

Version 2.34 Update:

1. Deleted file SUMMARY.DAT which was distributed as “Read-only” file
2. winTWQ.exe: added error message for case when user forgets to select phases
3. winTERSX.exe: recognizes DEC06.DAT as the default thermodynamic data file

winTWQ: version 2.32 changes – a quick list

1. Database change: the version 2.02 database has been revised and should now be considered obsolete. The main changes in the version 2.32 database are:
 - a. improved mixing and endmember properties for biotite, which incorporate estimates of Fe³⁺ and allow better thermometry (e.g. gt-bi) and barometry (e.g. gt-bi-plg-qz barometer with the equilibrium: $An + Phl = Gr + Py + Eas + Qz$)
 - b. most CMS phases and clinocllore have been added (like the version 1.02 database), however not tschermakite or pargasite yet
2. Program bugs/changes
 - a. Updated documentaton related to selecting specific equilibria, as opposed to all equilibria possible
 - b. Batch runs for multiple calculations: cmp.log, twq.log, intsx.log has list of completed calculations
 - c. winCMP:
 - i. Batch reading of cmp extension (e.g. CM1, CM3) in file batch.dat
 - ii. Has new option for estimating Fe³⁺ in biotite and garnet
 - d. winTERSX:
 - i. interactive fixed P or T added for batch or single file

winTWQ (version 2.32) Documentation

This file gives a brief introduction to the WINDOWS version of TWQ, which supercedes the earlier DOS versions, but incorporates their essential features. One major difference is that winTWQ provides a convenient way to base P-T results on specific equilibria rather than all possible equilibria. This can be an independent set of equilibria, but needn't be. An abbreviated list of suggested equilibria (presently considered most robust because of direct experimental constraints) can be easily modified by users. Of particular importance in this specific equilibria approach to geothermobarometry, as opposed to average P-T results (e.g. calculated with THERMOCALC; Powell et al., 1998; or INVEQ; Gordon, 1992), is the recognition that some equilibria have significantly higher closure temperatures than others, and thus should not be averaged with others. See, for example, the documented differences in "Al in Opx" vs. Fe-Mg based temperatures for orthopyroxene-garnet (Begin & Pattison, JMetmGeol, 12, 411-428; Aranovich and Berman, 1997, AmerMin, 82, 345-353). It is also important to recognize the TWQ's specific equilibria approach differs enormously from "standard, i.e. old-fashioned" thermobarometry in which applied equilibria are not internally consistent with one another, i.e. each incorporates a different set of thermodynamic properties for participating minerals.

Version 2.32 of winTWQ allows convenient use of either of the thermodynamic data base distributed with the earlier DOS version 1.02, or a revision (DEC06.DAT, DEC06.SLN) of the version 2.02 database with improved biotite properties (see below) and added CMS phases. Other revisions of the database, and more complete documentation are planned for distribution soon – if you have registered for winTWQ via email (rberman@nrcan.gc.ca), you will be notified of all updates. Below this introduction to winTWQ is the documentation distributed with the earlier DOS versions of the software.

If you publish the results of this software, please make sure to state and cite not only the program (Berman, 1991, Can Mineral, 29, 833-856) and version (2.3), but also the database version (1.02 = Berman, 1988, JPet, 29, 445-522; 2.02 = Berman and Aranovich, 1996, CMP, 126, 1-24; 2.32 = Berman & Aranovich, in prep), as well as citing other solution models that were used in the calculations. Please also note that the version 2.32 database may undergo other revisions in 2007, so check with Berman before using the 2.32 database for any publications.

Software Overview:

The main steps in using winTWQ are similar to the DOS versions (details are discussed further below for each step):

1. winTWQ.FIG: edit this text file to set up your preferences
2. winCMP.EXE: convert probe data to structural formula
 - a. create either .CM1, CM2, or CM3 files that are compatible with TWQ thermodynamic data of versions 1.02, 2.02, or 2.32 (with Fe3+ option chosen)
3. winTWQ.EXE: calculate P-T results, with interactive input to:
 - a. select thermodynamic database
 - b. specify chemical system, phase diagram variables & options
 - c. select endmembers to consider
 - d. specify solution model & file of mineral compositions (usually made by winCMP.EXE)
 - e. specify whether to calculate all equilibria, a set of recommended equilibria (which can be user-modified), or specific equilibria
 - f. results are written to a TWQ graphics file (plot.plt) that is accessed by other winTWQ programs (see below), a DXF graphics file (for import into other graphics programs), and a text file (summary.dat)
4. winCLEAN.EXE: clean up the appearance of calculated phase diagrams, by repositioning labels on equilibrium curves to avoid overlap
5. winPLOT.EXE or PLOT.EXE: on-screen viewing of calculated phase diagrams (plot.plt generated by winTWQ.EXE) or compositional plots (*.p files generated by winCMP.EXE)
6. winDXF.EXE: convert plot files for import into graphics programs (e.g. CORELDRW, AUTOCAD) and printing
7. winTERSX.EXE: calculate average results from intersections of equilibria calculated by winTWQ.EXE (plot.plt file)

Thermodynamic Data:

Calculated phase diagrams and thermobarometric results are dependent on thermodynamic data, making the quality of results a direct reflection on the quality of thermodynamic data. It is therefore essential to use internally consistent thermodynamic data, i.e. data that were derived from, agree with, and can thus reproduce primary experimental constraints on both individual phase properties (H, S, V, Cp, a, B) as well as phase equilibrium boundaries. Since the pioneering work of Helgeson et al. (1978), most focus has been on internally consistent thermodynamic data for mineral endmembers. The TWQ databases also incorporate internally consistent solid solution data, i.e. data that when used with TWQ endmember data, reproduce experimental observations (and some natural data sets) involving solid solutions. The emphasis over the past decade has been on the accuracy of reproducing experimental data with sometimes more complex solution models (e.g. asymmetric nonideal mixing), rather than expansion of thermodynamic data to more endmembers and minerals. WinTWQ allows users to use either of the thermodynamic databases distributed with the DOS versions 1 and 2, as well as a 2006 revision of the version 2 database. In due course, a new database will be distributed that merges and improves upon these databases which are briefly described below. Make sure you are a registered winTWQ user to receive notice of updated thermodynamic data.

Version 1.02 thermodynamic data (JUN92.GSC, JUN92.SLN)

This database contains thermodynamic data from Berman (1988, J. Pet., 29, p. 445-522) with preliminary/provisional/unpublished properties for andradite, baddelyite, Fe cordierite, geikelite, hedenbergite, hercynite, kalsilite, leucite, nepheline, staurolite, and zircon, as well as

1. Pumpellyite & glaucophane from Evans (1990, Lithos, v. 25)
2. Amphibole endmembers from Mader et al. (1994, Can J Earth Sci, 31, 1134-1145)
3. nonideal solution properties of:
 - a. garnet (Berman, 1990, Amer. Mineral., 75, p. 328-344)
 - b. biotite (McMullin et al., 1991, Can Mineral, 29, p. 889-908)
 - c. amphibole (Mader et al., 1994, Can J Earth Sci, v. 31, p. 1134-1145)
 - d. plagioclase (Furhman & Lindsley, 1988, Am Mineral, v. 73, p. 201-215)
 - e. white mica (Chatterjee & Froese, 1975, Am Mineral, v. 60, p. 985-993)
 - f. olivine (preliminary, unpublished data of Berman & Aranovich, 1993)

Version 2.02 thermodynamic data (BA96a.DAT, BA96A.SLN, BA96a.RCP)

This database uses Berman (1988) thermodynamic data for minerals & fluids for K-Na-CASH phases, along with data for the following minerals that have been derived by MAP analysis of relevant experimental data discussed in detail in the references below:

1. anthophyllite, talc, rutile, as well as components of the following solid solutions: olivine (fo, fa), orthopyroxene (en, fs, al-opx), cordierite (Mg-, Fe-; both of which are assumed to follow the same hydration energetics), garnet (alm, py), ilmenite (Fe-, gk) (Berman & Aranovich, 1996, CMP, 126, 1-24)
2. hedenbergite and Mg-Fe-Al (M1) clinopyroxene mixing properties (Berman et al., 1995, Contrib Mineral Petrol 119:30-42)

3. provisional properties for biotite (phl, annite, siderophyllite, eastonite), and Mg-Fe spinel, based on unpublished data of Berman & Aranovich (1997).

Note that because some Mg endmembers have changed (fo, en, cd, py, sp), you cannot use other Mg-, CaMg, or MgAl phases from Berman (1988) with this data set. If you need to use phases that are not included in the present database (e.g. most amphibole endmembers, CaMg phases, some MgAl phases), you will have to perform these calculations with the version 1 database. DO NOT mix thermodynamic data between versions as this will destroy their internal consistency! Lastly, note that this version of thermodynamic data are NOT identical to the data in the above references or in version 2.01 of TWQ because version 2.02 data are based on simultaneous analysis of ALL data, whereas the earlier works considered each set separately.

Version 2.32 thermodynamic data (DEC06.DAT, DEC06.SLN)

This database uses Berman (1988) thermodynamic data for minerals & fluids for K-Na-CASH phases, along with data for the following minerals that have been derived by mathematical programming analysis of relevant experimental data discussed in detail in the references below:

1. following from Berman & Aranovich (1996, CMP, 126,1-24): solution properties and components of the following solid solutions: olivine (fo, fa), orthopyroxene (en, fs, al-opx), cordierite (Mg-, Fe-; both of which are assumed to follow the same hydration energetics), garnet (alm, py), ilmenite (Fe-, gk), including as well these other endmembers: anthophyllite, talc, rutile
2. endmembers dependent on the above changes: periclase, brucite, chrysotile, antigorite, merwinite, akermanite, monticellite, dolomite (all following Berman, 1988)
3. hedenbergite and Mg-Fe-Al (M1) clinopyroxene mixing properties (Berman et al., 1995, Contrib Mineral Petrol 119:30-42)
4. revised properties for biotite (phl, annite, siderophyllite, eastonite), with:
 - a. endmember properties and Fe-Mg-Al-Ti mixing based on:
 - i. Al solubility data for Fe-Al, Mg-Al, Fe-Mg-Al biotite (Berman et al. 2007; Am Mineral, v.92, in press)
 - ii. ol-bi Fe-Mg exchange data for Fe-Mg-Ti biotite (Zhou 1994)
 - iii. highest-T (least oxidized annite) experiments for Annite = Mt + San + Qz + H₂O (Cygan et al. 1996)
 - b. All properties refined by analysis of gt-bi and gt-bi-plg-qz/GASP applications to natural assemblages
5. revised Mn-Fe-Mg mixing properties of garnet, and endmember properties of spessartine based on the experimental data of Feenstra and Peters (1996, CMP, 126, 109-120) and Feenstra and Engi (1998, CMP, 131, 379-392), along with natural datasets of Williams & Grambling (1990).
6. Pyrite, pyrrhotite, sphalerite from Froese and Berman (1994) – winTWQ calculates the stable pyrrhotite composition for any equilibria involving pyrrhotite and sulfur gas
7. Tremolite following Evans et al. (2000)
8. Clinocllore – approximate properties derived by consideration of the effects of variable Al content of chlorite calculated with the activity model of Hunziger (2002);
9. Fe-staurolite – from phase equilibrium data of Ganguly (1972), Rao & Johannes (1979), and some brackets of Richardson (1968)

Feedback on how the current database works for your rocks is much appreciated, and could lead to further improvements in thermodynamic data.

Note that if you want to do amphibole barometry with the tschermakite or pargasite endmembers, you still need perform these calculations with the version 1 database. There is a definite plan to add amphibole endmembers early in 2007, so do not despair! Remember: DO NOT mix thermodynamic data between versions as this will destroy their internal consistency! Lastly, note that this version of thermodynamic data are NOT identical to the data in the above references because version 2.32 data are based on simultaneous analysis of ALL data, whereas the earlier works considered each set separately.

