

Introduction

This page outlines the structure and format of the thermodynamic data file read by Perple_X. This file contains the basic data for chemically pure entities. Here pure is used to mean the entity has a fixed chemical composition. Normally the entities correspond to real phases, i.e., stoichiometric compounds or phases corresponding to the endmember compositions of a solution phase, but in some cases the entity may correspond to a hypothetical state of matter or a function that is used to constrain a chemical potential as a function of pressure and temperature.

HSC/SUPCRT Apparent Gibbs Energy Conventions

In applied thermodynamics, energies are invariably computed relative to an arbitrary reference condition. There is no particular convention built into Perple_X, rather the convention is defined by the thermodynamic data. While there are many possible conventions only two, referred to here as the HSC and SUPCRT conventions, are widely used. In both, the Gibbs energy at elevated pressure and temperature is

$$G(T, P) = G\theta - \text{integral}(S(T, P_r), T=T_r..T) + \text{integral}(V(T, P), P=P_r..P)$$

where $S(T, P_r)$ and $V(T, P)$ are the absolute specific entropy and volume, respectively, and the subscript r denotes the reference condition (invariably 298.15 K and 1 bar). In the SUPCRT convention $G\theta$ is the Gibbs energy of formation from the elements at the reference condition, $G_f(T_r, P_r)$, whereas in the HSC convention

$$G\theta = H_f(T_r, P_r) - T_r \cdot S(T_r, P_r).$$

where $H_f(T_r, P_r)$ is the enthalpy of formation from the elements. Given that

$$G_f(T_r, P_r) = H_f(T_r, P_r) - T_r \cdot (S(T_r, P_r) - S^{\text{elements}}(T_r, P_r))$$

where $S^{\text{elements}}(T_r, P_r)$ is the stoichiometrically weighted sum of entropies of the elements in their respective stable forms at the reference condition, the apparent Gibbs energies computed by the SUPCRT and HSC conventions differ by a constant

$$G\theta^{\text{HSC}}(T, P) - G\theta^{\text{SUPCRT}}(T, P) = T_r \cdot S^{\text{elements}}(T_r, P_r).$$

Thus, while it is clear that thermodynamic data can easily be converted from one convention to the other, it is important not to simply cut and paste data from one thermodynamic data file to another unless the data have the same convention.

The SUPCRT (Helgeson et al. 1978) and DEW (Harrison & Sverjensky 2013) programs and most early Perple_X data files assume the SUPCRT convention. In contrast, CALPHAD, THERMOCALC (Holland & Powell 1990), HSC (Roine 2002), and recent Perple_X data files generally assume the HSC convention.

HSC/SUPCRT Convention Conversion

To avoid the headache of keeping track of Apparent Gibbs Energy Conventions, Perple_X 6.7.8+ has an automatic facility for converting the HSC convention to SUPCRT convention. If this option is enabled by the presence of the HSC_conversion keyword in the data file header, then data from either convention may be entered in the thermodynamic file. In data files where conversion is enabled, HSC convention reference state Gibbs are identified by the tag "GH", while SUPCRT convention values are identified by the "G0" tag. If HSC_conversion is enabled, the components section of the thermodynamic data file header must specify

[`elements\(\$T_r, P_r\$ \)`](#) for each component after the atomic weight of the component.

Commonly Used Thermodynamic files

The following annotated list summarizes the most commonly used thermodynamic data files. The sources for data files not listed here can usually be found in the comments within the header section of the data file. These files can be downloaded from the [datafile](#) directory. Full references are listed in the [bibliography](#). Endmembers are generally identified by abbreviated names, in some data files the header section contains a comprehensive list of abbreviations and the corresponding names and formulae (e.g., [hp02ver.dat](#)), it is always possible decipher unknown names by locating the individual entries within the relevant file. In a few cases, indicated below, the data base phase notation has been summarized in separate files.

- **b89ver.dat, b92ver.dat** - Berman (1988) data base and update. [SUPCRT convention](#).
- **bb84ver.dat** - Berman & Brown (1984), CaO-Al₂O₃-SiO₂ liquidus data base. [SUPCRT convention](#).
- **ba96ver.dat** - Berman & Aranovich (1996) data base. [SUPCRT convention](#).
- **cr_hp02ver.dat** - a modification of the hp02ver.dat data base that includes some Cr endmembers. The modifications are documented by Klemme et al. (2009, updated by Ziberna et al. 2013). [SUPCRT convention](#).
- **DEW13ver.dat** - Harrison & Sverjensky (2013) aqueous species data base for the Deep Earth Water (DEW) Model (deepcarbon.net/feature/deep-earth-water-model-download-now#.V1WiwPl965M). This compilation is an extension and revision of the SUPCRT data base for aqueous species. The DEW spreadsheet data can be converted to Perple_X format using the Perple_X program DEW_2_ver, which allows the user to choose the elements of interest and apparent Gibbs energy convention, the on-line version of this file assumes the [SUPCRT convention](#).
- **DEW13HP02ver_elements.dat** - the DEW13ver.dat data base combined with the hp02ver.dat condensed phase data base. Formatted in terms of element components. [HSC_conversion_enabled](#). Holland & Powell aqueous species data has been moved to HPAQver.dat.
- **DEW13HP02ver_oxides.dat** - the DEW13ver.dat data base combined with the hp02ver.dat condensed phase data base. Formatted in terms of oxide components. [HSC_conversion_enabled](#). Holland & Powell aqueous species data has been moved to HPAQver.dat.
- **DEW13HP622ver_elements.dat** - the DEW13ver.dat data base combined with the hp622ver.dat condensed phase data base. Formatted in terms of element components. [HSC_conversion_enabled](#). Holland & Powell aqueous species data has been moved to HPAQver.dat.
- **DEW13HP622ver_oxides.dat** - the DEW13ver.dat data base combined with the hp622ver.dat condensed phase data base. Formatted in terms of oxide components. [HSC_conversion_enabled](#). Holland & Powell aqueous species data has been moved to HPAQver.dat.
- **DEW17HP622ver_elements.dat** - the May 19, 2017 revision of the DEW aqueous species data base (www.dewcommunity.org/resources.html) combined with the hp622ver.dat condensed phase data base. Formatted in terms of element components. [HSC_conversion_enabled](#). Holland & Powell aqueous species data has been moved to HPAQver.dat.
- **DEW17HP622ver_oxides.dat** - the May 19, 2017 revision of the DEW aqueous species data base (www.dewcommunity.org/resources.html) combined with the

