

## **Perple\_X PROGRAM DOCUMENTATION**

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November 5, 2002

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## 1. INTRODUCTION

Perple\_X is a collection of FORTRAN 77 programs for computing phase diagrams, as described by Connolly (1990), and general thermodynamic calculations. The most important of these programs is VERTEX, which can be used to calculate composition diagrams, Schreinemakers projections, mixed variable diagrams, fixed-bulk composition sections, and stability fields. VERTEX is not an interactive program, but an ancillary program, BUILD, is provided to permit users to interactively construct the input file describing computational options for VERTEX. VERTEX is designed to represent the compositional variation of solution phases using the pseudocompound approximation of Connolly and Kerrick (1986, Connolly 1990). However, petrologists most often make calculations assuming fixed thermodynamic activities. To accommodate such calculations, which are generally not thermodynamically valid, the program ACTCOR is provided. ACTCOR reads a thermodynamic data file and for each entry asks the user if the entry should be retained and if so, if an activity correction or ideal solution model should be applied. The retained entries are then written to a new file which can then be processed by VERTEX and/or BUILD. PSVDRAW is a program which can be used to generate PostScript files from the plot files generated by either FRIENDLY or VERTEX. ADIABAT and ISOKOR are programs to convert a Gibbs function thermodynamic data file to a Helmholtz, Enthalpy, or internal energy function based data file. Such files can then be processed by VERTEX for calculations of adiabatic, isolated, or isochoric thermodynamic systems. These programs can be coupled with computer graphics by system executive programs to make the use of VERTEX relatively straightforward for inexperienced users.

FRIENDLY is essentially a petrologic thermodynamic calculator. FRIENDLY reads, and optionally writes, a thermodynamic data file and can be used to calculate the thermodynamic properties of an individual phase or reaction, or to calculate the equilibrium coordinates of a reaction. FRIENDLY also permits activity corrections, data modification, and the creation of new entries in a thermodynamic data file. RK is a program which calculates the thermodynamic properties of mixed volatile fluids. COHSRK, SPECIES, ISO and RK are programs for the calculation of the properties and speciation of molecular fluids.

VERTEX, FRIENDLY, and BUILD all make use of a common set of subprograms in the files flib.f, tlib.f and rlib.f. Programs COHSRK and RK also use subprograms from tlib.f and flib.f, and PSVDRAW requires the subprogram library in the file pslib.f. For additional information on compiling Perple\_X programs refer to the README file.

All of the Perple\_X programs read data from a thermodynamic data file with a common format, FRIENDLY may also write entries to this same file (depending on the operating system). The thermodynamic data file consists of standard state data, variable names, component names, compositional data, finite difference increments, and numerical "zero" criteria. VERTEX also reads two additional files, a computational option file, usually generated by BUILD, and a file that contains data describing the excess properties of chemical solutions and subdivision schemes used to generate pseudocompounds. ACTCOR, ADIABAT, and ISOKOR write a thermodynamic data file with the same format as that which they read. VERTEX and FRIENDLY generate files for both printing and plotting. Input and output from all programs, with the exception of VERTEX is relatively simple, therefore this document is concerned entirely with the I/O

data structure of VERTEX.

Additional information on Perple\_X programs and their use is given in the Perple\_X Tutorial.

### 1.1. Correspondence of Data Files and FORTRAN Logical Units in VERTEX

The FORTRAN logical units (LUN's) used by VERTEX are designated by the variables N1, N2, ..., N9. These variables are stored in common block CST41 and are initialized in the BLOCK DATA subprogram to the values 21, 22, 23, 24, 25, 26, 25, 6, 29. All files used by VERTEX are formatted and sequential. LUN's N1, N2, N7, and N9 are used only to read input data. The file read from LUN N1 is the computational option file, this file is named by the user and may be generated with BUILD. The file read from LUN N2 is the thermodynamic data file. The file read from LUN N9 is the solution model file. The names of these files are specified in the computational option file. In the present version of VERTEX, and for batch systems in general, N1 and N7 are equivalent. For interactive systems N7 may be assigned to a terminal to allow limited interactive use of VERTEX.

LUN's N3, N4, and N8 are used only to write data. Data written to LUN N3 provides a written summary of the calculation done by VERTEX. Data written to LUN N4 is intended as input for computer graphics programs. The names of the files attached to LUN's N3 and N4 are specified in the computational option file. Some error messages and prompts (on interactive systems) are written to N8. For batch systems N3 and N8 should be made equivalent.

Data files may be both read and written to LUN's N5 and N6. The file on N6 is a scratch file which is necessary if a graphics file is to be generated. The data file on N5 is used, optionally, to store a permanent list of phase fields. This list is maintained to force a consistent phase-field numbering scheme for multiple executions of the program.

### 1.2. VERTEX Variables

The composition space, and therefore the compositional variables, for calculations with VERTEX are determined by the unconstrained components selected by the user. In addition, five other parameters, designated V(1), V(2), V(3), V(4) and V(5), may be specified. V(3) always corresponds to a compositional parameter of a saturated phase, if a calculation does not involve such a phase this parameter has no significance. For petrologic calculations the saturated phase is almost invariably a C-O-H-S fluid and a variety of different routines are provided for this case in the file flib.f. The identities of the other parameters are, in part, determined by the dependent state function tabulated in the thermodynamic data file. V(1) and V(2) correspond to the natural independent potentials of this state function. V(4) and V(5) are defined, at the users option, to be potentials conjugate to the natural independent extensities of the dependent state function tabulated in the thermodynamic data file. In the remainder of this document it will be assumed that the dependent state function is the Gibbs free energy; in which case the identities  $P=V(1)$  and  $T=V(2)$  are applicable, and V(4) and V(5), when defined, will correspond to independent chemical potentials.

In phase diagram calculations one or more of the parameters V(1-5) may be made a variable. For Schreinemakers diagram and stability field calculations the axes variables are designated the default "dependent" and "independent" variables. A third variable, designated the "sectioning" variable, may be incremented during a calculation to define multiple sections. The identities of these variables are indicated by the elements of array IV, where V(IV(1)), V(IV(2)), and V(IV(3)) are, respectively, the default independent, dependent, and sectioning variables. In mixed variable diagram calculations V(IV(2)) is treated as a sectioning parameter. The assignments V(IV(3)), V(IV(4)), and V(IV(5)) are ignored if the corresponding parameter is undefined; for example, the assignment IV(3)=3 has no effect if the requested calculation does not involve a phase saturation constraint. **NOTE:** because variables V(3), V(4), and V(5) may be undefined, it useful to have an array containing only the indices of the IPOT defined variables. This array is named JV, and it is often used to output results.

### 1.3. Thermodynamic Equations of State

The basic equation of state used by VERTEX for Gibbs function data bases requires: an isobaric heat capacity function, a volumetric function, a standard state molar Gibbs free energy, a standard state molar third law entropy, and a standard state molar volume. The units of these parameters must be consistent

with the gas constant 8.31441 J/mol-K given by the variable R assigned in the BLOCK DATA subprogram. The analytic function for the molar isobaric heat capacity is

$$C_p^m = a + bT + cT^{-2} + dT^2 + eT^{-1/2} + fT^{-1} + gT^{-3}. \quad (1)$$

Several different volumetric functions are presently supported, the specific function used for a given phase by Perple\_X is determined by the parameter  $b_8$ .

If  $b_8 = 0$  the volumetric function is

$$V^m = V(P_r, T_r) + b_2(T - T_r) + b_7(T - T_r)^2 + b_4(P - P_r) + b_6(P - P_r)^2 \quad (2.1)$$

where  $P_r$  and  $T_r$  are the standard state pressure and temperature and  $V(P_r, T_r)$  is the standard state molar volume. Eq 2.1 includes the polynomials used in early versions of Holland and Powell's (1990) data bases, and those currently used by Berman (1988, Berman and Aranovich 1996). The advantage of these polynomials is that they are numerically simple, but they do not extrapolate well to high pressure (> 4 GPa).

If  $b_8 < 0$  the volumetric function is

$$V^m = V(P_r, T_r) \exp [b_3(T - T_r) + b_8(P - P_r)]. \quad (2.2)$$

Eq 2.2 is currently used by Gottschalk (1997).

If  $b_8 > 0$  the Murnaghan equation of state for volume is used:

$$V^m = V(P_r, T) \left[ 1 - \frac{K'P}{K_T + K'P} \right]^{\frac{1}{K'}} \quad (2.3)$$

where  $V(P_r, T)$  is:

$$V(P_r, T) = V(P_r, T_r) \left[ 1 + \int_{T_r}^T \alpha dT \right] \quad (2.4)$$

and

$$\alpha = b_1 + b_2 T + b_3 T^{-1} + b_4 T^{-2} + b_5 T^{-1/2}. \quad (2.5)$$

The bulk modulus  $K_T$  is:

$$K_T = b_6 + b_7 T \quad (2.6)$$

and the pressure derivative of the bulk modulus,  $K'$ , is a constant:

$$K' = b_8. \quad (2.7)$$

Lambda-type transitions may be treated by the Landau model, following Holland and Powell (1990), or by the empirical methods used by Helgeson et al. (1978) or Berman and Brown (1985). The Landau model is based on two parameters  $T_c^0$ , the critical temperature of the transition, and  $V_{max}$  and  $S_{max}$ , the maximum volume and entropy changes due to the phase transition. The Gibbs free energy difference with respect to the disordered state is then given by the expression:

$$\Delta G_{order} = h'_r - T s'_r + \int_{P_r}^P v' dP + \Delta G_{Land} \quad (3)$$

where:

$$h'_r = S_{max} T_c^0 \left( Q_r^2 - \frac{1}{3} Q_r^6 \right) \quad (3.01)$$

$$s'_r = S_{max} Q_r^2 \quad (3.02)$$

$$v'_r = V_{max} Q_r^2 \left[ 1 - \frac{K'P}{K_T + K'P} \right]^{\frac{1}{K'}} \left[ 1 + \int_{T_r}^T \alpha dT \right] \quad (3.03)$$

$$T_c = T_c^0 + P \left( \frac{V_{\max}}{S_{\max}} \right) \quad (3.04)$$

$$Q_r = \left( 1 - \frac{T_r}{T_c^0} \right)^{\frac{1}{4}} \quad (3.05)$$

$$\text{if } T < T_c, \quad Q = \left( 1 - \frac{T}{T_c} \right)^{\frac{1}{4}}, \quad \text{else } Q = 0 \quad (3.06)$$

and

$$\Delta G_{\text{Land}} = S_{\max} ((T - T_c) Q^2 + \frac{1}{3} T_c Q^6). \quad (3.07)$$

The parameters used to evaluate Eq 3.03 are those relevant for the phase of interest as in Eq 2.1.

For transitions treated by Helgeson's method the temperature of the transition at  $P_r$ , the  $dP/dT$  of the transition phase boundary, the entropy change of the transition, and the heat capacity function (Eq 1) for the high-temperature phase, are required. For transitions treated by Berman and Brown's method the "lambda component" of the Gibbs energy is evaluated given the parameter  $T' = T + T_d$ , where  $T_d = T_{\lambda}^P - T_{\lambda}^r$ . The lambda component of the heat capacity function is then obtained from the equation:

$$C_{p,\lambda}^P = T'(I_1 + I_2 T)^2 \quad (3.1)$$

which is integrated over the interval  $t_r$  to  $T(\leq T_{\lambda}^P)$ , where  $t_{\text{ref}} = T_{\text{ref}} - T_d$ . In addition, three other parameters may be provided: (i)  $\Delta_{\text{fudge}}H$  which is the difference between the enthalpy change computed from equation (3) and that desired for the transition; (ii)  $(dV/dT)$  is a constant approximating the expansivity of the phase; and (iii)  $(dV/dP)$  is a constant approximating the compressibility of the phase.

