PAUL SCHERRER INSTITUT	Registrierung **TM-44-01-07**
Titel: **PMATCHC: A Program to MAnage ThermoCHemical data, written in C++ (Version 1.1, 31-08-2001)**	Ersetzt
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Abstract:

PMATCHC manages databases of thermodynamic data for use with geochemical modelling programs. It includes descriptions of reactions and their properties, as required for aqueous speciation and reaction codes based on the law of mass action (LMA), such as PHREEQC and MINEQL, and the properties of elements, aqueous species, solids and gases as required for Gibbs Energy minimisation (GEM) codes like GEM-Selektor. It is written in C++ and operates in MS Windows and Linux environments. It allows both interactive and batch operation for data entry, manipulation and output in user-specified formats. It performs calculations that maintain internal consistency among data entered in various forms, and provides messages to the user when data inconsistencies exist that the program cannot resolve internally.

PMATCHC is based on PMATCH, a code prepared to support the development of the earlier Nagra TBD of 05/92 in response to the need to compare data of different types and sources. PMATCHC was intended to support compilation and use of the new Nagra/PSI TDB. Its development has included translation of PMATCH from a Pascal DOS command line format to a C++ program running interactively in a windows environment. It has also included the addition of a number of additional data fields to make the program capable of managing data for a wider variety of geochemical modelling programs, and expansion of the internal calculation schemes to encompass these new types.

This document describes the data management capabilities of PMATCHC, including the data fields in the program and the calculations it performs to maintain consistency among data entered in various forms. The output capabilities of the program are also discussed, including the commands available.

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Total	47
Seiten	53
Beilagen	-
Informationsliste	
D 1 2 3 4 5 8 9 A	
Visum ~~Abt./Laborleitung~~: B.	

CONTENTS

FIGURES

TABLES

1 INTRODUCTION

PMATCHC manages databases of thermodynamic data for use with geochemical modelling programs. It includes descriptions of reactions and their properties, as required for aqueous speciation and reaction codes based on the law of mass action (LMA), such as PHREEQC (PARKHURST & APPELO 1999) and MINEQL (WESTALL *et al.* 1976), and the properties of elements, aqueous species, solids and gases as required for Gibbs Energy minimisation (GEM) codes like Selektor (CHUDNENKO *et al.* 1995; KARPOV *et al.* 1997) and GEM-Selektor (http://les.web.psi.ch/Software/GEMS-PSI/). It is written in C++ and operates in MS Windows and Linux environments. It allows both interactive and batch operation for data entry, manipulation and output in user-specified formats. It performs calculations that maintain internal consistency among data entered in various forms, and provides messages to the user when data inconsistencies exist that the program cannot resolve internally.

PMATCHC is based on PMATCH, a code prepared to support the development of the earlier Nagra TBD of 05/92 in response to the need to compare data of different types and sources, as discussed in Section 3.1. PMATCH was described by PEARSON *et al.* (1993) and in several Nagra internal reports (PEARSON & AVIS 1989, CHALMERS & PEARSON 1992, and PEARSON & MOORE 1995). PMATCHC was intended to support compilation and use of the new Nagra/PSI TDB (HUMMEL *et al.* 2001). Its development has included translation of PMATCH from a Pascal DOS command line format to a C++ program running interactively in a windows environment. It has also included the addition of a number of additional data fields to make the program capable of managing data for a wider variety of geochemical modelling programs, and expansion of the internal calculation schemes to encompass these new types.

This document describes the data management capabilities of PMATCHC, including the data fields in the program and the calculations it performs to maintain consistency among data entered in various forms. The output capabilities of the program are also discussed, including the commands available. It was intended that PMATCHC would be self-documenting through the use of copious help files. For the most part, these help files have not yet been prepared, so this document must be used as the user manual for this version of the code.

In the section following this introduction, the data types managed within PMATCHC are described. This is followed by a section discussing the calculations made by the program, and the thermodynamic relations behind them. Finally, the output capabilities of the code are discussed, and the commands available within that facility are described.

1.1. PROGRAM DISTRIBUTION

Programming of PMATCHC is discussed in Section 6 below. The PMATCHC distribution package will be posted on the web at "http://les.web.psi.ch/Software/PMATCHC/". The distribution package will include the source code and executable files for Windows and Linux, a sample database, example script files and this document (as a pdf file).

2 DATA FIELDS IN PMATCHC

The bulk of the data managed by PMATCHC are thermodynamic properties of elements, aqueous species, solids and gases, and of reactions among them. Records for four types of entities are considered: ELEMENTS, MASTER aqueous species, PRODUCT aqueous species, SOLIDS and GASES. In addition, there are fields for auxiliary data required by the geochemical modelling programs which PMATCHC is intended to support.

This section begins with a description of the various thermodynamic quantities that are managed by PMATCHC. This is followed by a discussion of the auxiliary data managed by the data base. Finally, the data fields included in each record type are described in Section 2.3 for ELEMENTS, MASTER species, PRODUCT aqueous species, SOLIDS and GASES. Fields for both thermodynamic properties and associated auxiliary data are included in these records.

2.1. THERMODYNAMIC QUANTITIES AND EQUILIBRIUM CONSTANTS

Selected thermodynamic data for reactions refer to the reference temperature T° of 298.15 K (25°C) and pressure of 0.1 MPa (1 bar) and, for aqueous species, infinite dilution ($I = 0$).

2.1.1. Units

Thermodynamic data in PMATCHC can be entered, displayed and (or) output in Joules (and kJ) or in calories (and kcal). Internally, the program calculates and stores data as Joules and kJ. The user chooses the units entered, displayed or output using the OUTPUT mode **units** command, as discussed in Section 4.1. In the equations below, units of Joules are used for illustration purposes.

The conversion factors used in this version of PMATCHC are given in Table 1. They may also be found in the program itself using the "Factors" command in any "Help" window except that of the opening window.

Table 1: Conversion factors used in this version of PMATCHC.

FACTOR	VALUE
Calories	4.184 Joules
R (gas constant)	8.31451 J/K/mol
$\ln_e(10)$	2.30259
T^0 ref	298.15 K

2.1.2. Reactions, Elements, Solute Species, Minerals and Gases

The reaction parameters include

$\log_{10}K°$ the equilibrium constant of the reaction, logarithmic

$\Delta_r G_m°$ the molar Gibbs free energy of reaction (kJ · mol^{-1})

$\Delta_r H_m^\circ$	the molar enthalpy of reaction	$(kJ \cdot mol^{-1})$
$\Delta_r S_m^\circ$	the molar entropy of reaction	$(J \cdot K^{-1} \cdot mol^{-1})$
$\Delta_r C_{p,m}^\circ$	the molar heat capacity of reaction	$(J \cdot K^{-1} \cdot mol^{-1})$

The equilibrium constant, K°, is related to $\Delta_r G_m^\circ$ according to the following relation,

$$\Delta_r G_m^\circ = -R \cdot T^\circ \cdot \ln(10) \cdot \log_{10} K^\circ \quad (2.1)$$

and the molar quantities $\Delta_r G_m^\circ$, $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$ are related according to the Gibbs-Helmholtz equation:

$$\Delta_r G_m^\circ = \Delta_r H_m^\circ - T^\circ \cdot \Delta_r S_m^\circ \quad (2.2)$$

Thermodynamics of individual entities are tabulated using standard state properties of formation from the elements in their reference state,

$\Delta_f G_m^\circ$	the standard molar Gibbs free energy of formation	$(kJ \cdot mol^{-1})$
$\Delta_f H_m^\circ$	the standard molar enthalpy of formation	$(kJ \cdot mol^{-1})$
$\Delta_f S_m^\circ$	the standard molar entropy of formation	$(J \cdot K^{-1} \cdot mol^{-1})$
$\Delta_f C_{p,m}^\circ$	the standard molar heat capacity of formation	$(J \cdot K^{-1} \cdot mol^{-1})$

or the absolute quantities,

S_m°	the standard molar entropy	$(J \cdot K^{-1} \cdot mol^{-1})$
$C_{p,m}^\circ$	the standard molar heat capacity	$(J \cdot K^{-1} \cdot mol^{-1})$

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

$$\Delta_r X_m^\circ = \Sigma \Delta_f X_m^\circ(\text{products}) - \Sigma \Delta_f X_m^\circ(\text{reactants}) \quad (2.3)$$

where X represents the thermodynamic property and Σ throughout this report is the stoichiometric sum, the sum of the products of the property of the product or reactant times its stoichiometric coefficient.

The standard molar quantities $\Delta_f G_m^\circ$, $\Delta_f H_m^\circ$ and $\Delta_f S_m^\circ$ are related according to the Gibbs-Helmholtz equation:

$$\Delta_f G_m^\circ = \Delta_f H_m^\circ - T^\circ \cdot \Delta_f S_m^\circ \quad (2.4)$$

For neutral species

$$\Delta_f S_m^\circ = S_m^\circ - \Sigma S_m^\circ(\text{elements}) \quad (2.5)$$

$$\Delta_f C_{p,m}^\circ = C_{p,m}^\circ - \Sigma C_{p,m}^\circ(\text{elements}) \quad (2.6)$$

and for charged species

$$\Delta_f S_m^\circ = S_m^\circ - \Sigma S_m^\circ(\text{elements}) + n\, S_m^\circ(e^-) \quad (2.7)$$

$$\Delta_f C_{p,m}^\circ = C_{p,m}^\circ - \Sigma C_{p,m}^\circ(\text{elements}) + n\, C_{p,m}^\circ(e^-) \quad (2.8)$$

in which n is the charge. The values of $S_m^\circ(e^-)$ and $C_{p,m}^\circ(e^-)$ are 1/2 $S_m^\circ(H_2, g)$ and 1/2 $C_{p,m}^\circ(H_2, g)$ because e^- and $H_2(g)$ are related by:

$$1/2\ H_2(g) - e^- = H^+ \quad (2.8a)$$

and all properties of H^+ are zero by convention (SILVA *et al.* 1995 Sect II.1.6.5, WAGMAN *et al.* 1982 p. 2-22).

NOTE: In order to calculate correctly, the present version of PMATCHC requires that $S_m^\circ(e^-)$ and $C_{p,m}^\circ(e^-)$ equal the **negative** of $1/2 S_m^\circ(H_2, g)$ and $1/2\ C_{p,m}^\circ(H_2, g)$. This is due to a legacy from GEMS in which the fictive species zz ($= -e^-$) is used instead of e^- itself.

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):

$$S_m^\circ(\text{bar}) - S_m^\circ(\text{atm}) = R \cdot \ln(1.01325/1.0) = 0.1094\ J \cdot K^{-1} \cdot mol^{-1} \quad (2.9)$$

2.2. AUXILIARY DATA

In addition to the thermodynamic properties, certain other data are needed for geochemical solution modelling. Fields that can be used for such data are included in PMATCHC records.

Master species and product species records include five fields on which no calculations are made and that can be used for any data the user requires. These are named DHA, DHB, SIT1, SIT2, and SIT3. In the Nagra/PSI thermodynamic database, these fields are used for the parameters of two types of activity coefficient expressions (HUMMEL *et al.* 2001, Section 2.2). The DHA and DHB fields are used for parameters of the extended form of the Debye – Hückel expression used in PHREEQC (PARKHURST & APPELO 1999, PARKHURST 1990),

$$\log \gamma_i = -Az_i^2 \left(\frac{\sqrt{I}}{1 + Ba_i^0 \sqrt{I}} \right) + b_i I, \quad (2.9a)$$

in which the symbols have their usual meanings with a_i^0 and b_i ion specific parameters. Field DHA is used for a_i^0 the ion size parameter and DHB for b_i. The SIT1, SIT2, and SIT3 fields are used for parameters of the SIT equation (GRENTHE *et al.* 1997) as described below in Section 2.3.1.

Records for master species and product species also include a field for alkalinity (ALK). Alkalinity is an important operational parameter used in many analyses of natural waters (HEM 1989 p. 105 although it is modelled only in U.S. Geological Survey programs such as PHREEQC (PARKHURST & APPELO 1999 p. 25, 55). Alkalinity is the number of equivalents of strong acid required to titrate a solution to a pH of 4.5. The alkalinity of a solute species is the number of mols of H^+ required to transform a mol of that species to its predominant form at pH 4.5. For example, the alkalinity of HCO_3^{-1} is 1 and that of CO_3^{-2} is 2. Using this formalism, the alkalinity of H^+ is -1.

The alkalinity of secondary master species and product species can be calculated from the alkalinities of its primary master species and reaction stoichiometry. Such calculations could

be made to find correct alkalinity values for secondary master and product species or to check entered values. They are not included in the present version of PMATCHC, however.

For databases designed for PHREEQC, alkalinity values need not be entered for secondary master and product species because they are calculated from master species values within PHREEQC.

The OPV (operational valence) was used in modelling redox reactions in PHREEQE (PARKHURST *et al.* 1980), the predecessor to PHREEQC. A field for this property is retained in PMATCHC for compatibility with earlier databases designed for PHREEQE. PMATCHC also retains the ability to calculate OPV values for secondary master species, product species and minerals for check purposes (see Section 5.3, "Calculate OPV" command).

2.3. RECORD TYPES IN PMATCHC

Data in PMATCHC are organised in records, each of which corresponds to an entity in the database, such as an ELEMENT, a MASTER species, a PRODUCT species, a MINERAL or a GAS. Each record contains fields for thermodynamic and auxiliary data that are appropriate to the entity.

Although each record contains many fields, it is not necessary that the user enter data in each one. Many of the thermodynamic properties are inter-related by the equations of classical chemical thermodynamics, as described in Sections 2.1 and 2.3.1 of HUMMEL *et al.* (2001), and in Sections 2.1 and 3.2 of this report. PMATCHC is designed to take whatever combination of property values are entered and, from them, to calculate values of as many other properties as possible. These calculations are described below in Section 3.3.

As described in Section 2.1.1, the energy units associated with the thermodynamic properties are J or kJ. PMATCHC is also able to accept data in cal or kcal and to convert between data entered in either unit. The unit in which given data are entered is chosen from the screen at the time of data entry, or can be set using the OUTPUT command word **units** described in Section 4.1, below.

2.3.1. ELEMENTS

This record type contains the following fields (See Figure 1):

NAME	Element name
SYMBOL	Chemical symbol for element
ATOMIC_NO	Position of element in periodic chart
ATOMIC_MASS	grams per mol atoms
VALENCE	The default oxidation state of the element when included in chemical formulae in the database. PMATCHC and GEM-Selektor use this as a default value when parsing chemical formulae of all compounds (see DMYTRIYEVA *et al.* 1999 for details).
V0	Molar volume per atom at STP (standard temperature and pressure).
S0	S_m° ,the standard molar entropy in **units** $\cdot$ K^{-1} $\cdot$ mol^{-1}.

Cp0	$C_{p,m}°$, the standard molar heat capacity in **units** · K^{-1} · mol^{-1}.
COMMENT	Text field.
REFERENCE	Text field.

Following conventional practice, $\Delta_f G_m°$ and $\Delta_f H_m°$ values of the elements are zero at standard state, reference temperature and pressure.