hp622ver.dat condensed phase data base. Formatted in terms of oxide components. [HSC_conversion_enabled](#). Holland & Powell aqueous species data has been moved to HPAQver.dat.

- **g97ver.dat** - Gottschalk (1997). [SUPCRT convention](#).
- **hpha02ver.dat** - The data in this file, provided courtesy of Oliver Jagoutz, a brilliant, tenureable, assistant professor at MIT, are identical to hp02ver.dat except that it includes: 1) a piecewise linear fit to the properties of quartz (Ohno et al., Phys Chem Min 33:1-9, 2006) that is intended to represent the anomalous behavior of quartz in the vicinity of the alpha-beta transition (the piecewise fit is manifest by four different quartz phases: q, q_anom, bq_anom, bq); and 2) linear fits to the adiabatic bulk and shear moduli data base of Hacker & Abers (2004). The virtues of this data base are that: 1) the elastic properties of quartz are poorly represented by Holland & Powell's Landau model as implemented in the original hp02ver.dat data file; and the Hacker & Abers (2004) compilation of elastic moduli is less haphazard than that in hp02ver.dat. The compilation is recommended particularly for applications involving quartz-bearing rocks. To use the linear models for bulk modulus provided with this data base, as opposed to bulk moduli derived from Holland & Powell's equation of state, the keyword [explicit_bulk_modulus](#) must be set to true in perplex_option.dat. [SUPCRT convention](#).
- **hpha622ver.dat** - this file is the Holland & Powell (2011, DS6.22 revision) data base augmented by elastic moduli from Abers and Hacker (2016 as entered by William Shinevar in hpha02ver.dat), courtesy of Fanny Goussin. Note that this file does not contain explicit moduli for all phases (see comments in header) and does not include all the endmembers present in hp622ver.dat. This file is not maintained and may be missing make definitions required for recent solution models, if this becomes an issue copy the make definitions from hp622ver.dat.
- **hp02ver.dat** - The Holland & Powell (1998) data base as revised by the authors in 2002, [database notation](#). This data base provides the most comprehensive chemical model for silicates in the lithosphere. The hp02ver.dat file is appropriate for calculations at depths < 440 km. The Holland & Powell database has been augmented by shear moduli for seismic velocity calculations. The references for these moduli are summarized in Connolly & Kerrick (2002) and Connolly (2005). [SUPCRT convention](#).
- **hp04ver.dat** - The Holland & Powell (1998) data base as revised by the authors in 2004. The primary difference between the 2002 and 2004 revisions is that in the 2002 version the aluminosilicate triple point is at 3.8 kbar and 780 K consistent with Holdaway's (1971) estimate; in the 2004 revision the properties of the aluminosilicates have been adjusted to place the triple point at 4.4 kbar and 823 K to satisfy a petrological argument of Pattison (1992). It is doubtful that this change is otherwise significant. The hp04ver.dat file does not contain shear moduli and therefore cannot be used (without modification) for seismic velocity calculations. The hp02ver.dat file is appropriate for calculations at depths < 440 km. [SUPCRT convention](#).
- **hp11ver.dat** - The TC-DS610 version of the Holland & Powell (2011) data base, generated Nov 13, 2011. This data base is based on an equation of state that is intended for use over the entire pressure range from the Earth's surface to the core-mantle boundary. It includes some lower mantle phases, but, at present, provides a less complete model for the lower mantle than the Stixrude & Lithgow-Bertelloni (2011) data base. This data base is not consistent with most of the current solution models for crustal and upper mantle silicates provided by Holland & Powell and coworkers in THERMOCALC. hp11ver.dat does not include shear moduli and therefore cannot be used to compute seismic wave speeds (except sound speed). [HSC convention](#).