WinTWQ setup:

Unzip winTWQ.zip in a directory c:\wintwq. Preferences for all winTWQ executables are controlled with text strings in the file winTWQ.fig. The order of these text strings in the file does not matter. Use any text editor to change preferences. Make sure to save as a text file without formatting. Some of the control words, with examples, are:

CONTROL WORD	Function
PATH=c:\myrocks\	location of input (.oxi, .cm1, .cm2, .cm3) and output (plot.plt) files, if different from location of executables
FONTFILE=c:\wintwq\romansim.fnt	location of font file used by winPLOT.EXE
MINERAL DATA=DEC06.DAT	default endmember thermodynamic data used by winTWQ
SOLUTION DATA=DEC06.SLN	default solid solution data used by winTWQ
AQUEOUS DATA=hkf81.aqu	default aqueous solution data used by winTWQ
SOH STD STATE= 0	0 = 1 bar, T std state for S2, H2, O2; 1 = P,T std state
PLOTFILE=PLOT.plt	Name of file with graphical output from winTWQ
RESTARTFILE=RESTART.RES	Name of file used for rerunning winTWQ
SUMMARYFILE=SUMMARY.DAT	Name of file with tabular output from winTWQ
METASTABLE EQUILIBRIA?=YES	WinTWQ plots metastable equilibria/extensions
PRINT ACTIVITIES?=YES	WinTWQ print activities along equilibria in the file "activities"
SLOPE DIFFERENCE=15	Angular threshold for parallel curves used in winTERSX program
CMP-START=1	Starting column to search for mineral abbreviation (winCMP)
CMP-COMMENT=0	# of comment lines before line with name of oxides (winCMP)
CMP-FERRIC=yes	Ferric Iron included?
CMP-3%FE3GT=yes	Assume Fe3+ is 3% of total Fe in garnet?
CLEAN LABEL SIZE=0.2	Default label size
CLEAN OPTION=-4	Forces labels on all curves

NOTE: When calculating activity diagrams involving S2, H2, or O2 gas, the default standard state in winTWQ has been changed to 1 bar and T. Previous versions used a standard state for these gases of P and T. This option is controlled with the "SOH STD STATE" keyword.

winTWQ.exe (to calculate phase diagrams or thermobarometric results)

winTWQ.EXE reads thermodynamic data and compositional data for rock samples, and then calculates the positions of all or a selected subset of equilibria that can be written among the selected minerals endmembers or species. For elaboration on some operational points, please read the relevant documentation for DOS version 1, included at the end of this document. Interactive input for winTWQ is required in the form of 6 windows to:

1. select batch mode operation for processing multiple files (described at the end of this documentation)
2. select the thermodynamic database
3. change/select file names; specify path for files; specify if a restart file will be used to control operation of the program
 - a. by default, the file RESTART.RES is written each time winTWQ is run. For minor changes on subsequent runs (e.g. different file of mineral compositions), this option saves having to interactively set up program operation.
4. select type of diagram
5. input chemical elements in system ("e" for charged aqueous species), P-T range, mole fraction of H₂O, CO₂, etc.
6. select minals, species to include in calculation by clicking with mouse
 - a. for activity diagrams, input the variable name which must be spelled exactly as shown in the list of minals or species; some acceptable variables involving aqueous species are K⁺/H⁺, Mg⁺⁺/H⁺², etc.
 - b. check whether all listed minals, species should be included
 - c. check whether specific equilibria will be selected on next screen, or whether all equilibria will be considered
 - d. check whether fixed, reduced activities or any special options should be included with any minals; if so, input will be prompted on another window for each mineral
7. if the "specific equilibria" option was selected on the prior screen (c):
 - a. highlight with the mouse which equilibria to calculate, or
 - b. check whether all equilibria are to be calculated, or
 - c. check "suggested equilibria only" option; these equilibria are indicated with an asterisk in the list of all equilibria. The list of suggested equilibria can be changed by editing the file "rxtns_fe.cal", being careful to follow their format and to use the abbreviations of phases used in the thermodynamic database. At present, these files contain an abbreviated, i.e. *incomplete* list of equilibria (maximum # of equilibria = 100 for now) that have been experimentally calibrated, and thus are considered most reliable. If you add three equilibria that are linearly related, e.g. an Fe- endmember equilibrium, and Mg-endmember equilibrium, and the linearly dependent Fe-Mg exchange equilibrium, winTWQ will use the first two listed in "rxtns_calib.dat" if you link all three with a letter of the alphabet that has not been used for other equilibria in the file.

NOTE: at present, use of the "specific equilibria" option is limited to systems with less than 3000 possible equilibria; for calculations involving more than 3000 equilibria, do not use this option (i.e. leave the "specific equilibria" box unchecked on the previous screen)

Output of winTWQ is directed to a text file (SUMMARY.DAT), a plot file (PLOT.PLT), and a graphics file (either PLOT.DXF or xxx.DXF, with xxx being the name of the composition file used in the calculation). View PLOT.PLT with winPLOT.exe (on-screen only; nice options, but no printing) or wPLOT.exe (few options, allows low-res printing). Import PLOT.DXF into a graphics package (e.g. CORELDRAW, AUTOCAD) for high-res printing.

Note: the plot file generated by winTWQ will contain labels giving the name of the file from which mineral compositions were read, as well as the solution model used for each mineral.

winPLOT.exe (for on-screen viewing of plot files)

Configuration is controlled with text strings in the file winTWQ.fig. The “FONTFILE=” string is searched to tell winPLOT.exe where to find the font file (ROMANSIM.FNT). The default is the directory “c:\winTWQ\ROMANSIM.FNT”. Make sure to include the proper path.

The program winTWQ.exe produces graphical output in the file PLOT.plt. When you double click on PLOT.plt the first time (or right click on it), instruct WINDOWS to always open *.plt files with the program winPLOT.exe (in the directory where you have put it, usually “c:\wintwq”). When winPLOT.exe starts, you may get a system error message about opening the COM port. Click on “ignore” and the program should work. If anyone knows a way to avoid this error message, please let me know!

Once the diagram is drawn, you are prompted for the next action. To access any of the menu commands, click with your mouse in the appropriate box, or type the first letter of the command. The options are:

- Type ESC or 'q' to quit the program.
- Type 'b' to blowup a portion of the diagram.

Crosshairs will appear near the center of the diagram. Using a mouse or the arrow keys, move the crosshairs to the lower left corner of the area you want to see enlarged and type CR. Repeat this process to select the upper right corner of the diagram. Note that the HOME, END, PGDN, and PGUP allow diagonal movements, and holding the SHIFT key with any of the others results in larger movements.

- Type 'o' to redraw the original diagram.
- Type 'n' to remove all labels from the diagram.
- Type 'r' to relabel the diagram.
- Type 'l' to add a label on the diagram.
- Type 'f' to superimpose another plot file on the present one.
- Type 'd' to delete a superimposed plot file.
- Type 'p' to plot symbols or draw lines.
- Type 's' to save a modified plot to a file of your choice.

wPLOT.exe (for med-resolution printing and on-screen viewing of plot files)

This program is best for taking a quick peek at plot files and making a medium-resolution printout. For a closer on-screen look with more options, use winPLOT.EXE. For high-resolution printouts, use winDXF to convert plot files, and import the plot.DXF file into a graphics package such as CORELDRAW or AUTOCAD.

To run wPLOT.EXE, double click on the program. Use “File, options” to specify the path for files. Use “File, open” to open the plot file. Use “File, print” to print the plot file

winCMP (a program for converting oxide analyses into mineral formulae)

Each set of thermobarometric calculations uses a file that contains mineral compositions to compute displaced equilibria. Normally this file is created with the winCMP program (see below), and has the extension CM1, CM2, or CM3, depending on which version of thermodynamic data is used. This file contains all compositional information for one 'equilibrium assemblage' (unless a fixed activity for endmembers is interactively input during winTWQ operation). The expected compositional terms relate to the sites that are defined in the file defining solid solutions (DEC06.SLN, BA96a.SLN, JUN92.SLN) described below. The files CMPTEST.CM1, CMPTEST.CM2, and CMPTEST.CM3 can be used as templates for composition files compatible with version 1.02 (JUN92.SLN), version 2.02 (BA96a.SLN), and version 2.32 (DEC06.SLN) solid solution data, respectively.

Abbreviations for each mineral must match those used to define the solution phase (e.g. in files DEC06.SLN, BA96a.SLN, JUN92.SLN). The order and number of entries for each phase corresponds to the number of components and number of sites upon which mixing takes place in the solution phase. All compositions are input as mole fractions, which can be up to 6 digits including the decimal point. They must be aligned within the square brackets of the appropriate component on the preceding line.

For convenience in some situations, you can also put in fixed activities for any phase component that override fixed activities specified during interactive input or in the restart file. These fixed activities are input in the compositional file by typing lines as follows (capital letters must be used):

```
FIXED ACTIVITY
SILLIMANITE=0.9
ORTHOENSTATITE=.5
ENDFIX
```

The phase names must match exactly those used in the thermodynamic data file. If the activities are less than 0, they are assumed to be natural log activities. Any activities input in this way are applied during the calculation, even if activities are further reduced based on mineral compositions that may be present in this file.

winCMP.EXE provides an easy way to make a CMP file for some solid solutions (see list below). Type in your oxides as shown in the sample file CMPTEST.OXI - the order of oxides is not important as long as the order is specified on the second line. A file of this format can usually be obtained directly from the microprobe. The program scans the first part of each line for key letters that identify which mineral the analysis corresponds to:

b=biotite, f or p=plag, o=opx, g=garnet, c=cpx, h or a=amph, cd=cord, i = ilmenite; ol=olivine; s=spinel; k=K-feldspar; z=any other FeMg mineral (for which only XFe and XMg will be calculated)

The file winCMP.FIG controls how many comment lines precede the oxide list line, and also the starting column that is searched for the above mineral abbreviation. Please note: the most common

way to crash this program is to have the wrong abbreviation for the analysis, ie. if “h” occurs before “p” in the label, the program assumes it’s an amphibole, not plagioclase. winCMP.EXE assumes the input file has the .OXI extension, and output is interactively directed to a file with the .CM1, CM2, or CM3 extension, depending on the version of thermodynamic data to be used in the calculation. Additional graphics file output is written to XXXX.p files (XXXX is garn, plag, opx, cpx, cord, biot depending on which minerals are in your input file. Use winTWQ's winPLOT.EXE to view these files on screen, wPLOT.EXE to view and print these files, or winDXF to convert them to DXF files that can be imported into a number of different graphics packages (e.g. CorelDraw or AutoCad).

For the minerals below other than biotite and amphibole, Fe³⁺ can be calculated by stoichiometry, but, in general this is not recommended due the extreme sensitivity to microprobe errors for SiO₂, and because thermodynamic calibrations mostly assumed Fe²⁺ in experimental run products. For most FeMg minerals, the CM1 or CM2 files will show Fe³⁺ cations that are calculated by stoichiometry, and the amount used in the structural formula (zero if this option was selected). For version 2.32, an option has been added to estimate Fe³⁺ in biotite (12% of total Fe) and garnet (3% of total Fe).