Note that atomic masses, $S_m°$,the standard molar entropy and $C_{p,m}°$, the standard molar heat capacity, are entered per mol of atoms, not per mol of the element in its standard state. This has consequences for certain thermodynamic calculations, as discussed in the descriptions of the ***SFE*** and ***CPFE*** fields below. Figure 2 shows how the element H, which is diatomic in its standard state, is entered.

It is necessary to include the electron as a master species, so there must be a corresponding element "electron" as well. This is illustrated in Figure 3 and shows that $S_m°$ and $C_{p,m}°$ of e^- are the negative of those of H (see discussion and the note in Section 2.1.2 above).

The calculations made using data from the ELEMENTS field are described below in sections 3.3.6.

2.3.2. MASTER Species

MASTER species are the aqueous species which react to form all PRODUCT species, SOLIDS and GASES in the database. There are two types of MASTER species: primary and secondary. Primary MASTER species are not defined by reactions, while secondary MASTER species are described by reactions among primary MASTER species. Primary and secondary MASTER species correspond to the strict and auxiliary basis species of EQ3/6 (WOLERY 1992) data sets. Primary MASTER species also correspond, in part, to the SOLUTION_MASTER_SPECIES of PHREEQC. Secondary MASTER species, together with PRODUCT species make up the SOLUTION_SPECIES of PHREEQC. The reactions corresponding to secondary MASTER species may include only primary MASTER species. Reactions for PRODUCT aqueous species, SOLIDS and GASES may contain both types of MASTER species.

Primary MASTER species records include the following fields (See Figure 4):

NAME	Record name. For aqueous species, this is usually the composition.
COMPOSITION:	The chemical formula of the species written using the element symbols defined in the elements records. Multipliers and parentheses are written in the usual form. The valence of redox-active elements is specified between vertical bars, *e. g.* sulphate = S|6|O4-2, hydrogen sulphide = H2S|-2|, aluminate ion = Al(OH)4-. The valence of a redox-active element need not be specified in the COMPOSITION field for a given species if it is the same as the default VALENCE specified in the element record. The contents of the COMPOSITION field can be output with or without the valence specifier by setting the

prnt_valence OUTPUT command to YES or NO, as described in Section 4.1.

CHARGE Species charge. The charge is also specified in the COMPOSITION field. Value entered.

OPV Operational valence. This parameter is described in Section 2.2. The field is retained from the predecessor program PMATCH and required for databases to be used with earlier versions of PHREEQE (PARKHURST *et al.* 1980). See the PHREEQE or PMATCH documentation for its definition. Value entered.

ALK Alkalinity. This parameter is described in Section 2.2 and in the PHREEQC documentation. Value entered.

DHA

DHB As discussed in Section 2.2, These fields are not used for calculations in PMATCHC and so they can be used for any data the user would like. In the Nagra/PSI TDB, DHA and DHB are the ion-size and WATEQ parameter for the WATEQ Debye-Hückel activity coefficient expression (see Section 2.2, above and Section 2.2.3 of HUMMEL *et al.* 2001). Value entered.

V0 Specific volume. Value entered.

S0 $S_m°$, the standard molar entropy of the species in **units** · K^{-1} · mol^{-1}. Value entered.

US0 Uncertainty in $S_m°$. Value entered.

CP0 $C_{p,m}°$, the standard molar heat capacity of the species in **units** · K^{-1} · mol^{-1}. Value entered.

As discussed in Section 2.2, fields SIT1, SIT2 and SIT3 are not used for any calculations in PMATCHC and so they can be used for any data the user would like. No data for SIT parameters have been entered in the electronic version of the Nagra/PSI TDB. However, the fields could be used as follows: (see Section 2.2 above, and Section 2.2.3 of HUMMEL *et al.* 2001).

SIT1 SIT parameter for: Cl^-, if CHARGE > 0,
Na^+ if CHARGE < 0,
NaCl if CHARGE = 0

SIT2 SIT parameter for: ClO_4^-, if CHARGE > 0,
Li^+ if CHARGE < 0,
(Li, Na)ClO_4 if CHARGE = 0

SIT3 SIT parameter for: NO_3^-, if CHARGE > 0,
K^+ if CHARGE < 0,
KNO_3 if CHARGE = 0

The ***SIT1, SIT2,*** and ***SIT3*** fields are coefficients for the SIT activity coefficient expression. If the data are to be used solely for modelling natural waters, only one SIT coefficient is likely to be needed, ***SIT1***, for NaCl. However, the data may also be used

for modelling experimental results, so fields for two additional parameters, ***SIT2*** and ***SIT3***, are included as well. These permit the modelling of experiments carried out in (Li or Na)ClO_4 and KNO_3 media, respectively. The SIT model and these coefficients are described in Section 2.2.4 of HUMMEL *et al.* (2001).

GFW Gram formula weight of the species. Calculated in PMATCHC from the COMPOSITION and ATOMIC_MASSes of the elements, or may be entered manually.

GF $\Delta_f G_m°$, the standard molar Gibbs free energy of formation, in **units** · mol^{-1}. Value entered or calculated if corresponding $\Delta_f H_m°$and $\Delta_f S_m°$ values are available. See Section 2.1, equation (2.4).

HF $\Delta_f H_m°$, the standard molar enthalpy of formation, in **units** · mol^{-1}. Value entered or calculated if corresponding $\Delta_f G_m°$ and $\Delta_f S_m°$ values are available. See Section 2.1, equation (2.4).

SF $\Delta_f S_m°$, the standard molar entropy of formation, in **units** · mol^{-1}. Value entered or calculated if corresponding $\Delta_f G_m°$, and $\Delta_f H_m°$ values are available. See Section 2.1, equation (2.4).

NOTE: If SF is entered or can be calculated, its value is compared to SFE, and the difference, if any, is displayed to the user. If there are not sufficient data to calculate SF, it is assigned the value of SFE. See Section 3.3.6.

NOTE: User should enter only 2 of the three properties ***GF, HF,*** or ***SF***. To maintain strict internal consistency in the data base, PMATCHC should calculate the third. If values for all three are entered, PMATCHC displays a warning message and gives options to: "Change input data." or "Continue".

SFE $\Delta_f S_m°$ calculated from $S_m°$ of species, $S_m°$ values of elements and the COMPOSITION of the species using :

$$\Delta_f S_m° = S_m° - \Sigma S_m°_{elements} + n * S_m°(e^-) \qquad (2.10)$$

where n is the species charge. See discussion of the electron as an element in Section 2.3.1.

CPAF

CPBF

CPCF These are entered or calculated values for the *a*, *b* and *c* coefficients of the Maier-Kelley equation for the molar heat capacity of the species as a function of temperature. See Section 3.2.

VF Standard volume of formation of species. Value entered.

CP25F $\Delta_f C_{p,m}°$, the standard molar heat capacity of formation of the species in **units** · K^{-1} · mol^{-1}. Value entered or calculated from Maier-Kelley equation (MAIER & KELLEY 1932) if values for *a*, *b*, and(or) *c* are available. If CP25F is entered or there are sufficient data to calculate it, its value is compared to that of

CP25FE, and the difference, if any, displayed to the user. If there are not sufficient data to calculate CP25F, it is assigned the value of CP25FE. See Section 3.3.6.

CP25FE $\Delta_f C_{p,m}^\circ$, calculated from $C_{p,m}^\circ$ of species, $C_{p,m}^\circ$ values of elements and the COMPOSITION of the species using :

$$\Delta_f C_{p,m}^\circ = C_{p,m}^\circ - \Sigma C_{p,m}^\circ{}_{elements} + n\, C_{p,m}^\circ(e^-) \qquad (2.11)$$

where n is the species charge. See discussion of the electron as an element in Section 2.3.1, above.

COMMENT Text field.

REFERENCE Text field.

There must be a MASTER species defined for each entity in every reaction in a PMATCHC data base. If redox reactions are written using the electron, a MASTER species "electron" must be present. This is illustrated in Figure 5.

Secondary MASTER species records are differentiated from those of primary MASTER species by ***PS_FLAG*** which indicates whether a species is a primary (P) master species (PRI_MAST) or a secondary (S) master species (SEC_MAST). Records for secondary master species (SEC_MAST) (PS_FLAG = S), include all the primary MASTER species field plus the following additional fields for reaction data, see Figure 6:

ALGK
BLGK
CLGK
DLGK
ELGK These are the coefficients A, B, C, D, and E for equation (3.2), the expression for $\log_{10}K^\circ(T^\circ)$ as a function of temperature. Values entered or calculated.

LGK25 $\log_{10}K^\circ(T^\circ)$, the equilibrium constant at the reference temperature T° (25°C) for the association reaction for the species described in the stoichiometry (STOICH) field below. Entered or calculated, as described below.

ULGK Uncertainty of ***LGK25***. Value entered.

DGR $\Delta_r G_m^\circ$, the molar Gibbs free energy of reaction in **units** · mol^{-1}. Value entered or calculated from $\Delta_r H_m^\circ$, and $\Delta_r S_m^\circ$, if available, or from $\Delta_f G_m^\circ$of this and reacting primary master species based on STOICH.

DHR $\Delta_r H_m^\circ$, the molar enthalpy of reaction in **units** · mol^{-1}. Value entered or calculated from $\Delta_r G_m^\circ$ and $\Delta_r S_m^\circ$, if available, or from $\Delta_f H_m^\circ$ of this and reacting primary master species based on STOICH.

DSR $\Delta_r S_m^\circ$, the molar entropy of reaction in **units** · K^{-1} · mol^{-1}. This value is entered or, if not, is calculated in one of three ways, depending on data availability:

a): from $\Delta_r G_m°$ and $\Delta_r H_m°$ using equation (2.2);
b): from $\Delta_f S_m°$ of this and reacting primary master species based on STOICH using equation (2.3);
c): from the absolute entropies of this and reacting primary master species based on STOICH using:

$$\Delta_r S_m° = \Sigma S_m°(\text{products}) - \Sigma S_m°(\text{reactants}) \quad (2.12)$$

NOTE: User should enter only 2 of the three properties ***DGR, DHR,*** or ***DSR***. To maintain strict internal consistency in the data base, PMATCHC should calculate the third. If values for all three are entered, PMATCHC displays a warning message and gives options to: "Change input data." or "Continue".

D25CPR $\Delta_r C_{p,m}°$, the molar heat capacity of reaction in **units** $\cdot K^{-1} \cdot mol^{-1}$. This value is entered or, if not is calculated in one of three ways depending on data availability:

a): from $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ using the Meier-Kelley equation (3.1);
b): from $\Delta_f C_{p,m}°$ of this and reacting primary master species based on STOICH using equation (2.3);
c): from the absolute heat capacities of this and reacting master species based on STOICH using:

$$\Delta_r C_{p,m}° = \Sigma C_{p,m}° \text{ (products)} - \Sigma C_{p,m}° \text{ (reactants)} \quad (2.13).$$

DACPR
DBCPR
DCCPR These are values for coefficients $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ of the Maier-Kelley equation for the molar heat capacity of the reaction as a function of temperature. See Section 3.2, equation (3.1). Values entered or calculated.

DVR $\Delta_r V^0$. Value entered or calculated.

STOICH Reaction stoichiometry. Entered.

2.3.3. PRODUCT Species

PRODUCT species records include all the fields in secondary MASTER species records described in the previous section (see Figure 7).

2.3.4. HKF Parameters

Records for MASTER and PRODUCT species include fields for parameters of the revised Helgeson-Kirkham-Flowers equation of state (TANGER & HELGESON 1988, ANDERSON & CRERAR 1993 and references therein). When a new record is opened, PMATCHC queries whether HKF parameters will be included. If so, the record is defined to include these fields and a data entry screen like that shown in Figure 8 appears. Note that if a record has been defined without HKF parameters, they cannot be added from within PMATCHC itself. To

add them, it is necessary to write a backup file, add the HKF fields manually to the backup file and read it back into a new database. See Sections 4 and 5 below.

2.3.5. SOLIDS and GASES

The records for SOLIDS, called MINERALS in PMATCHC, and GASES contain the same fields as in secondary MASTER species and PRODUCT species records except that CHARGE and ALK are not present in mineral or gas records (see Figure 9 and Figure 10).

3 THERMODYNAMIC EQUATIONS AND CALCULATIONS

PMATCHC provides fields for the thermodynamic data described in Section 2.3. There is considerable redundancy in these data and the program is able to calculate many values for a reaction, aqueous species, solid or gas from other data entered for it and from master species data. Section 3.1 provides an overview of the calculations in PMATCHC and the rationale behind the order in which they are carried out. Section 3.2 includes a review of the equations of chemical thermodynamics which relate the data included in PMATCHC. Section 3.3 describes the various types of calculations of which the program is capable.

3.1. OVERVIEW OF CALCULATION SCHEME

Virtually all geochemical modelling of the behaviour of aqueous solutions is done using programs based on the law of mass action (LMA). Such modelling requires descriptions of reactions among aqueous solutes, minerals and gases and the equilibrium constants for these reactions at the modelling temperature. Data from experimental studies are sometimes given in this form and can be used directly for modelling. Examples include the works of Plummer and Busenberg (PLUMMER & BUSENBERG 1982, BUSENBERG *et al.* 1984, and BUSENBERG & PLUMMER 1986) on alkaline earth carbonates and of Wesolowski and Palmer (WESOLOWSKI 1992, PALMER & WESOLOWSKI 1992, and PALMER & WESOLOWSKI 1993) on the solution chemistry of aluminium.

Compilations of data for use with geochemical solution models usually contain standard state equilibrium constants at 25 degrees C ($\log_{10}K^0(T^0)$) for specified reactions. Commonly they also include parameters that allow calculation of logK values at other temperatures. These may be $\Delta_r H^0(T^0)$ or coefficients for expressions for logK as f(T). The paper by NORDSTROM *et al.* (1990) and the database for the U.S. Environmental Protection Agency Geochemical Model (MINTEQA2, ALLISON *et al.* 1991) are examples of such compilations.

Compilations of thermodynamic data intended for broader applications are usually given as the standard state properties of formation at the reference temperature for solids, gasses, liquids and aqueous species. The compilations of CODATA, NPS (now NIST), and NEA are of this type. Other compilations, such as those of Helgeson, Shock, Sverjensky and their colleagues, include additional parameters for calculation of properties of temperatures far removed from their reference values (*e. g.* HELGESON *et al.* 1981, SHOCK *et al.* 1997, SVERJENSKY *et al.* 1997). These authors use the revised HKF equation of state for solutes. Helgeson and his colleagues express the temperature variation of heat capacity of solids and gases using the three-term Maier-Kelley equation (*e.g.* HELGESON *et al.* 1978). The NEA uses a six-term equation for the heat capacity but points out that most temperature variations can be described using only the three terms of the Maier-Kelley equation (the NEA compilation

also includes the data for reactions from which their formation properties were calculated. They point out that experimental uncertainties are correctly reflected in the logK data but may be overestimated in the uncertainties assigned to the properties of formation they tabulate).

PMATCH (PEARSON *et al.* 1993) was intended to be a tool that would accept data in any of the forms in which they are conventionally given and convert them to any other forms desired. That is, it would calculate properties of formation from reaction data and properties of given reactions from formation data with the intent of maintaining strict internal consistency within a single database. PMATCH was also given flexible output formatting capabilities so that databases for use with specific modelling programs could be written directly from it.

