
C
      LSAVE=0
      OPEN(UNIT=8,STATUS='UNKNOWN')
      INQUIRE(UNIT=8,NAME=PROMPT)
      INTER=0
      IF(PROMPT(1:3).EQ.'TT:')INTER=1
      PROMPT='DIR'

```

```

-----
amended to
-----

```

```

C      OPEN INPUT & OUTPUT
C
      LSAVE=0
      OPEN(UNIT=8,STATUS='UNKNOWN')
      INQUIRE(UNIT=8,NAME=PROMPT)
      INTER=0
      IF(PROMPT(1:3).EQ.'PER:')INTER=1
      PROMPT='DIR'

```

Finally, the header title has been commented out:

```

C
C      OUTPUT PROGRAM HEADER
C
      CALL DATE(DAY)
      CALL TIME(HMS)
      IF(INTER.EQ.0)THEN
        WRITE(LO,1)PNAM,DAY,HMS
1  FORMAT(/' THERMODATA SYSTEM VERSION V  - PROGRAM ',A,
      &' - DATE ',A,' TIME ',A)
        CPU=JOB(3)
        WRITE(LO,2)CPU
2  FORMAT(' A.G.TURNBULL - DIVISION OF MINL CHEMISTRY - ',A,
      &' - PHONE (03)6470211')
        WRITE(LO,3)
3  FORMAT(' & M.W.WADSLEY - P.O.BOX 124, PORT MELBOURNE, V',
      &'ICTORIA 3207 - TELEX 34349'//)

```

PLOTHP.F77

The function of this routine is to submit plots to the HP plotter. This facility is not available on the DG, and the entire routine was therefore commented out.

GETREF.F77

The VAX allows for the keyword READONLY be to included in the open statement. This essentially places a writelock on the respective file. The DG does not have this facility, so that lines 106, 114, 121, 128 had to be changed, as shown for line 121:

```

      OPEN(UNIT=1,FILE=FILE1(1:LF1),
      &      STATUS='OLD',READONLY,IOSTAT=IOS)
-----
amended to
-----

```

```

      OPEN(UNIT=1,FILE=FILE1(1:LF1),
&        STATUS='OLD',IOSTAT=IOS)

```

FILES.F77

The IO facilities on the DG is somewhat tricky, and the rules for operations are extensive (see Data General FORTRAN users guide). Changes in this routine are fairly extensive. All open statements that deal with sequential access files are padded viz:

```

C
C      SEQUENTIAL ACCESS FILE
      IF(IAC.EQ.1.AND.IFO.EQ.1)THEN
        OPEN(UNIT=LUN,ACCESS='SEQUENTIAL',ERR=300,
&          STATUS='OLD',FORM='FORMATTED',FILE=ENAM,IOSTAT=IOS)

```

```

C
C      SEQUENTIAL ACCESS FILE
      IF(IAC.EQ.1.AND.IFO.EQ.1)THEN
        OPEN(UNIT=LUN,ACCESS='SEQUENTIAL',ERR=300,PAD='YES',
&          STATUS='OLD',FORM='FORMATTED',FILE=ENAM,IOSTAT=IOS)

```

If at any stage, the program should prematurely end with the error message "End of File encountered at record ... " one possible solution to this is the file has been opened without the padding option.

The second amendment deals with the problem of opening new files. The DG does not have the facility of version numbers in file names. Hence, it is not possible to open a new file of the same name as an existing file, and preserve both as unique files. Should a new file be created, any file of the same name **within a SEARCHLIST** is destroyed. To lessen the possibility of overwriting an existing file, an inquire statement has been included. The additional code will result in a warning should a file exist, with an option for the user to terminate the job.