- **hp62ver.dat** - The TC-DS620 version of the Holland & Powell (2011) data base as used in Green et al (2016). [HSC convention](#).
- **hp622ver.dat** - The TC-DS622 version of the Holland & Powell (2011) data base as used in Jennings & Holland (2015). [HSC convention](#).
- **hp633ver.dat** - The TC-DS633 version of the Holland & Powell (2011) data base as used in Holland et al (2018). [HSC convention](#).
- **koma06ver.dat** - the Komabayashi & Omori (2006) data base for dense hydrous Mg-silicates. To use this data base set approx_alpha and Anderson-Gruneisen to False. [SUPCRT convention](#).
- **sfo05ver.dat** - Stixrude & Lithgow-Bertelloni (2005) augmented for mid- and lower-mantle phases as described by Khan et al. (2006). See the header section of this file for a list of solution models to be used with the data base.
- **stx08ver.dat** - Xu et al. (2008). See the header section of this file for a list of solution models to be used with the data base.
- **stx11ver.dat** - Stixrude & Lithgow-Bertelloni (2011). The most comprehensive data base for mantle phase relations and seismic wave-speed calculations. See the header section of stx11ver.dat for a list of solution models to be used with the data base. **NOTE:** This thermodynamic data base requires the solution model file named stx11_solution_model.dat.
- **stx21ver.dat** - Stixrude & Lithgow-Bertelloni (2021). An update to stx11ver.dat. See the header section of stx21ver.dat for a list of solution models to be used with the data base. **NOTE:** This thermodynamic data base requires the solution model file named stx21_solution_model.dat.
<https://doi.org/10.1093/gji/ggab394>
- **sup92ver.dat** - The SUPCRT database (for aqueous species see DEW13ver.dat), Johnson et al (1992), [database notation](#). [SUPCRT convention](#).

Comment, Numerical data, and Keyword format

Thermodynamic data files consist of a header section followed by the data for individual entities. The different sections of the data base are identified by left justified, case sensitive, keywords. Numerical data is unformatted but individual numbers cannot be longer than 14 characters. Comments are indicated by the "|" character, comments can be placed on the same line as data, but, in general, comments should not be placed on the same line as a keyword that indicates the beginning or end of a section or data entry. Comments may also be written free form at the end of the header section before the "end" keyword.

Header Section

The subsections of the header section ([Figure 1](#)) are listed sequentially below:

Title: the first non-blank, non-comment, line is the data base title. The title may be up to 80 characters long.

Standard variables:

this section
specifies names,
reference values,
and finite
difference
increments for the
standard variables
of the data base.

Figure 1. Thermodynamic data file header section.

```
| comments are indicated by the | character.
This is the uninformative title of the data base
begin_standard_variables
P(bar)      1.00   0.1E-3 | if you don't like a
```

The beginning of this section is indicated by the

```
T(K)      298.15    0.1E-4 | variable name, change it.
Y(CO2)     0.00     0.1E-6
mu(C1)      0.00     0.1E-2
mu(C2)      0.00     0.1E-2
end_standard_variables

tolerance   .1E-2

HSC_conversion | this is an optional keyword

begin_components | < 6 chars, molar weight (g), elemental entropy (R)
Na2O  61.9790  205.175
MgO    40.3040  135.255 | a comment can be added like this
Al2O3 101.9610  364.425
SiO2   60.0840  223.96
K2O    94.1960  231.935 | the component names can be changed
CaO    56.0770  144.205 | to whatever you prefer, e.g., LIME
TiO2   79.8660  235.87  | or CAO, BUT remember to change the
FeO    71.8440  129.855 | name in the formulae of individual
O2     31.9990  205.15  | data entries.
H2O    18.0150  233.255
CO2    44.0100  210.89
end_components

begin_special_components
H2O
CO2
end_special_components

begin_makes
    | some make definition examples:

    | a biotite solution endmember
fbi = 1 east -1/2 cor 1/2 hem
dqf_fbi = 13.45e3 J/mol
    | quartz-fayalite-magnetite O2 buffer
qfm = 2 mt 3 q -3 fa
dqf_qfm = 0
    | a melt endmember with modified stoichiometry
sil8L = 8/5 sill
dqf_sil8L = 0
    | a dqf corrected endmember
ts_dqf = 1 ts
dqf_ts = 10000 J/mol

end_makes

end
```

"begin_standard_variables" keyword and it is terminated by the **"end_standard_variables"** keyword. The specification of each variable is on a single line and consists of a left justified name (<9 characters), a number representing the variables reference or default value, and its finite difference increment. The increment is used only in unconstrained minimization calculations for tracing univariant phase fields (see page 15, card 6, of the somewhat out-of-date documentation [vdoc](#) for more information on the increments stored in array DELT). The units for thermodynamic potentials are J, K, bar and mol, these units are determined by the value of the universal gas constant as assigned in the block data subprogram (file tlib.f).

Tolerance: specified by the keyword **"tolerance"** followed by a numeric value. This tolerance is used only for unconstrained minimization calculations. This tolerance (**DTOL**) is used to determine whether a phase is stable with respect to a divariant assemblage with the same bulk composition as the phase in question. The tolerance

has units of J/mol. The tolerances used to locate univariant (**UTOL**) and invariant (**PTOL**) equilibria are linear functions of DTOL (see page 15, card 6, of the out-of-date documentation [vdoc](#) for more information on DTOL/UTOL/PTOL).