These intentions are maintained in PMATCHC. PMATCHC also includes the new record type ELEMENT, and fields for properties of formation from the elements and for the HKF parameters of aqueous species. The properties of the elements are used to calculate or check entered formation properties of solutes, solids, and gases. The HKF parameters are not used for calculation in this version of PMATCH. Instead, when such data are available, SUPCRT (JOHNSON *et al.*, 1992) is used to calculate properties of reaction, which are then entered in PMATCHC. An obvious improvement to PMATCHC would be to include SUPCRT-like calculations directly or an ability to run SUPCRT externally from within PMATCH.

The order of calculations in PMATCH reflects its initial design to support LMA codes with their need for reaction data and the fact that reaction data are also closer to experimental data than are properties of formation. The calculation cases, which are described below, begin with reaction data entered for logK values and their temperature coefficients, followed by cases in which thermodynamic properties of reaction are entered. Cases in which properties of formation are entered are next and certain cases with mixed data types are last.

In practice, this is important to the way PMATCHC treats redundant data. If only logK data are entered, PMATCHC will calculate $\Delta_r G^0$ and $\Delta_f G^0$ from them as described below. If both logK and $\Delta_f G^0$ data are entered, it will calculate $\Delta_r G^0$ from the logK information rather than from $\Delta_f G^0$. However, it will not recalculate $\Delta_f G^0$ if it should be inconsistent with the logK value. Thus, to maintain a fully internally consistent database, the user must be vigilant not to enter redundant data.

With the calculation scheme in the present version of PMATCH, it may also possible to generate thermodynamic data that do not exist. This is discussed in Section 3.4 along with suggestions about how data should be entered to minimise the risk of data generation.

3.2. THERMODYNAMIC EQUATIONS

The equations given in this section are largely duplicates of those given in Sections 2.1 through 2.3 of HUMMEL *et al.* (2001).

The equation of MAIER & KELLEY (1932) is widely used to express the variation of the molar heat capacity at constant pressure, $C_{p,m}^\circ$, with absolute temperature, T. When applied to a reaction, this equation is written:

$$\Delta_r C_{p,m}^\circ(T) = \Delta_r a + \Delta_r b \cdot T - \Delta_r c / T^2 \qquad (3.1)$$

where $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ are constants. It can also be applied to heat capacities of formation:

$$\Delta_f C_{p,m}^\circ(T) = \Delta_f a + \Delta_f b \cdot T - \Delta_f c / T^2 \quad (3.1a)$$

where $\Delta_f a$, $\Delta_f b$ and $\Delta_f c$ are constants.

Integration of equation (3.1) leads to the following equation relating $\log_{10} K^\circ(T)$ values to temperature:

$$\log_{10} K^\circ(T) = A + B \cdot T + C / T + D \cdot \log_{10}(T) + E / T^2 \quad (3.2)$$

This equation is embodied in PMATCHC and PHREEQC, and has been adopted for the Nagra/PSI thermochemical data base.

The following equations show the relations between the temperature dependent equilibrium constant, $\log_{10} K^\circ(T)$, and such other thermodynamic properties of reaction as $\Delta_r G_m^\circ$, $\Delta_r H_m^\circ$, $\Delta_r S_m^\circ$, $\Delta_r C_{p,m}^\circ$ and $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ of the heat capacity equation.

$$\Delta_r G_m^\circ(T) = -R \cdot T \cdot \ln(10) \cdot \log_{10} K^\circ(T) \quad (3.3)$$

$$\Delta_r G_m^\circ(T) = -R \cdot \ln(10) \cdot (A \cdot T + B \cdot T^2 + C + D \cdot T \cdot \log_{10}(T) + E / T) \quad (3.4)$$

$$\Delta_r H_m^\circ(T) = R \cdot T^2 \cdot \ln(10) \cdot (\partial \log_{10} K^\circ(T) / \partial T) \quad (3.5)$$

$$\Delta_r H_m^\circ(T) = R \cdot \ln(10) \cdot (B \cdot T^2 - C + D \cdot T / \ln(10) - 2 \cdot E / T) \quad (3.6)$$

$$\Delta_r S_m^\circ(T) = -\partial \Delta_r G_m^\circ(T) / \partial T \quad (3.7)$$

$$\Delta_r S_m^\circ(T) = R \cdot \ln(10) \cdot (A + 2 \cdot B \cdot T + D / \ln(10) \cdot (1 + \ln(T)) - E / T^2) \quad (3.8)$$

$$\Delta_r C_{p,m}^\circ(T) = \partial \Delta_r H_m^\circ(T) / \partial T \quad (3.9)$$

$$\Delta_r C_{p,m}^\circ(T) = R \cdot \ln(10) \cdot (2 \cdot B \cdot T + D / \ln(10) + 2 \cdot E / T^2) \quad (3.10)$$

$$\Delta_r a = R \cdot D \quad (3.11)$$

$$\Delta_r b = 2 \cdot R \cdot \ln(10) \cdot B \quad (3.12)$$

$$\Delta_r c = -2 \cdot R \cdot \ln(10) \cdot E \quad (3.13)$$

If sufficient experimental data are available to define all five coefficients A through E, the values of the Gibbs energy, enthalpy, entropy, heat capacity, and all three coefficients $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$ of the heat capacity expression, can be found using the above equations.

It is also necessary to be able to calculate values of the coefficients A through E of the $\log_{10} K^\circ(T)$ equation from thermodynamic properties of a reaction. 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 are calculated according to:

$$E = -\Delta_r c / (2 \cdot R \cdot \ln(10)) \quad (3.14)$$

$$D = \Delta_r a / R$$

$$B = \Delta_r b / (2 \cdot R \cdot \ln(10)) \quad (3.16)$$

The coefficient C is calculated using $\Delta_r H_m^\circ$ at the reference temperature T°:

$$C = B \cdot T°^2 + D \cdot T° / \ln(10) - 2 \cdot E / T° - \Delta_r H_m°(T°) / (R \cdot \ln(10))$$

$$C = (\Delta_r b / 2 \cdot T°^2 + \Delta_r a \cdot T° + \Delta_r c / T° - \Delta_r H_m°(T°)) / (R \cdot \ln(10)) \quad (3.18)$$

A is calculated from $\Delta_r S_m°$ at the reference temperature T°:

$$A = \Delta_r S_m°(T°) / (R \cdot \ln(10)) - 2 \cdot B \cdot T° - D / \ln(10) \cdot (1 + \ln(T°)) + E / T°^2 \quad (3.19)$$

$$A = (\Delta_r S_m°(T°) - \Delta_r b \cdot T°^2 - \Delta_r a \cdot (1 + \ln(T°)) - \Delta_r c / (2 \cdot T°^2)) / (R \cdot \ln(10)) \quad (3.20)$$

If $\Delta_r C_{p,m}°$ is known only at the reference temperature T°, it is often assumed to be constant with temperature. In this case, $\Delta_r C_{p,m}° = \Delta_r a$ and $\Delta_r b = \Delta_r c = 0$, so that B = E = 0, and the expression for $\log_{10} K°(T)$ has the form:

$$\log_{10} K°(T) = A + C / T + D \cdot \log_{10}(T) \quad (3.21)$$

This equation is called the three-term approximation of temperature dependence. From the equations above it follows that:

$$D = \Delta_r C_{p,m}° / R$$

$$C = (\Delta_r C_{p,m}° \cdot T° - \Delta_r H_m°(T°)) / (R \cdot \ln(10)) \quad (3.23)$$

$$A = (\Delta_r S_m°(T°) - \Delta_r C_{p,m}° \cdot (1 + \ln(T°)) / (R \cdot \ln(10)) \quad (3.24)$$

For most reactions, $\Delta_r C_{p,m}°$ is not known and it must be assumed that $\Delta_r H_m°$ is constant with temperature. In this case, B = D = E = 0, and the expression for $\log_{10} K°(T)$ has the form:

$$\log_{10} K°(T) = A + C / T \quad (3.25)$$

This equation is called the two-term approximation of temperature dependence. From the equations above it follows that:

$$C = - \Delta_r H_m°(T°) / (R \cdot \ln(10)) \quad (3.26)$$

$$A = \Delta_r S_m°(T°) / (R \cdot \ln(10)) \quad (3.27)$$

and that:

$$\log_{10} K°(T) = \log_{10} K°(T°) + \Delta_r H_m°(T°) / (R \cdot \ln(10)) \cdot (1 / T° - 1 / T) \quad (3.28)$$

Equation (3.28) is the integrated van't Hoff equation as used in MINEQL, PHREEQC and other geochemical programs.

3.3. CALCULATIONS

The calculation scheme in PMATCHC is designed to derive the maximum amount of information from whatever data have been entered into the data base by the user, while maintaining

the priority given to reaction data. Numerical records in PMATCHC are in one of three possible states: Entered, Calculated or Null, as described for the output mode command **real** (see Section 4.1). Calculated values are flagged within the data base (and indicated by an asterisk on the record display screens) so they can be distinguished from data entered by the user.

A number of calculation pathways are necessary to allow for the various permutations and combinations of data which can be entered. This section describes these calculations so the user will recognise the relative priorities given to the types of data within PMATCHC.

The following Sections 3.3.1 through 3.3.6 outline the thermodynamic calculations. The equation numbers are those used in Sections 2.1 and 3.2. There are 23 calculation cases which are summarised in Table 2. PMATCHC checks the data entered in the database and performs the first calculation for which sufficient data are available. The order in which the cases are checked is: 1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 116, 16, 117, 17, 21, 22, 18, 19, 20.

No attempt has been made to include all possible permutations and combinations of thermodynamic data entry in the calculation schemes run by PMATCHC. Rather, a user with a combination of data for a species, solid or gas that does not match any of the cases included in PMATCHC and discussed below is expected to modify the form available for data entry to one of the existing cases by judicious addition of zero values or calculations external to PMATCHC . Case 17a is an example of the type of intelligent user input required.

3.3.1. Calculations Based on Two or More LGK Coefficients

Case 1. User entered data for A, B, C, D, E coefficients of the $\log_{10}K°(T)$ equation (3.2).
Calculations of reaction properties at 25°C:

$\Delta_r G^0$	- equation (3.4)
$\Delta_r H^0$	- equation (3.6)
$\Delta_r S^0$	- equation (3.8)
$\Delta_r a$	- equation (3.11)
$\Delta_r b$	- equation (3.12)
$\Delta_r c$	- equation (3.13)
logK(25°C)	- equation (3.2)
$\Delta_r Cp^0$	- equation (3.1)

If the properties of formation of all constituent master species are in the data base, $\Delta_f G^0$, $\Delta_f H^0$, $\Delta_f S^0$, $\Delta_f a$, $\Delta_f b$, $\Delta_f c$ and $\Delta_f Cp^0$ are calculated using equation (2.3).

Case 2. User entered data for A, B, C, D coefficients of $\log_{10}K°(T)$ equation (3.2).
For calculations of reaction properties at 25°C:

E and $\Delta_r c$	are set to zero

and the calculations are made as for case 1.

Case 3 User entered data for A, C, D coefficients of $\log_{10}K°(T)$ equation (3.2).
For calculations of reaction properties at 25°C:

B, E, $\Delta_r b$ and $\Delta_r c$ are set to zero

and the calculations are made as for case 1.

Case 4 User entered data for A and C coefficients of the $\log_{10}K°$(T) equation (3.2).
For calculations of reaction properties at 25°C:

B, D, E, $\Delta_r a$, $\Delta_r b$, $\Delta_r c$ and $\Delta_r Cp^0$ are set to zero

and the calculations are made as for case 1.

Case 5: Case Number not used in PMATCHC.

Other combinations of coefficients for the logKT equation are also possible. These can be included in PMATCHC data bases by manually entering values of zero for unknown coefficients as necessary to make the input data set correspond to any of cases 1 through 4. If this is done, the calculation results must be carefully checked to be certain that entering zero in a field that should be blank (have a null value) does not cause the program to calculate values that should not be present.

3.3.2. Calculations Based on other Properties of Reactions

Case 6 User entered data for any two of $\Delta_r G^0$, $\Delta_r H^0$ or $\Delta_r S^0$ and all three of $\Delta_r a$, $\Delta_r b$ or $\Delta_r c$. Note the entering values for all three of $\Delta_r G^0$, $\Delta_r H^0$ or $\Delta_r S^0$ could lead to an internal inconsistency in the data base. For this reason, a warning message appears if values for all three are entered.
Calculations for missing values at 25°C:

Missing value of $\Delta_r G^0$, $\Delta_r H^0$ or $\Delta_r S^0$:	- equation (2.2)
B	- equation (3.16)
D	- equation (3.15)
E	- equation (3.14)
C	- equation (3.17)
A	- equation (3.19)
logK(25°C)	- equation (3.2)
$\Delta_r Cp^0$	- equation (3.1)

If the properties of formation of all constituent master species are in the data base, $\Delta_f G^0$, $\Delta_f H^0$, $\Delta_f S^0$, Δ_fa , Δ_fb, Δ_fc and $\Delta_f Cp^0$ are calculated using equation (2.3).

Case 7 User entered data for any two of $\Delta_r G^0$, $\Delta_r H^0$ or $\Delta_r S^0$ and $\Delta_r a$ and $\Delta_r b$.
For calculating non-entered data at 25°C:

$\Delta_r c$ and E are set to zero

and the calculations are made as for case 6.

Case 8 User entered data any two of $\Delta_r G^0$, $\Delta_r H^0$ or $\Delta_r S^0$ and $\Delta_r a$.

For calculating non-entered data at 25°C:

$\Delta_r b$, $\Delta_r c$, B and E — are set to zero

and the calculations are made as for case 6.

Case 9 User entered data any two of $\Delta_r G^0$, $\Delta_r H^0$ or $\Delta_r S^0$ and $\Delta_r Cp^0$.

For calculating non-entered data at 25°C:

$\Delta_r a$ — is set to $\Delta_r Cp^0$

$\Delta_r b$, $\Delta_r c$, B and E — are set to zero

and the calculations are made as for case 6.

Case 10 User entered data any two of $\Delta_r G^0$, $\Delta_r H^0$ or $\Delta_r S^0$

For calculating non-entered data at 25°C:

$\Delta_r a$, $\Delta_r b$, $\Delta_r c$, $\Delta_r Cp^0$, B, D and E are set to zero

and the calculations are made as for case 6.

3.3.3. Calculations Based on Properties of Formation

These calculations can be made only if the properties of formation of all constituent master species are in the data base. $\Delta_f G^0$ and/or $\Delta_f H^0$ must be entered directly. $\Delta_f S^0$ and $\Delta_f Cp^0$ can be entered directly or calculated if S^0 or Cp^0 is entered, and S^0 or Cp^0 properties of the constituent elements are also present. The CODATA compilation commonly gives $\Delta_f H^0$ and S^0 values.

Note that having values for all three of $\Delta_r G^0$, $\Delta_r H^0$ and $\Delta_r S^0$ could lead to an internal inconsistency in the data base. For this reason, a warning message appears if values for all three are present before calculation.

As discussed below for Cases 21 and 22, values for $\Delta_r S^0$ and $\Delta_r Cp^0$ can be calculated from S^0 or Cp^0 values of the species themselves even if all required data for the elements are not available.