Below are the mole fractions required for specific phases:

Summary of site fractions compatible with version 1.02 solid solutions (JUN92.SLN):

The following is a list of the mole fractions compatible with version 1.02 solution models.

```
GARN [-Gr-][-Py-][-Alm][-Sp-]
GARN  .072  .112  .789  .027
MICA [-xK-][-xNa][xAl-][-xOH]
MICA  .826  .174  .913  1.00
BIOT [xMg-][xFe-][-xTi][-xAl][-xK-][-xOH]    Note: 3 equivalent
octahedral sites
BIOT  .384  .431  .038  .147  .870  .970
PLAG [-An-][-Ab-][-Or-]
PLAG  .277  .719  .004
CPX  [MgM1][AlM1][FeM1][CaM2][NaM2][FeM2]
CPX   .58   .14   .28   .84           .16
OPX  [xMgM1][xFeM1][xMgM2][xFeM2]
OPX   .340  .630  .35   .64
CORD [xMg-][xFe-]
CORD  .430  .550
AMPH [NaA ][K A ][v A
][MgM2][FeM2][AlM2][Fe3M][TiM2][CaM4][MgM4][FeM4][MnM4][MgM1][FeM1
][MnM1][SiT1][AlT1][O O3][OH03][F O3]    See Mader et al. 1994, Can
J Earth Sci, 31, 1134-1145
AMPH .3885 .2907 .3208 .2849 .2704 .1978 .1613 .0857 .9480 .0015
.0505 .0000 .2394 .7565 .0041 0.6079.3921 .0857 .9143 .0000
```

Summary of site fractions compatible with version 2.02 solid solutions (BA96a.SLN):

Opx: 1-site model with En-Fs-Ok (orthocorundum) endmembers.

M(1):xEn,xFs,xOk

where, for a 6-oxygen formula,

$$xOk = Al/4$$

$$xFs = Fe/2$$

$$xEn = Mg/2$$

Nonideal Mg-Fe-Al interactions are given by Berman & Aranovich (1996)

Cpx: 2-site model with equal partitioning of Fe-Mg between sites, octahedral Al assumed to be tschermakitic, except for jadeite component (=Na)

M1(1):xMg,xFe,xAl,xTi-M2(1):xCa,xMg,xFe,xNa

$$Na = Na - Fe3 \text{ (acmite)}$$

$$AlM1 = Na + (Al-Na)/2 \text{ (increase AlM1 by jadeitic Al)}$$

$$mgfe = Mg/(Mg+Fe2)$$

$$sum1 = 1 - Ti - AlM1 - Fe3$$

$$FeM1 = (1 - mgfe) * (sum1)$$

$$MgM1 = (mgfe) * (sum1)$$

$$Sum2 = 1 - Na - Ca - Mn$$

$$FeM2 = (1 - mgfe) * sum2$$

$$MgM2 = (mgfe) * sum2$$

Nonideal Mg-Fe-Al interactions are given by Berman & Aranovich (1996a)

Biotite: 4-site model assuming Al, Ti on 1 M1 site (Circone & Navrotsky, 1993); random mixing on 4 tetrahedral sites

M2(2):Mg,Fe,F3-M1(1):Mg,Fe,Ti,Al,F3,v-T(4):Al,Si-A(1):K

Nonideal Mg-Fe-Ti-Al mixing corrections are given by Berman & Aranovich (unpublished data)

Garnet

C(3):xCa,xMg,xFe,xMn

Nonideal Mg-Fe-Ca-Mn interactions *based on* analysis of Berman & Aranovich (1996)

Cordierite

M1(2):xMg,xFe

Nonideal Mg-Fe interactions *based on* analysis of Berman & Aranovich (1996)

Olivine

M(2):xMg,xFe

Nonideal Mg-Fe interactions *based on* analysis of Berman & Aranovich (1996)

Ilmenite

M(1):xMg,xFe, xMn

Nonideal Mg-Fe interactions *based on* analysis of Berman & Aranovich (1996)

Mica

A(1):K,Na-M(2):Al-H(2):OH

Nonideal mixing corrections for K-Na are available from Chatterjee & Froese (1975).

Plagioclase

I(1):Ca,Na,K

Nonideal Ca-Na-K interactions are given by Fuhrman & Lindsley (1988).

Spinel

X(1):Mg,Fe-Y(2):Al

Nonideal Mg-Fe interactions are given by Berman & Aranovich (unpublished data)

Note that winCMP also writes the file:

HBPL.DAT – contains amphibole and plagioclase analyses in a format that can be run with Holland & Blundy's HBPL program

Summary of site fractions compatible with version 2.32 solid solutions (DEC06.SLN):

Same site assignments as version 2.02 above, except for biotite, with solution properties of ol, opx, grt, cd, ilmenite following the analysis of Berman and Aranovich (1996, CMP, 126, 1-24).

Biotite: 4-site model assuming Al, Ti on 1 M1 site (Circone & Navrotsky, 1993); random mixing of Al-Si on 2 tetrahedral sites

M2(2):Mg,Fe,Fe³⁺-M1(1):Mg,Fe,Ti,Al,Fe³⁺,v-T(2):Al,Si-A(1):K

Nonideal Mg-Fe-Ti-Al mixing corrections are given by Berman & Aranovich (unpublished data), with Mg-Fe-Al interactions following the analysis of Berman & Aranovich (2006, AmMin, in review)

winCLEAN.exe (convert plot files for import into graphics packages)

This program is used to clean up the appearance of plot files (e.g. plot.PLT from winTWQ) by repositioning labels so that they do not overlap. Output files are ****.CLN (the new plot file) and ****.LST (listing the equilibria with numbers that may be used on the new plot), with **** being the prefix of the original plot file name.

winDXF.exe (convert plot files for import into graphics packages)

This program is used to convert plot files (e.g. plot.PLT from winTWQ, plot.CLN from winCLEAN.EXE, and ****.P files from winCMP.EXE) to DXF files read by AUTOCAD, CORELDRW, etc.

Some options are:

1. # of output files; the 4 files will separate lines, axis tic marks, axis labels, and labels onto different layers
2. convert bars to kilobars

winTERSX.exe (average P-T results from equilibria intersections)

This program reads the plot file generated by TWQ and computes an average P and T (or other axis variable) from all intersections between curves, weighted towards those equilibria with the highest ΔS , ΔV and smallest $\ln K'$, and which intersect most orthogonally. See Berman (1991, CanMin, 29, 833-856) for details.

Input the name of the plot file to be averaged (e.g. myrk1.plt), and the thermodynamic data files used by winTWQ.exe to compute the plot file (check near the top of the plot file if you have forgotten!). The default thermodynamic data files set in the winTWQ.fig file are shown at the bottom of the screen. You can override these files by clicking on the buttons for version 1 or version 2 thermodynamic data. Output is written to the file "myrk1.avg". If you want to average results at a fixed pressure or temperature (not both!), input the pressure in kbar or temperature in degrees Celsius.

Some control over the results of this program are possible by changing the slope difference in the winTWQ.fig file. This value is the limit below which two equilibria are considered to be parallel and discarded from the calculations. Generally, use of a limit less than 20 degrees results in less robust solutions, but in calculations with only several equilibria a lower limit must be used to obtain any results whatsoever. You can also average selected equilibria by making a copy of the plot file and deleting unwanted equilibria. Plans are afoot to make this process easier in later versions.

Batch Runs (for winCMP, winTWQ, WinTERSX):

Operation in batch mode is useful particularly in order to perform the same calculations on a number of different composition files, whether these are for a number of different samples, or whether they are "perturbed" compositions for one sample used for Monte Carlo error analysis. Batch mode can be used to run WinCMP, WinTWQ, or WinTERSX.

1. Use the template in the file “BATCH.DAT” to specify on each line: path, restart file, file with endmember thermo data, file with solution properties, file containing a list of composition files that will be used in the batch run, and finally the extension of the composition file used with winTWQ.
2. If an asterisk occurs before a file name, the file is assumed to be located in the present directory, not in the directory given by the path specified in BATCH.DAT.
3. The path is limited to 40 or fewer characters
4. The path+composition file name is limited to 60 or fewer characters
5. Run the program, checking the “Batch Run” box.
6. A summary of the TWQ batch run results is listed in the file BATCH.LOG.

In the example of BATCH.DAT below, calculations will be performed on the files listed first in \cc\fer\samples.dat, then in \cc\ghe\samples.dat, \cc\hoi\samples.dat, and finally in \cc\hua\samples.dat. Any number of files can be listed in the samples.dat; any number of lines can be specified in BATCH.DAT:

```
c:\cc\FER\,*92gchps.res,jun92.gsc,jun92.sln,samples.dat,cm1
c:\cc\ghe\,*92ghps.res,jun92.gsc,jun92.sln,samples.dat,cm1
c:\cc\hoi\,*96gops.res,ba96a.dat,ba96a.sln,samples.dat,cm2
c:\cc\hua\,*96gcps.res,ba96a.dat,ba96a.sln,samples.dat,cm2
```

NOTE: Note that the file extensions given in samples.dat should be either CM2 (if winTWQ version 2 is used) or CM1 (if winTWQ version 1 is used).

NOTE: The files BATCH.DAT and SAMPLES.DAT must be text files without any formatting!

TWEEQU (version 1.0)
 Thermobarometry With Estimation of EQUilibration state
 February 9, 1992

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 RECOMMENDED CITATIONS:

When publishing thermobarometric results calculated with this software, please cite the program itself (Berman, 1991) as well as the thermodynamic data used, including end-member properties (Berman, 1988; 1990) and the solid solution models that you used (see below). Full references are listed near the end of this document.

 INTRODUCTION

TWQ (version 1.0) replaces what used to be called PTAXSS. It is basically the same program but has been renamed to better distinguish it from the UBC distributed GE0CALC program called PTAX. The new name, abbreviated from TWEEQU (Thermobarometry With Estimation of EQUilibration state) emphasizes the important thermobarometric

application of being able to test the assumption that all mineral compositions used in a calculation last equilibrated at the same P-T. For the perfectly behaved system (all minerals equilibrate at same P,T; perfectly known mineral compositions, standard state and mixing properties), the calculated phase diagrams should have all equilibria intersecting at a unique point. So much for perfection! The degree of scatter in the intersections gives an indication of the validity of these assumptions as well as a qualitative measure of the uncertainties in the calculation. In many cases, this uncertainty can be substantially reduced by omitting from the calculations minerals for which standard state or mixing properties are poorly known. As we gain more confidence in thermodynamic properties it should be possible to use this program to tell whether all minerals equilibrated at the same P-T conditions. See Berman (1991) for a detailed description of the philosophy of this program and several examples of applications.

Several TEST files have been included on the distribution disc so that you may make sure you are using the software correctly. Run TWQ and include the elements: K Fe Mg Ca Al Si O H when requested. On the next screen include the endmembers: ALMANDINE, ANNITE, ANORTHITE, GROSSULAR, MUSCOVITE, PHLOGOPITE, PYROPE, ALPHA QUARTZ, SILLIMANITE, all with default activities equal to unity. On the next screen, type 'a' to take the default solution models. Type TEST.CMP for the file of compositional data. The program should calculate all equilibria and produce a file PLOT.DAT that should be identical to the file TEST.PLT on the distribution disc. View this file by typing PLOT PLOT.DAT. Run CLEAN, take all defaults, and you should get a file named CLEAN.DAT that is identical to the file TEST.CLN. View this file by typing PLOT CLEAN.DAT. Run INTERSX, type TEST.CMP when asked for the file of compositional data, and you should get averaged results in the file PLOT.AVG that are identical to those in the file TEST.AVG. View these results using any text editor or by typing TYPE PLOT.AVG at the DOS prompt. Full instructions for running all programs are given below.

If you wish to be informed of upgrades of this software and associated data (e.g. amphibole, biotite, orthopyroxene, clinopyroxene endmembers and solution properties) send a BITNET/INTERNET message to: BERMAN@GSC.EMR.CA.

A Macintosh version of this program will be available sometime in 1996 from Martin Engi. You can reach him at "engi@mps.unibe.ch".