HSC_conversion: the presence of the "HSC_conversion" keyword instructs Perple_X programs to convert [HSC convention](#) standard state Gibbs energies identified by the tag "GH" in data entries to SUPCRT convention Gibbs energies. The keyword also indicates that the components section of the thermodynamic data file header specifies [selements](#)(T_r, P_r) for each component after its atomic weight. If the HSC_conversion keyword is removed the data is evaluated as entered. Currently conversion is uni-directional, HSC convention Gibbs energies can be converted to SUPCRT convention, but SUPCRT convention cannot be converted to HSC.

Components: this section assigns the names and gram-formula weights of the chemical components for the the data base. The beginning of this section is indicated by the "**begin_components**" keyword and it is terminated by the "**end_components**" keyword. The definition of each component is on a single line and consists of a left justified name (<6 characters), and the gram-formula weight of the component. The Perple_X program CTRANSF can be used to transform a data base from one set of components to another, provided the final components are a linear combination of the initial components.

Special components: this optional section identifies a subset of the data base components as special components. The beginning of this section is indicated by the "**begin_special_components**" keyword and it is terminated by the "**end_special_components**" keyword. Ordinarily special components are the chemical components of a phase whose chemical composition can be used as an independent phase diagram variable (i.e., a saturated phase).

Make definitions: this optional section specifies make definitions. The beginning of this section is indicated by the "**begin_make_definitions**" keyword and it is terminated by the "**end_make_definitions**" keyword. Make definitions define the Gibbs energy of thermodynamic entities (e.g., chemical potential buffers, endmembers, etc.) as a linear combination of the Gibbs energies of real entities in the data section thermodynamic file. The definition optionally includes a pressure-temperature dependent increment, sometimes referred to as a DQF correction, that is added to the Gibbs energy of the linear combination.

The format of a make definition consists of two lines (<240 characters):

```
name = num1 * name1 + num2 * name2 + .... + numj * namej
dnum1 dnum2 dnum3
```

where name is the name of the entity to be created, num_i is a number or fraction (i.e., two numbers separated by a '/') indicating the stoichiometric proportion of an entity name_i that exists as a data entry in the second part of the data file. The Gibbs energy of the made entity is

$$G_{\text{name}} = \text{num}_1 \cdot G_{\text{name1}} + \text{num}_2 \cdot G_{\text{name2}} + \dots + \text{num}_j \cdot G_{\text{namej}} + G_{\text{dqf}} \quad [2]$$

and

$$G_{\text{dqf}}[\text{J/mol}] = \text{dnum}_1 + T[\text{K}] \cdot \text{dnum}_2 + P[\text{bar}] \cdot \text{dnum}_3 \quad [3]$$

Perple_X 6.7.3+ allows more flexible input format for the coefficients of equation [3], the format is described at [FAQ](#).

Made entities are excluded from calculations in Perple_X if they are included in the excluded phase list in the problem definition file (e.g., "in"); however, real entities to the right of the equals sign in a make definition are not effected by

the excluded phase list. For example, if qL (liquid silica) is excluded, the make definition

q8L = 4 qL

will function, but qL will not be considered as a possible phase in the Perple_X calculation.

End-of-Header: the end of the header section is indicated by the "end" keyword.

Data Entries

The first line of data entries (Figure 2) for thermodynamic entities consist of a left justified name (<9 characters) for the entity followed by the **EoS** keyword, an equals sign, and an integer (the EoS keyword value) indicating the equation of state to be used for the entity. The EoS keyword may take the following values:

- 1 - normal polynomials for V , α , C_p (e.g., Helgeson et al. 1978; Berman 1988)
- 2 - normal polynomials for α , C_p , K_T ; Murnaghan for V (e.g., Holland & Powell 1998)
- 3 - normal polynomial for C_p ; Ghiorso (2003) polynomial on α , K_T ; Birch-Murnaghan on pressure
- 4 - normal polynomials for α , C_p , K_T ; Birch-Murnaghan for V (e.g., Saxena & Fei 1992)
- 5 - Debye Mie-Gruneisen (e.g., Stixrude & Bukowinski 1993)
- 6 - Debye Mie-Gruneisen (e.g., Stixrude & Lithgow-Bertelloni 2005b)
- 7 - normal polynomials for α , C_p ; exponential polynomial for V (e.g., Haas et al. 1986; Gottschalk 1997)
- 8 - normal polynomial for C_p ; Mie-Gruneisen Einstein oscillator for thermal pressure; modified Tait for V (Holland & Powell, 2010)
- 9 - normal polynomials for C_p , α , K_T ; Tait for V (Holland & Powell, 2010)
- 10 - ideal gas, normal polynomial for C_p
- 11 - Mie-Gruneisen Liquid (e.g., Stixrude et al. 2009)
- 12 - Brosh/CALPHAD format
- 13 - normal polynomial for C_p ; Komabayashi & Omori (2006) polynomial on α , K_T , K' ; Murnaghan on pressure
- 14 - Brosh/CALPHAD format for two part interpolative models
- 15 - Anderson Density Extrapolation model for aqueous species (Anderson et al. 1991)
- 16 - revised HKF formulation for aqueous species (Tanger & Helgeson 1988, Shock et al. 1992, Sverjensky et al. 2013)
- >100 - special EoS