Case 11 User entered data any two of $\Delta_f G^0$, $\Delta_f H^0$, or $\Delta_f S^0$, and all three of $\Delta_f a$, $\Delta_f b$, and $\Delta_f c$.

Calculations for any missing values at 25°C:

Missing value of $\Delta_f G^0$, $\Delta_f H^0$ or $\Delta_f S^0$:	- equation (2.4)
$\Delta_f Cp^0$	- equation (3.1a)
$\Delta_r G^0$, $\Delta_r H^0$, $\Delta_r S^0$	- equation (2.3)
$\Delta_r a$, $\Delta_r b$, $\Delta_r c$:	- equation (2.3)
$\Delta_r Cp^0$	- equation (3.1)
B	- equation (3.16)
D	- equation (3.15)
E	- equation (3.14)
C	- equation (3.17)

A	- equation (3.19)
logK(25°C)	- equation (3.2)

Case 12 User entered data for any two of $\Delta_f G^0$, $\Delta_f H^0$, or $\Delta_f S^0$, and for $\Delta_f a$, and $\Delta_f b$.
For calculating non-entered data at 25°C :

$\Delta_f c$	is set to zero

and the calculations are made as for case 11.

Case 13 User entered data for any two of $\Delta_f G^0$, $\Delta_f H^0$, or $\Delta_f S^0$, and for $\Delta_f a$.
For calculating non-entered data at 25°C:

$\Delta_f b$ and $\Delta_f c$	are set to zero

and the calculations are made as for case 11.

Case 14 User entered data for any two of $\Delta_f G^0$, $\Delta_f H^0$, or $\Delta_f S^0$, and for $\Delta_f Cp^0$.
For calculating non-entered data at 25°C:

$\Delta_f a$	is set to $\Delta_f Cp^0$
$\Delta_f b$ and $\Delta_f c$	are set to zero

and the calculations are made as for case 11.

Case 15 User entered data for any two of $\Delta_f G^0$, $\Delta_f H^0$, or $\Delta_f S^0$.
For calculating non-entered data at 25°C:

Missing value of $\Delta_f G^0$, $\Delta_f H^0$, or $\Delta_f S^0$:	- equation (2.4)
$\Delta_r G^0$, $\Delta_r H^0$, $\Delta_r S^0$:	- equation (2.3)
$\Delta_r a$, $\Delta_r b$, $\Delta_r c$ and $\Delta_r Cp^0$:	- set to zero
$\Delta_f a$, $\Delta_f b$, $\Delta_f c$ and $\Delta_f Cp^0$:	- equation (2.3)
B, D, E:	- set to zero
C	- equation (3.17)
A	- equation (3.19)
logK(25°C)	- equation (3.2)

3.3.4. Calculations Based on Mixed Sets of Properties

Case 16 User entered data for logK(25°C), $\Delta_r H^0$ or $\Delta_r S^0$.
For calculating non-entered data at 25°C:

$\Delta_r G^0$	- equation (2.1)

The calculations are then made as for case 10.

Case 116 User entered data for logK(25°C), $\Delta_r H^0$ or $\Delta_r S^0$ and $\Delta_r Cp^0$ or values for $\Delta_r a$, $\Delta_r b$ and (or) $\Delta_r c$.
For calculating non-entered data at 25°C:

$\Delta_r G^0$ - equation (2.1)

116a) If user entered values for $\Delta_r a$, $\Delta_r b$ and $\Delta_r c$, make calculations as for case 6.

116b) If user entered values for $\Delta_r a$ and $\Delta_r b$, make calculations as for case 7.

116c) If user entered values for $\Delta_r a$, make calculations as for case 8.

116d) If user entered values for $\Delta_r Cp^0$, make calculations as for case 9.

Case 17 User entered data for logK(25°C), $\Delta_f H^0$ or $\Delta_f S^0$:

For calculating non-entered data at 25°C:

$\Delta_r G^0$ - equation (2.1)

$\Delta_f G^0$ - equation (2.3)

The calculations are then made as for case 15.

Case 117 User entered data for logK(25°C), $\Delta_f H^0$ or $\Delta_f S^0$ and $\Delta_f Cp^0$ or values for $\Delta_f a$, $\Delta_f b$ or $\Delta_f c$.

For calculating non-entered data at 25°C:

$\Delta_r G^0$ - equation (2.1)

$\Delta_f G^0$ - equation (2.3)

117a) If user entered values for $\Delta_f a$, $\Delta_f b$ and $\Delta_f c$, make calculations as for case 11.

117b) If user entered values for $\Delta_f a$ and $\Delta_f b$, make calculations as for case 12.

117c) If user entered values for $\Delta_f a$, make calculations as for case 13.

117d) If user entered values for $\Delta_f Cp^0$, make calculations as for case 14.

Case 17a This case is not programmed in PMATCHC, but is described here as an example of how user interaction can extend the capabilities of the program.

There are user entered data for logK(25°C) but not for $\Delta_f H^0$ or $\Delta_f S^0$. S^0 and possibly Cp^0 data are also entered. S^0 and possibly Cp^0 data are available for all other reactants and elements. As described below in Section 3.3.6, PMATCHC calculations give values for SFE and possibly CP25FE. If these calculated values are entered for $\Delta_f S^0$ (SF) and $\Delta_f Cp^0$ (CP25F), a recalculation will follow according to case 17 (if only $\Delta_f S^0$ is entered) or 117 (if $\Delta_f S^0$ and $\Delta_f Cp^0$ are entered).

3.3.5. Calculations Based on Single Value Sets of Properties

Case 18 User entered data for $\log_{10}K(25°C)$.

Calculations for any missing values at 25°C:

A	- set to $\log_{10}K(25°C)$
Δ_rG^0	- equation (2.1)
Δ_fG^0	- equation (2.3)

In the data base itself, all other values are left blank.

Case 19 User entered data for Δ_rG^0 .

Calculations for any missing values at 25°C:

$\log_{10}K(25°C)$	- equation (2.1)
A	- set to $\log_{10}K(25°C)$
Δ_fG^0	- equation (2.3)

In the data base itself, all other values are left blank.

Case 20 User entered data for Δ_fG^0 ,

Calculations for any missing values at 25°C:

If properties of formation of all constituent master species are in data base:

Δ_rG^0	- equation (2.3)

Then as for case 19.

3.3.6. Calculations based on absolute entropies and heat capacities

Entities in PMATCHC data bases may have values for $\Delta_fS_m°$ and $\Delta_fC_{p,m}°$ that have been entered directly or calculated from data for master species in the reactions by which they are formed. (See, for example, calculation cases 1 through 10.) There is also provision for entry of $S_m°$ and $C_{p,m}°$ values for the elements and other entities in the data base. If such data are available for an entity and all its constituent elements, values for $\Delta_fS_m°$ and $\Delta_fC_{p,m}°$ can be calculated using equations (2.10) and (2.11). It is possible that the two calculations paths could reach conflicting values for these properties.

To overcome this possible conflict, there are two fields for entropy of formation and heat capacity formation for each MASTER and PRODUCT species, MINERAL and GAS. One is the ***SF*** or ***CP25F*** field, which is calculated from values for Δ_fG^0 and Δ_fH^0 which have been entered or calculated from reaction data, as shown in Sections 3.3.1 and 3.3.2 . The other is the ***SFE*** or ***CP25FE*** field calculated from ELEMENTS data and the $S_m°$ and $C_{p,m}°$ values entered for the entity.

If sufficient data are present that calculations can be made for both fields, the values are compared and a screen message appears showing the comparison. If only a value for ***SFE*** or ***CP25FE*** from the elements can be calculated, it can manually be entered in the ***SF*** or ***CP25FE*** field as described for case 17a. In the data base itself, all other values are left blank.

Table 2: Summary of PMATCHC calculation cases.

Property	PMATCHC Field Name	logK(T) Coefficients Entered				Properties of Reaction Entered				
		1	**2**	**3**	**4**	**6**	**7**	**8**	**9**	**10**
EQUILIBRIUM CONSTANT										
A Coef. logK(T) expression	ALGK	E	E	E	E	3.19	3.19	3.19	3.19	3.19
B Coef. logK(T) expression	BLGK	E	E	set to 0	set to 0	3.16	3.16	3.16 ⇒ 0	3.16 ⇒ 0	3.16 ⇒ 0
C Coef. logK(T) expression	CLGK	E	E	E	E	3.17	3.17	3.17	3.17	3.17
D Coef. logK(T) expression	DLGK	E	E	E	set to 0	3.15	3.15	3.15	3.15	3.15 ⇒ 0
E Coef. logK(T) expression	ELGK	E	set to 0	set to 0	set to 0	3.14	3.14 ⇒ 0	3.14 ⇒ 0	3.14 ⇒ 0	3.14 ⇒ 0
logK(25°C)	LGK25	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2
PROPERTIES OF REACTION										
$\Delta_r G_m^0$	DGR	3.4	3.4	3.4	3.4	E or 2.2	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r H_m^0$	DHR	3.6	3.6	3.6	3.6	E or 2.2	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r S_m^0$	DSR	3.8	3.8	3.8	3.8	E or 2.2	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r C_{p,m}^0$	D25CPR	3.1	3.1	3.1	3.1 ⇒ 0	3.1	3.1	3.1	E	set to 0
Δ_ra: Maier-Kelley	DACPR	3.11	3.11	3.11	3.11 ⇒ 0	E	E	E	set to $\Delta_r C_{p,m}^0$	set to 0
Δ_rb: Maier-Kelley	DBCPR	3.12	3.12	3.12 ⇒ 0	3.12 ⇒ 0	E	E	set to 0	set to 0	set to 0
Δ_rc: Maier-Kelley	DCCPR	3.13	3.13 ⇒ 0	3.13 ⇒ 0	3.13 ⇒ 0	E	set to 0	set to 0	set to 0	set to 0
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION										
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E	E	E
$\Delta_f G_m^0$	GF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f H_m^0$	HF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f S_m^0$	SF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f C_{p,m}^0$	CP25F	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
a: Maier-Kelley	CPAF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
b: Maier-Kelley	CPBF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
c: Maier-Kelley	CPCF	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION										
S_m^0	S0									
$C_{p,m}^0$	CP0									

Legend:

E	Data entered
3.4	Calculated using equation (3.4)
3.1 ⇒ 0	Calculated to be zero from equation (3.1)
–	Blank: Not entered or insufficient data to calculate

Table 2: Continued.

Property	PMATCHC Field Name	Properties of Formation Entered					Mixed and Single Value Properties Entered			
		11	**12**	**13**	**14**	**15**	**16**	**116a**	**116b**	**116c**
EQUILIBRIUM CONSTANT										
A Coef. logK(T) expression	ALGK	3.19	3.19	3.19	3.19	3.19	3.19	3.19	3.19	3.19
B Coef. logK(T) expression	BLGK	3.16	3.16	3.16	3.16	3.16 ⇒ 0	3.16 ⇒ 0	3.16	3.16	3.16 ⇒ 0
C Coef. logK(T) expression	CLGK	3.17	3.17	3.17	3.17	3.17	3.17	3.17	3.17	3.17
D Coef. logK(T) expression	DLGK	3.15	3.15	3.15	3.15	3.15 ⇒ 0	3.15 ⇒ 0	3.15	3.15	3.15
E Coef. logK(T) expression	ELGK	3.14	3.14	3.14	3.14	3.14 ⇒ 0	3.14 ⇒ 0	3.14	3.14 ⇒ 0	3.14 ⇒ 0
logK(25°C)	LGK25	3.2	3.2	3.2	3.2	3.2	E	E	E	E
PROPERTIES OF REACTION										
$\Delta_r G_m^0$	DGR	2.3	2.3	2.3	2.3	2.3	2.1	2.1	2.1	2.1
$\Delta_r H_m^0$	DHR	2.3	2.3	2.3	2.3	2.3	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r S_m^0$	DSR	2.3	2.3	2.3	2.3	2.3	E or 2.2	E or 2.2	E or 2.2	E or 2.2
$\Delta_r C_{p,m}^0$	D25CPR	3.1	3.1	3.1	3.1	set to 0	set to 0	3.1	3.1	3.1
Δ_ra: Maier-Kelley	DACPR	2.3	2.3	2.3	2.3	set to 0	set to 0	E	E	E
Δ_rb: Maier-Kelley	DBCPR	2.3	2.3	2.3	2.3	set to 0	set to 0	E	E	set to 0
Δ_rc: Maier-Kelley	DCCPR	2.3	2.3	2.3	2.3	set to 0	set to 0	E	set to 0	set to 0
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION										
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E	E	E
$\Delta_f G_m^0$	GF	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	2.3	2.3	2.3	2.3
$\Delta_f H_m^0$	HF	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	2.3	2.3	2.3	2.3
$\Delta_f S_m^0$	SF	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	2.3	2.3	2.3	2.3
$\Delta_f C_{p,m}^0$	CP25F	3.1a	3.1a	3.1a	E	2.3	2.3	2.3	2.3	2.3
a: Maier-Kelley	CPAF	E	E	E	set to $\Delta_f C_{p,m}^0$	2.3	2.3	2.3	2.3	2.3
b: Maier-Kelley	CPBF	E	E	set to 0	set to 0	2.3	2.3	2.3	2.3	2.3
c: Maier-Kelley	CPCF	E	set to 0	set to 0	set to 0	2.3	2.3	2.3	2.3	2.3
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION										
S_m^0	S0									
$C_{p,m}^0$	CP0									

Table 2: Continued.

Property	PMATCHC Field Name	Mixed and Single Value Properties Entered						
		116d	**17**	**117a**	**117b**	**117c**	**117d**	**17a**
EQUILIBRIUM CONSTANT								
A Coef. logK(T) expression	ALGK	3.19	3.19	3.19	3.19	3.19	3.19	3.19
B Coef. logK(T) expression	BLGK	3.16 ⇒ 0	3.16 ⇒ 0	3.16	3.16	3.16	3.16	3.16
C Coef. logK(T) expression	CLGK	3.17	3.17	3.17	3.17	3.17	3.17	3.17
D Coef. logK(T) expression	DLGK	3.15	3.15 ⇒ 0	3.15	3.15	3.15	3.15	3.15
E Coef. logK(T) expression	ELGK	3.14 ⇒ 0	3.14 ⇒ 0	3.14	3.14	3.14	3.14	3.14
logK(25°C)	LGK25	E	E	E	E	E	E	E
PROPERTIES OF REACTION								
$\Delta_r G_m^0$	DGR	2.1	2.1	2.1	2.1	2.1	2.1	2.1
$\Delta_r H_m^0$	DHR	E or 2.2	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_r S_m^0$	DSR	E or 2.2	2.3	2.3	2.3	2.3	2.3	2.2
$\Delta_r C_{p,m}^0$	D25CPR	E	set to 0	3.1	3.1	3.1	3.1	3.1
Δ_ra: Maier-Kelley	DACPR	set to $\Delta_r C_{p,m}^0$	set to 0	2.3	2.3	2.3	2.3	2.3
Δ_rb: Maier-Kelley	DBCPR	set to 0	set to 0	2.3	2.3	2.3	2.3	2.3
Δ_rc: Maier-Kelley	DCCPR	set to 0	set to 0	2.3	2.3	2.3	2.3	2.3
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION								
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E
$\Delta_f G_m^0$	GF	2.3	2.3	2.3	2.3	2.3	2.3	2.3
$\Delta_f H_m^0$	HF	2.3	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	2.4
$\Delta_f S_m^0$	SF	2.3	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E or 2.4	E see NOTE
$\Delta_f C_{p,m}^0$	CP25F	2.3	2.3	3.1a	3.1a	3.1a	E	E see NOTE
a: Maier-Kelley	CPAF	2.3	2.3	E	E	E	set to $\Delta_f C_{p,m}^0$	set to 0 or $\Delta_f C_{p,m}^0$
b: Maier-Kelley	CPBF	2.3	2.3	E	E	set to 0	set to 0	set to 0
c: Maier-Kelley	CPCF	2.3	2.3	E	set to 0	set to 0	set to 0	set to 0
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION								
S_m^0	S0							E see NOTE
$C_{p,m}^0$	CP0							E see NOTE

NOTE: Values for $\Delta_f S_m^0$ and $\Delta_f C_{p,m}^0$ (designated SFE and CP25FE) can also be calculated from S_m^0 and $C_{p,m}^0$ data for elements and other entities using equation (2.10) or (2.11). If values for both SF and SFE, and for CP25F and CP25FE are present they are compared. If they differ by more than 0.01, an error message appears on the screen. For case 17a, SFE and possibly CP25FE are available and can be used to enter the missing SF and CP25F.