```

C
C - BECAUSE THE DATA GENERAL IS UNABLE TO CREATE NEW VERSIONS OF
C   EXISTING FILES, THIS ADDITIONAL CODE WARNS OF OVERWRITING
C   FILES.
C
      EXT = .FALSE.

```

```

        INQUIRE(FILE=ENAM,EXIST=EXT)
        IF (EXT) THEN
            WRITE(6,700) ENAM
700    FORMAT(1X,'FILE',A,'ALREADY EXISTS ',/,1X,'CONT [Y]:',,$)
            READ(5,710) IANS
710    FORMAT(A1)
            IF (IANS.EQ.'N'.OR.IANS.EQ.'n') STOP
            STR80 = '          '
            STR25 = 'DELETE/1=IGNORE/2=IGNORE '
            STR80 = STR25//ENAM
            CALL CLI(STR80,IER)
        ENDIF

```

If the user opts to continue, a CLI command to delete the existing file is issued, and the new file is created. This precaution has now been commented out again, after careful testing.

FILRUN.F77

The absence of multiple versions also presents a problem in FILRUN, as one of the functions of this FILER routine is to update/replace data bank files. . On the VAX, the process for any modification of the database is to create a new file of the same name with the next higher version number. The modified data is written into the new file, and finally the old version of the data file is deleted. As this cannot be done on the DG, the process had to be changed slightly. The file will change name from +.DAT to +.OLD. A new file +.DAT is then created and the update is written into the new file. The OLD file is then deleted.

FILRUN required the following addition from line 164

```

C
C -----
C
C--- CHECK FOR EXISTING FILE ... IF SO , CHANGE NAME TO +.OLD
C

```

```

    IF (IRUN.EQ.1) THEN
    HNAM=NAM
    GNAM=NAM
    EXT = .FALSE.
    IF(NCHARS(TYP).GT.0)HNAM=HNAM(1:NCHARS(NAM))//'. '//TYP
    INQUIRE(FILE=HNAM,EXIST=EXT)
    IF (EXT) THEN
        WRITE(6,*) ' RENAMING FILE FROM ',HNAM
        WRITE(6,*) ' TO '
        TYP = 'OLD'
        GNAM=NAM
        GNAM=GNAM(1:NCHARS(NAM))//'. '//TYP
        WRITE(6,*) ' ',GNAM
        WRITE(6,*) ' '
        CALL EXCOMS(HNAM,GNAM)
        CALL FILES(LR,4)
        TYP = 'DAT'
    ELSE
        CALL FILES(LR,4)
    ELSIF
    ELSE
        CALL FILES(LR,4)
    END IF

```

```

C
C -----

```

The call EXCOMS (see below) renames the files , e.g. from HNAM to GNAM.

SEARCH.F77

DG will not allow a specified record length with sequential files. On line 80, 'RECL' was changed to 'MAXRECL', specifying a maximum record length.

```

C
    CALL SETKEY
    OPEN(LT,STATUS='SCRATCH',RECL=170,
    &      ACCESS='SEQUENTIAL',FORM='FORMATTED')
-----
amended to
-----

```

```

CALL SETKEY
OPEN(LT,STATUS='SCRATCH',MAXRECL=170,
&      ACCESS='SEQUENTIAL',FORM='FORMATTED')

```

QUICK.F77

THERMODATA requires the use of channels 10 and 11 for scratch files. The DG has these two channels allocated as preconnected IO units. Before they can be used, they must be closed, i.e from line 23:

```

LOGICAL OPN
C
INQUIRE(UNIT=10,OPENED=OPN)
IF (OPN) CLOSE(UNIT=10)
INQUIRE(UNIT=11,OPENED=OPN)
IF (OPN) CLOSE(UNIT=11)
OPEN(10,STATUS='SCRATCH',RECL=170,
&      ACCESS='SEQUENTIAL',FORM='FORMATTED')
OPEN(11,STATUS='SCRATCH',RECL=170,
&      ACCESS='SEQUENTIAL',FORM='FORMATTED')

```

FILER.F77

Main program unit requiring a call to IO, line 108 . A call to ASSIO is required to assign input and output files.