The name and EoS keyword line is followed by a line that specifies the molar composition of the entity in terms of the [data base components](#). The format of this composition

name₁(num₁)name₂(num₂)name₃(num₃)

where name_{*i*} is the case-sensitive name of a component and num_{*i*} is its stoichiometric coefficient in the molar formula unit of the entity. A component can occur

Figure 2. A thermodynamic data file entry.

```
an      EoS = 2 | anorthite <= this is a comment
AL203(1)SiO2(2)CaO(1)
G0 = -4007795 S0 = 200 V0 = 10.079
c1 = 371.6 c2 = .12615E-1 c3 = -4110200 c5 = -2038.4
```

```

only once in the composition, the composition must be
written on a single line and cannot be separated from the name/EoS line by blank lines, but it can be
separated from the name/EoS line by lines containing the comment character.
Entities without mass (e.g., an entity representing a balanced chemical reaction)
are indicated by the word "null" on the composition line.

b1 = .238E-4 b5 = -.238E-3 b6 = 960100 b7 = -137.85 b8 = 4
m0 = 421000 m1 = 3.48 m2 = -43
transition = 1 type = 1 t1 = 2300 t2 = 11 t3 = .5E-1
end

```

The remaining lines assign values to the keywords: G0, S0, V0, c1-c7, d1-d10, m1-m3, and transition. The keywords can be listed in any order, if a keyword is not listed its value defaults to zero. The thermodynamic significance of the keyword values is dependent on specific keyword values, the possibilities are described here in two categories: the standard formulation (EoS 1-4, 7-10) and Mie-Gruneisen formulations (EoS 5, 6, 11). The EoS keyword can also be used to indicate certain internal equations of state.

Individual entries are terminated by the "end" keyword.

Standard Formulation (EoS 1-4 and 7-9)

In the standard formulation, the **G0** (or **GH**), **S0**, and **V0** are the [reference state Gibbs energy](#) (J/mol), entropy (J/K/mol), and volume (J/bar) at the reference pressure (P_r) and temperature (T_r) of the data base. In data files where [HSC_conversion](#) is enabled, the **G0** tag indicates a SUPCRT convention reference state Gibbs energy whereas the **GH** indicates an HSC reference state Gibbs energy.

Isobaric Heat Capacity, c1-c7

The values of **c1-c7** correspond to the coefficients of the polynomial

$$C_p(T, P_r) = c1 + c2 \cdot T + c3/T^2 + c4 \cdot T^2 + c5/T^{1/2} + c6/T + c7/T^3 + c8 \cdot T^3 \quad [4]$$

that describes the isobaric heat capacity (C_p) at the reference pressure.

Volumetric functions, b1-b8

The values of **b1-b8** characterize the pressure-temperature dependence of the volume (V).

$V(T, P)$: EoS 1

Volume (V , J/bar) at pressure (P) and temperature (T) is

$$V(T, P) = V0 + b2 \cdot (T - T_r) + b4 \cdot (P - P_r) + b6 \cdot (P - P_r)^2 + b7 \cdot (T - T_r)^2 \quad [5]$$

$V(T, P)$: EoS 7

Volume at pressure and temperature is

$$V(T, P) = V0 \cdot \exp[b3 \cdot (T - T_r) + b8 \cdot (P - P_r)] \quad [6]$$

Temperature dependent volumetric functions: EoS 2, 4

The isobaric expansivity (α) at the reference pressure is

$$\alpha(T, P_r) = b1 + b2 \cdot T + b3/T + b4/T^2 + b5/T^{1/2} \quad [7]$$

that describes the isobaric expansivity (α) at the reference pressure. Volume at the reference pressure is

$$V(T, P_r) = V_0 \cdot [1 + \text{integral}(\alpha(T, P_r), T=T_r..T)] \quad [8]$$

if the perplex_option.dat keyword [approx_alpha](#) is T (the default), or

$$V(T, P_r) = V_0 \cdot \exp[\text{integral}(\alpha(T, P_r), T=T_r..T)] \quad [9]$$

if [approx_alpha](#) is F.

The isothermal bulk modulus is

$$K(T, P_r) = b_6 + b_7 \cdot (T - T_r) \quad [10]$$

if the perplex_option.dat keyword [Anderson-Gruneisen](#) is F, or

$$K(T, P_r) = b_6 \cdot \exp[-K' \cdot \text{integral}(\alpha(T, P_r), T=T_r..T)] \quad [11]$$

if [Anderson-Gruneisen](#) is T.

Temperature dependent volumetric functions: EoS 3

Volume at the reference pressure is computed as

$$V(T, P_r) = V_0 + b_1 \cdot (T - 1673) \quad [12]$$

and the isothermal bulk modulus is

$$K(T, P_r) = V(T, P_r) / [b_2 + b_3 \cdot (T - 1673)] \quad [13]$$

Temperature dependent volumetric functions and $V(T, P)$: EoS 13

The isobaric expansivity (α) at the reference pressure is as in equation [7]. For consistency with Komabayashi & Omori (PEPI 156:89-107, 2006) [approx_alpha](#) and [Anderson-Gruneisen](#) are ignored.