Note to GE0-CALC users: Since 1992, PTAX has been completed. This program combines GE0-CALC's earlier PTX and PTA programs into one program, and adds the general solid solution equations incorporated in TWQ. It will be distributed for a modest fee by:

GE0-CALC SOFTWARE
Department of Geological Sciences
University of British Columbia
Vancouver, British Columbia, Canada V6T 2B4
604-228-4653

The only difference between PTAX and the enclosed program, TWQ, is that the latter program is designed specifically for thermobarometry applications. It always calculates and plots all equilibria whether they are stable or metastable (both are equally informative). You will have to order PTAX through the above address if you wish to compute stable phase diagrams with all metastable extensions removed.

 HIGHLIGHTS FOR 'OLD-TIME' USERS (look below for details):

Changes in the latest TWQ version (v 1.01):

- Bugs in fluid choice routine removed (discard results using fluids with TWQ (v 1.0)
- INTERSX correctly prints the number of independent reactions

The newest features that have been added to TWQ (v 1.0):

- A new program (INTERSX) reads the plot file generated by TWQ and computes an average P and T (or other axis variable) from all intersections between curves, weighted towards those equilibria with the highest ΔS , ΔV and smallest $\ln K'$, and which intersect most orthogonally. To use this program after TWQ, type INTERSX, and the output will be directed to the file PLOT.AVG as well as to the video monitor.
 - A new plot program (PLOT) replaces PLOTS, and offers mouse support, menu options, multiple file reads, change saves, and more graphics card support. The PTAXCON.FIG file is set up for a VGA card and monitor ("/e:5") at end of first line. Change this to "/e:4" for EGA cards. See the more detailed notes below.
 - Multi-site mixing: Multisite nonideal mixing can now be handled in a general way (see below) by defining mixing models in the file SOLID.SLN (replaces MINERAL.SLN).
 - Note: Old CMP files will work with the new program, except for OPX compositions. These need to be entered anew (see below).
 - Activities of any phase can be fixed in the CMP file that gives mineral compositions (see below).
 - Operation in 'batch' mode
 - New equation of state for CO₂ that better extrapolates to high P Mader & Berman (1991)
 - Endmember and mixing properties of amphiboles. See Mader & Berman (1992).
- Other less recent changes that have been added over the last two years:
- Bug which kept the hydration model for cordierite from being applied has been corrected
 - Optional suppression of printing of the SUMMARY.DAT file
 - The early versions of PTXSS had unfortunate inconsistencies in the properties of Fe-cordierite, staurolite, hercynite, and chloritoid (FEB89.RGB). These were introduced when almandine properties were revised to accommodate garnet mixing properties (Berman, 1990). These inconsistencies have now been removed (NOV89.RGB).
 - A typo on the Cp of hydrogen gas has now been corrected (FEB90.RGB)
 - The Nov89 version of PTAX did all mixed volatile calculations with ideal H₂O-CO₂ mixing. This is now corrected.
 - Annite properties adjusted slightly (AUG90.RGB) due to analysis of natural data yielding nonideal Ti,Al mixing parameters in biotite (McMullin et al. 1991).

 OVERVIEW

TWEEQU is a software package consisting of a program for calculation of phase equilibrium curves, a thermodynamic database for minerals, and auxiliary programs for plotting, printing, and averaging of computed curves. The minimum hardware requirements for using this software are a IBM-compatible personal computer with 640 K memory, math coprocessor, and

graphics card (CGA, EGA, VGA, or HERCULES).

The main part of this package is the FORTRAN 77 program TWQ which calculates phase equilibria in pressure-temperature (P-T), temperature-composition (T-XH₂O-CO₂), pressure-composition (P-XH₂O-CO₂), T-activity, P-activity, or activity-activity sections. The program structure and equations of state are discussed briefly in Appendix II. The output of TWQ can be plotted for visual representation or inspected from a table. The program evaluates all possible reactions in the user-specified compositional and PTX space, and labels each equilibrium curve.

This software is distributed with the thermodynamic database of Berman (1988), but options for a variety of other equations of state are provided so that the programs can be used with different data sets. Run time options include setting the P, T, X limits of the diagram, the selection of ideal or non-ideal H₂O-CO₂ mixing, choice of solid solution models, the specification of fixed phase activities, and the choice of mineral compositions read from an external file.

TWQ allows one to calculate any equilibrium curve using the variables P, T, XCO₂, or activity. The user should be ever aware that the accuracy of calculated phase diagrams is a direct function of the quality of thermodynamic input data. The database distributed with this software is that presented by Berman (1988) and modified by Berman (1990) for the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂. Details of the procedure used to derive this data set are given by Berman et al. (1986). Appendix I shows the list of minerals in the database along with their chemical formulae, abbreviations, and reliability levels (see Berman, 1991 for a description of the reliability definitions). Users should be aware that calculations involving reliability level 3 phases should be interpreted with some caution, and that feedback on which phases seem to give reasonable results and which don't is required (and appreciated!) in order to improve some of our thermodynamic representations of these phases.

I strongly discourage users from replacing or modifying any parameters in this data set because doing so will destroy the internal consistency of the database. Users may wish to add phases which are not included in the data set, and I advise reading the Berman et al. (1986) paper cited above for guidelines of how best to derive reliable thermodynamic parameters.

Also note: This software has been tested extensively, and reasonable efforts have been made to remove ambiguities and known bugs. Nevertheless, I can safely assume that some problems have escaped our detection. If you do have problems with this software, I ask your patience in dealing with them and remind you that this software is distributed as a research tool, not as a guaranteed commercial product. Please do not phone for help unless absolutely necessary. I will be happy to assist you in solving problems, but the most efficient way to receive help is to describe the problem in a brief letter including a self-addressed envelope for return. Also include a high density floppy disc that contains the input/output files (RESTART.RES, SUMMARY.DAT, and PLOT.DAT) that were used/generated during the problem run. This will provide me with the necessary information to solve your problem. The floppy disc will be used to respond to you, and include any program/data modifications that are necessary.

The most common steps in using this software package are:

- 1) Setup computer for TWQ operation
- 2) Use text editor to make files containing analytical data for minerals
- 3) Use TWQ.EXE to calculate phase equilibria
- 4) Use CLEAN.EXE to improve legibility of phase diagram
- 5) Use PLOT.EXE for an on-screen preview of phase diagram
- 6) Use PRINTER.EXE or LASER to make high resolution hard copy
- 7) Use INTERSX.EXE to compute average thermobarometric results

Each of these steps is described in detail below.

----- SETUP/CONFIGURATION

Most users will want to keep this software in a directory which I assume will be called 'TWQ'. Use the DOS command 'MKDIR TWQ' to make this directory, and then 'CD TWQ' to change to this directory. Copy all files on the two distribution discs to your hard drive using the DOS command: 'COPY a:*. *'.

Before you run TWQ, you must configure your system to allow a minimum of 20 files to be open. Using any line editor, edit the DOS file 'CONFIG.SYS'. Add the line:

```
FILES=20
```

If you do not have the 'CONFIG.SYS' file in your root directory, you must create first it (see your DOS manual for details). Before running PT-System, you need to restart your computer so that this file is processed. Press the 'CTRL', 'ALT', and 'DEL' keys simultaneously to reboot your system, or turn your computer off and then on again.

The file 'PTAXCON.FIG' contains information on lines 1-4 related to the hardware being used to run these programs, default names for input/output files on lines 5-10, and default options on lines 11-14. If this file is not found by the program, default names (same as below) stored by the program are assumed. The file as distributed contains the following lines:

```
EGA,GRAPH/e:5
COLOR,01,14,05,07
EPSON
HARD DISK
PLOT.DAT
JAN92.RGB,HKF81.AQU
RESTART.RES
SUMMARY.DAT
CLEAN.DAT
CLEAN.LST
METASTABLE CURVES
NO SUMMARY
DON'T PRINT ACTIVITIES
SLOPE DIFF=20
```

With a text editor, change these values to match your system configuration. Each line specifies:

1. Graphics card (EGA,CGA,HERC); GRAPH or TEXT mode for TWQ operation.
The characters after the '/' are used by the PLOT.EXE to specify the type of graphics card your system has. The various options are listed in the file CARD.DOC.

2. COLOR or MONOCHROME monitor (#'s give different color choices)
3. EPSON or OTHER type of printer
4. HARD or FLOPPY disc system configuration
5. Default name of plotfile generated by TWQ
6. Default names of mineral and aqueous species thermo data files
7. Default name of restart file
8. Default name of file summarizing results in tabular form
9. Default name of plotfile generated by CLEAN program
10. Default name of file that lists equilibria made by CLEAN program
11. ignored by TWQ
12. SUMMARY or NO SUMMARY - controls printing of text summary file
13. PRINT or DON'T PRINT 'SCR' file that contains computed activities for each mineral component at each point on all computed equilibria (this file can get lengthy!)
14. SLOPE DIFF=20 (change this value to control the lower limit that INTERSX uses for testing for parallelism of two equilibria)

 DEFINITION OF SOLUTION PHASES

All solution minerals (limited to 12 in this version) are defined in the file SOLID.SLN. The SOLID.SLN file on the distribution disk contains calibrations for computing activity coefficients for garnet, plagioclase, biotite, white mica, orthopyroxene, and clinopyroxene. Additional calibrations (up to 4 per mineral) for these and other minerals (up to the maximum of 12) can be added as long as the entropy of mixing of these minerals can be described by the random distribution of cations over energetically equivalent sites (see below). The calibrations included in this version of TWQ include:

garnet - Berman (1990); Berman & Koziol (1991)
 plagioclase - Fuhrman & Lindsley (1988)
 biotite - McMullin et al. (1991)
 mica - Chatterjee & Froese (1975)
 opx - ideal mixing (Newton, 1983)
 cpx - ideal mixing (Newton, 1983)

When reported thermobarometric results, be sure to state that these models were used. Other calibrations can be added (carefully!!) as described below. (Note carefully that the properties of annite were derived from Ferry and Spear's (1978) garnet-biotite data, and are thus linked to the Fe-Mg mixing properties of garnet. If you include annite in a calculation you MUST use the Berman(1990) garnet model for consistency. If you want to use another calibration of Fe-Mg garnet mixing, then change the annite properties in the file JAN92.RGB to regain consistency with Ferry and Spear's garnet-biotite data.)

A brief description of the format of the SOLID.SLN file is given below in order that solution parameters can be updated as each model is refined and so that additional solution phases can be added. Each solution phase is defined in blocks with this format:

```
BIOT 2      Biotite
M(3):Mg,Fe,Ti,Al-A(1):K-H(2):OH
PHLOGOPITE      Mg(3)-K(1)-OH(2)
ANNITE          Fe(3)-K(1)-OH(2)
M90      McMullin (1991)
1-13      58865.
```

```

1-14      75000.
1-23      30921.
1-24      63721.
END
IDEAL
END

```

The first line gives a four character abbreviation, the number of components, and up to 20 character name for the phase. (Any abbreviation can be used with the exception of that for plagioclase (PLAG), which has a specific section of the program (accessed with this abbreviation) devoted to calculation of the idiosyncracies of its solution model. The block ends with a blank line. The second line of the block defines the different sites and all cations assumed to occur on these sites for the purposes of the calculation. The format is the name of the site (up to 2 characters), the site multiplicity in parentheses, a colon, followed by a list of all species on this site (maximum of 2 characters for each, separated by commas); each site is separated from the next by a hyphen, except for the last. The maximum number of sites per solution is 4, and species per site is 5.

Next the name of each component is written on separate lines (in order for activity coefficients to be calculated for these components, these names must match the names of the phases as defined in the thermodynamic database (JAN92.RGB). No spaces are allowed in these names. A maximum of 8 components is allowed for each solution phase. For each component, the name and number of cations on each site of the phase are defined as in the examples above.