Table 2: Continued.

Property	PMATCHC Field Name	Mixed and Single Value Properties Entered			Absolute Entropy (and Absolute Heat Capacity) Entered			
		18	**19**	**20**	**21a**	**21b**	**22a**	**22b**
EQUILIBRIUM CONSTANT								
A Coef. logK(T) expression	ALGK	set to logK (25°C)	set to logK (25°C)	set to logK (25°C)	3.19	3.19	3.19	3.19
B Coef. logK(T) expression	BLGK	--	--	--	3.16 ⇒ 0	3.16 ⇒ 0	3.16 ⇒ 0	3.16 ⇒ 0
C Coef. logK(T) expression	CLGK	--	--	--	3.17	3.17	3.17	3.17
D Coef. logK(T) expression	DLGK	--	--	--	3.15 ⇒ 0	3.15	3.15 ⇒ 0	3.15
E Coef. logK(T) expression	ELGK	--	--	--	3.14 ⇒ 0	3.14 ⇒ 0	3.14 ⇒ 0	3.14 ⇒ 0
logK(25°C)	LGK25	E	2.1	2.1	3.2	3.2	3.2	3.2
PROPERTIES OF REACTION								
$\Delta_r G_m^0$	DGR	2.1	E	2.3	2.2	2.2	2.3	2.3
$\Delta_r H_m^0$	DHR	--	--	--	2.3	2.3	2.2	2.2
$\Delta_r S_m^0$	DSR	--	--	--	2.12	2.12	2.12	2.12
$\Delta_r C_{p,m}^0$	D25CPR	--	--	--	set to 0	2.13	set to 0	2.13
Δ_ra: Maier-Kelley	DACPR	--	--	--	set to 0	set to $\Delta_r C_{p,m}^0$	set to 0	set to $\Delta_r C_{p,m}^0$
Δ_rb: Maier-Kelley	DBCPR	--	--	--	set to 0	set to 0	set to 0	set to 0
Δ_rc: Maier-Kelley	DCCPR	--	--	--	set to 0	set to 0	set to 0	set to 0
PROPERTIES OF FORMATION OF ALL ENTITIES IN REACTION								
Reaction Stoichiometry	STOICH	E	E	E	E	E	E	E
$\Delta_f G_m^0$	GF	2.3	2.3	E	2.3	2.3	E	E
$\Delta_f H_m^0$	HF	--	--	--	E	E	2.3	2.3
$\Delta_f S_m^0$	SF	--	--	--	2.4	2.4	2.4	2.4
$\Delta_f C_{p,m}^0$	CP25F	--	--	--	2.3	2.3	2.3	2.3
a: Maier-Kelley	CPAF	--	--	--	2.3	2.3	2.3	2.3
b: Maier-Kelley	CPBF	--	--	--	2.3	2.3	2.3	2.3
c: Maier-Kelley	CPCF	--	--	--	2.3	2.3	2.3	2.3
ABSOLUTE PROPERTIES OF ALL ENTITIES IN REACTION								
S_m^0	S0				E	E	E	E
$C_{p,m}^0$	CP0				--	E	--	E

Two cases are included in PMATCHC that automatically transfer results of calculations using S^0 and Cp^0 to other data fields.

Case 21 User entered data for $\Delta_f H^0$, S^0 (*case 21a*) and, possibly, Cp^0(*case 21b*)
Calculations for any missing values at 25°C:
If properties of formation of all constituent master species are in data base:

$\Delta_r H^0$	– equation (2.3)
$\Delta_r S^0$	– equation (2.12)
$\Delta_r Cp^0$	– equation (2.13)

Then as for case 10, or case 9 if Cp^0 is also entered.

Case 22 User entered data for $\Delta_f G^0$, S^0(*case 22a*) and, possibly, Cp^0(*case 22b*).
Calculations for any missing values at 25°C:
If properties of formation of all constituent master species are in data base:

$\Delta_r G^0$	– equation (2.3)
$\Delta_r S^0$	– equation (2.12)
$\Delta_r Cp^0$	– equation (2.13)

Then as for case 10, or case 9 if Cp^0 is also entered.

3.4. PRIORITY GIVEN TO INPUT DATA AND POSSIBLY MISLEADING CALCULATION RESULTS

There are three principal shortcomings of the calculation scheme in this version of PMATCHC.

First, with two exceptions, PMATCHC does not prevent the user from entering redundant data that could lead to an internally inconsistent database. One exception is the case where a user enters all three of the values for $\Delta_r G^0$, $\Delta_r H^0$, and $\Delta_r S^0$ or for $\Delta_f G^0$, $\Delta_f H^0$ and $\Delta_f S^0$. The program suggests that only two of each trio of values be should entered and that for greatest consistency PMATCHC should calculate the third value. The second exception is when values of $\Delta_f S^0$ and/or $\Delta_f Cp^0$ can be calculated both from reaction data and from data on elements. In this case PMATCHC notes any disagreement between two values calculated and includes both values in data display windows.

Second, in its calculations, PMATCHC does not always distinguish between parameters with values that are unknown and parameters with values that are known but equal to zero. In the data base itself and in the display screens for the various record types, calculated values are always distinguished from entered data. Also, in PMATCHC output, it is possible to distinguish among entered, calculated and null (blank) values. (See output command **real.**)

Third, in several calculation cases (10, 15, 16, 17, 21a, 22a), the present version of PMATCHC may calculate meaningless values for $\Delta_f a$, $\Delta_f b$, $\Delta_f c$ and $\Delta_f Cp^0$. In these cases $\Delta_r a$, $\Delta_r b$, $\Delta_r c$ and $\Delta_r Cp^0$ are assumed to be zero. Therefore, the values for $\Delta_f a$, $\Delta_f b$, $\Delta_f c$ and $\Delta_f Cp^0$ depend on how the formation reaction is formulated, i.e. which master species are used.

Table 3: Output format specifiers.

Specifier	Data Type	Description
Fm.n	Real	writes a real number right justified in a field m characters wide using standard notation with n decimal places. n must be greater than or equal to zero and less than or equal to ten. m must be greater than or equal to n+3 and less than 256.
Em.n	Real	writes a real number right justified in a field m characters wide using scientific notation with n digits. n must be greater than zero and less than or equal to 10. m must be greater then or equal to n+7 and less than 256.
Gm	Real	writes a number right justified in a field m characters wide using a 'best' notation with approximately 6 decimal places of accuracy. m must be greater than zero and less than 256.
Im	Integer	writes an integer right justified in a field m characters wide. m must be greater than zero and less than 256.
Am	Alpha	writes a character string left justified in a field m characters wide. m must be greater than zero and less than 256.
Tm	Control	starts the next output field at position m in the output line. m must be greater than zero and less than 256.
mX	Control	moves the output position m characters to the right.
/	Control	starts a new line of output
'literal'	Control	writes the text within the quotation marks
S	Stoich	causes the current STOICH format to be invoked once for each term in the stoichiometry of the species being written
C(n)	Comment	causes the current COMMENT format to be substituted once for each line of text in the comment. If the optional n is given (n>0) a maximum of n lines of text will be output.
R(n)	Reference	causes the current REFERENCE format to be substituted once for each line of text in the reference. If the optional n is given (n>0) a maximum of n lines of text will be output.
- (minus)	Real	when placed immediately in front of an F, E, or G, multiplies the associated real number by -1.0 before output.

Note: If the **star** specifier is used (see **real** command), an asterisk is written just to the right of the field defined by the format specifier. As a consequence, the width of an output line is increased by *n* characters if the **star** option is switched on *n* times.

4 OUTPUT FORMATTING OPTIONS

PMATCHC can write the data it manages in a number of user-specified formats. The OUTPUT Mode and the commands associated with it are described in this section.

Because a series of commands will usually be needed to format and write output data, it is convenient to set up external text, or script files to control output formatting and writing. Script file names can be in any form recognised by the environment in which the program is being run. The files themselves are simple text files containing lists of the output commands described here. They can be written from within PMATCHC or using external text processors. Script files are described in Section 4.2.

Facilities for generating output are quite flexible, and as a consequence, relatively complex. In addition to examples given with the descriptions, several script files of output commands are included with the program package. These are simple ASCII files that can be opened with the PMATCHC line editor, described below, or with any text editor. The files are run from within PMATCHC as described below.

The output commands available are described here as they are used in script files. Default values for many of the formatting variables that can be defined using output commands are shown and can also be changed from the opening Formatted Output screen (Figure 11).

4.1. OUTPUT COMMANDS

The following output commands are available. Some appear as choices while running the program, and others as commands in script files.

format delformat stoich units comment reference

real outdev write prnt_valance

The output command **backup** is also described in this section, although it is run from the database window.

format *formname formspec formspec formspec*

The format command is used to specify output formats. The user can create a number of named formats. These are similar to FORTRAN format statements and use many of the same field specifiers as FORTRAN. The first parameter for the command is the name of the format statement. The name is used when referring to the format with **delformat** and **write** commands. It must be a unique name, less than 15 characters long, with no spaces or punctuation.

The *formspec* fields are the actual format specifiers. With a few exceptions they follow FORTRAN usage fairly closely. The format specifiers and their meanings are given in Table 3.

A number of rules apply to creating formats:

- repetition counts are allowed for F, E, G, I, A, X, and / specifiers. The maximum repetition count is 20. For example: 5X, 2A6, 2F10.2, 3/
- when displaying formats, PMATCHC will not show repetition counts but will display each element as an individual specifier. Thus, the format above will be displayed as: 5X, A6, A6, F10.2, F10.2, / , /, /

- parenthetic repetitions are not allowed. For example, T10, 3(A5, 3A, G10) is unacceptable.
- a minus sign placed immediately in front of a real format specifier (F, E, G) will cause any data value associated with the format specifier to be multiplied by -1.0 prior to output. The main purpose of this facility is to allow output of reactions in both association and dissociation forms. If a repetition counter is used on the format, the minus sign must be placed after the repetition counter (*e.g.* 10-F12.5)

There is no practical limit to the length of a user defined format statement. However, format statements of any length can be broken into several lines by using '+'.

delformat ALL | *[formname formname ....]*

The **delformat** command is used to delete user-defined formats. If the **ALL** parameter is given all user-defined formats are deleted. Otherwise only the named formats are deleted.

stoich *formspec formspec formspec ...*

The **stoich** command is used to define the format used to write individual terms in reaction stoichiometry. When writing output a using user-defined format containing an "S" format specifier, the currently defined **stoich** format is substituted for each term in the stoichiometry. The **stoich** format can include literal characters, control format specifiers, and alpha, integer, and real specifiers. Alpha specifiers are used to write master species names in reactions, integer specifiers cause the record number of master species to be written, and real specifiers are used for writing stoichiometric coefficients.

Examples of the use of the **stoich** command are given in the script files included with the PMATCHC package

units [JOULES | CALORIES | KILO | ONE]

The **units** command is used to set the input and output units for the thermodynamic properties of formation and reaction (see Section 2.1.1). The first two parameter choices are used to specify the base unit system as either CALORIES or JOULES. The third and fourth parameter choices are used to specify the multiplier used for $\Delta_r H^0$, $\Delta_r G^0$, $\Delta_f H^0$, and $\Delta_f G^0$. If KILO is specified ΔH and ΔG data are displayed and input is expected in kilojoules or kilocalories. Specifying ONE causes ΔH and ΔG data to be displayed and input expected in base units (either JOULES or KILOS).

If the **units** command is given with no parameters, an information message describing the current setting is displayed. The default setting for PMATCHC **units** is joules and kilo, and PMATCHC stores data internally in joules.

Examples:

units JOULES ONE -	System Joules, ΔH and ΔG in Joules, ΔH and ΔG multiplier unchanged.
units KILO -	System unchanged, ΔH and ΔG multiplier in Kilo units.
units CALORIES KILO -	System Calories, ΔH and ΔG multiplier in Kilo units.
units -	Displays information message giving current unit settings.

comment *formspec formspec formspec ...*

The **comment** command is used to define the format used to write individual lines of comment text. When writing output using a user-defined format containing a "C" format specifier (Table 3), the currently defined format is substituted for each line of comment text to be written. The comment format can include literal characters, control format specifiers, and alpha specifiers. As an example of use, consider writing a species with the following comment text:

Line 1 of comment

Line 2 of comment

Line 3 of comment

Example output appearances for various user defined ,and **comment** formats are:

User Format	Comment	Output
		12345678901234567890123456789012 3456
10X, C	10X, A20, /	Line 1 of comment Line 2 of comment Line 3 of comment
10X, C2	10X, A20, /	Line 1 of comment Line 2 of comment
'Comment', C	T20, A15, /	Comment Line 1 of comment Line 2 of comment Line 3 of comment
'Comment', C2	T10, A20, /	Comment Line 1 of comment Line 2 of comment
C1	A80, /	Line 1 of comment

reference *formspec formspec formspec ...*

The **reference** command is identical in use and function to the **comment** command except it is used to substitute for "R" format specifiers (Table 3) when writing the text of references.

real *status_type display*

where

status_type = **entered** | **calculated** | **null**

display = **default** | **blank** | **star** | 'literal'

PMATCHC records containing real numbers can have one of three possible states: user-entered, calculated, or null. User-entered real numbers are those with values specified by the user. Calculated real numbers are thermodynamic properties which have been calculated by PMATCHC. Null real numbers are in those fields for which the user has not entered data and which are not calculated. Examples of null real data are DHA and DHB fields for a product species with a charge of 0. By default, null real numbers are given the value 0.0.