Phases with temperature dependent disordering may be treated as described by Berman and Brown (1985) or Berman (1988). With Berman and Brown's method, parameters for the "disorder" component of the heat capacity is evaluated from the function:

$$C_{p,\text{dis}}^P = d_0 + d_1 T^{-1/2} + d_2 T^{-2} + d_3 T^{-3} + d_4 T^{-1} + d_5 T + d_6 T^2 \quad (4)$$

in the interval  $T_{\text{dis,ref}} < T < T_{\text{dis}}$ , where  $T_{\text{dis,ref}}$  is the temperature at which disordering commences, and  $T_{\text{dis}}$  is the temperature at which it is completed. In addition, the parameter  $d_3$  from the equation:

$$\Delta_{\text{dis}}V^T = \Delta_{\text{dis}}H^T d_3^{-1} \quad (5)$$

is also required.

### 1.3.1. Equations of State for Solutions

The Gibbs free energy of solution phases is computed from the relation:

$$G = G^{\text{mix}} - T S^{\text{conf}} + G^{\text{excess}}. \quad (6)$$

The mechanical mixture properties of a solution ( $G^{\text{mix}}$ ,  $S^{\text{mix}}$ ,  $V^{\text{mix}}$ ,  $C_p^{\text{mix}}$ , etc.) are computed from end-member properties by the Bragg-Williams summation. For a molar property  $\Psi$ , of a solution with  $n$  independent mixing sites, this summation is:

$$\Psi^{\text{mix}} = \beta(\Psi_{i_1 \dots i_n}) = \sum_{i_1=1}^{s_1} \dots \sum_{i_n=1}^{s_n} X_{1i_1} \dots X_{ni_n} \Psi_{i_1 \dots i_n}, \quad (7)$$

where  $\Psi_{i_1 \dots i_n}$  is the value of  $\Psi$  for the endmember with molecular species  $i_1$  through  $i_n$  on sites 1 through  $n$ , respectively,  $s_n$  is the number of molecular species mixing on site  $n$ , and  $X_{ni_n}$  is the site fraction of species  $i_n$  on site  $n$ . For a solution with a single independent mixing site, equation (7) becomes:

$$\Psi^{\text{mix}} = \beta(\Psi_{i_1}) = \sum_{i_1=1}^{s_1} \Psi_{i_1} X_{1i_1},$$

and for a solution with two independent sites:

$$\Psi^{\text{mix}} = \beta(\Psi_{i_1 i_2}) = \sum_{i_1=1}^{s_1} \sum_{i_2=1}^{s_2} \Psi_{i_1 i_2} X_{1i_1} X_{2i_2}$$

In the case of a solution in which the endmembers are completely ordered, the molecular site fraction  $X_{ij}$  is equivalent to the atomic site fraction  $Z_{ij}$ . More generally this is not true, for example consider a hypothetical single site solution between a disordered endmember AB and  $B_2$ , if the solution is an equal mixture of the endmembers, then  $X_{11}=X_{12}=0.5$ , but  $Z_{1A}=0.25$  and  $Z_{1B}=0.75$ .

For solutions with ordered endmembers, and without coupled substitutions, the ideal configurational entropy in equation (6),  $S^{\text{conf}}$ , is computed as:

$$S^{\text{conf}} = -R \sum_{i=1}^n \sum_{j=1}^{p_i} q_i X_{ij} \ln(X_{ij}). \quad (8.1)$$

In equation (8.1),  $p_i$  is the number of species mixing on the  $i^{\text{th}}$  site,  $q_i$  is the number of such sites per molar unit. For solutions with one or more disordered endmembers, or with coupled substitutions, the more general expression is adopted:

$$S^{\text{conf}} = R \ln \Omega - \beta(S_{i_1 \dots i_n}^{\text{conf}}) \quad (8.2)$$

in which:

$$\ln \Omega = - \sum_{k=1}^m \left( q_k \sum_{l=1}^{s_k} Z_{kl} \ln Z_{kl} \right) \quad (8.3)$$

where  $m$  is the total number of non-equivalent mixing sites per formula unit, i.e. both dependent and independent sites,  $s_k$  is the number of atomic species on site  $k$ ,  $q_k$  is the multiplicity of site  $k$ ,  $\beta$  is the Bragg-Williams summation operator of equation (7), and  $S_{i_1 \dots i_n}^{\text{conf}}$  is the ideal configurational entropy of the endmember with molecular species  $i_1 \dots i_n$  on sites 1 through  $n$ , respectively. The atomic site fractions  $Z_{kl}$  in equation (8.3) are expressed as functions of the molecular site fractions  $X_{ij}$  in the form:

$$Z_{kl} = \alpha_{kl} + \sum_{i=1}^{p_{kl}} \alpha_{kli} \left( \prod_{j=1}^{r_{kij}} X_{u_{kij} v_{kij}} \right) \quad (8.4)$$

where the coefficients  $\alpha_{kl}$  and  $\alpha_{kli}$ , the counters  $p_{kl}$  and  $r_{kij}$ , and the indices  $u_{kij}$  and  $v_{kij}$  are specified by the user. The values of  $S_{i_1 \dots i_n}^{\text{conf}}$  in equation (8.2) are computed by vertex as:

$$S_{i_1 \dots i_n}^{\text{conf}} = R \ln \Omega \quad \text{when} \quad X_{1i_1} = \dots = X_{ni_{i_n}} = 1. \quad (8.5)$$

As an example of the application of equation (8.2), consider  $(\text{Mg,Fe})_4^{\text{M1}}(\text{Mg,Fe,Al})_2^{\text{M2}}\text{Si}_2(\text{Si,Al})_2^{\text{T2}}\text{O}_{10}(\text{OH})_8$  chlorite. Charge balance constraints for this chlorite require that  $n_{\text{Al}}^{\text{M2}} = n_{\text{Al}}^{\text{T2}}$ , therefore although mixing occurs on three nonequivalent sites, the site populations are completely determined if the site fractions are known on the binary M1 and T2 sites (assuming that neither Fe or Mg is preferentially partitioned on these sites). Thus, this chlorite can be described by a model with two independent mixing sites, M1 and T2. If the M1 and T2 sites are designated sites 1 and 2, respectively, and clinochlore (cl)  $(\text{Mg}_4)^{\text{M1}}(\text{MgAl})^{\text{M2}}\text{Si}_2(\text{SiAl})^{\text{T2}}\text{O}_{10}(\text{OH})_8$  is designated as the endmember with species 1 on site 1 and species 1 on site 2 (endmember 11) the identities  $X_{11}=X_{\text{Mg}}^{\text{M1}}$ ,  $X_{21}=X_{\text{SiAl}}^{\text{T2}}$ ,  $X_{12}=X_{\text{Fe}}^{\text{M1}}$ , and  $X_{22}=X_{\text{AlAl}}^{\text{T2}}$  are implicit. Further this implies that daphnite (da)  $(\text{Fe}_4)^{\text{M1}}(\text{FeAl})^{\text{M2}}\text{Si}_2(\text{SiAl})^{\text{T2}}\text{O}_{10}(\text{OH})_8$  is endmember 21, amesite (am)  $(\text{Mg}_4)^{\text{M1}}(\text{Al}_2)^{\text{M2}}\text{Si}_2(\text{Al}_2)^{\text{T2}}\text{O}_{10}(\text{OH})_8$  is endmember 12, and ferroamesite (fam)  $(\text{Fe}_4)^{\text{M1}}(\text{Al}_2)^{\text{M2}}\text{Si}_2(\text{Al}_2)^{\text{T2}}\text{O}_{10}(\text{OH})_8$  is endmember 22. To apply equation (8.2) the atomic site fractions on all three nonequivalent sites (M1, M2, and T2) must be expressed in the form of equation (8.4) in terms of the molecular site fractions on the two independent mixing sites (M1 and T2). Note that the indexing of the sites and species for equation (8.2) is independent of the indexing of the molecular species and independent sites for equation (7); for example M1 and Mg have been designated the first site and first species on M1, respectively, for calculating mechanical mixture properties from equation 7, but  $Z_{11}$  could be defined through equation (8.4) to be the atomic site fraction of Si on T2. Here, with reference to equations (8.2-8.4), Mg and Fe will be designated the first and second species on site M1 = site 1; Si and Al as the first

and second species on site T2 = site 2; and Al, Mg, and Fe the first, second, and third species on site M2 = site 3. Given these assignments, on M1 the site fractions are:

$$Z_{Mg}^{M1}=Z_{11}=X_{Mg}^{M1}=X_{11} \quad (i)$$

$$Z_{Fe}^{M1}=Z_{12}=X_{Fe}^{M1}=X_{12} \quad (ii)$$

which implies:

$$\begin{aligned} q_1=4 \quad s_1=2 \quad \alpha_{11}=\alpha_{12}=0 \quad p_{11}=p_{12}=1 \quad \alpha_{111}=\alpha_{121}=1 \\ r_{111}=r_{121}=1 \quad u_{1111}=1 \quad v_{1111}=1 \quad u_{1211}=1 \quad u_{1211}=2. \end{aligned} \quad (iii)$$

On T2 the site fractions are:

$$Z_{Si}^{T2}=Z_{21}=X_{AlSi}^{T2}/2=X_{21}/2 \quad (iv)$$

$$Z_{Al}^{T2}=Z_{22}=1/2 + X_{AlAl}^{M1}/2=1/2 + X_{22}/2 \quad (v)$$

which implies:

$$\begin{aligned} q_2=2 \quad s_2=2 \quad \alpha_{21}=0 \quad \alpha_{22}=1/2 \quad p_{21}=p_{22}=1 \quad \alpha_{211}=\alpha_{221}=1/2 \\ r_{211}=r_{221}=1 \quad u_{2111}=2 \quad v_{2111}=1 \quad u_{2211}=2 \quad u_{2211}=2. \end{aligned} \quad (vi)$$

And on M2 the site fractions are:

$$Z_{Al}^{M2}=Z_{31}=Z_{Al}^{T2}=1/2 + X_{22}/2 \quad (vii)$$

$$Z_{Mg}^{M2}=Z_{32}=Z_{Mg}^{M1}(1 - Z_{Al}^{M2})=X_{11}/2 - X_{11}X_{22}/2 \quad (viii)$$

$$Z_{Fe}^{M2}=Z_{32}=Z_{Fe}^{M1}(1 - Z_{Al}^{M2})=X_{12}/2 - X_{12}X_{22}/2 \quad (ix)$$

which implies:

$$\begin{aligned} q_3=2 \quad s_3=3 \quad \alpha_{31}=1/2 \quad \alpha_{32}=\alpha_{33}=0 \quad p_{31}=1 \quad p_{32}=p_{33}=2 \quad \alpha_{311}=\alpha_{321}=\alpha_{331}=1/2 \quad \alpha_{322}=\alpha_{332}=-1/2 \\ r_{311}=r_{321}=r_{331}=1 \quad r_{322}=r_{332}=2 \\ u_{3111}=2 \quad v_{3111}=2 \quad u_{3211}=1 \quad v_{3211}=1 \quad u_{3311}=1 \quad v_{3311}=2 \quad u_{3221}=1 \quad v_{3221}=1 \quad u_{3321}=1 \quad v_{3321}=2 \\ u_{3222}=u_{3322}=2 \quad v_{3222}=v_{3322}=2. \end{aligned} \quad (x)$$

The  $G^{\text{excess}}$  term of equation (6) is computed by the polynomial expansion:

$$G^{\text{excess}} = \sum_{k=1}^s W_k \left( \prod_{m=1}^{t_k} X_{u_{km} v_{km}} \right) \quad (9)$$

where k indexes the s terms in the expansion and  $X_{u_{km} v_{km}}$  represents molecular site fractions the indices of which are specified by the user. The P-T dependence of the  $W_k$  parameters is given by the expression:

$$W_k = w_{k1} + w_{k2}T + w_{k3}P + w_{k4}T \ln T + w_{k5}T^2 + w_{k6}T + w_{k7}T^3 + w_{k8}T^{1/2} + w_{k9} \ln T + w_{k10}T^2 + w_{k11}PT \quad (10)$$