Each solution phase may contain up to 5 alternate sets of solution parameters which are defined on the lines after the name of the components and before the blank line signifying the end of the definition of each solution phase. Each set begins with a string of up to eight characters which uniquely identifies the solution parameter set. 'IDEAL' is reserved for use with ideal solutions. Each set ends with an END line. Any lines occurring between the first line and the END line are assumed to give parameters (maximum of 20) for a general Margules solution (Berman and Brown, 1984). Each line contains up to four entries:

- a) an integer followed by a hyphen defining the number of the site this parameter applies to, and abbreviation in terms of up to 4 subscripts of the interaction parameter (for symmetric models: W12; for asymmetric models: W112,W122);
- b) excess enthalpy parameter (WH);
- c) excess entropy parameter (WS); and
- d) excess volume parameter (WV).

Also note that all parameters are in Joules per mole, not per cation, and that if the Wohl(1953) equation is desired, the ternary constants must be converted for use with the Berman and Brown (1984) general Margules equation:

$$nRT \ln G_m = \text{Sum for all parameters of } Q_m X_i X_j X_k \dots X_p / x_m - (p-1) X_i X_j X_k \dots X_p$$

where n is the site multiplicity, p is the number of subscripts (degree of polynomial used for G_{excess}) and Q_m is the sum of how many of the ijk...p subscripts are equal to the m subscript. For a third degree polynomial (asymmetric) model, Wohl ternary parameters (C_{ijk}) are converted to ternary parameters given by the

above equation (Wijk) by:

$$Wijk = (Wiij + Wijj + Wiik + Wikk + Wjjk + Wjkk)/2 - Cijk$$

In other words, if you want to set the Wohl ternary $Cijk = 0$, then the Wijk ternary entries in the SOLID.SLN file should be set equal to the sum of the parameters of the three bounding binaries, all divided by 2.

----- TWQ OPERATION

You are now ready to run TWQ. In the following description CR refers to the 'carriage return' key, ESC refers to the key labelled 'ESC', and ^ followed by a letter (e.g. ^Q) indicates that the 'CTRL' key should be pressed at the same time as the letter.

Type 'TWQ' followed by CR. The first of several screens requesting input will appear.

FIRST SCREEN (DIAGRAM TYPE, FILE ASSIGNMENT): Move the cursor with the right or left arrow key or the space bar to the type of diagram you wish to calculate.

Type ESC to continue.

The default files for input and output will appear in a window on the screen. If you wish to change any of these files, use the up or down arrows to move to the file to be changed, and type the new file name (including the drive designation and directory if these are different from the current drive and directory), followed by CR. Type ESC to continue after all files are selected. If any of the selected files cannot be found, this screen will repeat. Note: the only valid files for unit #5 (interactive input) are 'CON:' (the console) or 'RESTART.RES' (the file containing a list of the responses used in calculating the last phase diagram). If a file other than these is typed, unpredictable results can be expected.

SECOND SCREEN (GLOBAL OPTIONS): Enter the elements in the desired chemical system, separated by blanks or commas, and followed by CR. There is no default set of elements. The phases provided in the database distributed with this software (JAN92.RGB) are composed of the elements: Na, K, Ca, Mg, Fe, Al, Ti, Si, O, H, and C. Any combination of these elements may be typed in response to this question. Don't forget oxygen!

After a CR is typed, the cursor will move to the portion of the screen where the default limits (minimum and maximum pressure in bars, temperature in degrees Celsius, mole fraction of CO₂) of the phase diagram can be changed. If you wish to change any of these values, select the value(s) to be changed with the cursor, and type the new value(s) (don't forget a decimal point) followed by CR.

If you are calculating a P-T diagram and want a gas phase to be present, move the cursor to the line showing the mole fractions of gas species. The default values for all gas species are '0.0'. Use the cursor or space bar to select the value(s) for any species to be changed, and type the new value(s) (with a decimal point) followed by CR. For example, if you want the gas to be pure H₂O, change the first '0.0' to '1.0'. If you wish the gas to be pure CO₂, change the second '0.0' to '1.0'. If you want to

use a specific H₂O-CO₂ mixture, change both of the first two values, such that they sum to 1. Note: If you select non-zero mole fractions for both gas species, the program forces them to sum to 1. If you make a mistake and need to change either or both of these non-zero values, you will need to first reset one of the mole fractions to zero, and then type in the desired mole fractions. This procedure must be followed in order to bypass the built-in function that checks the sum of the mole fractions of both gas species.

If the mole fraction of either H₂O or CO₂ is specified to be non-zero, or if you are calculating a T-XCO₂ or P-XCO₂ diagram, the equation of state used to calculate gas properties will be highlighted. Move the cursor to the abbreviation of the model you wish to use for calculation of fugacities of pure gases. If the mole fractions of both H₂O and CO₂ are non-zero, the default option of non-ideal mixing using the equation of state of Kerrick and Jacobs (1981) is highlighted. Other options can be selected by moving the cursor to the appropriate field and typing CR. Note: The Kerrick and Jacob mixing model does not work below about 350°C. If you choose this mixing model, the program will set the minimum temperature of the diagram to 350°C if the requested temperature is below this value.

Note: The thermodynamic data of Berman (1988; 1990) were derived using the Kerrick & Jacobs equation of state for pure CO₂ and H₂O-CO₂ mixing, and the Haar et al. (1984) equation for pure H₂O. To preserve the internal consistency of this database these same models should be used in calculations, although the model of Mader & Berman (1991) for pure CO₂ has been derived in such a way as to also preserve this consistency.

In the TWQ program, one cannot specify that stable segments of equilibrium curves be plotted. To implement this option, you will need to purchase GEO-CALC's PTAX program (see above). In addition, there is a choice of using full mineral names or abbreviations (the default). To change the default values for either of these options, select your choices with the cursor and type CR.

When all choices have been made, type ESC to continue to the next screen. Note that only the elements in the system need be specified to calculate a phase diagram. For all other choices, the default options can be used. At any time in the selection of the various options, the cursor can be moved up or down to correct previous entries.

THIRD SCREEN (ENDMEMBER SELECTION): After exiting the second screen, the program will read the thermodynamic database and put a list of endmembers in the selected chemical system on the screen. The user must select which endmembers are to be considered in the calculations and what their activities are (activity = 1.0 for pure endmember). In selecting endmembers, keep in mind that diagram complexity and time of calculation increase dramatically as the number of endmembers considered increases. Note: If you do not see an endmember that you wanted to consider, it means you did not type in the proper elements on the previous screen or that the endmember is not in the database. Type ^Q to exit the program and start again.

Initially all endmembers are assumed to be excluded from consideration. Move the cursor with the arrow keys to each endmember in turn that is to be included in the calculation. Type CR to include the endmember, or 'i' to include the endmember in all reactions that are

considered. After choosing one of these options, you are prompted for the activity of the endmember. Type the activity (don't forget the decimal point) followed by CR, or simply type a CR to accept the default activity of 1.0 (pure endmember). Any fixed activity that is input at this time will be applied in addition to that based on mineral compositions supplied (see below). If you want to remove a previously chosen endmember, move the cursor to this endmember, and type `-' . Note: Projecting from endmembers ('p') should not be used in the TWQ program. Including endmembers ('i') forces these endmembers in all reactions that are considered.

If you want to include all endmembers in a given calculation, type `a'. You are then prompted to confirm this action. Type `y' or `n'. Previous or subsequent selection of any option for a given endmember (`i' or `-') overrides the inclusion of endmembers with this `a' option. Thus, if you want to include all but several endmembers, you may find it more convenient to type `a', and then remove these few endmembers with the `-' option.

If more endmembers occur in the chemical system than will fit on one screen (45 endmembers), use the `PgDn' key to access these endmembers and proceed with the selection as described above. Press `PgDn' to view the next page of endmembers and `PgUp' to return to the previous page.

Once the endmember selection is complete, type ESC to continue to the next screen.

FOURTH SCREEN (SOLID SOLUTION MODELS): This screen only appears if one of the end-members that you included is defined as a component of a solid solution model defined in the file SOLID.SLN (defined below). A numbered list of all solution phases will appear. The default state is that no solution models are used. Type `a', `n', or an integer to select all, none, or a specific solution phase to be included. Default solution models (the first option for each solution phase defined in the SOLID.SLN file) for each solution phase are chosen if `a' is typed. If an integer is typed, the solution model options are listed; type the number of the option desired. When your selection is complete, type `ESC'. If any solution phase is to be included you will be prompted for the name of the file that contains mineral compositions (default file is ROCK.CMP). Type the name followed by a carriage return or type QUIT if you can't remember a valid file name. The calculation should then proceed with all equilibrium curves being displaced with fixed activities input on the previous screen as well as activities computed for the compositions of minerals in ROCK.CMP and the solution parameters chosen from SOLID.SLN.

If any solution models are used, a record of these as well as the file containing mineral compositions appears in the upper right corner of the plot output.

A major advantage of this program is that it is set up to allow one to see the sensitivity of results to choices of solution models. This is accomplished most easily by editing the RESTART.RES file (contains a record of the last TWQ run) to change the name of the solution model desired for each solution phase to any of the models assigned in the SOLID.SLN file. It can also be done in batch mode, by referring to different `restart' files on each line of the BATCH.DAT file (see below).

NOTE: GEO-CALC's original PTX program had specific solution models

defined for calcite, aluminous enstatite, and hydrous cordierite which were accessed through a solution model menu similar to that described above. In the thermodynamic database accompanying the present version, only those for the variable hydration of cordierite have been retained. Two mineral names appear. If CORDIERITE, or FE_CORDIERITE are selected the hydration model is used. If CORDIERITE (DRY), or FE_CORDIERITE (DRY) are selected the hydration model is not used.

FIFTH SCREEN (CALCULATION OF DIAGRAM): At this point the program proceeds to calculate the phase diagram by considering one reaction at a time. The progress of the calculation is summarized either in TEXT or GRAPH mode, depending on which option is specified on the first line of the PTAXCON.FIG file.

In text mode, progress is summarized on a screen which contains three windows. The top window indicates how many reactions are possible among the selected phases. The maximum number that can be printed is 2 billion, although there is no limit to the number that may be calculated. In addition, this window displays the clock time at which the calculation began. The middle window shows the current reaction being examined, the clock time at the beginning of calculation of this reaction, and the status of the reaction. The bottom window gives the running total of the number of reactions examined, calculated, that have portions written to the plot file, and an estimate (very approximate) of the percentage of reactions remaining to be calculated.

In graph mode, the program's attempts to locate and follow each equilibrium curve is viewed on the video monitor. The current equilibrium is printed at the top of the screen, and approximate percentage remaining at the bottom of the screen.

You may switch between modes by typing ^T or ^G. You may QUIT, PAUSE, or STEP through the calculations by typing ^Q, ^P, or ^S. These commands take effect after the current reaction is completed.

When the diagram is complete, the results are summarized on the final screen which shows the clock time at the beginning and end of the calculation, the number of reactions examined, and the number plotted. Type ESC to finish execution of TWQ and return to DOS.

If selected on line 12 of the PTAXCON.FIG file, the results of the phase diagram calculation may be seen in tabular form in the SUMMARY.DAT file. Type `TYPE SUMMARY.DAT' to display the results on your monitor. The SUMMARY.DAT file is 132 columns wide and should be printed by first typing `MODE LPT1:132,8' to set up the printer for condensed printing. Then type `PRINT SUMMARY.DAT' and the file will be printed on your attached printer. See your DOS manual for further explanation of the TYPE , MODE, and PRINT commands.