The **real** command can be used to differentiate among the three states of real data when real values are output. The first parameter for the command is used to indicate the data states being addressed. The second parameter governs the output format as follows:

default	write according to format specified for the field
blank	write as blanks using width of format specified for field
star	convert according to format specified for the field. Add an asterisk character one space to the right of the data
'literal'	write the literal characters right justified using width of format specified for field

The following are examples of output of a real number field containing the value 100.0 for various combinations of format specifiers and the *display* parameters of the **real** command. The examples script files include additional illustrations.

Format Spec	Display	Output
		12345678901234567890
F10.1	DEFAULT	100.0
-F10.1	DEFAULT	-100.0
F10.1	STAR	100.0*
F5.3	DEFAULT	*****
F5.3	STAR	******
F5.3	'example'	examp
E15.3	STAR	1.000E+02*
E10.3	DEFAULT	1.000E+02

E10.3	'example'	example
G5	'example'	examp
G5	DEFAULT	100

offset *[integer]*

The **offset** command is used to specify an integer value which is added to the record number for index field output (see **write** command). This can be useful when preparing input data fields for programs such as PHREEQE (PARKHURST *et al.* 1980) where product species numbers must have a value greater than the largest permissible number of master species. Issuing the command with no parameters is equivalent to **offset** 0.

outdev [file *filename* **]**

The outdev command is used to specify the file name where the output from **write**, **backup**, and **script** commands will be directed. The text file *filename* will be opened the first time output is sent to it using the **write**, **backup** or **script** commands. If the file already exists, the user will be asked to confirm overwriting the file. The file is closed after each **write** command and re-opened immediately before the next **write** so that no data should be lost if the program or computer crashes. The link to the file specified by **outdev** is maintained until another **outdev** command is issued. The text file is automatically closed when the program is closed and after **backup** or **save** commands are processed.

write *datatype formname fieldname fieldname fieldname ...*

or

write *formname*

where

datatype = **ALL | ELEMENT | PRI_MAST | SEC_MAST | PRODUCT | MINERAL | GAS**

The first form of the **write** command is used to extract all data records of type *datatype* from the data base and write them to the current file according to the user defined format *formname*. If the **all** value is used for the parameter *datatype*, all records in the data base are written. The specified format is invoked once for each record written.

The *fieldname* parameters select the record fields to be output. Each fieldname must be a valid field for the selected data type. In addition, the fields **TYPE**, **INDEX**, and **NULL** are also defined for all data types. **TYPE** is a character string reflecting the type of data being written. **INDEX** is the record number in the PMATCHC data base of the record being written. The current **offset** value is added to the PMATCHC record number for output. **NULL** is a general purpose field which outputs blanks for alpha fields and zero values for integer and real numeric fields.

There must be a one to one correspondence between the field names and non-literal / non-control format specifiers in the format being used. Furthermore, the type of field name must be compatible with the type of matching format specifier. Format specifiers compatible with field names and shown in the following table.

The second form of the write command is used for writing formats that consist of control and literal specifiers only. This form can be used for writing titles and headers.

The example script files include several examples of the use of the write command to produce headings.

COMPATIBILITY OF FIELD NAMES AND FORMAT SPECIFIERS

Field Name	Format Specifiers	Comments
NAME	A	
CHARGE	F, E, G	
STOICH	I, S	if an integer format specifier is used, the number of stoichiometric terms will be output, otherwise the STOICH format will be used to write out each term
COMMENT	I, C	if an integer format specifier is used, the number of lines of comment text will be output, otherwise the COMMENT format will be used to write out each line
REFERENCE	I, R	see COMMENT
TYPE	A	
INDEX	I	

backup

The **backup** command is issued from the Database|File screen of PMATCHC. This commend writes all records in the data base to the output device using a free format. This is useful for maintaining backups of data bases and is also useful for rebuilding a data base that has become fragmented through many data base maintenance and editing file operations. Examples backup files are included in the PMATCHC program package and in Appendix C of DMYTRIYEVA *et al.* (1999).

Note that **backup** files include only data entered by the used.

script

The **script** command translates all current user format, real settings, and **stoich**, **comment** and **reference** formats to a sequence of commands that can be read as a script file. The commands are translated and sent to the current output device.

Example script files are given in the PMATCHC program package

prnt_valence | YES | NO |

In the COMPOSITION field of all record types except ELEMENTS, the valence of elements in oxidation states other than that specified in the VALENCE field of the ELEMENT record is indicated using "|x|", where x is the valence of the element in the COMPOSITION. For some purposes, such as printing tables, it may be useful to include this valence indication when COMPOSITION is output. For other purposes, such as writing files to be used as data input to modelling programs, the valence indication should not be output. The **prnt_valence** command specifies whether the valence information, "|x|", is included when the COMPOSITION field is output.

4.2. SCRIPT FILES

There may be common sequences of commands that the user wishes to perform frequently. Rather than forcing the user to type in each command, PMATCHC offers a facility for saving groups of commands as standard text files and for reading and executing the commands in such files. These files, known as script files, can be written, edited and run from the Formatted Output screen or external to PMATCHC using any text editor.

Several example script files are included in the PMATCHC program package.

5 PROGRAM OPERATION

USER NOTE: Many of the windows described below have "Help" buttons. In this version of PMATCHC, these buttons may lead nowhere in some cases. In other cases they may lead to text from an earlier version of PMATCH that is present merely as a place-holder. Thus, DISREGARD any help information given from within the program itself and refer instead to this documentation.

5.1. MAIN WINDOW

When PMATCHC.EXE is first run, the Main window will appear (Figure 12). The first step is to open an existing database or define (name) a new database.

5.2. DATABASE MANAGER WINDOW

The "Database" button opens the Database Manager window (Figure 13). This window provides the path and name of the open database and information about the types and numbers of records it contains. When no database is open, the File Path is "undefined" and the numbers of all records are 0.

Select "File" to open the panel of file management commands.

"New Database" opens a file management window allowing the user to select a directory and enter the name of a new file into which data will be entered manually or by reading a backup file. Note that no suffix following the period should be given when a new file name is defined.

"Open Database" opens a file management window allowing the user to select the directory and name of an existing PMATCHC file to be opened. A PMATCHC database is stored in four files: name.ELM, name.MST, name.PMG, and name.PTX, where "name" is the database name. The suffixes indicate that the files contain, respectively:

ELEMENTS data,

MASTER Species data,

PRODUCTS, MINERALS AND GASES data,

Text fields (Comments and References) associated with all records.

Selecting any of the four files will open the full database.

To read a backup file into a new database after it has been named, choose "Read Backup". This opens a file management window allowing the user to select the directory and name of the backup file to read. If the backup file is read successfully, a pop-up appears stating this fact and the numbers of records in the new database appear in the database manager window. If the backup file is not read successfully, a notice to this effect also appears. In this case, it is necessary to modify the backup file with a text editor until it can be read successfully. Backup files are discussed in Section 4.1.

"Import Data" does nothing in this version of PMATCHC.

To write a backup file for a database open in PMATCHC, select "Write Backup". A file management window will open allowing the location and name of the backup file

to be specified. Note that backup files can also be written from the "Files" panel of the Formatted Output Controls window.

When a database is open, the "Close Crtl+F4" command returns the program to the main window. At this point, the main window will show the database name and the types and numbers of valid records it contains

5.3. RECORDS WINDOWS

When a new or existing database is open, the record type to be examined or entered is selected from the Main window using the buttons labelled "Elements", "Master Species" or "Product species, Minerals and Gases". A panel then appears listing the names of records of the type selected. The "Product species, Minerals and Gases" window opens showing records of all three of these types. It is possible to list only one or two record types by selecting that type in the listing window.

Selecting any of the items and pressing "Ok" brings up the appropriate data entry window. To enter data in a new record select, any existing record and choose "Record", "Create", as described below. Pressing "Cancel" from the data listing window will also bring up a blank data entry window in which new data can be entered or which can be closed if some other record type is of interest.

The data entry windows for the various record types are shown in Figures 1, 4, 6, 7, 9 and 10 and are described in Section 2.3, above. The fields in the various types of data entry windows differ but the selection of commands and the tool bar available in all data entry windows are the same. (Note that the icons in the tool bar are contained in directory BMP. This directory must be a subdirectory of the directory that contains PMATCHC.EXE). The toolbar commands are merely shortcuts to operations available from the menu The toolbar itself can be moved around the window as usual in window environments.

Note that entries and changes in a record and the command to delete a record do not become a part of the saved database until the "Save" command is given. This feature makes it possible to test combinations of data entries without changing the saved records.

Selecting "Record" opens the panel of commands to:

"Show F6" a list of the entries of this record type,

"Create" a new record of this type,

Shift to the "Next" or "Previous" entry of this record type,

"Save" or "Delete" the data in this record or

"Close F4" this window.

"Record List" has two choices:

"Delete List" opens a list of the entries of this record type. It is possible to select one or all of the items for deletion.

"Units" allows the selection of the units in which the thermodynamic properties are displayed. Changing the units causes the record on the window to empty, however, it can be restored with data in the new units by simply selecting it again. Units are described above.

"Calculate" has four choices:

"Calculate Thermo" calculates all possible values from the data available in the database.

"Calculate OPV", "Calculate Charge" and "Check" calculate the OPV or charge of the record entry or to check that all necessary fields have been entered. Note that these commands are for use principally with old PMATCH databases and have little effect in databases designed specifically for PMATCHC.

"Erase" opens a panel from which to choose specific records or all records to be erased.

5.4. FORMATTED OUTPUT CONTROL WINDOW

The "Formatted Output" button in the Main window opens the Formatted Output Controls window, from which output formats can be specified and script files written, edited and run. As discussed in Section 4.1 above, PMATCHC has elaborate output formatting capabilities. These are not described in great detail in this document, but several example script files are included with the PMATCHC program package that illustrate the use of many of the formatting commands. Study of these files and experimentation with PMATCHC itself should permit the user to develop any type of formatting desired.

Note that PMATCHC includes a line editor permitting the user to make new or edit existing script files. However, it is often convenient to write and edit script files external to PMATCHC using any text editor of the user's choice. These files can be "RUN" directly or saved with names of the user's choosing and then run using the "Run" command of the "Scripts" panel below.

The Formatted Output Control window displays the values of a number of formatting options and offers "Files", Formats" and "Scripts" commands.

The "Files" command opens a panel with the additional commands:

"Setup" allows the user to change the default formats displayed on the Formatted Output Control window. Formats can also be set using Output Mode Commands

"Output file" opens a file management window allowing the user to select a directory and name the output file to be written. The output file can also be specified using the Output Mode Command **outdev** in script files.

"Write format" has no function in this version of PMATCHC.

"Write Backup" writes a backup file of the open database to the specified "Output file". This command mirrors the "Write Backup" command available in the "File" panel of the Database Manager Window.

"Export data" has no function in this version of PMATCHC.

"Close F4" closes the window.

The "Formats" command opens a panel with the additional commands:

"New" opens an Edit window in which a format type can be named and then specified. See Output Mode command **format**

"Edit" opens a window in which to select an existing format followed by an edit window.

"View" opens a window in which to select an existing format to be displayed in the Formatted Output Controls window.

"Delete" opens a window to select an existing format(s) to be deleted.

The "Scripts" command opens a panel with the additional commands:

"New script" opens the Script Editor for entry of a new script file. One can than "Save" or "Run" the script.

"Open script" opens a file management window to select an existing file which is then opened in the Script Editor.

"Run Script" opens a file management window to select an existing file which is then run. A splash window announces whether the run was successful or not.

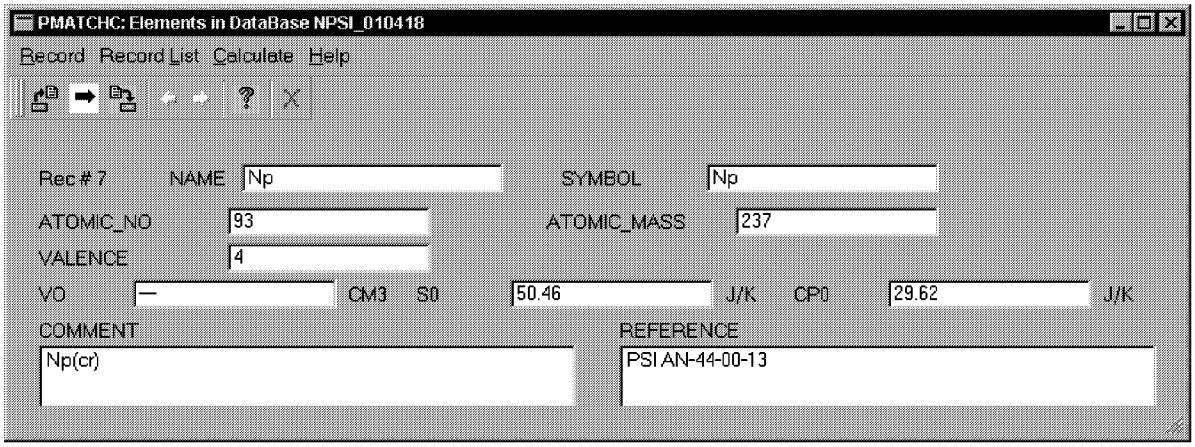

Figure 1: Example ELEMENTS screen for data entry and manipulation.

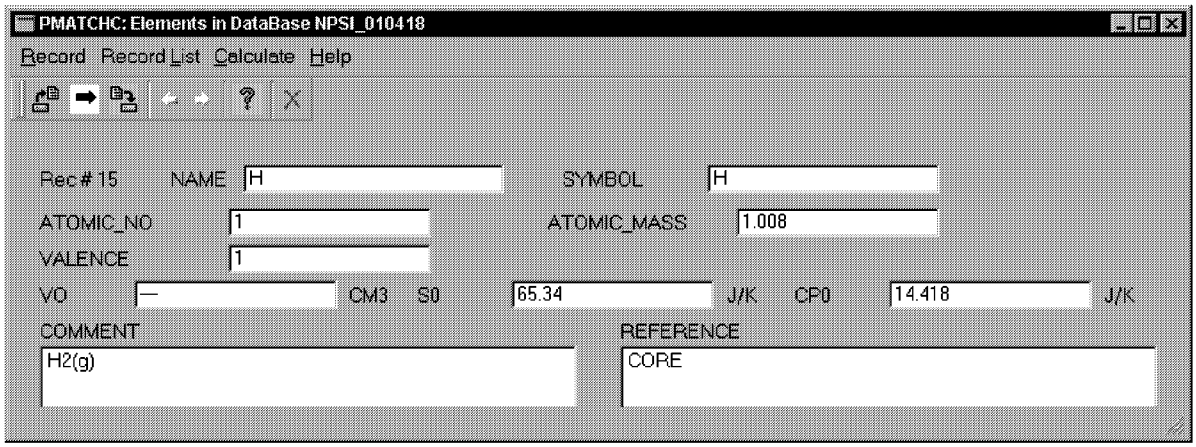

Figure 2: ELEMENTS data screen for $H_2(g)$ illustrating data entry per atom rather than per molecule.