As an example of the application of equation (10) consider the Margules expansion for the excess Gibbs energy for ternary feldspar (endmembers Ab, An, and Or) as given by Ghiorso (1984), Green and Usdansky (1986), and Fuhrman and Lindsley (1988) (in contrast to these authors, configurational entropy is not considered here to be part of  $G^{\text{excess}}$ ):

$$\begin{aligned} G^{\text{excess}} = & W_{OrAb}(X_{Or}X_{Ab})(X_{Ab} + X_{An}/2) + W_{AbOr}(X_{Or}X_{Ab})(X_{Or} + X_{An}/2) + W_{OrAn}(X_{Or}X_{An})(X_{An} + X_{Ab}/2) \\ & + W_{AnOr}(X_{An}X_{Or})(X_{Or} + X_{Ab}/2) + W_{AbAn}(X_{Ab}X_{An})(X_{An} + X_{Or}/2) + W_{AnAb}(X_{An}X_{Ab})(X_{Ab} + X_{Or}/2) \\ & + W_{AbAnOr}(X_{Ab}X_{Ab}X_{Or}). \end{aligned} \quad (i)$$

Making the assignments  $X_{Ab}=X_{11}$ ,  $X_{An}=X_{12}$ , and  $X_{Or}=X_{13}$ , equation (i) can be rearranged in the form of equation (10) as:

$$G^{\text{excess}} = W_1 X_{11} X_{11} X_{13} + W_2 X_{11} X_{13} X_{13} + W_3 X_{12} X_{12} X_{13} + W_4 X_{12} X_{13} X_{13}$$

$$+ W_5 X_{11} X_{12} X_{12} + W_6 X_{11} X_{11} X_{12} + W_7 X_{11} X_{12} X_{13} \quad (\text{ii})$$

which implies  $s=7$  and  $t_k=3$  for all  $s$  terms in equation (9), and the identities:

$$\begin{aligned} W_1 &= W_{\text{OrAb}} & W_2 &= W_{\text{AbOr}} & W_3 &= W_{\text{OrAn}} & W_4 &= W_{\text{AnOr}} & W_5 &= W_{\text{AbAn}} & W_6 &= W_{\text{AnAb}} \\ W_7 &= W_{\text{OrAnAb}} + (W_{\text{OrAb}} + W_{\text{AbOr}} + W_{\text{OrAn}} + W_{\text{AnOr}} + W_{\text{AbAn}} + W_{\text{AnAb}})/2 \end{aligned} \quad (\text{iii})$$

**NOTE:** The sign of  $w_{2k}$  is positive, thus if a Margules coefficient  $W_G$  is given as  $W_H - T W_S + P W_V$ , then  $w_{2k} = -W_S$ . The units of the  $W_k$  coefficients are Joules per mole, i.e., they are formulated on the basis of a molecular model. However, many solution models are formulated on the basis of an ionic model, i.e., per mole cation. In such cases the  $W_k$  coefficients entered for vertex must be multiplied by the number of cations per endmember formula unit.

#### 1.4. Pseudocompound Subdivision Schemes for Solutions

The compositional variation of a solution phase is modeled in VERTEX generating a grid over the composition space for the solution. VERTEX computes the phase relations and properties of a compound, i.e. a pseudocompound, which has the properties of the solution at each mesh point in this grid. The generation of such a grid is referred to here as subdivision (Connolly and Kerrick 1987, Connolly 1990, Connolly and Trommsdorff 1991) Three basic kinds of subdivision schemes for the range of compositions on a given mixing site are supported by VERTEX, Cartesian, barycentric, and transform (a stretching transformation). Transform subdivision can only be used for binary sites and barycentric subdivision can only be used for ternary sites. Cartesian and barycentric subdivision provide relatively uniform compositional resolution over a specified portion of a site composition space. In Cartesian subdivision pseudocompounds are generated with a prescribed compositional spacing, the advantage of this method is that it is easy to control the range of pseudocompound compositions. In barycentric subdivision (Connolly & Kerrick 1987) three points in a ternary composition space are specified, the triangular region thus defined is then subdivided by barycentric starring, each star being taken as pseudocompound composition. This method provides the most efficient and uniform representation of a site composition space. Another advantage of barycentric subdivision is that the compositional resolution obtained in the ternary composition space is equivalent to that obtained for the lower order subcompositions (i.e., the resolution for the ternary phase relations is equivalent to the resolution of the phase relations in each binary subsystem). In contrast, Cartesian subdivision provides better resolution in the binary subsystems, than it does for the full ternary space. With transform subdivision the compositional spacing of pseudocompounds for a binary solution can be made to increase exponentially towards one or both of the compositional extremes of the solution. Transform subdivision is particularly useful if the phase relations at the compositional extremes of a nonideal binary solution are of interest. In symmetric transform subdivision pseudocompounds are generated with a spacing which decreases away from either side of the barycenter; and in asymmetric transform subdivision pseudocompounds are generated, from a specified point, with decreasing spacing towards a compositional limit. Different subdivision schemes can be specified for each site of a multi-identisite solution model.

**NOTE:** when specifying subdivision schemes, care should be take to insure that the pseudocompounds used to represent different solutions are not compositionally degenerate. VERTEX is not able to determine the true variance of equilibria involving compositionally degenerate compounds. Such degeneracy is easily avoided by specifying slightly different compositional increments and starting and end points. For example, consider the almandine-pyrope and enstatite-ferrosillite solutions. If both solutions are represented by compounds with  $X_{\text{Mg}}$  ranging from 0.1 to 0.9 in 0.1 increments, then any garnet-pyroxene pair with the same  $X_{\text{Mg}}$  would be linearly degenerate. This does not occur, if one solution, say garnet, is represented by pseudocompounds with  $X_{\text{Mg}}$  ranging from 0.10001 to 0.90001 in 0.1 increments.

#### 1.5. Chemical Potential Buffers

For many geologic problems it is useful to calculate phase diagram sections for which the potential of a chemical species equal to that consistent with the equilibrium of a particular phase assemblage (e.g., as in the calculation of a P-T phase diagram in which the chemical potential of Oxygen is determined by a buffering assemblage such as magnetite-hematite). To do this with VERTEX, you must first create an entry in the thermodynamic data file which defines the potential consistent with the buffer assemblage. This entry



must have the chemical composition of the buffered potential. Then when you run VERTEX, you must specify that the system is saturated with respect to this composition, and you must exclude all phases with the same composition except for the buffer.

**EXAMPLE 1:** calculation of a phase diagram for a system in which the chemical potential of oxygen is always equal to that consistent with the equilibrium of quartz( $\text{SiO}_2$ ) + fayalite( $\text{Fe}_2\text{SiO}_4$ ) + magnetite( $\text{Fe}_3\text{O}_4$ ).

- (i) Create the  $\text{O}_2$  buffer, called QFM, by linear combination of thermodynamic parameters and compositions according to the equation:  
$$\text{QFM} = 2 \text{ magnetite} - 3 \text{ fayalite} + 3 \text{ quartz}$$
You can do this by hand, or FRENDLY (option 2) can do it for you.
- (ii) Add the parameters for QFM to the thermodynamic data file (this can also be done by FRENDLY automatically).
- (iii) Run BUILD to create the input for VERTEX.
  - (a) When build asks if you want to do calculations with saturated components, respond yes, and select the component  $\text{O}_2$ .
  - (b) When build asks you if you want to exclude any phases, respond yes, and exclude all phases with the composition  $\text{O}_2$ , with the exception of QFM. If you do not exclude these phases, at any P-T-X condition VERTEX will calculate  $\mu_{\text{O}_2}$  from  $\text{O}_2$  buffer or phase with the lowest  $\mu_{\text{O}_2}$ , which may or may not be QFM.
- (iv) Run VERTEX.

**EXAMPLE 2:** calculation of a phase diagram section as a function of fluid composition in which HF fugacity is known ( $10^{-6}$  bar) and fluorine fugacity is buffered by graphite, but the fluid is assumed to consist essentially of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . (This calculation requires an C and  $\text{F}_2$  components in the thermodynamic data file).

- (i) Create the  $\text{O}_2$  buffer, called CCO2, by linear combination of thermodynamic parameters and compositions according to the equation:  
$$\text{CCO2} = \text{CO}_2 - 2 \text{ graphite}$$
You can do this by hand, or FRENDLY (option 2) can do it for you.
- (ii) Create the function to calculate HF free energy as a function of P and T by adjusting the reference state S and G of HF as follows:  
$$S = S - R \ln f_{\text{HF}}$$
$$G = G + T_r R \ln f_{\text{HF}}$$
Alternatively, this adjustment is done automatically when you run ACTCOR if you enter the fugacity when ACTCOR prompts you for an activity. Call the adjusted thermodynamic data entry HF(10-6).
- (iii) Finally create the  $\text{F}_2$  buffer, called F2buf, by linear combination of thermodynamic parameters and compositions according to the equation:  
$$\text{F2buf} = 0.5\text{CCO}_2 + 2 \text{ HF}(10-6) - \text{H}_2\text{O}$$
- (iv) Run BUILD to create the input for VERTEX.
  - (a) When build asks if you want to do calculations with saturated components, respond yes, and select the component  $\text{F}_2$ .
  - (b) When build asks you if you want to exclude any phases, respond yes, and exclude all phases with the composition  $\text{F}_2$ , with the exception of F2buf.
- (iv) Run VERTEX.

## 1.6. Fictive Composants

Any calculation done by VERTEX is necessarily done over the entire composition space defined by a positive linear combination of the specified independent components. The algorithm of VERTEX requires that there must be at least one stable phase with a thermodynamic composition equivalent to that of each component, i.e., there must be a composant for every component. Often data for real composants may be

lacking, in which case VERTEX can still be used by if the user provides fictive composants in the thermodynamic data file. In specifying a fictive composant care should be taken to ensure that the free energy of the composant is high enough that it is never stable with respect to a real composant. It is also important to recognize that any phase relations involving such a composant are arbitrary, but serve to indicate the limits of the thermodynamic data being used.

**EXAMPLE:** T- $Y_{\text{CO}_2}$  phase diagram calculation for the system CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> using a data base that contains no data for a pure CaO phase. To make this calculation it is first necessary to create a fictive composant in the data file, arbitrarily this phase will be named CaO (this step can be done with FRENLY, option (4)). The composition of the CaO is specified as being literally CaO, and to ensure that the presence of this composant does not affect any real phase relations, it can be given a standard state free energy of zero (relative to a formation from the elements standard state), all other properties for CaO can also be made zero. Consider now what happens if  $Y_{\text{CO}_2}$  is decreased from the calcite stability field, calcite cannot be stable in a pure water fluid, so regardless of how CaO has been specified, calcite must eventually become metastable to CaO. Therefore VERTEX will determine a Calcite + CaO phase field, calcite cannot be stable at more water rich-conditions than this field, but in fact calcite would probably become metastable at considerably more CO<sub>2</sub>-rich conditions if real composants (e.g., lime) were included in the data.

Although, the free energy of a fictive composant should be large relative to other phases, it should not be too large because large numbers will destabilize the matrix inversions done by VERTEX (zero is a safe choice, given formation from the elements standard states in joules). On the other hand, if you make a fictive composant too stable then you will observe non-degenerate reactions involving the composant, In the above example this would be the case if wollastonite were to react to form CaO plus quartz.