If the second to last line of the PTAXCON.FIG file contains the string "NO SUMMARY", then the program will not write the calculated equilibria to the SUMMARY.DAT file. For those of us who make exclusive use of the plot output (PLOT.DAT), the size of the SUMMARY.DAT file can be annoying, especially on batch runs.

The results may also be viewed in graphical form using the PLOT.EXE, PRINTER.EXE, or LASER.EXE programs described below.

RERUNNING TWQ WITH MINOR CHANGES: Use of the RESTART.RES file to recalculate phase diagrams is extremely efficient for performing repetitive calculations with different files of mineral compositions and different options for selected solution models. Almost any changes can be incorporated by editing this file, the two exceptions being when a) a different chemical system is used, and b) when a different type of diagram is chosen (e.g. TX instead of PT). Examples of common changes to the restart file are:

- a. change P, T range of diagram
- b. change phases included (0 = include; 1 = exclude)
- c. change fixed activities of any phase
- d. change solution models selected
- e. change file containing mineral compositions
- f. change fluid phase options

Rerunning TWQ with a different set of mineral compositions: The first line after the list of minerals present in the chemical system selected during the last TWQ run gives the name of the file containing the compositions of all minerals in a given rock. Change this name to that of another file with different mineral compositions, and rerun TWQ. If no general solution models were used on the previous run, the first 15 columns of this line will be blank.

Rerunning TWQ to see the effect of different solution models: The lines after that giving the name of the file containing the mineral compositions show which solution model was used on the previous TWQ run for each solution phase. The first character will be "Y" or "N", depending on whether the model was used. The next field of eight characters (separated from the previous field by 1 space) indicates the specific solution model selected for each mineral. These keywords are defined for each possible solution model in the SOLID.SLN file. The last field of 20 characters (separated from the first by 1 space) shows the name of the solution phase.

Note: the last few lines of the restart file contain the stoichiometry of any reactions that were found to be stable on the last run of TWQ. The default operation is that the program always computes all possible reactions on each run. If you want to only calculate the reactions that were stable on the last run of TWQ, change the alignment of the last digit of the second line of the file by moving it one column to the left.

2. Rerunning TWQ
 - a. Type TWQ
 - b. Select type of diagram <ESC>
 - c. Type ^R

AUXILIARY PROGRAMS

PLOT.EXE: This program displays graphical output on video monitors using various graphics cards. Appendix IV lists these graphic cards and the code ('/' followed by 1 or 2 characters) that should be added to the PTAXCON.FIG file or to the end of the command line. To execute this program, type `PLOT file/?', where file is the name of the file containing the graphical output

(the default output file of TWQ is PLOT.DAT), and ? is the appropriate code listed in Appendix IV for your graphics card. You can change the default colors by appending four 2-digit numbers between 0 and 15, beginning with and separated by commas, to the end of the second line of this file. The 4 numbers correspond to the default background, axis, message, and calculated curve colors.

Once the diagram is drawn, you are prompted for the next action. To access any of the menu commands, click with your mouse in the appropriate box, or type the first letter of the command. The options are:

- Type ESC or 'q' to quit the program.
- Type 'b' to blowup a portion of the diagram.

Crosshairs will appear near the center of the diagram. Using a mouse or the arrow keys, move the crosshairs to the lower left corner of the area you want to see enlarged and type CR. Repeat this process to select the upper right corner of the diagram. Note that the HOME, END, PGDN, and PGUP allow diagonal movements, and holding the SHIFT key with any of the others results in larger movements.

- Type 'o' to redraw the original diagram.
- Type 'n' to remove all labels from the diagram.
- Type 'r' to relabel the diagram.
- Type 'l' to add a label on the diagram.
- Type 'f' to superimpose another plot file on the present one.
- Type 'd' to delete a superimposed plot file.
- Type 'p' to plot symbols or draw lines.
- Type 's' to save a modified plot to a file of your choice.

PRINTER.EXE: This program makes high resolution hard copies of the graphical output on EPSON-compatible dot matrix printers. The file `CHARB.FON' must be in the directory.

After turning on your printer, type `PRINTER' or `PRINTER file', where file is the name of the file containing the graphical output (the default output file of TWQ is PLOT.DAT). The extension `.DAT' is assumed for this file and can be omitted. If the file name is followed by a period (`,`), the program assumes that the file has no extension. The first screen allows you to change this file name by typing the new name followed by CR. Press ESC to print the diagram. The complete diagram will take from 4-10 minutes to complete depending on the speed of your computer and printer.

LASER.EXE: This program makes high resolution hard copies of the graphical output on HP Laserjet printers. The file `CHARB.FON' must be in the directory. It runs the same way as PRINTER.EXE described above.

CLEAN.EXE: The graphical output (PLOT.DAT) of TWQ is often difficult to read because reaction labels overlap one another in reasonably complex phase diagrams. The TWQ.EXE program cannot improve diagram appearance because it deals with one reaction at a time and does not store information regarding label positions of previously calculated reactions.

The CLEAN program can be used to improve diagram legibility. This program reads the plot file, shifts label positions if there is space to write a label, or replaces labels with a number if there is not enough space for the entire label. Two output files are written: a more legible plot file (default name is CLEAN.DAT) which can be viewed using the PLOT.EXE, LASER.EXE, or PRINTER.EXE programs described above, and a file (CLEAN.LST)

that contains a numbered list of all reactions with the high pressure assemblage (in P-T or P-X diagrams) or the high temperature assemblage (in T-X diagrams) written on the left hand side of the equality sign. The numbers of each reaction correspond to any reaction numbers that are written in the improved plot file (CLEAN.DAT).

To run this program (after completion of the TWQ program), type 'CLEAN' or 'CLEAN file', where file is the name of the plot file to be cleaned. The extension '.DAT' is assumed for this file, and can be omitted. If the file name is followed by a period ('.'), the program assumes that the file has no extension.

The first screen gives you the option of changing the input/output files. If you do not want to use the default files, move the cursor to the appropriate field using the arrow keys or space bar, and type the new file name followed by CR. Type ESC to continue.

Next you are prompted for the size of all labels on the cleaned-up diagram. If you don't want the default label size (0.25), type the new label size, including a decimal point, followed by CR. If you type a CR alone, the default value is assumed. The lower limit for label sizes is 0.1. A few tries running this program with different label sizes, followed by printing the diagram with the PRINTER program will allow you to judge what label sizes to expect.

You are next shown the various global options which can be chosen for the new plot file. Type the number of the option you want (0 = default). If you prefer to select options for each reaction individually, type the numbers of each of these reactions, separated by a comma or a space. The global options are:

0: the default option of writing all labels that will fit, replacing labels with numbers centered on the curve, or, if numbers will not fit, replacing labels with numbers that are removed from the curve and connected to it with a dotted line.

- 1: no reaction labels are written
- 2: no reaction labels or numbers are written
- 3: numbers are forced on all reactions
- 4: labels are forced on all reactions
- 5: labels or numbers are forced on all reactions

If any number or numbers are typed other than those above, the program assumes that they refer to the numbers of specific reactions for which you want to choose separate options. After a CR is typed, the program will read all the data from the plot file and prompt you for specific options as each curve is processed. Specification of options for individual curves is most useful for refining the appearance of plot files on subsequent CLEAN-up runs. Note: The program CLEAN cannot be used to process the file produced by a previous CLEAN run; it only reads data in the specific format of PLOT.DAT, the plot file produced by TWQ.EXE.

INTERSX.EXE: This program reads the plot file generated by TWQ and computes an average P and T (or other axis variable) from all intersections between curves, weighted towards those equilibria with the highest ΔS , ΔV and smallest $\ln K'$, and which intersect most orthogonally. To use this program after TWQ, type INTERSX, and the output will be directed to the file PLOT.AVG as well as to the

video monitor. Some control over the results of this program are possible by changing the slope difference on the last line of the PTAXCON.FIG file. This value is the limit below which two equilibria are considered to be parallel and discarded from the calculations. Generally, use of a limit less than 20 degrees results in less robust solutions, but in calculations with only several equilibria a lower limit must be used to obtain any results whatsoever.

BATCH MODE OPERATION:

This mode of operation bypasses normal interactive mode of operation, enabling the user to setup the computer to perform thermobarometric calculations for a large number of samples, with different options (e.g. end-members included, solution models, thermodynamic databases) selected. Both the TWQ and INTERSX programs can be run in batch mode.

Edit a file call BATCH.DAT. On each line there should be 5 entries separated by commas, with each entry < 20 characters. Although only entry#2 is required, 4 commas are expected. An example of this file is:

```
C:\path1\,assembl.res,*c:\twq\jan92.rgb,*c:\twq\hkf81.aqu,suitel.dat
C:\path1\,assembl.res,*c:\twq\jan90.hp,*c:\twq\hkf81.aqu,suitel.dat
C:\path2\,assembl.res,*c:\twq\jan92.rgb,*c:\twq\hkf81.aqu,suite2.dat
```

The 5 entries indicate:

1. Path: applied in search for next 4 file names. No path is allowed on next 4 file names unless this path is blank or unless these next entries begin with an asterisk (*). The plot and summary output files are written to this path. The names of the plot files and averaged result files are taken from the first part of the names of the composition files listed in the file which is the fifth entry (suitel.dat in example above). The extensions are 'P' and 'A' for the plot and averaged files, respectively, followed by the number of the line in the batch.dat file that controls the calculation (1, 2, or 3 in the example above).
2. Restart file name: Path from #1 ignored if first character = '*'.
3. Mineral data file: Path from #1 ignored if first character = '*'.
4. Aqueous species data: Path from #1 ignored if first character = '*'.
5. File name with list of files containing mineral compositions. Path from #1 is applied to all of these file names, unless the first character = '*'.

To activate batch mode operation of TWQ, type TWQ/b.

The file BATCH.LOG contains info regarding status of last run. Any errors in opening files are logged here.

To activate batch mode operation of the INTERSX program, type INTERSX/b.

REFERENCES

- Berman RG (1991) Thermobarometry using multiequilibrium calculations: a new technique with petrologic applications. Canadian Mineralogist, v. 29, 833-855.
- Berman, R.G. (1990) Mixing properties of Ca-Mg-Fe-Mn garnets. The American Mineralogist, 75, 328-344.
- Berman, R.G. (1988) Internally-consistent thermodynamic data for stoichiometric minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂. Journal of Petrology, 29, 445-522.
- Berman, R.G. and Brown, T.H. (1985) The heat capacity of minerals in the system

- Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂: representation, estimation, and high temperature extrapolation. *Contrib. Mineral. Petrol.*, 89, 168-183.
- Berman, R.G., Brown, T.H. (1984) A thermodynamic model for multicomponent melts, with application to the system CaO-Al₂O₃-SiO₂. *Geochimica Cosmochimica Acta*, 48, 661-678.
- Berman, R.G., Engi, M., Greenwood, H.J., Brown, T.H. (1986) Derivation of internally consistent thermodynamic properties by the technique of mathematical programming, a review with application to the system MgO-SiO₂-H₂O. *Journal of Petrology*, 27, 1331-1364.
- Berman, R.G. and Koziol, A.M. (1991) Ternary excess properties of grossular-pyrope-almandine garnets and their influence in geothermobarometry. *Amer. Mineral.*, 76, 1223-1231.
- Chatterjee, ND & Froese EF (1975) A thermodynamic study of the pseudobinary join muscovite-paragonite in the system KAlSi₃O₈-NaAlSi₃O₈-Al₂O₃-SiO₂-H₂O. *Amer. Mineral.*, 60, 985-993.
- Ferry, J.M., and Spear, F.S. (1978) Experimental calibration of partitioning of Fe and Mg between biotite and garnet. *Contrib. Mineral. Petrol.*, 66, 113-117.
- Fuhrman, M.L. and Lindsley, D.H. (1988) Ternary-feldspar modeling and thermometry: The American Mineralogist, 73, 201-216.
- Holland TJB and Powell R (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: the system K₂O-Na₂O-CaO-MgO-MnO-FeO-Fe₂O₃-Al₂O₃-TiO₂-SiO₂-C-H₂O₂. *J. Meta. Geol.*, 8, 89-124.
- Kerrick & Jacobs (1981) A modified Redlich-Kwong equation for H₂O, CO₂, and H₂O-CO₂ mixtures at elevated pressures and temperatures. *American Journal of Science*, v. 281, p. 735-767.
- Mader UK and Berman RG (1991) An equation of state for carbon dioxide to high pressure and temperature. *Amer. Mineral.*, 76, 1547-1559.
- Mader UK, Berman RG (1992) Amphibole thermobarometry: a thermodynamic approach. *Current Research, Part E, Geological Survey of Canada Paper 92-1E:393-400*
- McMullin D, Berman RG, Greenwood HJ (1991) Calibration of the SGAM thermobarometer for pelitic rocks using data from phase equilibrium experiments and natural assemblages. *Can. Mineral.*, v. 29, 889-908.
- Newton, R.C. (1983) Geobarometry of high-grade metamorphic rocks. *American Journal of Science*, 283-A, 1-28.
- Wohl, K. (1953) Thermodynamic evaluation of binary and ternary liquid systems. *Chemical Engineering Progress*, 49, 218-219.