The isobaric expansivity (α) at the reference pressure is

$$\alpha(T, P_r) = b_1 + b_2 \cdot T + b_3/T + b_4/T^2 \quad [34]$$

The bulk modulus at the reference pressure is

$$K(T, P_r) = 1 / (b_5 + b_6 \cdot T + b_7 \cdot T^2 + b_8 \cdot T^3) \quad [35]$$

and its pressure derivative is

$$K' = b_9 + b_{10} \cdot (T - T_r) \cdot \ln(T/T_r). \quad [36]$$

$V(T, P_r)$ is computed as in equation [9] and $V(T, P)$ is computed as in equation [14] below.

$V(T, P)$: EoS 2, 3, 4

Perple_X uses the Murnaghan or Birch-Murnaghan isothermal equations of state (third order) to compute volume depending on the value of b_8 . If $b_8 > 0$, b_8 is the pressure derivative of the bulk modulus (K') and the Murnaghan equation is used

$$V(T, P) = V(T, P_r) \cdot [1 - K' \cdot P / \{K' \cdot P + K(T, P_r)\}]^{1/K'} \quad [14]$$

is used. Otherwise if $b_8 < -3$, $b_8 = -K'$ and the Birch-Murnaghan equation

$$P = 3 \cdot K(T, P_r) \cdot f \cdot [1 + 2 \cdot f]^{5/2} \cdot [1 + \{3 \cdot (K' - 4)/4\} \cdot f], \quad [15]$$

where

$$f = [\{V(T, P_r)/V(T, P)\}^{2/3} - 1]/2, \quad [16]$$

is used and solved numerically for $V(T, P)$.

$V(T, P)$: EoS 8 and 9

Documentation pending publication of Holland & Powell (2010, JMG)

EoS 8

b1 - α_0 (1/K)
b5 - Debye T (K)
b6 - K_0 (J/mol)
b7 - K_0'' (1/bar)
b8 - K_0'

EoS 9

b1 - α_0 (1/K)
b5 - dK/dT (bar/K)
b6 - K_0 (J/mol)
b7 - K_0'' (1/bar)
b8 - K_0'

Adiabatic Shear Modulus, m_0 - m_2

Refer to Stixrude & Lithgow-Bertelloni (2005a,b) for details of the computation of the adiabatic shear modulus for EoS 5-6. For all other EoS, the explicit adiabatic shear modulus (bar) is computed as

$$\mu_S(T, P) = m_0 + m_1 \cdot (P - P_r) + m_2 \cdot (T - T_r) \quad [17]$$

if the `perplex_option.dat` keyword [poisson_ratio](#) is **off** or **on**. If m_0 - m_2 are not specified and [poisson_ratio](#) is **on**, or if [poisson_ratio](#) is **all**, then

$$\mu_S(T, P) = \nu \cdot K_S(T, P) \quad [18]$$

where the Poisson ratio ν is specified by the second value of the [poisson_ratio](#) keyword and the adiabatic bulk modulus $K_S(T, P)$ is computed by differentiation of the Gibbs energy (Equation 4 of [Connolly & Kerrick 2002](#)).

Adiabatic Bulk Modulus, k_0 - k_2

By default, Perple_X computes the adiabatic bulk modulus $K_S(T, P)$ by differentiation of the Gibbs energy (Equation 4 of [Connolly & Kerrick 2002](#)). This method has the virtue that the modulus is consistent with the equation of state used to compute phase relations. The importance of this consistency for seismic velocity is debatable because phase relations depend directly on the Gibbs energy, whereas $K_S(T, P)$ is dependent primarily on second order derivatives of the Gibbs energy. Thus it can be argued that in some cases empirically calibrated expressions for $K_S(T, P)$ are more accurate than the values obtained from an EoS intended only for phase equilibrium calculations (e.g., Holland & Powell 1998). To accommodate this case, the adiabatic bulk modulus (bar) can be specified explicitly in the thermodynamic data file by the expression

$$K_S(T, P) = k_0 + k_1 \cdot (P - P_r) + k_2 \cdot (T - T_r). \quad [18.1]$$

This explicit expression for the $K_S(T,P)$ is used only if the `perplex_option.dat` keyword `explicit_bulk_modulus = T` (true). If the coefficients are not specified or `explicit_bulk_modulus = F`, then $K_S(T,P)$ is computed by differentiation of the Gibbs energy.

Mie-Gruneisen Formulations for Solids (EoS 5-6)

The Mie-Gruneisen type formulations of Stixrude & Bukowinskii (1993) and Stixrude & Lithgow-Bertelloni (2005b) are specified in `Perple_X` by EoS values 5 and 6, respectively. Both formulations use the Debye thermal model for which the isochoric Helmholtz free energy is

$$A(T,V) = (\theta/T)^{-3} \cdot \text{integral}((\theta/T)^2 \cdot \ln\{1 - \exp[-(\theta/T)]\}, (\theta/T)) \quad [19]$$

and the third-order [Birch-Murnaghan](#) equation of state. The formulations differ from each other in the dependence of the Debye temperature (θ) on volume. In the Stixrude & Bukowinskii (1993) formulation, the Debye temperature is

$$\theta = \theta_0 \cdot \exp\{-\gamma_0[\{V/V_0\}^{q_0} - 1]/q_0\} \quad [20]$$

and in the Stixrude & Lithgow-Bertelloni (2005b) formulation

$$\theta = \theta_0 \cdot [1 + (a_1 + a_2 \cdot f/2) \cdot f]^{1/2} \quad [21]$$

with

$$a_1 = 6 \cdot \gamma_0 \quad [22]$$

$$a_2 = a_1 \cdot [a_1 - 2 - 3q_0] \quad [23]$$

and f as in equation 16.