### 1.7. Reducing VERTEX's Memory Requirement

The amount of memory required to use VERTEX is strongly dependent on the maximum number of thermodynamic components permitted for a calculation. The dimensioning for the number of pseudocompounds, and the number of invariant and univariant equilibria is also an important factor. The default dimensioning in VERTEX is for 12 component systems, 2000 pseudocompounds, and 3000 univariant and invariant equilibria, and requires about 6 Mbytes. This capability is excessive for most geologic problems and can be drastically reduced by modification of the parameter statements within the code, to this you may use global edits, but remember that the code to be modified is in many files (vertex.f, flib.f, rlib.f build.f, tlib.f, cohsrk.f, actcor.f and frendly.f). Table 1 indicates the significance and default value of the dimensioning parameters used in VERTEX.

TABLE 1. Dimensioning parameters for VERTEX		
Parameter	Value	Significance
Phase Counters		
k1	2000	maximum number of phases
k10	200	maximum number of stoichiometric compounds
Component and Subsystem Counters		
k5	12	maximum number of thermodynamic components
Assemblage Counters		
k2	3000	maximum number of high variance ( $p > c$ ) assemblages
j9	40000	maximum number of low variance ( $p < c+1$ ) assemblages
Miscellaneous Counters		
h5	3	maximum number of component saturation constraints
h6	20	maximum number of composants per component saturation constraint
h8	80	maximum number of excluded phases
k4	16	number of parameters in thermodynamic equation of state
k9	50	maximum number of phases with lambda-type transitions
j8	800	maximum number of pseudo-facets
l2	5	maximum number of independent potentials
l4	2	maximum number of saturated phase components
m6	3	maximum number of lambda transitions per phase
m7	9	number of parameters used to describe a lambda transition
m8	9	number of parameters used to describe T-dependent ordering
m9	50	maximum number of phases with T-dependent ordering

### 1.8. Adding Equations of State for the Saturated Phase (Fluid)

The composition of a saturated phase can be used as an independent variable ( $V(3)$ ) in calculations with vertex. Normally the saturated phase is a binary fluid, but other types of phases (e.g., mineral solutions) can also be used, provided a subroutine with the appropriate equation of state is added to the program library fib.f. Such subroutines must have a common block named CST5 for nine double precision variables, which will be the independent variables  $V(1-5)$ , the reference state values for variables  $V(1)$  and  $V(2)$ , the gas constant, and a variable used for calculations in which  $V(1)$  (usually pressure) for the saturated phase can vary independently of that for the other remaining phases. The subroutine should then output the natural log of the activity (relative to the reference state, usually an ideal gas at  $P_r$  and  $T$ ) of the two chemical potentials related to  $V(3)$  as double precision variables in a common block named CST11. In addition subroutines cfluid and rfluid (fib.f) and fluid (rk.f) must be modified to call the subroutine.

### 1.9. PSVDRAW: PostScript Plotting

Because of the great variety in graphics hardware and software VERTEX is no longer provided with interactive graphics; however, the program PSVDRAW (files psvdraw.f, pslib.f) can be used to plot output from either VERTEX or FRENLY on PostScript interpreters/printers. These programs are written in FORTRAN77 and generate a standard PostScript file with the name of the input file plus the suffix ".ps". PSVDRAW requires two special files named pro.ps and epi.ps, these files must be located in the working directory from which PSVDRAW is executed. The PostScript file generated by PSVDRAW contains comments which can be interpreted by the IDRAW program in X-Windows (IDRAW can be obtained by anonymous ftp from Interviews.stanford.edu, IP no. 36.22.0.175). Users with access to an X-Windows system can use IDRAW to modify or redraft output from PSVDRAW. The PostScript output from PSVDRAW can also be viewed with the PAGEVIEW and PSVIEW utilities available under Open-Windows and NEWS, respectively, on Sun Computers. PSVDRAW output cannot be read by the Adobe Illustrator program. At present PSVDRAW only recognizes Schreinemakers and ternary composition diagrams.

PSVDRAW has several useful options for plotting Schreinemakers diagrams, these options can be invoked if the user answers yes to the prompt which asks whether the user would like to modify the default

plot. Most of these options control the appearance and labeling of the diagram; however, it is also possible to restrict the phase fields shown in the diagram. PSVDRAW can be instructed to show only phase fields which (i) contain a particular phase assemblage, (ii) contain one or more phases from a list, or (iii) do not contain any of the phases from a list. In specifying solution phase identities for PSVDRAW the user has the option of specifying the name of the solution phases, or a specific pseudocompound composition for the solution. For example, the user may ask PSVDRAW to show all phase fields in which garnet, chlorite, and staurolite solutions coexist; or the user may ask PSVDRAW to show only those phase fields in which these solutions have specific compositions (as represented by pseudocompounds).

## 2. THE COMPUTATIONAL OPTION FILE

Data read from LUN's N1 and N7 describe computational options. The file read from N1 is the computational option file, this file may be generated interactively with program BUILD. The only read done from N7 (in routine CHMCAL) is done after all reads have been done from N1 (in routines INPUT1 and INSTB). Thus, if N7 is equated with N1, data read from N7 should be appended to the file on N1. The variables read on each card image and their significance are as follows (FORTRAN format and variable types are also indicated):

Card 1 - N2FNAM - (A80) - C\*80 -

Name of the thermodynamic data file to be read on LUN N2.

Card 2 - IO3, IO4, IO5 - format-free - I -

Flags indicating if output is to be generated on N3 (print file), N4 (graphics file), or N5 (phase field list file), respectively. If a value of 1 is supplied, data is not written to the corresponding LUN, for any other value data is written. IO5 also determines if phase field lists are read from LUN N5.

Card 3 - N3FNAM - (A80) - C\*80 -

Name of the print file written to LUN N3. This card may be left blank if IO3 = 1.

Card 4 - N4FNAM - (A80) - C\*80 -

Name of the graphics file written to LUN N4. This card may be left blank if IO4 = 1.

Card 5 - N5FNAM - (A80) - C\*80 -

Name of the phase field list file written to LUN N5. This card may be left blank if IO5 = 1.

Card 6 - ICOPT, ISEC, JPOT, JTEST, IFULL, IMSG, IO3P - format-free - I -

ICOPT is a flag indicating the kind of calculation desired: 0 - composition diagram; 1 - Schreinemakers projection; 2 - options 0 or 1 with a fixed or constrained bulk composition; and 3 - mixed variable diagram. ISEC is a flag indicating the level of reliability and efficiency desired for the Schreinemakers-type diagram calculations. ISEC may take values from 1 to 5, 1 giving the highest reliability and the lowest efficiency, and 5 giving the lowest reliability and highest efficiency, the (default) value of 4 is recommended. High values of ISEC increase the probability that a univariant equilibrium may be skipped. JPOT is a flag which, if 0, signals that whenever a composition diagram is calculated the dependent potentials for each phase assemblage should also be output. JTEST is a flag which, if 0, signals that additional tests for the thermodynamic consistency should be made in the computation of composition phase diagrams, these tests are only for debugging (default: JTEST = 1). IFULL is a flag that determines the format used for univariant reaction equations: IFULL = 0 (default) - reaction equations include only phases from the thermodynamic composition space (e.g.,  $a = b$ ); IFULL = 1 - equations include saturated phases (e.g.,  $a = b + q$ , where  $q$  is a saturated phase or component); IFULL = 2 - equations include entropy, saturated components and volume (e.g.,  $a + V = b + q + S$ ); IFULL = 3 - equations include saturated phases and stoichiometric coefficients (e.g.,  $1 a = 2 b + 3 q$ ); IFULL = 4 - equations include entropy, saturated components, volume and entropy, and stoichiometric components (e.g.,  $1 a + 2 V = 3 b + 4 q + 5 S$ ). IMSG is a flag that determines whether progress messages are written to the console during a computation (IMSG = 0, default), if IMSG = 1, no messages are written. IO3P is a flag that determines whether the short (IO3P = 1, default) or long form (IO3P = 0) of the print file is written. The short form of the print file does not include univariant equilibrium coordinates.

Card 7 - ITRANS, ICMPN - format free - I -

ITRANS is a flag indicating the number of component transformations to be performed on the

ICMPN components defined in the thermodynamic data base.

If ITRANS is nonzero:

Card 8-(7+ITRANS) - ((TCNAME(I),ICTR(I),CTTRANS(J,I),J=1,ICMPN),I=1,ITRANS)

- (A5,1X,I2,15(1X,F6.2)) - C\*5, I, R - TCNAME(I) is the name of the I<sup>th</sup> transformed component, which will replace the ICTR(I)<sup>th</sup> data base component. This transformation is defined as a linear combination of the ICMPN data base components, where the elements (CTTRANS(J,I),J=1,ICMPN) are the stoichiometric coefficients in the transformation.

Card ITRANS+8 - (RNAME(J),J=1,K6) - 7(A5,1X) - C\*5 -

The names of the unconstrained thermodynamic components. K6 (see Table 1) components may be specified. The nonblank elements of RNAME are copied to the elements CNAME(J), J=1,ICP, where ICP is a counter for thermodynamic components.

Card ITRANS+9 - (RNAME(J),J=1,H5) - 7(A5,1X) - C\*5 -

the names of components subject to component saturation or functional constraints. H5 (see Table 1) constraints may be specified. If there are no such constraints this card is left blank, but included. The nonblank elements of RNAME are copied to the elements CNAME(J), J = ICP + 1, ICP + ISAT, where ISAT is a counter for components subject to saturation or functional constraints.

Card ITRANS+10 - (RNAME(J), J=1,2) - 7(A5,1X) -

the names of the components subject to a phase saturation constraint. Two components may be constrained (for the routines provided with VERTEX). If no phase saturation constraint is requested this card is left blank, but included. The nonblank elements of RNAME are copied to the elements CNAME(J), J=ICP+ISAT+1,ICP+ISAT+IFCT, where IFCT is a counter for the components subject to a phase saturation constraint.

Card ITRANS+11 - (RNAME(J), J=1,2) - 5(A5,1X) -

the names of the chemical species associated with variables V(4) and V(5) (see section 1.2 for further explanation). If these variables are not defined this card is left blank, but included. The nonblank elements of RNAME are copied to the elements CNAME(J), J = ICP + ISAT + IFCT + 1, ICP + ISAT + IFCT + IMCT, where IMCT is a counter for the chemical species of which the chemical potentials are independent variables. The character names entered on Cards ITRANS+8 - ITRANS+11 must match the names on Cards (2\*IDAT+8)-(2\*IDAT+9) (array CMPNT) of the thermodynamic data file.

Card ITRANS+12 - JBULK - format free - I -

The number of constrained components for fixed bulk composition calculations (i.e., ICOPT = 2). If ICOPT = 2, JBULK must be greater than 2 and less than ICP + ISAT.

Card ITRANS+13 - (CBULK(I),I=1,JBULK) - format free - R -

The molar proportions of the JBULK components.

Cards ITRANS+12-ITRANS+26 - (EXNAME(I),I=1,H8) - 6(A8,1X) - C\*8 -

The names of phases or chemical species to be excluded from consideration during a calculation. These cards are left blank, but included, if no phases are excluded. The names given here should match phase or species names defined in the thermodynamic data file, if matches are not found by the program execution will continue and no warning message will be issued. **NOTE:** the number of cards read will depend on the H5 parameter (see table 1), it is currently set to 80 (14 cards)

Card ITRANS+27 - (VMAX(J), J=1,5) - format-free - R -

the maximum values for variables V(1)-V(5), respectively. VMAX(3)-VMAX(5) must be assigned values even if they have no significance.

Card ITRANS+28 - (VMIN(J), J=1,5) - format-free - R -

the maximum values for variables V(1)-V(5), respectively. The values assigned to VMIN(1)-VMIN(5) are also the default values for V(1)-V(5). VMIN(3)-VMIN(5) must be assigned values even if they have no significance. To avoid possible errors, if a variable has no significance the corresponding elements of VMIN and VMAX should be assigned equivalent values.