APPENDIX II: TWQ PRINCIPLES AND EQUATIONS

TWQ Program Structure

The problem of calculating curves in PTX space can be broken into discrete steps. These include:

- a) specification of the PTX space and chemical system,
- b) reading of the thermodynamic data base and evaluation of which phases occur in this component space,
- c) generation of reaction coefficients for all reactions in this system using matrix methods
- d) calculation of the equilibrium points on each individual curve in turn,
- e) evaluation of the stability of each of these equilibrium points with respect to all other phases in the specified system,
- f) labelling of the stable assemblages on both sides of the curves,

- g) output of equilibrium curves and labels to a plot file,
- h) pruning the remaining list of reactions of those containing totally metastable phases or assemblages.

Some of the more essential steps are briefly discussed below.

The location of any equilibrium point in PTX space is specified by the condition that the Gibbs free energy change of reaction must be zero. The program starts in the center of the diagram and, using a gradient method, tries to locate any point with the zero free energy value. If no such points are found, then any reactions containing the metastable assemblage will be removed from further consideration. If an equilibrium point is located, then the curve is followed, making use of the last two calculated points to estimate the position of each subsequent point. Step size is varied (as a function of the range of the axis values and of the curvature of the equilibrium) so as to produce smooth curves. At each point on every equilibrium curve, the stability level of the reaction assemblage is tested against all other phases by comparing each phase's Gibbs free energy to the chemical potential plane defined by the reaction assemblage. If the respective stability level of any two points on a curve changes, the location of the invariant point is found by interval halving.

All equilibria are followed until they have intersected the diagram boundaries a minimum of two times, unless they form a closed loop within the range of the diagram boundaries. Subsequently, the sign of the free energy change of the reaction is checked around the edges of the diagram, so that all segments of each equilibrium curve are located. The program structure is such that one equilibrium is calculated in entirety before the next reaction is generated and followed.

Equations of State

The programs are distributed with the database derived by Berman (1988; 1990), but a number of options have been incorporated in the software that enable users to calculate phase diagrams with alternate data sets (e.g. Helgeson, Delany, Nesbitt, and Bird, *American Journal of Science*, 278-a, 1978; Robie, Hemingway, and Fisher, *U.S. Geological Survey Bulletin* 1452, 1978; Powell and Holland, *Journal of Metamorphic Geology*, 3, 327-342, 1985; Holland and Powell, 1990). Potential users must recognize that predicted phase relations are only as accurate as the thermodynamic data used in the calculations, and we recommend the Berman et al. database because of its high degree of consistency with both calorimetric and phase equilibrium data. These thermodynamic data were derived by mathematical programming analysis (Berman et al., 1986) of all relevant data using equations of state that were chosen for their accuracy as well as their capacity for extrapolation. For the greatest accuracy in predicted phase diagrams, the internal consistency of the database must be maintained, and the user must opt for the same equations of state that were used in derivation of the database. These are noted below, along with alternate equations that may be used in conjunction with different databases.

The thermodynamic properties of pure H₂O, CO₂, and H₂O-CO₂ mixtures are computed with the equations of state developed by Haar, Gallagher, and Kell (NBS/NRC Steam Tables, Hemisphere Publishing Co., Washington, 1984), Mader and Berman (1991), and Kerrick and Jacobs (1981), respectively. Options are also provided to use the models of Kerrick and Jacobs (1981) for CO₂ and Holland and Powell (1990) for H₂O, CO₂, and H₂O-CO₂ mixtures.

Regardless of what database is used, the programs evaluate equilibrium conditions by calculating the apparent Gibbs free energy of formation from the elements (Gf) of each phase, using the equation:

$$G_f = H_f - T S_o + \int_{T_o}^T C_p dT - T \int_{T_o}^T (C_p/T) dT + \int_{P_o}^P V dP + G_{\text{transition}} + G_{\text{disorder}} + G_{\text{solution}} \quad (1)$$

H_f and S_o are the enthalpy of formation from the elements and the third law entropy at the reference temperature (298.15 K) and pressure (1 bar). V is the molar volume which, for minerals, is independent of temperature and pressure in the database of Berman et al. (1985). For a reaction, this approximation introduces very little error for pressures up to 10 kilobars. The expansivity and compressibility function:

$$V_{P,T} / V_{1 \text{ bar}, 298} = 1 + v_1(T-298) + v_2(T-298)^2 + v_3(P-1) + v_4(P-1)^2 \quad (2)$$

is provided in the software so that databases which include these terms can be used.

Heat capacity, C_p , is calculated using the equation:

$$C_p = k_0 + k_1 T^{-1/2} + k_2 T^{-2} + k_3 T^{-3} + k_4 T^{-1} + k_5 T + k_6 T^2 \quad (3)$$

where k_0 - k_6 are fit parameters. The database distributed with this software (Berman et al., 1985) uses only the first four terms of equation 3, thus defaulting to the C_p equation of Berman and Brown (1985; Contributions to Mineralogy and Petrology, v. 89, p. 168-183). The additional terms are included so that phase diagrams can be calculated with other data sets that use C_p equations such as proposed by Maier and Kelly (Journal of the American Chemical Society, 54, 3243-3246, 1932) and Haas and Fisher (American Journal of Science, 276, 525-545, 1976).

The energetic consequences of polymorphic transitions are incorporated with an additional term in equation 1, $G_{\text{transition}}$. In the case of lambda or second-order transitions, this term is computed with an empirical function (Berman and Brown, 1985) representing the variation of the heat capacity over temperature range of the transition.

The free energy contribution resulting from temperature dependent disordering, G_{disorder} , is computed from

$$G_{\text{disorder}} = H_{\text{disorder}} - T S_{\text{disorder}} + V_{\text{disorder}}(P-1) \quad (4)$$

H_{disorder} and S_{disorder} are represented in a manner similar to that discussed by Helgeson and others (1978) by integrating the extended heat capacity equation

$$C_{p\text{disorder}} = d_0 + d_1 T^{-1/2} + d_2 T^{-2} + d_3 T^{-1} + d_4 T + d_5 T^2 \quad (5)$$

between a reference temperature that marks the onset of disordering and an upper temperature limit at which the phase is fully disordered. V_{disorder} has the same temperature dependence as $C_{p\text{disorder}}$ and is calculated with one parameter that scales the heat capacity to the volume of disorder.

Solid solution effects are added with an additional term, Gsolution, that is calculated in a separate subroutine. Use of this subroutine is indicated in the thermodynamic data file by assigning a four-character phase name abbreviation which is recognized by the subroutine and specifies which activity model to use. At present, this routine contains an activity model hydrous cordierite (McPhail et al., 1990).

APPENDIX III: DESCRIPTION OF THE I/O FILES

The following pages describe the various files used by the program TWQ. These descriptions are provided so that users can modify these files, particularly the thermodynamic data file (JAN92.RGB) and output plot file (PLOT.DAT), to suit specific needs as they may arise.

The Thermodynamic Database: Input to Unit 3

All thermodynamic and compositional data are read from the file assigned to unit 3, which corresponds in format to the UBC/TICTM thermodynamic base. The file is an ordinary sequential file that can be copied safely and is easily edited with any text editor. The format is general with no constraints on the number of the phases nor on the presence or absence of data for a given phase.

The data base has two parts. The first identifies the elements and their atomic weights, while the second contains thermodynamic and compositional data for all of the solids and gases that have been included in the compilation.

Part one

Part one identifies the atomic symbols and the atomic weights of all elements that are used in the data base. Blank lines cannot occur within this portion of data, but they are allowed between this portion and the next.

The variables and format in this portion are:

```

NUMEL, DBASE      (Number of elements, Database abbreviation; I4,1x, A20
                  format)
SYMBOL(I), I = 1, NUMEL (Atomic symbols, one for each element,
                          7 per line, each separated by one or
                          more blanks. Maximum of eight
                          characters per symbol.)
WEIGHT(I), I = 1, NUMEL (Atomic weights in grams/mole, one for
                        each element, 7F10 format)

```

The order and number of these lines are fixed; they must be exactly as given.

Part Two

This part contains all of the thermodynamic, compositional and physical data for every solid and gas in the compilation. The data for solids and gases occupy separate sections and are identified by a unique heading. The section headings must be one of the following:

****MINERAL DATA****
 ****GAS DATA****
 ****REFERENCES****

These sections are not in any definite order and can be repeated as often as needed. The minimum number of asterisks preceeding and ending each section heading is one; there is no maximum. The first asterisk should occur within the first five columns of the line.

The data in each of the sections uses the same general format: lines containing the phase name, formula, and abbreviation are followed by lines containing the thermodynamic data. The data is order independent, with each line of data having a unique character designation code occurring within the first five columns of each line.

****MINERAL DATA**** indicates that the following data refers to thermodynamic, compositional and physical information for solid phases. The data has the form:

PHASE NAME	FORMULA	ABBREVIATION
	Standard state data (ST)	
	Heat capacity data (C1,C2,C3)	
	Transition data (T1,T2)	
	Disorder data (D1,D2)	
	Expansivity/compressibility data (V1)	
	Solid solution Flag (ADD)	

Appendix II shows the equations of state used by the program. The segments (standard state data, heat capacity data, transition data, disorder data, expansivity/compressibility, solid solution flag) can be in any order. Each segment need be included only when necessary. An exclamation point as the first non-blank character on a line indicates a 'comment line' that is ignored by the program.

The first line for each phase must contain the phase name, mineral formula, and abbreviation, each separated by a minimum of four spaces. The mineral formula contains the elements (in upper case) followed by their amounts in parantheses (see Appendix I). The numbers in parantheses may be integers or real numbers.

The standard state segment contains ST as the first non-blank characters on the line. The remainder of the line tabulates the Gibbs free energy of formation from the elements (Jmol⁻¹), the enthalpy of formation from the elements (Jmol⁻¹), the third law entropy (JK⁻¹mol⁻¹) and the molar volume (Jbar⁻¹), all at the reference conditions of 298.15 K and 1 bar. The enthalpy of formation from the elements, third law entropy, and molar volume are the minimum amount of data for a solid phase; any other data is optional. If a phase does not have the minimum amount of information or it has an enthalpy greater than 99999, it is ignored.