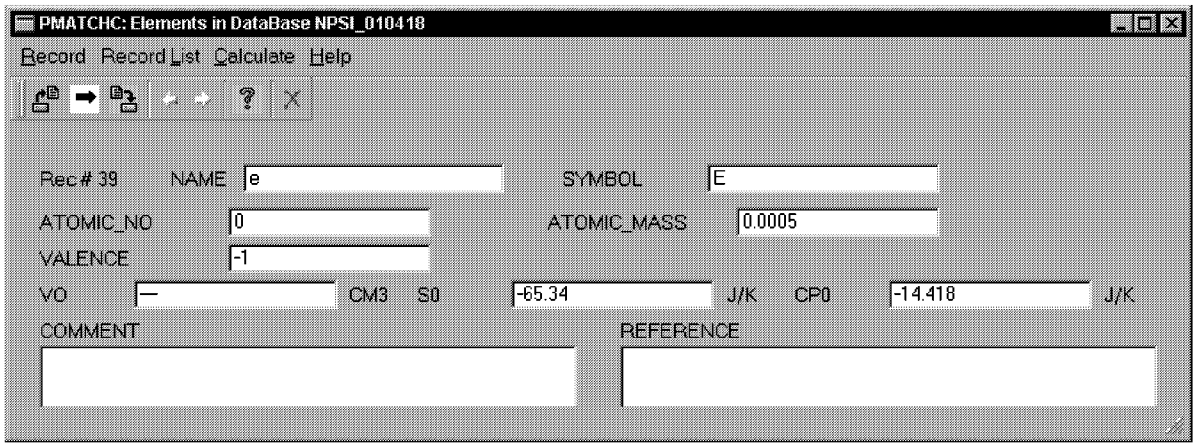

Figure 3: ELEMENTS data screen for the electron. See discussion and note in Section 2.1.2.

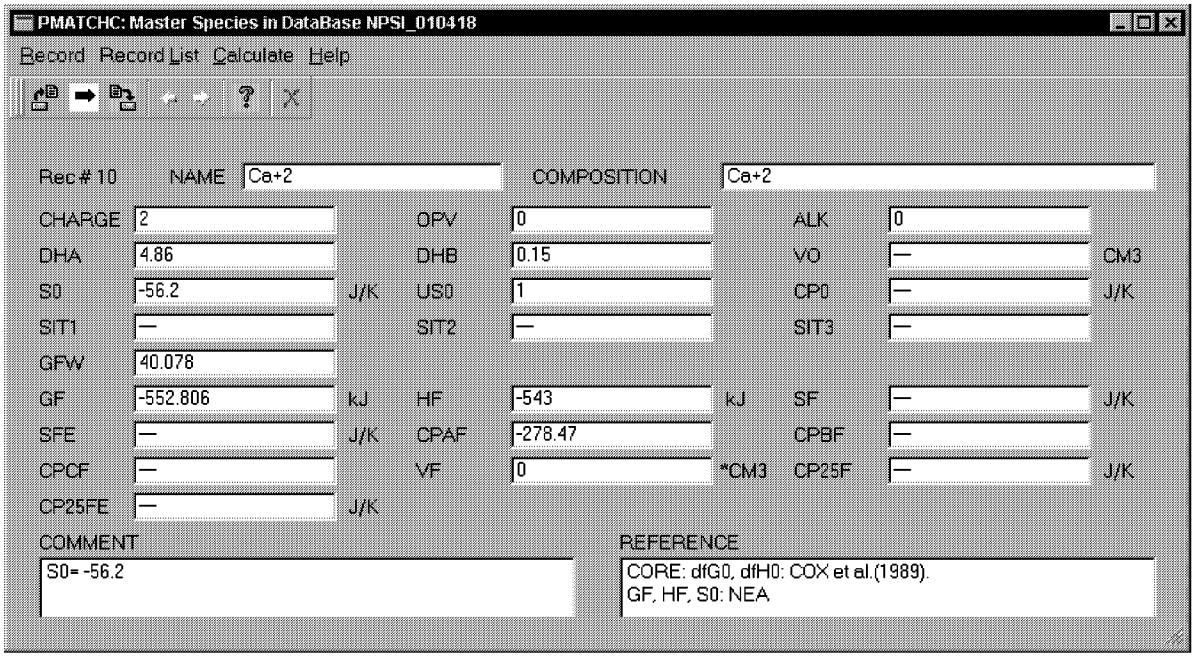

Figure 4: Example Primary Master species data entry and manipulation screen.

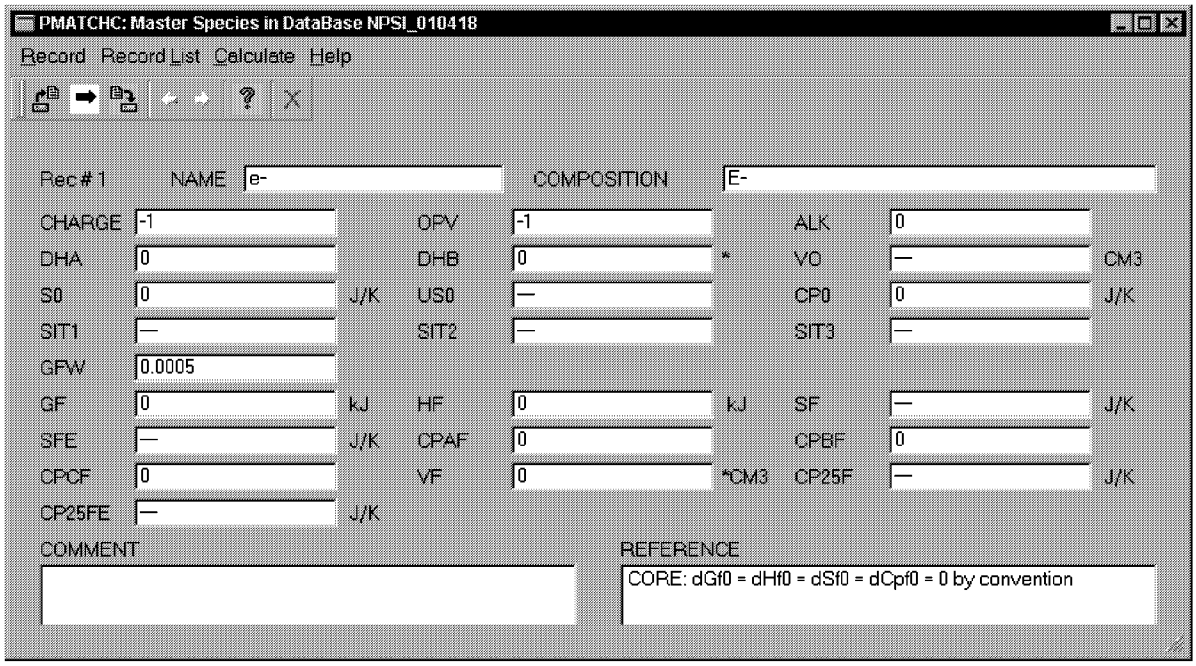

Figure 5: Primary MASTER species data screen for electron.

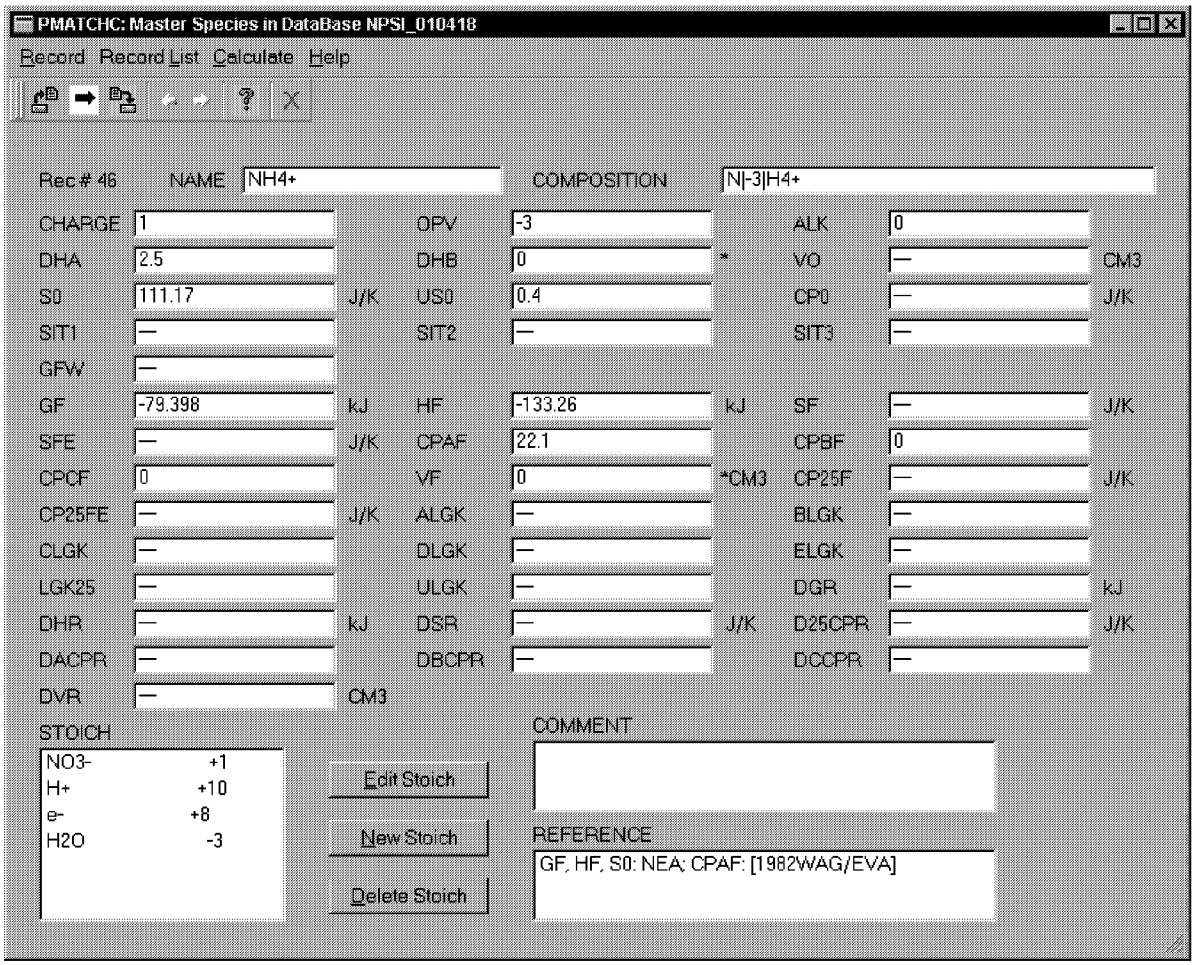

Figure 6: Secondary MASTER species data entry and manipulation screen.

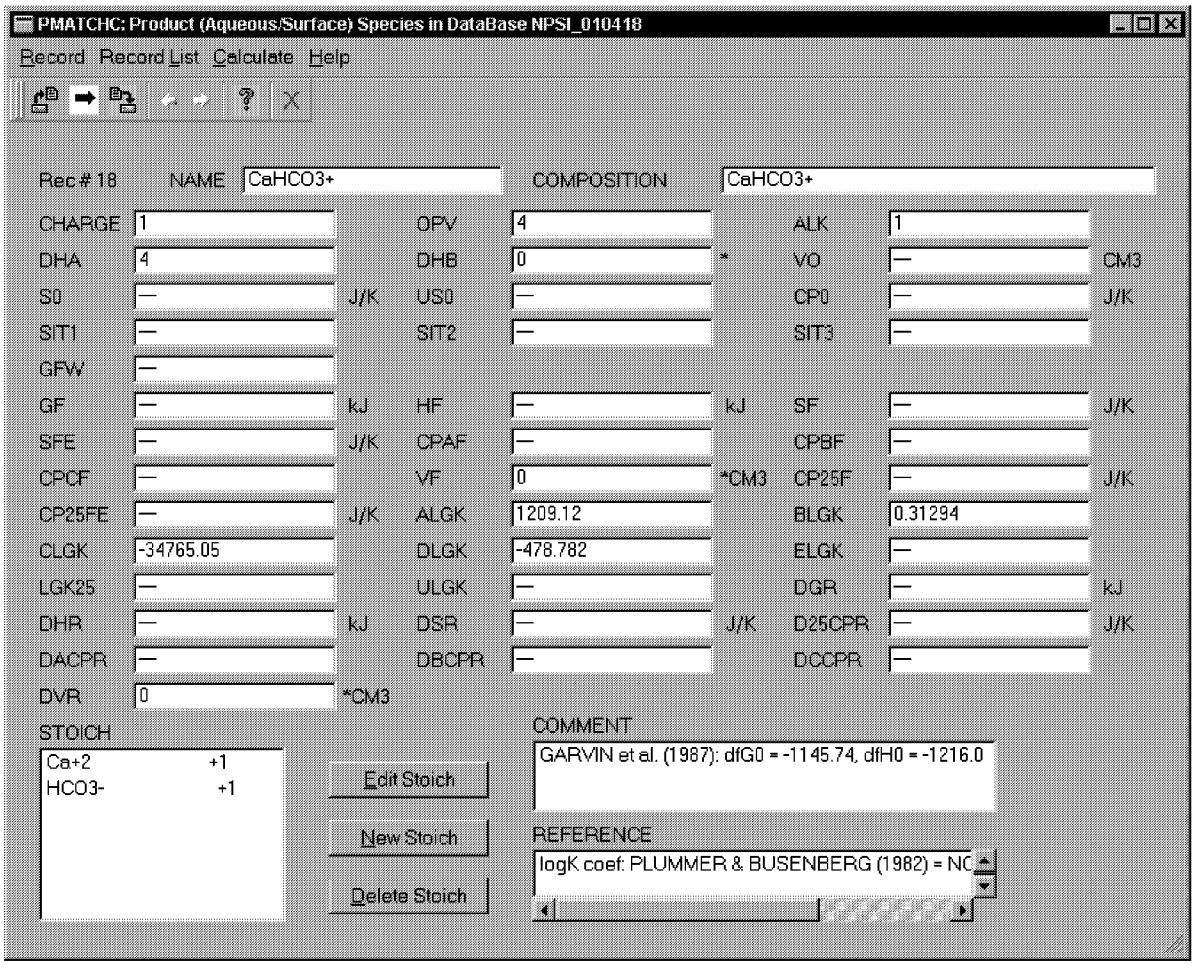

Figure 7: PRODUCT species data entry and manipulation screen.