Card ITRANS+29 - (DV(J), J=1,5) - format-free - R -

the default increment values for the variables V(1)-V(5), respectively. These are relevant only if

ICOPT $\neq$ 0. The increment DV(IV(J)) is ordinarily assigned values of about (VMAX(IV(J))-VMIN(IV(J)))/40 for J=1 or 2. The increment DV(IV(3)) determines the spacing and number of sections computed if VMAX(IV(3)) $\neq$ VMIN(IV(3)), where the number of sections is given by (VMAX(IV(3))-VMIN(IV(3)))/DV(IV(3))+1. If VMAX(IV(3)) $\neq$ VMIN(IV(3)) one section at constant V(IV(3)) (=VMIN(IV(3))) is calculated. DV(IV(4)) and DV(IV(5)) have no significance but must be assigned values.

Card ITRANS+30 - (IV(J), J=1,5) - format-free - I -

the elements of the array IV(1-5) determine the status of the corresponding variables V(1-5), the significance of these assignments varies depending on the computational option specified by ICOPT as follows: ICOPT=1 or 2 - V(IV(1)), V(IV(2)), and V(IV(3)) are, respectively, the dependent, independent, and sectioning variables, and V(IV(4)) and V(IV(5)) are held constant. ICOPT=3 - V(IV(1)) is the independent variable; V(IV(2)), V(IV(4)), and V(IV(5)) are held constant; and V(IV(3)) is taken as the sectioning variable. ICOPT=0 - the assignments determine the order in which the values of the variables V(JV(I)), I=1,IPOT) are read after Card 21, see comments below. See also section 1.2 for further explanation.

Card ITRANS+31 - IDBASE - format-free - I -

The numeric code which identifies the thermodynamic data-base to be used for the calculation. This code must match one of the codes defined in the data thermodynamic data file.

Card ITRANS+32 - IFUG - format-free - I -

The numeric code which identifies the equation of state to be used for the saturated phase. This card is read even if there is no phase saturation constraint imposed for a calculation. Six equations of state are provided for the evaluation of the properties of pure H<sub>2</sub>O and CO<sub>2</sub> and mixed fluids, these are indicated by the codes (this is out-of-date): 0 - the modified Redlich Kwong (MRK) equation of De Santis (1974), with parameters from De Santis (1974), Holloway (1977), and Connolly (1981); 1 - the hard sphere modified Redlich Kwong (HSMRK) equation of Kerrick and Jacobs (1981); 2 - a hybrid equation (QRKMRK) which uses the HSMRK to calculate the fugacity of pure species, and calculates the activities of species in mixed volatile fluids with the MRK; 3 - the equation of state of Bottinga and Richet (1981) for pure CO<sub>2</sub> fluids, this equation of state is computationally inefficient and requires special values in the array DELT defined in the thermodynamic data file; 4 - the equation of state of Saxsena and Fei (1984), this equation of state assumes ideal mixing; 5 - CORK (Holland & Powell 1990, 1996) a very good general equation of state for a wide range of P-T conditions; 6 - a hybrid equation (PRK, Connolly and Bodnar 1983) which calculates the properties of pure H<sub>2</sub>O and CO<sub>2</sub> with the equations of Haar et al. (1979) and Bottinga and Richet (1981), respectively, and calculates the activities of species in mixed volatile fluids with an MRK type equation; 7 - the Holland and Powell 1990 pseudo-virial equation; and 8 - the MRK equation (as in ifug = 0, above) with COH speciation computed to be consistent graphite saturation and a selected oxygen fugacity buffer. The QRKMRK equation is less costly to use than the PRK and is recommended for most purposes. User defined equations of state can be accommodated by modifying routine UFLUID.

IF IFUG = 7 the following data must follow Card ITRANS+32:

IBUF, DBUF - format free - I, R -

IBUF specifies the oxygen fugacity buffer, at present only one buffer can be selected (QFM). DBUF is a constant, in units of ln(fO<sub>2</sub>), to be added to the ln(fO<sub>2</sub>) computed for the buffer specified by IBUF.

Cards ITRANS+33-ITRANS+35 - (FNAME(I),I=1,18) - 6(A10,1X) -

The names of chemical solutions considered for the calculation. These names must match with solutions described in the data file on N9. These cards are left blank, but included, if no chemical solutions are to be considered. The names given here should match chemical solution names defined in the file on N9, if matches are not found by the program execution will continue, but a warning message will be issued.

Card ITRANS+36 - N9FNAME - (A80) - C\*80 -

Name of the file containing solution models. This card is only written if FNAME has non-blank

elements (cards 27-29).

Card ITRANS+37 - ISUDO - format-free - I -

A flag indicating if pseudoinvariant or pseudounivariant phase fields are calculated. If assigned a value of 1 pseudounivariant and pseudoinvariant fields are not calculated, for any other value these fields are calculated.

Card ITRANS+38 - TITLE - A72 -

A title for the phase diagram calculation.

Card ITRANS+38 is the last card read for a Schreinemakers or mixed variable phase diagram calculation. If ICOPT = 0, i.e., composition phase diagram calculations have been requested, the following data is read for each calculation from N7 in routine CHMCAL. In the present version of VERTEX N7 and N1 are equivalent and BUILD appends this data to the computational option file. If interactive calculation of composition diagrams is desired, the commented statements in CHMCAL should be restored, and N7 given a value appropriate to read input from the users terminal (usually this means N7 = 5).

Card ITRANS+39 -(V(I),I=1,5) - format-free - R -

This card is read for each composition diagram calculation. The array V contains the values for the five computational variables (normally P, T,  $Y_{CO_2}$ ,  $\mu_1$ , and  $\mu_2$ ) for each diagram. Values must be supplied for all elements of V, even if some values are irrelevant for a given calculation, e.g., if  $\mu_1$  is not a variable for a calculation, a value for V(4), such as zero, must still be provided. After the data for the last calculation is entered, Card 32 must be repeated one more time with the value of -9999 for V(1), this signals the end of calculations to VERTEX.

If ICOPT = 2, i.e., stability field calculations are requested the following data is read:

Card 33 - ISTBCT - format-free - I -

A counter indicating the number of high variance phase fields to be calculated.

Cards 34-(34+ISTBCT) - (SNAME(I), I=1,ICP) - 5(A8,1X) - C\*8 -

the names of the phases or pseudocompounds which define each of the high variance phase fields to be calculated (these cards are read by routine INSTB). These cards should not be included if ICOPT $\neq$ 2.

If N7 $\neq$ N1 and ICOPT= 0, 1, or 3 an end-of-file test is done after Card 31, or if N7 $\neq$ N1 and ICOPT=2 this test is done after Card (22+ISTBCT+1). If the end-of-file test is true execution terminates, otherwise it is assumed that a second set of input has been appended and data is read accordingly (i.e., beginning with Card 2 as described above). If N7=N1 and ICOPT=0 the program will read format-free cards which define the variables V(1)-V(5), until a trailer card containing -9999, 0, 0, 0, 0 is read. After this trailer is read the end-of-file test is made, with the same consequences as already mentioned.

Figures 1 and 2 are examples of the input to VERTEX, on N1, used to generate the data for Figures 3.4 and 3.8 of Connolly (1988) The data for Figure 3.5 would be generated from the input shown in Figure 3.4, by changing the value on Card 2 from 1 to 0. A series of four isobaric sections from 2000 to 8000 bar, spaced at 2000 bar increments, could also be generated from this data by changing the value of VMAX(3) from 2000 to 8000. The data for Figure 3.6 could be generated from the input shown in Figure 1 by changing the value on Card 21 from 1 to 0.

### 3. THE THERMODYNAMIC DATA FILE

The thermodynamic data file read from LUN N2 is divided in two parts. The first part identifies the data-bases stored in the file and initializes computational parameters which are not subject to frequent changes by users. The remainder of the file consists of data which defines the standard state properties, heat capacity functions, and volumetric functions of phases and chemical species. All reads from LUN N2 are done from subroutine INPUT2.

For the first part of the thermodynamic data file the variables read on each card image and their significance are as follows (FORTRAN read format or variable types are also indicated):

Card 1 - IDAT - format-free - I -

IDAT is a counter indicating the number of data-bases stored in the data file.

- Card 2 - (VNAME(I), I=1,3) - 3(A8,18X) -  
the character names for variables V(1), V(2), and V(3) for print output (to LUN's N3 and N8).
- Cards 3-5 - (IG(I), GNAME(I), I=1,3) - (I2, A78) -  
the number of characters and the graphics code names for variables V(1), V(2), and V(3). The graphics code names are written to N4, but have no other significance in VERTEX.
- Card 6 - (DELT(J), J=1,5), DTOL - format-free - R -  
the values of DELT are the finite difference increments for the variables in the array V and are used to estimate Clapeyron slopes (equation (28), equation numbers > 20 refer to Connolly 1989) and to solve equation (26) (routines SLOPE and UNIVEQ). DTOL is the numerical zero for testing condition (23) (DTOL is used in most of the routines called by subprogram BOSSOP). DTOL is also used to define two additional tolerances UTOL (-DTOL/10) and PTOL (-3\*DTOL) in topn2. UTOL is the numerical zero for satisfying equation (26) (routine UNIVEQ), and PTOL is the numerical zero used to locate invariant fields in Schreinemakers projections (routine PCHK). The values of DELT, DTOL, UTOL, and PTOL can effect program stability and efficiency. As a general rule the elements of DELT may be assigned values four or five orders of magnitude less than the typical corresponding values of DV. An exception to this rule occurs when Bottinga and Richet's CO<sub>2</sub> equation of state is used, in this case the values DELT(1) and DELT(2), must be at least 0.01 and 0.001. DTOL, UTOL and PTOL have the same units as the free energy function of equation (1). Normally DTOL, UTOL, and PTOL should be assigned values such that  $|UTOL| < DTOL < |PTOL|$ . The value of DTOL is dictated by the amount of round-off error associated with solving equation (22), which is generally quite small. On the other hand, small values of UTOL and PTOL can lead to excessive iteration. UTOL should always be less than PTOL/2.
- Card 7 - ICODE, P, T - format-free - I, 3\*R -  
ICODE is an integer code identifying one of the data-bases stored in the file. P and T are the standard state values for V(1) and V(2) (usually pressure and temperature).
- Card 8 - DNAME(ICODE) - A40 -  
the character name for the data-base identified by ICODE.
- Cards 7 and 8 are repeated for each data-base stored in the file, the final card being 2\*IDAT+6.
- Card (2\*IDAT+7)- ICM PN - format-free - I -  
for the Gibbs function, these are the chemical species which are taken to define the chemical composition of all phases and species in the data-base. More generally, the number of extensities for the dependent state function tabulated in the data-base.
- Cards (2\*IDAT+8)-N- (CMPNT(J), J=1,ICMPN) - 6(A5,1X) -  
for the Gibbs function, CMPNT contains the character names of the independent chemical species. More generally, the character names for the extensities for the dependent state function.
- Card N+1- IDS1,IDS2 - format-free - I -  
the indices of the elements of the array CMPNT which correspond to chemical species subject to a phase saturation constraint (i.e., any species which may be specified on Card 9 of the file on N1). If there are no such species assign values of zero.
- Card N+2- Comments - a3 -  
Comments may be placed after Card N+1, the list of comments is terminated by a left justified "end" comment.

The "end" card ends the first part of the data file. Note that the value of Figure C.3 shows an example of this part of the data file setup for five different data-bases. Because the variable names are assigned for all data in the file, care must be taken to insure that each data-base is consistent with these choices. There is no requirement that data should be available for all the species named on Cards (2\*IDAT+8)-(N+1).