The heat capacity segment contains either C1, C2 or C3 as the first non-blank characters. If the first characters are C1, then the remainder of the line contains the heat capacity coefficients, k0, k1, k2, and k3 of the equation proposed by Berman and Brown (1985). If the first characters are C2, then the remainder of the line contains the coefficients k4, k5 and k6. If the first characters of a line are C3, then the remainder of the line contains the coefficients k0, k5 and k2 which corresponds to the Maier-Kelley heat capacity equation. The use of the C3 line precludes the use of the C1 and C2 lines.

The transition data segment provides for up to three transitions which can

be either lambda-type or first order transitions. If the first non-blank characters are either T1, T3, or T5 (depending on the number of transitions), the remainder of the line contains the temperature of transition (K), a reference temperature (K) setting a lower integration limit, the l1 and l2 lambda Cp parameters defined by Berman and Brown (1985) in J0.5K-1 and J0.5K-2, and the assumed first order portion of the enthalpy of transition (J). For first order transitions, only the temperature of transition and the enthalpy of transition need be included. If the temperature of a lambda-type transition is a known function of pressure, the heat capacity will also be a function of pressure, and it may be necessary to include expansivity and compressibility terms which apply to the low-temperature polymorph. These terms are (optionally) input on a second line identified by the characters T2, T4, or T6 (depending on the number of transitions). The remainder of the line contains the slope of the transition (Kbar-1), the transition volume change (Jbar-1), and the derivatives of the volume with respect to temperature and pressure in Jbar-1K-1 and Jbar-2, respectively.

The disorder data segment contains either D1 or D2 as the first non-blank characters. Both D1 and D2 lines must be present. If the first characters on the line are D1, the remainder of the line contains the d0, d1, d2, d3 and d4 terms of equation 5. If the first characters on the line are D2, the remainder of the line contains the terms d5, d6, TMIN, and TMAX (the latter two terms define the temperature of onset of disordering and the temperature at which disordering is complete).

The expansivity/compressibility segment contains V1 as the first non-blank characters on a line. The remainder of the line contains the parameters v1(x105), v2(x105), v3(x105), and v4(x108).

The solution flag segment consists of one line with ADD as the first non-blank characters. The remainder of the line contains a unique code name with a maximum of 4 characters separated from ADD by at least one blank. This code name is used as a switch to identify which part of the solid solution subroutine is used to compute the solution properties.

****GAS DATA**** indicates that the following data is compositional and thermodynamic properties for gases. The data for each gas has the form:

NAME	FORMULA	ABREVIATION
	Standard State Data (ST)	
	Heat Capacity data (C1,C2)	

The definition of these segments is exactly the same as the mineral data. The volume is optional in the standard state data. The thermodynamic properties of gases at elevated pressures are computed using special routines discussed above.

****REFERENCE DATA**** indicates that subsequent information is text which is ignored until a new section heading is read.

Summary Output: Output to Files Assigned to Unit 7

The output to the file assigned to unit 7 is a listing of the file assignments, the data used, the diagram constraints, and the calculated points of the stable equilibria.

Plotting: Output to Files Assigned to Unit 8

The information generated by the TWQ is most usefully presented as plot

output. The program writes the plot information as a series of X-Y points on a file assigned to unit 8. This data can then be read by a other programs (e.g. PLOT.EXE, LASER.EXE, or PRINTER.EXE) and plotted. The format of the data written to unit 8 is as follows. The first three lines contain information related to the axes of the diagram. The following lines represent groups of data that are repeated for each curve, and which define the points on the curve and its associated labels.

X-AXIS TITLE: label for the X axis of the plot
 Y-AXIS TITLE: label for the Y axis of the plot
 X-MIN, X-MAX, Y-MIN, Y-MAX, X AXIS LENGTH, Y AXIS LENGTH (6F10. format):
 minimum and maximum axis values and scaling factors for axis lengths

NLBLS, NPTS, NSYM, NDOT: number of labels, number of X-Y points in data set, symbol number, line-type number (4I5 format)
 (X, Y, IPEN), repeated NPTS times: data points and pen control for plotting curve (7(2F10,I2) format). IPEN values of 2 and 3 indicate moves with the pen down and up, respectively.
 (X, Y, HT, ANGLE, LABEL), repeated NLBLS times: information for plotting a label (4F10, 5x, 120A1 format). X and Y are the coordinates of the first letter of a label; HT is height of label; ANGLE is a negative or positive angle measured from the horizontal in degrees. The labels consist of the reactants and products for the reaction positioned on their respective sides of the equilibrium. If a curve is broken by metastable segments, then each stable segment will be labelled. X and Y are given in the appropriate units for the diagram (bars, degrees, XCO2). HT has the same units as XSIZE and YSIZE. The X-Y position of the label is adjusted to the height of the labels and, therefore, is indirectly dependent on XSIZE and YSIZE.

Note: although all the details of the plot file format have been given above so that users can add or delete data as desired, the change most commonly made to it is simply to alter the minimum and maximum axis values on line 3 of the data file.

Rerunning a Program: Use of Output Written to Unit 10

The file assigned to unit 10 (RESTART.DAT) contains a record of the interactive input entered by the user on the last run of TWQ. If a diagram is to be recalculated, this file can be assigned to unit 5 (the interactive input unit) to avoid re-entering the input. Although this assignment can be done explicitly, it is more convenient to simply type '^R' on the 'Unit Assignment' screen, which makes this reassignment and begins processing of the 'restart' file.

In order that users may edit this file to make changes in the next phase diagram, details of the format of this file are provided below.

Line 1: shows the type of diagram that was last calculated.
 Line 2: contains (6F10.3,I5 format) the default axis limits (XMIN, XMAX, YMIN, YMAX), followed by the axis scale factors used for plotting (XSIZE, YSIZE), and lastly a non-zero digit in column 65 (IRST). The non-zero value for the IRST variable indicates that reaction coefficients of all stable reactions on the previous run of TWQ follow at the end of this file (see below).
 Line 3: is present only for PT diagrams and shows the mole fractions of H2O and CO2 in 2F10.3 format.
 Line 4: For TX or PX diagrams, and for PT diagrams in which both H2O and CO2 are involved, the next line indicates whether ideal (2) or nonideal (3)

gas mixing was chosen.

Line 5: shows whether only stable segments of equilibria are calculated (Y) or whether metastable segments are followed (N).

Line 6: shows the chemical elements selected.

Line 7: is present for historic purposes only and indicates that the following lines contain the list of all phases in the chemical system chosen.

Each phase in the specified compositional space is listed with two numbers. The first indicates whether the phase was included (0), ignored (1), included in all reactions (2), or projected from (3), while the second shows the activity of this phase. In the restart file, the name of the phase is listed next to these numbers in order to facilitate changes in the selection of phases.

Next line: shows name of file containing mineral compositions

Next lines: show options for solution phases in which selected endmembers belong

Next line: shows whether phase abbreviations were used to label curves (Y) or whether full names were used (N).

Following this line is a list of the reaction coefficients of all stable reactions that were calculated in the preceding run of TWQ. When re-running the program using this file, these reactions are read from this list rather than re-calculating all possible reactions.

If the restart file is edited and used to rerun the program, care must be taken not to change it so that equilibria other than those listed at the end of the file are stable. The following changes may lead to different stable equilibria necessitating that all possible reactions be calculated by setting the IRST variable (see lines 1 and 2 above) to zero:

-Changing the P-T, P-X or T-X space.

-Changing the composition of the fluid, pressure (for T-X diagrams), or temperature (for P-X diagrams).

-Changing the activity of any phase.

-Choosing a different routine for calculation of gas mixing properties.

When including a phase that was suppressed on the previous diagram or suppressing a phase that was previously included, all possible reactions must be recalculated; change the IRST variable (see above) to zero.

----- APPENDIX IV: GRAPHICS CARD OPTIONS FOR USE WITH PLOT.EXE

/A	AT&T Graphics Adaptor,	640x400 monochrome.
/A:1	AT&T Graphics Adaptor,	640x400 monochrome.
/A:2	AT&T Display Enhancement Board (DEB),	640x200 16-color.
/A:3	AT&T Display Enhancement Board (DEB),	640x400 16-color.
/B	Conographics ConoColor-40 Adaptor	640x400 16-color
/B:1	Conographics ConoColor-40 Adaptor	640x400 16-color
/B:2	Conographics ConoColor-40 Adaptor	512x512 16-color
/ IBM	Color Graphics Adaptor (CGA)	640x200 monochrome.
/C:1	IBM Color Graphics Adaptor (CGA)	640x200 monochrome.
/C:2	IBM Color Graphics Adaptor (CGA)	320x200 4-color.
/D	Sigma Design Color-400 Adaptor,	640x400 16-color.
/E	IBM Enhanced Graphics Adaptor (EGA)	640x200 16-color.
/E:1	IBM Enhanced Graphics Adaptor (EGA)	640x350 monochrome.
/E:2	IBM Enhanced Graphics Adaptor (EGA)	320x200 16-color.
/E:3	IBM Enhanced Graphics Adaptor (EGA)	640x200 16-color.
/E:4	IBM Enhanced Graphics Adaptor (EGA, 128Kb)	640x350 16-color.
/E:5	IBM PS/2 Video Graphics Array (VGA)	640x480 16-color.

/E:6	IBM Enhanced Graphics Adaptor (EGA)	640x350 2-color.
/E:7	IBM PS/2 MultiColor Graphics Array (MCGA)	640x480 2-color.
/G	MDS Genius Display Adaptor,	738x1004 monochrome.
/H	Hercules/AST Monochrome Graphics Adaptor,	720x348 monochrome.
/L	Tseng Labs EVA/480 or NEC GB-1 Adaptor,	640x480 16-color.
/M	Microsoft mouse,	bus version.
/M:1	Microsoft mouse,	serial version, COMM1.
/M:2	Microsoft mouse,	serial version, COMM2.
/M:D	Microsoft mouse driver,	bus or serial.
/N	Number Nine Revolution Adaptor,	512x512 256-color.
/O	Toshiba 3100,	640x400 monochrome.
/S	STB GraphicsPlus-II Adaptor,	640x352 monochrome.
/S:1	STB GraphicsPlus-II Adaptor,	640x352 monochrome.
/S:2	STB GraphicsPlus-II Adaptor,	320x200 16-color.
/S:3	STB GraphicsPlus-II Adaptor,	640x200 4-color.
/S:5	STB GraphicsPlus-III Adaptor	640x400 monochrome.
/T	Tecmar Graphics-Master Adaptor,	720x352 monochrome.
/T:1	Tecmar Graphics-Master Adaptor,	720x352 monochrome.
/T:2	Tecmar Graphics-Master Adaptor,	720x704 monochrome.
/T:3	Tecmar Graphics-Master Adaptor,	640x200 16-color.
/T:4	Tecmar Graphics-Master Adaptor,	640x400 16-color.
/U	Vega EGA+	640x480 16-color.
/U:1	Vega EGA+	640x480 16-color.
/U:2	Vega EGA+	720x480 16-color.
/V	Everex Edge Adaptor,	640x200 16-color.
/V:1	Everex Edge Adaptor,	640x200 16-color.
/V:2	Everex Edge Adaptor,	640x400 4-color.
/W	Wyse WY-700 Graphics Display,	1280x400 monochrome.
/W:1	Wyse WY-700 Graphics Display,	1280x800 monochrome.
/W:2	Wyse WY-700 Graphics Display,	1280x400 monochrome.
/W:3	Wyse WY-700 Graphics Display,	640x400 monochrome.
/X	IBM 3270 PC,	720x350 monochrome.
/X:1	IBM 3270 PC,	720x350 monochrome.
/X:2	IBM 3270 PC,	360x350 4-color.