For the Stixrude & Bukowinskii (1993, EoS=5) formulation the correspondence of the `Perple_X` keywords is [the zero subscript indicates a value at reference conditions]:

- G_0 = Helmholtz energy (F_0 , J/mol)
- S_0 = number of atoms per formula unit (n)
- V_0 = negative of the volume ($-V_0$)
- c_1 = isothermal bulk modulus (K_0 , bar)
- c_2 = pressure derivative of the isothermal bulk modulus (K')
- c_3 = Debye Temperature (θ_0 , K)
- c_4 = Gruneisen thermal parameter (γ_0)
- c_5 = Mie-Gruneisen exponent (q_0)
- c_6 = Shear strain derivative of the tensorial Gruneisen parameter (η_{S0})
- c_7 = Configurational (and magnetic) entropy (J/mol/K)
- m_1 = Adiabatic shear modulus (μ_{S0} , bar)
- m_2 = Pressure derivative of the adiabatic shear modulus (μ_{S0}')

The only difference from the above list in the parameter assignments for the Stixrude & Lithgow-Bertelloni (2005b, EoS=6) formulation is

- S_0 = negative of the number of atoms per formula unit ($-n$)

Modified Anderson Density Model for Aqueous Species (EoS 15)

EoS 15 implements the Anderson density model (Anderson et al. 1991) for estimation of the properties of aqueous species at elevated pressure and temperature as

modified by Holland & Powell (1998, page 313). The tags used to identify the parameters of this model in Perple_X thermodynamic data files are:

- G0 = reference state Gibbs energy (J/mol)
- S0 = reference state entropy (J/mol/K)
- V0 = reference state the volume (J/bar)
- c1 = reference state heat capacity (J/mol/K)
- c2 = temperature dependence of the reference state heat capacity (J/mol/K²)
- c3 = ionic charge
- b3 = a flag identifying the hydronium (b3 = 1) and hydroxyl (b3 = 2) ions (6.7.8+)

In addition to the above species specific parameters, the following solvent (water) properties (Anderson et al. 1991) are assumed for the evaluation of EoS 15:

- α_0 = reference state expansivity = $25.93 \cdot 10^{-5}/K$
- β_0 = reference state compressibility = $45.23 \cdot 10^{-6}/bar$
- $(d\alpha/dT)_0$ = reference state derivative of α with respect to $T = 9.5714 \cdot 10^{-6}/K^2$
- ρ = density (Pitzer & Sterner 1994).

Revised HKF Formulation for Aqueous Species (EoS 16)

EoS 16 implements the revised HKF formulation (Tanger & Helgeson 1988, Shock et al. 1992) for the estimation of the thermodynamic properties of aqueous species at elevated pressure and temperature. The tags, listed below, used to identify the parameters of this model in Perple_X thermodynamic data files correspond to the notation used in Shock et al. (1992) and the Deep Earth Water (DEW) Model (Harrison & Sverjensky, 2013).

- G0 = reference state Gibbs energy (J/mol)
- S0 = reference state entropy (J/mol/K)
- ω_0 = reference state Born coefficient (J/mol)
- c1 = caloric equation of state parameter (J/mol/K)
- c2 = caloric equation of state parameter (J-K/mol)
- a1 = volumetric equation of state parameter (J/mol/bar)
- a2 = volumetric equation of state parameter (J/mol)
- a3 = volumetric equation of state parameter (J-K/bar/mol)
- a4 = volumetric equation of state parameter (J-K/mol)
- HOH = a flag identifying the hydronium (HOH = 1) and hydroxyl (HOH = 2) ions (6.7.8+)

In addition to the above species specific parameters, the following solvent (water) properties/functions are assumed for the evaluation of EoS 16:

- θ = characteristic temperature, 228 K
- ψ = characteristic pressure, 2600 bar
- ϵ = dielectric constant (Sverjensky et al. 2013)
- $Y_\theta = (\partial \ln \epsilon / \partial T) / \epsilon$ [at T_r (298.15 K) and P_r (1 bar)] = $-5.79865 \cdot 10^{-5}/K$
- ρ = density of water (Zhang & Duan 2005)
- η = proportionality constant relating the Born constant to the inverse of electrostatic radius = $4.184 \cdot 1.66027 \cdot 10^5$ J-Angstrom/mol

Special EoS (EoS > 100)

Perple_X has a number of specialized internal EoS, a resume of these follows

- **101-117** invoke the molecular fluid equation of state specified by the [hybrid_EoS](#) Perple_X option or the Modified Redlich-Kwong EoS (DeSantis et al 1974), if no such option exists for the species in question. The values correspond to the species: H2O (101), CO2 (102), CO (103), CH4 (104), H2 (105), H2S (106), O2 (107), SO2 (108), COS (109), N2 (110), NH3 (111), O (112), SiO (113), SiO2 (114), Si (115), C2H6 (116), HF (117). The thermodynamic for the species should not include volumetric properties and it is assumed that the calorimetric properties are as described for EoS 1.
- **600-603** invokes the Komabayashi & Fei (2010) EoS for Fe-phases.
- **604** obsolete, replaced by EoS 114.
- **605** invokes the MRK for O in a mixed O-O2 fluid.
- **606** obsolete, replaced by EoS 115.
- **610-637** invokes internal EoS various Fe-Cr-C-Si condensed phase endmembers (Lacaze & Sundman 1990, Xiong et al. 2011, Golubkova et al. 2015).
- **700** obsolete, replaced by EoS 113.
- **701** obsolete, replaced by EoS 107.
- **702** obsolete, replaced by EoS 112.