The second part of the thermodynamic data file consists of the standard state data, heat capacity functions, and volumetric functions for individual phases and chemical species. With the exception of the first read for each phase, all subsequent reads are format-free; consequently, the data may be written on as many cards as necessary to accommodate it. However, data which is read in more than one read statement cannot be put on the same card. Comment cards may be placed between data entries provided the first eight



columns of the comment card are blank. The variables read by each FORTRAN read statement are as follows (FORTRAN read format and variable types are also indicated):

Read 1- NAME, IBASE, JMOD, ILAM, IDISO - A8, 4(I2) -

NAME is the character name for the phase. JMOD is a flag which if non-zero indicates whether additional data is provided for seismic velocity computations. Usually subdivision into pseudocompounds is done within VERTEX, and the option of specifying pseudocompounds on LUN N2 is used only in special cases. ILAM is a flag which indicates that the phase has one or more second-order or pseudo-second order transitions if not 0. If not 0, ILAM may have three ranges of values. If  $1 \leq ILAM \leq 3$ , the transition is to be treated as described by Berman and Brown (1985), the number of transitions for the phase is ILAM. If  $4 \leq ILAM \leq 6$ , the transition is to be treated as described by Helgeson et al. (1978) for all phases except Quartz and Coesite, the number of transitions for the phase is ILAM-3. If ILAM = 7, the transition is to be treated as described by Helgeson et al. for Quartz and Coesite. If ILAM = 10, the transition is to be treated by the Landau model (Holland and Powell 1990). In some cases high and low polymorphs may be treated as distinct phases, in which case data for each polymorph is entered separately and ILAM is assigned a value of 0 for each entry. IDISO is a flag which indicates that the phase has temperature dependent configurational disordering if 1, if temperature dependent configurational disordering does not occur, or if it is accounted for within the heat capacity function this IDISO is assigned a value of 0.

Read 2 - (COMP(J), J=1,ICMPN), (THERM(J), J=1,18) - format-free - R -

The array COMP contains the molar stoichiometric coefficients of the species corresponding to the species identified in the array CMPNT. THERM(1) is the standard state molar Gibbs free energy. THERM(2) is the standard state molar entropy. THERM(3) is the standard state molar volume. The values THERM(4)-THERM(10) correspond to the coefficients a-g of the molar heat capacity function given in equation (1). The values THERM(11)-THERM(18) correspond to the coefficients  $b_1$ - $b_8$  of the molar volumetric function given by equation (2).

Read 3 - ((TM(I,J), I=1,10), J=1, JLAM) - format-free - R -

This read is done only if ILAM $\neq$ 0. JLAM is the number of transitions, determined from ILAM (Read 1, above). Data may be provided for up to three transitions, each transition being indexed by the value of J. TM is dimensioned for up to three transitions; however only one transition per phase is permitted for transitions treated by Holland and Powell's (1990) method.

For transitions treated by the Landau model (Holland and Powell 1990): TM(1,J) is the temperature of the J<sup>th</sup> transition in Kelvin. TM(2,J) is the maximum entropy change of the J<sup>th</sup> transition. TM(3,J) is the maximum volume change of the J<sup>th</sup> transition.

TM(4-10,J) have no significance (but must be assigned values).

For transitions treated by Helgeson's method: TM(1,J) is the temperature of the J<sup>th</sup> transition in Kelvin. TM(2,J) is the slope (dP/dT) of the J<sup>th</sup> transition phase boundary. TM(2,J) should be set to zero, if the slope (dp/dT) is infinite or unspecified. TM(3,J) is the entropy change of the J<sup>th</sup> transition. TM(4-10,J) are the coefficients a-g, respectively, of the heat capacity function (Eq 1) for the high temperature phase after the J<sup>th</sup> transition.

For transitions treated by Berman and Brown's (1985) method: TM(1,J) is the value of  $l_1$  in equation (3) for the J<sup>th</sup> transition. TM(2,J) is the value of  $l_2$  in equation (3) for the J<sup>th</sup> transition. TM(3,J) is  $T_{\lambda}^P$ , the temperature of the J<sup>th</sup> lambda transition at the reference state pressure. TM(4,J) is the slope (dT/dP) for the J<sup>th</sup> transition phase boundary (assumed constant). TM(5,J) and TM(6,J) approximate the derivatives (dV/dT) and (dV/dP) for the phase. TM(7,J) is  $T_{ref}$ , the temperature of the beginning of the lambda spike for the J<sup>th</sup> transition at the reference state pressure. TM(8,J) is  $\Delta_{fudge}H$ , the "non-lambda enthalpy change" of the J<sup>th</sup> transition at the reference state pressure. TM(9-10,J) are not used in the current version of VERTEX. For additional explanation see Berman and Brown (1985) or Berman (1988).

Read 4 - (TD(I), I=1,9) - format-free - R -

This read is done only if IDIS $\neq$ 0. TD(1)-TD(7) are the parameters  $d_0$ - $d_6$ , respectively, in equations (4) and (5). TD(8) is the temperature of the onset of disordering ( $T_{dis,ref}$ ). TD(9) is the temperature

of complete disordering ( $T_{dis}$ ).

Figure C.4 shows an example of data read from the second part of the file on N2. The first phase, PYR (pyrophyllite), is an example of a phase with neither high order transitions nor temperature dependent disordering. The second phase, KF (orthoclase), is an example of a phase with temperature dependent configurational disordering. The third phase, Q (quartz) is an example of a phase with an assumed lambda transition. The fourth entry, CO2 (carbon dioxide, gas), is a species (or phase) for which the thermodynamic properties are calculated relative to an ideal gas fixed pressure standard state; note that because of this convention the molar volume is set to zero. The fifth entry defines an oxygen fugacity buffer for magnetite-hematite equilibrium.

#### 4. THE SOLUTION MODEL DATA FILE

The solution model data file describes the mixing properties of chemical solutions (see section 1.3.1) and the subdivision schemes used to generate pseudocompounds (see section 1.4) for these solutions. At present VERTEX is dimensioned to permit solution models with up to three independent mixing sites and up to three molecular species mixing on each site. The total number of mixing sites cannot exceed five, and no more than five species may be present on any site. The solution model file is read from LUN N9 by routine INPUT9, data for special configurational entropy models (see section 1.3.1) is read by subroutine RMODEL (called by INPUT9). With the exception of the first and third read statements for each solution, all other read statements are format-free; consequently, data may be written on as many card images as necessary to accommodate it. However, data which is read in more than one read statement cannot be put on the same card. Comment cards may be placed between data for solution models provided the first ten columns of the cards are blank. The format of the statements to read a solution model is described below.

Read 1 - TNAME - A10 - C\*10 -

The name of the solution phase.

Read 2 - ISITE - format-free - I -

The number of independent, nonequivalent, mixing-sites in the solution model (i.e.,  $n$  in equation (7)), ISITE must be less than four.

Read 3 - (ISP(I), IST(I), I=1,ISITE) - format-free - I -

ISP(I) is the number of species mixing on the  $I^{\text{th}}$  independent mixing-site (i.e.,  $s_i$  in equation (7)), ISP(I) must be less than four. IST(I) is the multiplicity of site I per formula unit of the solution (i.e.,  $q_i$  in equation (8.1)). For models in which equation (8.2) is used to compute configurational entropy, the values of IST(I) are read, but have no significance.

Read 4 - (((MNAME(I,J,K), I=1,ISP(1)), J=1,ISP(2)), K=1,ISP(3)) - 3(A8,1X) - C\*8 -

MNAME(I,J,K) is the name which identifies the solution endmember with the  $I^{\text{th}}$  species on site 1, the  $J^{\text{th}}$  species on site 2, and the  $K^{\text{th}}$  species on site 3. For models with less than three independent mixing sites (ISITE<3) only names for the relevant species/site indexes are read and the unused indexes are set to equal to one, e.g., for a single-site model the endmembers read are (MNAME(I,1,1), I=1,ISP(1)), and for a two-site model endmembers read are ((MNAME(I,J,1), I=1,ISP(1)), J=1,ISP(2)). These endmember names should match names defined in the thermodynamic data file. **NOTE:** the order in which the endmembers are entered defines the molecular species mixing on each site, e.g., in the two-site model for chlorite discussed in section 1.3.1, entering clinocllore and daphnite as the first and second names implies that the chlorite M1-site is the first site and Mg is the first species on that site. The remaining names must be entered so as to be consistent with these assignments, i.e., amesite must be the third endmember (1,2), and ferroamesite must be the fourth endmember (2,2). If amesite, instead of daphnite, was entered as the second endmember, this would imply that the chlorite T2-site is the first site, and that SiAl is the first species on T2, in this case daphnite must be the third endmember (1,2).

Read 5 - (((IEND(I,J,K), I=1,ISP(1)), J=1,ISP(2)), K=1,ISP(3)) - format-free - I -

IEND(I,J,K) is a flag which indicates if zero, that endmember MNAME(I,J,K) is to be considered part of the solution, this can effect the way in which VERTEX determines the variance or identity of some equilibria. If the flag is one, the endmember is considered in the calculation but is considered a true compound for computing variance. If the flag is two, after pseudocompounds have been generated,

the thermodynamic properties of the endmember are changed so that it will be metastable under most conditions (in effect, this is a way of eliminating the endmember from the calculation). As in read 4, in the case of models with less than three independent mixing sites, only values for the relevant species/site indexes are read.

Read 6 - ((XMN(I,J), XMX(I,J), XNC(I,J), J=1,ISP(I)-1), IMD(I), I=1,ISITE) - format-free - I -

XMN, XMX, and XNC are parameters describing the subdivision schemes to be used in generating pseudocompounds (see section 1.4) on the I<sup>th</sup> site, they have the following significance depending on the value of IMD(I) and the number of species (ISP(I)) mixing on the site.

**IMD(I)= 0, ISP(I)= 2 or 3 - Cartesian Subdivision.** XMN(I,J) and XMX(I,J) are the minimum and maximum values of the molecular site fraction of the J<sup>th</sup> species on the I<sup>th</sup> site and XNC(I,J) is the increment for this site fraction between pseudocompounds. For ternary sites the subdivision is done by incrementing  $X_{i2}$  and taking all valid values of  $X_{i1}$  between XMN(I,1) and XMX(I,1). Pseudocompounds are generated over the compositional range spanned by (XMN(I,1), XMN(I,2)), (XMX(I,1), XMN(I,2)), and (XMN(I,1), XMX(I,2)). **NOTE:** for ternary sites these values are not independent, i.e., XMX(I,1) must be  $\leq 1 - \text{XMN}(I,2)$  and XMX(I,2) must be  $\leq 1 - \text{XMN}(I,1)$ . If inconsistent limits are specified VERTEX redefines the limits and writes a warning message.

**IMD(I)= 1, ISP(I)= 2 - Symmetric Transform Subdivision.** XMN(I,1) is a stretching parameter for the transformation, XMN(I,1) must be greater than one; as XMN(I,1) approaches one an increased density of pseudocompounds at the compositional extremes of the solution is obtained; and as XMN(I,1) approaches infinity the pseudocompound density becomes uniform (Cartesian).  $2 * (\text{XNC}(I,1) - 1) - 1$  is the number of pseudocompounds to be generated. XMX(I,1) determines the compositional region to be considered. If XMX(I,1) is positive, then XMX(I,1) is the maximum mole fraction of the first species on the I<sup>th</sup> site. If XMX(I,1) is negative, then the absolute value of XMX(I,1) is the maximum mole fraction of the second species on the I<sup>th</sup> site. If XMX(I,1) is zero, or its absolute value is  $> 1$ , then the subdivision is done over the entire compositional range possible for the site.

**IMD(I)= 2, ISP(I)= 2 - Asymmetric Transform Subdivision.** XMX(I,1) defines the maximum site fraction of the first species on the I<sup>th</sup> site. XMN(I,1) is a stretching parameter for the transformation, XMN(I,1) must be greater than one; as XMN(I,1) approaches one, an increased density of pseudocompounds is obtained as the composition of the solution approaches  $X_{i1}=0$ .  $(\text{XNC}(I,1) - 1)$  is the number of pseudocompounds to be generated.