```

NDEL=0
NREP=0
CALL UNITS(0)
PNAM='FILER'
CALL HEADER

```

amended to

```

-----
NDEL=0
NREP=0
CALL ASSIO
CALL UNITS(0)
PNAM='FILER'
CALL HEADER

```

REACT.F77

Similar situation

```

NP=1
P(1)=1.
CALL UNITS(0)
PNAM='REACT'
CALL HEADER

```

amended to

```

NP=1
P(1)=1.
CALL ASSIO
CALL UNITS(0)
PNAM='REACT'
CALL HEADER

```

and SYSTEM.F77

```

TA(1)=298.15
CALL UNITS(0)
NOUT=2
PNAM='SYSTEM'
CALL HEADER

```

amended to

```

TA(1)=298.15
CALL ASSIO
CALL UNITS(0)
NOUT=2
PNAM='SYSTEM'
CALL HEADER

```

CHEMIX.F77

```

MA=0
CALL UNITS(0)
DO 10 I=1,4
10 NAMF(I)=BLANK
NROY=0
NP=1

```

amended to

```

MA=0
CALL ASSIO
CALL UNITS(0)
DO 10 I=1,4
10 NAMF(I)=BLANK
NROY=0
NP=1

```


EXERGY.F77

Similar situation

```

      DO 15 I=1,3
        JOB(I)='      '
    15 CONTINUE
C
C      SET DEFAULT UNITS
      CALL UNITS(0)

```

```

-----
amended to
-----

```

```

      DO 15 I=1,3
        JOB(I)='      '
    15 CONTINUE
C
C      SET DEFAULT UNITS
      CALL ASSIO
      CALL UNITS(0)

```

ESTIMA.F77

Similar situation line 48

```

      DO 5 J=1,3
    5 JOB(J)='      '
      CALL UNITS(0)
      PNAM='ESTIMA'
      CALL HEADER

```

```

-----
amended to
-----

```

```

      DO 5 J=1,3
    5 JOB(J)='      '
      CALL ASSIO
      CALL UNITS(0)
      PNAM='ESTIMA'
      CALL HEADER

```

VAPOUR.F77

```

C      INITIALIZE
      MA=0
      NNE=0
      CALL UNITS(0)
      PNAM='VAPOUR'
      CALL HEADER

```

```

-----
amended to
-----

```

```

C      INITIALIZE
      MA=0
      NNE=0
      CALL ASSIO
      CALL UNITS(0)
      PNAM='VAPOUR'
      CALL HEADER

```

REFER.F77

line 41

```

C      INITIALIZATION
      LI=8
      LO=9
      LDI=8
      LDO=9
      PNAM='REFER'
      CALL HEADER
C      SET PROMPT OFF
      INTER=0

```

```

-----
amended to
-----

```

```

C      INITIALIZATION
      LI=8
      LO=9
      LDI=8
      LDO=9
      CALL ASSIO
      PNAM='REFER'
      CALL HEADER

```

New subroutines

ASSIO.F77

Provides assignment of IO to channels LI, LO respectively. Prompts for input and output file names are all done through this routine. Hence, it is essential that this is called after channel numbers have been allocated, but before anything else.

EXCOM.F77

Renames a file from ... to ...

RNUM.F77

Performs an internal free format READ on the DG. The routine accepts a character string containing a set of numbers, and returns the decimal values of the numbers.

UCASE.F77

Returns the uppercase value of a string that is passed by reference.

CLI.F77

Executes a CLI command. The operation of this command relies on the library BMRLIB.OB. When a program is relinked using LINKLIB.CLI in the THERMO directory, a call is made to this library.

Additional CLI commands

The subdirectory CHRIS.PEG:THERMO:CMD contains three CLI routines written for the maintenance of the THERMODATA programs at BMR.

BEGIN.CLI

This command file works in the same manner as the VAX file BEGIN.COM by Turnbull and Wadsley ('Introduction'). It is suggested that all calls to THERMODATA programs are processed via the BEGIN command, because this establishes the searchlist to the DATA and EXEC directories.

REPLACE.CLI

Should any of the FORTRAN subroutines be modified in any way, the THERMO library will need to be updated using REPLACE. The routine name may be specified immediately following the command, or (if no argument is given), REPLACE will ask.

LINKLIB.CLI

After re-compilation of a modified subroutine it must be linked to all main programs that call this routine. This is done by the LINKLIB command.

Example for REPLACE/LINKLIB:

Suppose the subroutine FILES.F77 has been modified in some manner. First, the subroutine must be updated in the THERMO.LB library, thus :