Explicit Thermal Disorder, d1-d9

Coefficients **d1-d9** provide for an explicit expression of the energetic effects of thermal disordering (Berman & Brown 1984; Berman 1988) in a thermodynamic entity. The values **d1-d7** correspond to the coefficients of the polynomial

$$C_{P,dis} = d1 + d2 \cdot T + d3/T^2 + d4 \cdot T^2 + d5/T^{1/2} + d6/T + d7/T^2 \quad [24]$$

which represents the disorder component of the isobaric heat capacity. This component is added to the baseline [heat capacity](#) over the temperature(K) interval **d8** to **d9**.

Lambda Transitions, transition, type, t1-t11

The data for a Lambda (and mock-Lambda) transition of a thermodynamic entity is entered on a single line with the general format

transition = num₁ **type** = num₂ **t1** = num₃ ... **t11** = num₁₃

transition and **type** are mandatory keywords and must be the first and second entries for the transition, the remaining keywords are optional. The **transition** keyword value is the index of the transition; normally 1, but for phases with more than one transition the index indicates the transition's order of occurrence with respect to temperature at the reference pressure. The **type** keyword value indicates the model to be used to interpret the subsequent data keywords (t1-t12) and can take the following values:

- 1 - UBC style (e.g., Berman 1988)
- 2 - Standard (e.g., USGS, JANAF)
- 3 - Helgeson et al. (1978)
- 4 - Landau (e.g., Holland & Powell 1998)
- 5 - Bragg-Williams (e.g., Holland & Powell 1996)
- 6 - CALPHAD G

type = 1, UBC form

In the UBC lambda model, the lambda component of the Gibbs energy is evaluated in terms of the variable $T' = T + T_d$, where $T_d = t4 \cdot (P - P_r)$. The lambda component of the heat capacity is

$$C_{P\lambda} = T' \cdot (t1 + t2 \cdot T') \quad [25]$$

over the interval from $t_7 - T_d$ to the smaller of T' or $t_3 - T_d$. t_5 and t_6 approximate the $\partial V/\partial P$ and $\partial V/\partial T$ derivatives for the entity, and t_8 is an energetic correction.

type = 2, Standard form

In the standard lambda model, transitions are approximated as discontinuous transitions and each phase is characterized by a unique isobaric heat capacity function. No correction is made for the effects of pressure on the transition temperature. The parameters are

t_1 - transition temperature at the reference pressure
 t_3 - entropy change of the transition
 t_4 - t_{11} - coefficients c_1 - c_8 of the [heat capacity function](#) to be used at $T > t_1$

type = 3, Helgeson form

The Helgeson model is identical to the standard model except that it accounts for the pressure dependence of the transition by introducing the additional parameter

t_3 - Clapeyron slope ($\partial P/\partial T$) of the transition

type = 4, Landau form

The Landau model is based on three parameters: t_1 - the temperature T_0 at which the phase becomes fully disordered at the reference pressure; t_2 - the maximum entropy change of disorder, S_d ; t_3 - the maximum volume change of disorder, V_d . The Gibbs energy change of ordering due to a lambda transition is

$$\Delta G = h' - T \cdot s' + \text{integral}(v', P=P_r..P) + G_{\text{Landau}} \quad [26]$$

where

$$h' = S_d \cdot T_0 \cdot (Q_0^2 - Q_0^6/3) \quad [27]$$

$$s' = S_d \cdot Q_0^2 \quad [28]$$

$$v' = V_d \cdot Q_0^2 \cdot [1 - K' \cdot P / \{K' \cdot P + K(T, P_r)\}]^{1/K'} \cdot [1 + \text{integral}(\alpha(T, P_r), T=T_r..T)] \quad [29]$$

$$T_c = T_0 + P \cdot V_d / S_d \quad [30]$$

$$Q_0 = (1 - T_r / T_0)^{1/4} \quad [31]$$

$$\text{if } T < T_c, \text{ then } Q = (1 - T/T_0)^{1/4}, \text{ else } Q = 0 \quad [32]$$

$$G_{\text{Landau}} = S_d \cdot [(T - T_c) \cdot Q^2 + T_c \cdot Q^6/3] \quad [33]$$

and the unspecified properties are those of the completely disordered state.

type = 5, Bragg-Williams form

Documentation pending publication of Holland & Powell (2011, JMG)

t_1 - enthalpy change of disordering (J/mol)
 t_2 - volume change of disordering (J/bar/mol)
 t_3 - W_H (J/mol)
 t_4 - W_V (J/bar/mol)
 t_5 - n

t6 - if fac > 0, t6 = fac, else t6 = (-fac * n + 1) / (n + 1)

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