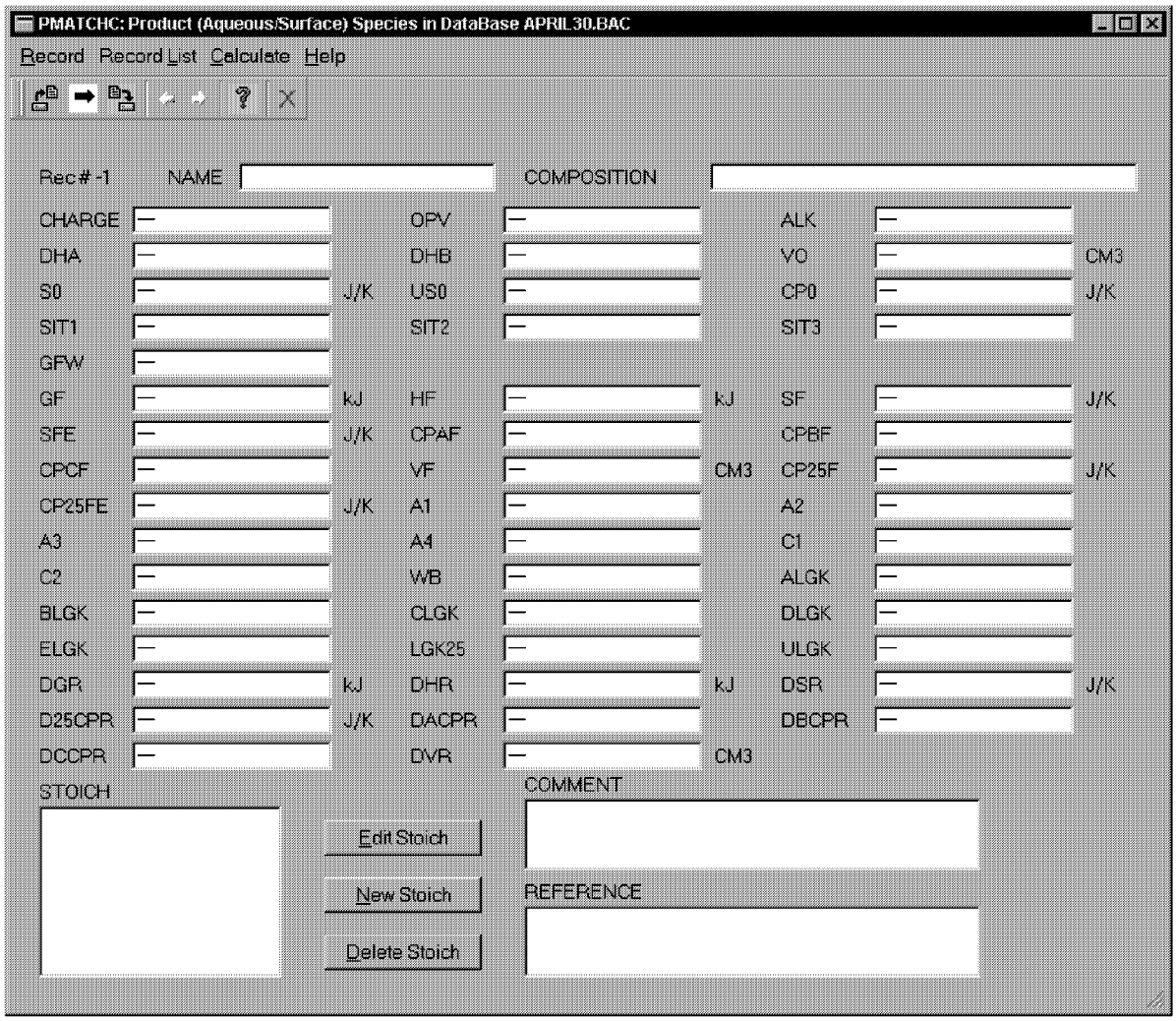

Figure 8: Data entry and manipulation screen for PRODUCT species with HKF data.

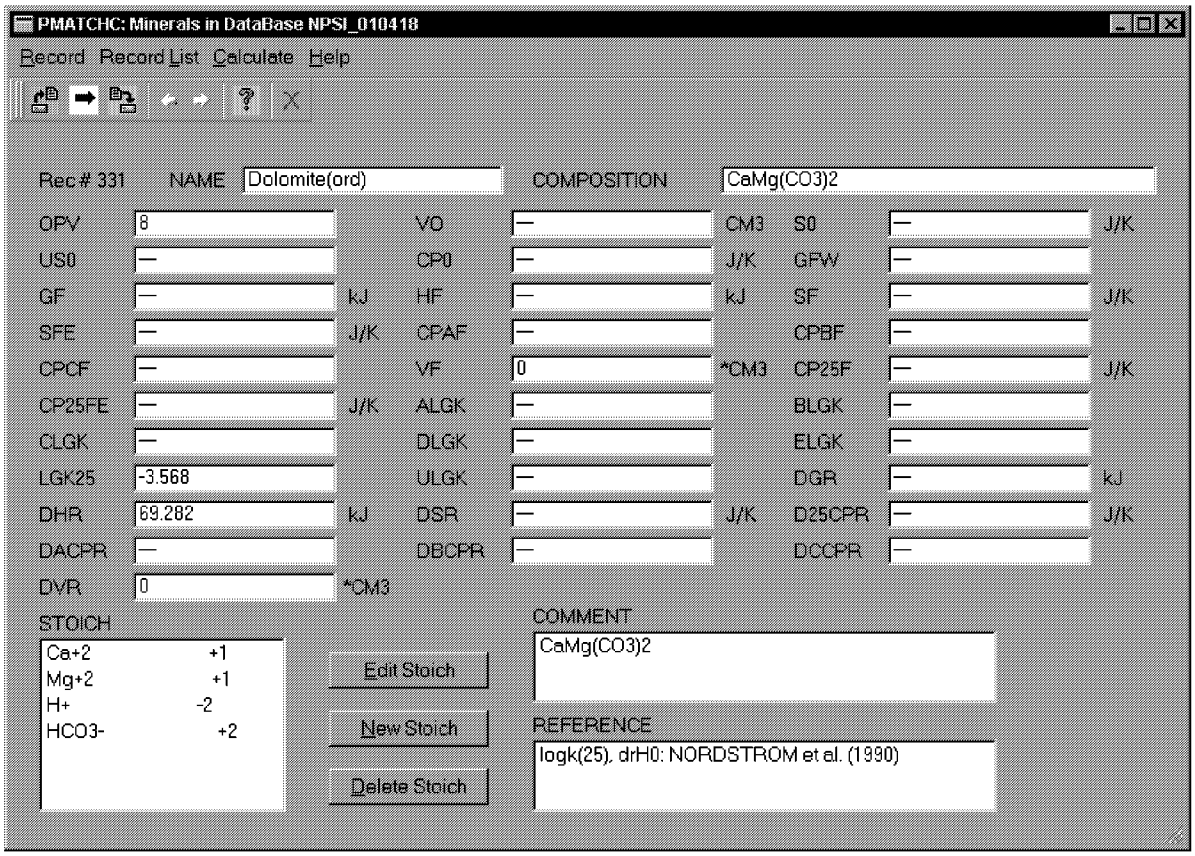

Figure 9: SOLID (Mineral) data entry and manipulation screen.

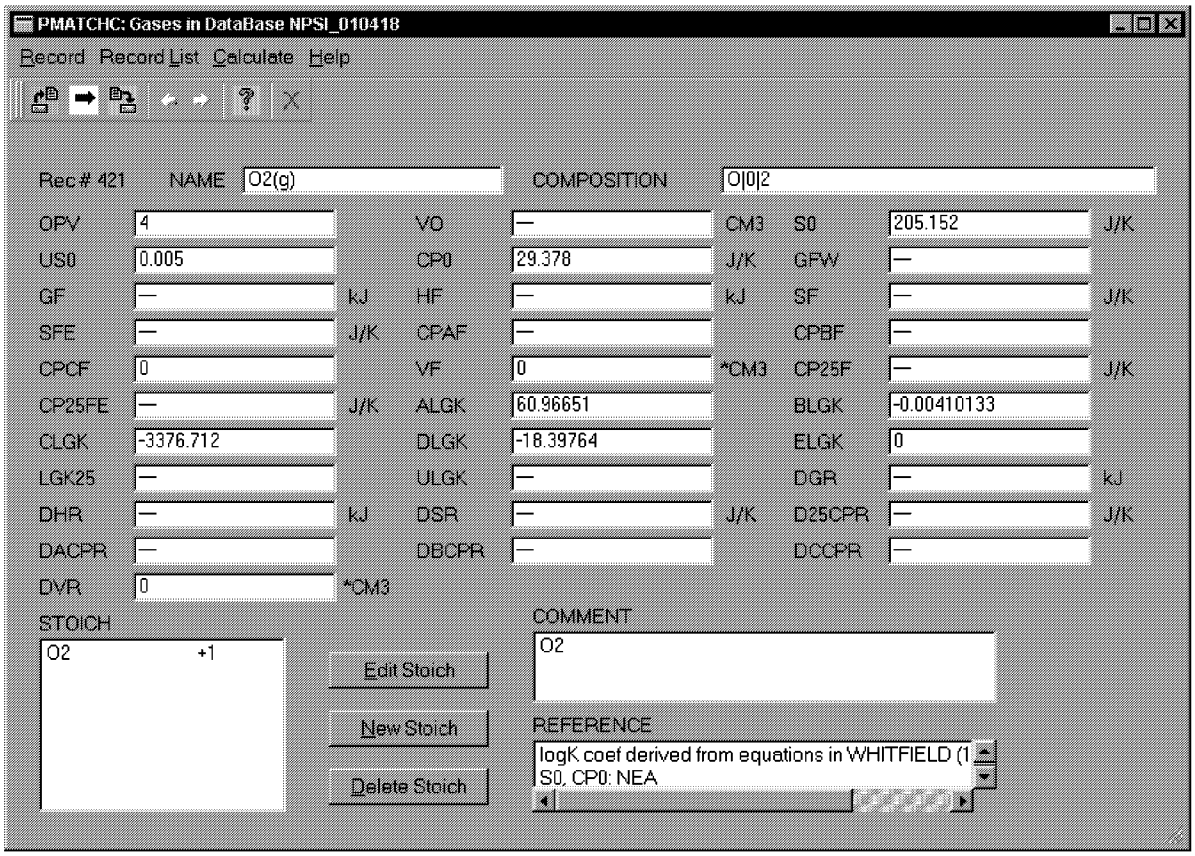

Figure 10: GAS data entry and manipulation screen.

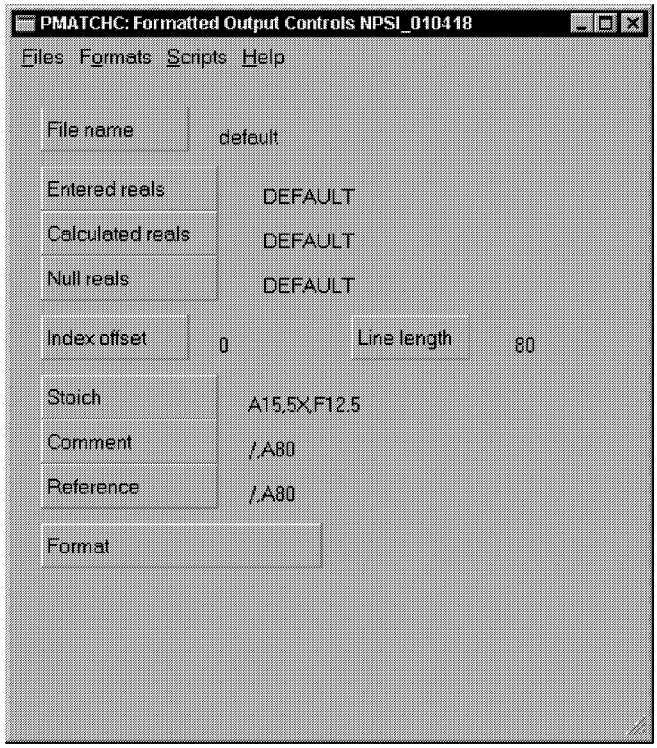

Figure 11: Formatted data screen.

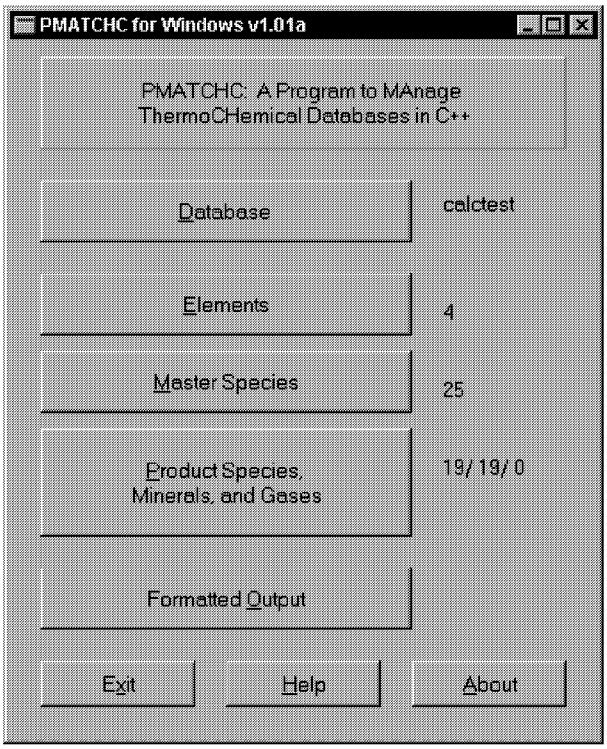

Figure 12: PMATCHC Main (opening) window.

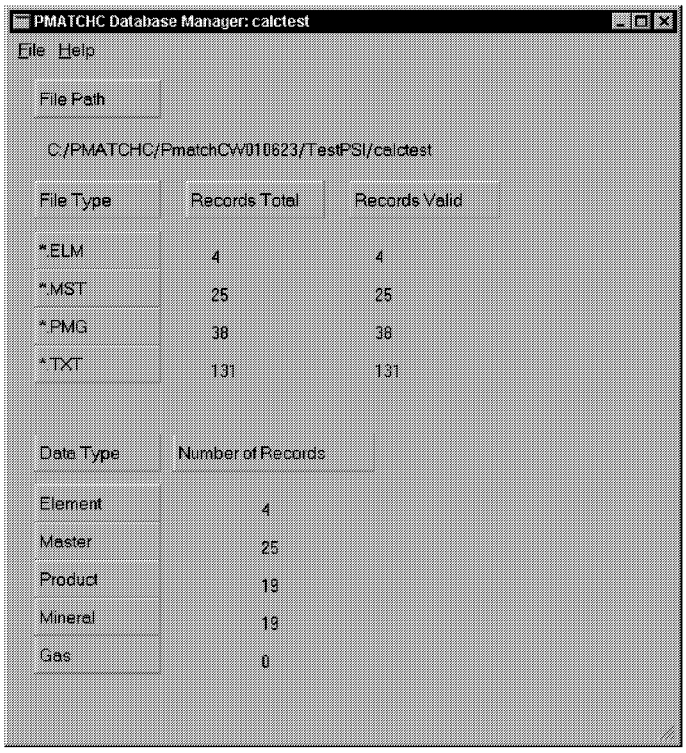

Figure 13: Database Manager window.

6 PROGRAMMING CONSIDERATIONS

The version of PMATCHC described in this documentation is available in executable files with source code for both MS Windows® and Linux operating systems. The source code for both versions is the same and requires compilation together with the Qt Toolkit, version 2.0 or higher (© Troll Tech AS, Norway). This toolkit was chosen because it allows PMATCHC to be used either under Linux or Win32 platforms. The Qt Toolkit (GNU licence for Linux, commercial licence #1435740 for Windows) was used by S. Dmytriyeva who programmed the PMATCHC code in C++ by translating the previous PMATCH code (PEARSON *et al.* 1993) written in Pascal. Borland C++ Builder 5 (standard) was used for compiling the Win32 version and GNU C++ (gcc, egcs) for compiling the Linux version.

The distribution package includes executable versions of PMATCHC for both MS Windows and Linux operating environments and the full source code.

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