```
FRED.PEG> REPLACE FILES <NL>
```

The command REPLACE will recompile the subroutine FILES, and replace it in the library. It is then necessary to re-link it with the main programs CHEMIX and FILER, thus :

```
FRED.PEG> LINKLIB CHEMIX <NL>
```

```
FRED.PEG> LINKLIB FILER <NL>
```

In this example this would be necessary for all programs, because FILES is an essential part of each of them. However, some of the routines require only a re-linking of one or two programs. Information about this is contained in the cross-reference list XREF.DOC.

How to get started

THERMODATA is installed in the account CHRIS.PEG with a directory access list (ACL) that allows reading and execution, but not deletion or overwriting, of all programs and example job files from **any** Petrology and Geochemistry user account, e.g. NEVILLE.PEG.

Setting-up links between your account and THERMODATA

The following two steps are required once only. The link will be retained after you log off from your first session.

Firstly, type from your top directory (<nl> = new line key):

```
CREATE/LINK CHRIS :UDD:CHRIS.PEG <nl>
```

which will create a link so that you can enter the account CHRIS.PEG, if you wish, to inspect data or retrieve example job files (see below).

Secondly, to be able to run THERMODATA jobs from your account, the directory :UDD:CHRIS.PEG:CMD must be included in your SEARCHLIST. This is best done once-off by including it in your log-on file IIPC.CLI; if it does not exist create one by typing a dummy file containing the following lines:

```
prefix [!user][!ascii 276]
searchlist :udd:NEVILLE.PEG :bmr_cmnds :util &
          :udd:chris.peg:cmd
```

and then copy it onto IIPC.CLI. After creating this file, run it by typing

```
IIPC <nl>
```

Running a THERMODATA job

Once you have established these links you can henceforth invoke THERMODATA from any subdirectory within your account, by typing

```
BEGIN <program> <input file> <nl>
```

for file input mode, or just

```
BEGIN <nl>
```

for interactive mode (which includes on-line HELP on the THERMODATA command language).

Inspection and retrieval of additional documentation and example job files

Due to the link established above, the command

```
DIR CHRIS
```

allows you to enter the account CHRIS.PEG. You can now safely move to any subdirectories, and access data or copy example jobs to your own account, but you are prevented from deleting or (over)writing any files.

The following subdirectories contain information that might be of general interest:

CHRIS.PEG:THERMO:HLP contains all of the original THERMODATA documentation by Turnbull and Wadsley, plus the contents of the present BMR Record in files with the extension

CHRIS.PEG:THERMO:TEST contains all example job input files documented in the green booklets by Turnbull and Wadsley.

CHRIS.PEG:THERMO:DEMO contains a variety of geochemical application jobs created for demonstrations at BMR, including the files SOH4.SYS and AUSOH14.CHE which were used in Figs. 1 to 4 (above). Input files for program SYSTEM have the extension .SYS, CHEMIXchemix jobs .CHE, etc.

Experience has shown that it is often most convenient to set up a new job by altering an existing job file. For example to set up a job to calculate an activity diagram using program SYSTEM, you might want to start with the example file SYSTEM1 of Turnbull and Wadsley. First enter the TEST subdirectory by typing

```
DIR THERMO <nl>  
DIR TEST <nl>
```

You have no privilege to change or run a job here, but you can move the job input file into your own directory area by typing

MOVE/NACL/V :UDD:NEVILLE.PEG SYSTEM1.EXA <n1>

Now return to your own directory by typing

HOME <n1>

and begin the calculation by:

BEGIN SYSTEM SYSTEM1.EXA <n1>

which will invoke SYSTEM to create a text output file SYSTEM1.OUT and a plot file VISUAL.PLT.

Graphics display

The binary graphics file VISUAL.PLT can be retrieved from the DG to a Cleveland IBM/PC for screen inspection. Currently the micros in Room 369 and 375 are equipped for this. Inspect in C:\CEO by typing

DISPLAY VISUAL.PLT

For hard-copy plots ask Chris Heinrich or Subhash Jaireth regarding a temporary solution.

Your problems and suggestions

Please add reports of any difficulties, errors in programs or data, suggestions etc. to the file PROBLEMS.DOC in the directory :UDD:CHRIS.PEG. This file is not write-protected.