**IMD(I)= 1-4, ISP(I)= 3 - Barycentric subdivision.** XMN(I,J) and XMX(I,J) are the minimum and maximum values of the molecular site fraction of the J<sup>th</sup> species on the I<sup>th</sup> site. (XMN(I,1), XMN(I,2)), (XMX(I,1), XMN(I,2)), and (XMN(I,1), XMX(I,2)) define a triangular region of the site composition space over which pseudocompounds are generated. The value of IMD(I) is the order of the subdivision and determines the number of compounds generated, for values from 1 to 4, the number of compounds is 7, 25, 121 and 673, respectively. The values of XNC(I,J) have no significance, but must be assigned.

Read 7 - ITERM, IORD - format-free - I -

ITERM is the number of terms in the solution model (i.e., s in equation 9). IORD is the maximum order of any term in the solution model (i.e., the maximum value of the index  $t_k$  in equation 9). For ideal solution models ITERM=0, and IORD has no significance.

Read statements 7a and 7b are executed sequentially ITERM times with the index K running from 1 to ITERM, if ITERM=0 these statements are not executed.

Read 7a - (ISUB(K,M), JSUB(K,M), M = 1, IORD) - format-free - I -

ISUB(K,M) and JSUB(K,M) are the values of the site and species index, respectively, for the M<sup>th</sup> molecular site fraction of the K<sup>th</sup> term of equation (9), i.e.,  $\text{ISUB}(K,M) = u_{km}$  and  $\text{JSUB}(K,M) = v_{km}$ . If  $t_k < \text{IORD}$ , the unused values of ISUB(K,M) and JSUB(K,M) must be assigned zero values.

Read 7b - (WG(K,L), L=1,11) - format-free - R -

The parameters (WG(K,J), J=1,11) correspond to the coefficients  $w_{k1} - w_{k11}$  in equation (10).

Read 8 - MSITE - I -

If MSITE is non-zero equation (8.2) is to be used to compute configurational entropy and the value of MSITE is the total number of nonequivalent mixing sites for the solution. Refer to section 1.3.1 for a

definition of parameters.

The following nested read statements (8a-8d) are executed MSITE times with the site index K running from 1 to MSITE, if MSITE=0 these statements are not executed. These read statements are executed from routine SMODEL.

Read 8a - NSP(K), SMULT(K) - format-free - I, R -

NSP(K) is the number of species mixing on site K ( $s_k$ , equation 8.2). SMULT(K) is the multiplicity of site K per formula unit of the solution ( $q_k$ , equation 8.2).

Read statement 8b is repeated following each execution of Read 8a NSP(K) - 1 times with the species index L running from 1 to NSP(K) - 1.

Read 8b - NTERM(K,L), A0(K,L) - format-free - I, R -

NTERM(K,L) is the number of terms used to describe the site fraction of the L<sup>th</sup> species on the K<sup>th</sup> site ( $p_{kl}$ , equation 8.4). A0(K,L) is the value of  $\alpha_{kl}$  in equation (8.4).

Read statement 8c is repeated following each execution of Read 8b NTERM(K,L) times with the term index I running from 1 to NTERM(K,L).

Read 8c - NTTY(K,L,I) - format-free - I -

NTTY(K,L,I) is the number of molecular site fractions which appear in the I<sup>th</sup> term of the expression for the site fraction of the L<sup>th</sup> species on the K<sup>th</sup> site ( $r_{kli}$ , equation 8.4).

Read 8d - ACOEF(K,L,I), (NSUB1(K,L,I,J), NSUB2(K,L,I,J), J = 1, NTTY(K,L,I)) - format-free - R, I -

ACOEF(K,L,I) is the value of  $\alpha_{kli}$  in equation (8.4), and NSUB1(K,L,I,J), NSUB2(K,L,I,J) are the values of the molecular site fraction indices  $u_{klij}$  and  $v_{klij}$ , respectively, in equation (8.4).

Read 9 - JFIX - format-free - I -

JFIX is a flag indicating the number of endmembers which have fixed composition (mole fraction) in the solution.

The following read statement is executed only if JFIX≠0.

Read 9a - (IDCF(I), XFX(I), I=1,JFIX) - format-free - I, R -

IDCF(I) is the index of an endmember in the array MNAME of which the composition will be held constant, and XFX(I) is the value of the composition. At present, an endmember composition may be held constant only if that endmember does not lie in the composition space of the system being considered by vertex, e.g., for example the spessartine content of a garnet may be held constant only if MnO is not a component in the calculation. In this case, an activity correction is made for such endmembers, and the solution composition is renormalized for the remaining endmembers. The composition of a solution may be held constant within the composition space of a system by setting XMAX=XMIN, in general such calculations (as are "fixed-activity" calculations) are thermodynamically invalid.

## 5. PRINTER/TERMINAL OUTPUT

The format of the data output to the print file on LUN N3 requires little explanation (I hope). To facilitate viewing of computational results on computer terminals, rather than in line printer output, the computational summaries have been made as brief as possible, and largely consists of logical records less than 80 characters long. Only information describing phase diagram geometry is output; however, VERTEX can be manipulated to output almost any kind of thermodynamic information relevant to phase diagram calculations and, it is hoped, such manipulations can be accomplished with little difficulty by experienced programmers. In the present version of VERTEX some error messages are written to the file (or terminal) designated by LUN N8, all other print output is written to LUN N3.

The output to LUN N3 for all types of calculations is prefaced by a title segment which is primarily an echo of the input data, an example of this segment generated from the data shown in Figures C.1 and C.3 is given in Figure C.8. The title segment is generated by routine OUTTIT and indicates: (i) The sequence of the calculation. (ii) The thermodynamic data base read from LUN N2. (iii) The equation of state used for the saturated phase (if a calculation was requested with such a phase). (iv) Potentials subject to external, saturation, or buffering constraints (chemical potentials are indicated only by the identity of the chemical species). (v) Thermodynamic components. (vi) The composition (as defined in equation (22) of

Connolly 1990) of those phases which have coordinates off saturation and buffering surfaces (these records are more than 80 characters long). (vii) Phases with representative coordinates which correspond with a saturation or buffering surface. (ix) Phases excluded from consideration.

### 5.1. Composition Diagrams

An example of the output following the title segment for composition diagram calculations is shown in Figure C.9. This output is for the calculation illustrated by Figure 3.5. Output for composition diagram calculations is generated by routine OUTCHM and indicates: (i) The stable phases (or buffering "species") on the specified component saturation ( $\alpha$ -Q) and buffering (Mt-Hm) surfaces. (ii) The values of the independent potentials (or the composition of the saturated phase, if appropriate). (iii) The stable phase assemblages (the integer flag (IASMBL) indicated parenthetically for each assemblage, has the following significance: IASMBL=1 - the assemblage is invariant; IASMBL=2 - the assemblage is pseudounivariant; IASMBL=3 - the assemblage includes an immiscible solution phase; IASMBL=4 - the assemblage consists entirely of pseudocompounds which comprise part of a true one-phase region) (iv) Whether or not immiscibility was detected in any solution phases. For binary systems the stable phases are listed in the order that they occur along the compositional join, buffering surface.

### 5.2. Schreinemakers, Mixed Variable, and Stability Field Diagrams

The output for Schreinemakers diagrams is illustrated by the example shown in Figure C.10, which was generated by a calculation similar to that shown in Figure 3.6, but over a more limited range of temperature (800-825 K) and  $Y_{CO_2}$  (0.0-0.2 mole). It should be noted that the output shown in Figure C.10 has been abridged and is intended only to show the general form of the file written to N3. This output consists of three major parts for each section at constant  $V(IV(3))$ : (i) The composition diagram at the conditions ( $V(IV(1)), V(IV(2))$ ) is summarized in the first part, this part is generated by routine OUTCHM. (ii) The  $V(IV(1))-V(IV(2))$  loci of the (pseudo-) univariant phase fields are summarized in the next part. This section is prefaced by a line which gives the names for the variables  $V(IV(1))$ ,  $V(IV(2))$ , and  $V(IV(3))$  (i.e.,  $VNAME(IV(1))$ ,  $VNAME(IV(2))$ , and  $VNAME(IV(3))$ ), and the value for the sectioning variable  $V(IV(3))$  (this line is written in routine NEWHLD). Each phase field is identified by the corresponding reaction equation, which is specified by the phase names and reaction coefficients and by a numeric code (VAR-NAMES). The coordinates for each phase field are given as  $V(IV(1))-V(IV(2))$  pairs. The data for univariant phase fields is written by routines OUTIER and OUTFRN. (iii) The third part is a summary of the (pseudo-) invariant phase fields and the conditions at which they occur, this part is written by the MAIN program segment. Each invariant phase field is identified with a two part numeric code, the first part of this code is a numeric label for the phase field, and the second part is a flag (IPVAR) which indicates if the field is invariant (IPVAR=1) or pseudoinvariant (IPVAR=2). After parts (i-iii) have been repeated for each section at constant  $V(IV(3))$ , cumulative lists, i.e., for all sections, of the univariant reactions and invariant phase fields are output by routine OUTLST. In the list of univariant reactions each reaction is identified by a numeric label and a flag (IVAR) which indicates if the reaction is univariant (IVAR=1) or pseudoinvariant (IVAR=2).

The structure of the data file written to LUN N3 for mixed variable diagrams, as illustrated by the example shown in Figure C.11, is similar to that written for Schreinemakers diagrams and the differences probably do not require explanation. The phase field identities and conditions for mixed variable diagrams are written by routine OUTIRN. Likewise, the output for stability field calculations is also essentially identical to that for Schreinemakers diagrams except that data for composition diagrams is not output (i.e., part (i), immediately above); and a line indicating the phase assemblage in question appears as the first part following the title segment. The (pseudo-) univariant phase field identities and conditions for stability field diagrams are written by routines OUTIER and OUTFRN.

## 6. OUTPUT FOR COMPUTER GRAPHICS

VERTEX produces a data file for computer graphics on LUN N4. VERTEX is capable of producing more complex output for generating three-dimensional phase diagrams and to allow comparisons of calculations. Because suitable graphics equipment is not generally available the version of the program presented here is tailored to produce a file for simple diagrams. An undocumented version of VERTEX with more

complex graphics file structure, and examples of appropriate graphics software, can be obtained from the author. The following sections describe the structure of the sequential card image graphics file for each type of calculation.

### 6.1. Composition Diagrams

The graphics file for composition diagram calculations is written by routine OUTGRF. Figure C.12 shows the graphics file used to generate Figure 6 (see also Figure C.9). The variables written by each FORTRAN write statement are as follows:

Write 1 - ICOPT - I3 -

ICOPT is a flag indicating the kind of data which follows, for composition diagrams ICOPT = 0.

Write 2 - ICP, ISTCT, IPHCT, IPOINT, IB, IFYN, ISYN, IPOT - 8(I3,1X) -

ICP is the number of thermodynamic components. ISTCT is the index of the first phase in the array NAMES (see below) whose coordinates do not lie entirely on a saturation or buffering surface. IPHCT is the total number of phases in the array NAMES. IPOINT is the index of the last true compound in the array NAMES. IB is the number of stable phase assemblages. IFYN is a flag which indicates that the calculation was done with a phase saturation constraint (i.e., if IFYN=0, otherwise IFYN=1). ISYN is a flag which indicates that the calculation was done with component saturation constraints (i.e., if ISYN=0, otherwise ISYN=1). IPOT is the number of independent potentials.

Write 3 - (IG(JV(I)), GNAME(JV(I)), I=1,IPOT) - (I2, A78) -

IG(JV(I)) is the number of characters in the name GNAME(JV(I)) of the JV(I)<sup>th</sup> independent potential as encoded for the graphics applications (see Cards 3-5 of data on N2).

Write 4 - (V(JV(I)), I=1,IPOT) - 5(G10.4,1X) -

The values of the independent potentials (for further explanation of JV and IPOT refer to section 1.2).

Write 5 - TITLE - (A72) -

Title for the phase diagram calculation as read from Card 31 of the computational option file read on LUN N1.

Write 6 - (NAMES(I), I=1,IPHCT) - 10(A8) -

The names of all possible phases (and real or fictive species) considered in the phase diagram calculation. NAMES(1) and NAMES(2) are the names of the independent components of the saturated phase specified for a phase saturation constraint, note that if such a constraint is not specified these names are specified by default (as (NAMES(I), I=2, ISTCT-1) are the names of phases or species which define buffering and component saturation constraints. (NAMES(I), I=ISTCT, IPHCT) are names of phases which may plot in the composition diagram.

Write 7 - ((X(I,J), J=1,ICP-1) I=ISTCT, IPHCT) - 11(F6.4,1X) -

The first c-1 (ICP-1) compositional coordinates of each of the phases which may plot in the composition diagram.

For binary systems:

Write 8 - (IDBV(1,I), I=1,IB) - 20(I3,1X) -

the indices of the stable phases (in the arrays NAMES and X) along the binary join, ordered by increasing X(I, 1).

For ternary systems:

Write 8 - ((IDTV(1,J, I), I=1,3), J=1,IB) - 20(I3,1X) -

the indices of the three stable phases in the J<sup>th</sup> phase field of the ternary join.

For quaternary systems:

Write 8 - ((IDQF(1,J, I), I=1,4), J=1,IB) - 20(I3,1X) -

the indices of the four stable phases in the J<sup>th</sup> phase field of the quaternary join.

For quinary systems:

Write 8 - ((IDCF(J, I), I=1,5), J=1,IB) - 20(I3,1X) -

the indices of the five stable phases in the J<sup>th</sup> phase field of the quinary join.

Write 9 - (IASMBL(J), J=1,IB) - 20(I3,1X) -

IASMBL(J) is a flag for the J<sup>th</sup> assemblage written in Write 8 with the following significance: IASMBL(J)=1 - the assemblage is invariant; IASMBL(J)=2 - the assemblage is pseudounivariant; IASMBL(J)=3 - the assemblage includes an immiscible solution phase; IASMBL(J)=4 - the assemblage consists entirely of pseudocompounds which comprise part of a true one-phase region). The value of IASMBL can be used to determine the graphics pattern used to represent the assemblage (cf., Figures 3.1 and 3.5).

The following data is written only if ISYN=0.

Write 10 - ISAT - I3 -

the number of buffering or component saturation constraints.

Write 11 - (IDSS(I), I=1,ISAT) - 3(I3,1X) -

IDSS(I) is the index of the equilibrium phases or species which define the buffering or component saturation surfaces, i.e., IDSS(I) is the index J of a phase in the arrays NAMES and X, where  $2 < J < \text{ISTCT}$ .

## 6.2. Schreinemakers and Stability Field Diagrams

The graphics file for Schreinemakers and stability field diagrams is generated by the MAIN program segment and by routines OUTFRN, OUTIER, and OUTLST. Figure C.14 shows an example of the graphics file complementary to the print file presented in part in Figure C.10 for a Schreinemakers diagram calculation. The format of the graphics files generated for stability field calculations is identical in every respect to that of the files generated for Schreinemakers diagrams. The variables written by each FORTRAN write statement are as follows:

Write 1 - ICOPT - I3 -

ICOPT is a flag indicating the kind of data which follows, for Schreinemakers diagrams ICOPT = 1, and for stability fields ICOPT = 3.

Write 2 - IPHCT, ISOCT - 2(I3,1x) -

IPHCT is a counter of the total number of compounds and pseudocompounds considered in the calculation, and ISOCT is a counter of the number of solution phases considered.

Write 3 - (NAMES(I), I=1,IPHCT) - (10A8) -

The alphanumeric names of compounds and pseudocompounds. This Write is only executed if IPHCT  $\neq$  0.

Write 3 - (IKP(I), I=1,IPHCT) - (26(I2,1x)) -

Flags which indicate whether the i<sup>th</sup> compound in the array NAMES is a true compound (IKP(I)=0) or not. If the i<sup>th</sup> compound is a pseudocompound, IKP(I) is a pointer to the corresponding solution name in the array SNames (see Write 4). This Write is only executed if IPHCT  $\neq$  0.

Write 4 - (SNames(I), I=1,ISOCT) - (8A10) -

The alphanumeric names of the solution phases. This Write is only executed if ISOCT  $\neq$  0.

Write 5 - (TITLE(I), I=1,4) - (A72) -

Title information for the phase diagram calculation.

Write 6 - IPOT - I3 -

The number of independent potentials (see section 1.2).

Write 7 - (IG(JV(I)), GNAME(JV(I)), I=1,IPOT) - I2, A78 -

IG(JV(I)) is the number of characters in the name GNAME(JV(I)) of the JV(I)<sup>th</sup> independent potential as encoded for the graphics applications (see Cards 3-5 of the thermodynamic data file and for further explanation of JV and IPOT refer to section 1.2).

Write 8 - (VMAX(JV(I)), VMIN(JV(I)), I=1,IPOT) - 6(G11.5,1X) -

VMAX(JV(1)) and VMIN(JV(1)) are the maximum and minimum values for the "independent" potential (i.e., the x-coordinates); and VMAX(JV(2)) and VMIN(JV(2)) are the maximum and minimum values for the "dependent" potential (i.e., the y-coordinates). (VMIN(JV(I)), I=3, IPOT) are the values of the independent potentials which were held constant for the calculation. For two-dimensional diagrams (VMAX(JV(I)), I=3, IPOT) have no significance.

Write statements 1-8 are executed from routine HEADER.

Write 8 - IPT2, IRD, IVAR, IVCT, (IDR(I), I=1,IVCT) - (20(I3,1X)) -

IPT2 is the number of V(IV(1))-V(IV(2)) coordinate pairs output for the (pseudo-) univariant phase field in Write 9. IRD is an integer code which identifies the reaction equation associated with this phase field. IVAR is a flag which indicates that the phase field is univariant (IVAR=1) or pseudo-univariant (IVAR=2). IVCT is a counter indicating the number of phases in the phase field. IDR contains pointers to the compounds of the phase field in the array NAMES. IRD may be used to identify the phase field in graphical output, and IVAR may be used to determine the line pattern used to draw the field.

Write 10 - (VNU(I), I=1,IVCT) - 7(G10.4,1X) -

VNU contains the reaction coefficients of the phases identified by the pointer array IDR.

Write 11 - (PTX(I), I=1,IPT2) - 3(1X,G10.4,1X,G10.4,3X) -

PTX contains the V(IV(1))-V(IV(2)) coordinate pairs which define the (pseudo-) univariant phase field associated with the values of IPT2, IRD, and IVAR written by write statement 8.

Write statements 8-11 are repeated for each (pseudo-) univariant phase field and are executed from routine OUTRXN. Following the last set of V(IV(1))-V(IV(2)) coordinate pairs the trailer card " 1 1 1 1 1.0 " is written to N4 from routine OUTIER. This card can be recognized as a trailer (i.e., distinguished from the output of Write 3) because the value of IPT2 written by write statement 3 cannot be less than two.

Write 13 - IPCT, ICP2 - format-free - I -

IPCT is the number of (pseudo-) invariant phase fields. ICP2 is the number of phases in each invariant phase field.

For each (pseudo-) invariant field (i.e., J=1,IPCT) the following write statements are executed:

Write 14 - IP1(J), IVARIP(J), (IDP(I), I=1,ICP2) - (20(I3,1X)) -

IP1(J) is an integer code which identifies the J<sup>th</sup> (pseudo-) invariant field; and IPVAR(J) is a flag which indicates if the J<sup>th</sup> field is invariant (IVARIP(J)=1) or pseudo-invariant (IVARIP(J) = 2). IDP contains pointers to the compounds of the J<sup>th</sup> phase field in the array NAMES. IVARIP(J) can be used to determine the graphics marker pattern for the associated phase field, and IP1(J) can be used to label the field.

Write 15 - (VIP(JV(I),J),I=1,IPOT) - (5(G11.5,1X)) -

((VIP(JV(I),J),I=1,IPOT) are the values of the potentials (V(JV(I)),I=1,IPOT) for the J<sup>th</sup> invariant field.

Write statements 14 and 15 are repeated for each invariant field.

Note that the data written by write statements 14 and 15 are actually written to a scratch file on LUN N6 from routine OUTIER. The scratch file is subsequently rewound in the MAIN program segment and then copied to N4 as character data (the C\*80 variable RECORD).

### 6.3. Mixed-Variable Diagrams

The graphics file for mixed variable phase diagrams is generated by routines OUTGRF and OUTIRN. Figure C.13 shows a graphics file for a mixed variable diagram, this example is for the same calculation summarized in Figure C.11. The variables written by each FORTRAN write statement are as follows:

Write 1 - ICOPT - I3 -

ICOPT is a flag indicating the kind of data which follows, for mixed variable diagrams ICOPT = 2.

Write statements 2-11 -

are done by routine OUTGRF and are exactly the same as described for composition diagrams in the preceding section. The composition diagram described by this portion of the file is calculated at the minimum value of the independent potential (i.e., V(IV(1))=VMIN(IV(1))).

Write 12 - (XNAME(J), J=1,ICP-1) - 5(A18) -

the names of the first c-1 compositional variables encoded for graphics output. The order of output corresponds to the order the components are entered on Card 7 of the input read from N1.

Write 13 - (IKP(I), I=1,IPHCT) - 20(I3,1X) -

IKP(I) is a flag which is assigned a value of 0 if the I<sup>th</sup> phase is not a pseudocompound. If the phase



is a pseudocompound IKP is given an integer value identifying the solution phase; i.e., all phases for which IKP=0 are true compounds, all phases for which IKP=n (an arbitrary value not equal 0) represent the same solution phase. The values of IKP can be used, in conjunction with the initial phase configurations (write 7, above) and the invariant reactions (write x, below), to determine the disposition of vertical and horizontal lines about invariant and pseudoinvariant points.

Write 14 - VMIN(IV(1)), VMAX(IV(1)) - format-free -

the minimum and maximum values for the independently variable potential.

Write 15 - (IR1(I), IRV(IR1(I)), IVARRX(IR1(I)), VIP(IV(1), IR1(I)),(IR(IR1(I),J), J=1,IRV(IR1(I))), I=1,IRCT) - 3(I3,1X),G12.5,1X,6(I3,1X) -

IRCT is the total number of invariant and pseudoinvariant (unless ISUDO=1, see Card 21 of input from N1) reactions which are represented in the diagram. IR1(I) is the numeric index of the I<sup>th</sup> reaction, note that unless IO5=1 IR1(I)=I (see Card 2 of input from N1). IRV(IR1(I)) is the number of phases in the I<sup>th</sup> reaction. IVARRX(IR1(I)) is a flag equal 1 if the I<sup>th</sup> reaction is invariant, and equal 2 if the reaction is pseudoinvariant. VIP(IV(1), IR1(I)) is the value of V(IV(1)) at the equilibrium condition for the I<sup>th</sup> reaction. (IR(IR1(I),J), J=1,IRV(IR1(I))) are the indexes of the phases (in the arrays NAMES and X) in the I<sup>th</sup> reaction. The reactions are written in order of increasing VIP(IV(1), IR1(I)).

Write statements 11-15 are executed in routine OUTIRN.

## 7. THE PHASE FIELD LIST FILE

The file on N5 is used to store a permanent list of phase fields. This list is maintained at the users option (see flag IO5, in Card 2 of the data on N1) to force consistent phase field numbering (i.e., the numeric codes assigned to each (pseudo-) univariant reaction and invariant field) for multiple executions of VERTEX. If the file assigned to N5 is initially empty VERTEX generates a list of fields. If the file already contains a list of fields, then during execution VERTEX checks each phase field identified in a calculation against this list; if new phase fields are identified during the calculation the permanent lists on N5 is updated. All data read from N5 is read in routine INPUT5, all data written to N5 is written from routine OUTLST. Ordinarily the data in N5 is formatted by VERTEX and does not require any initialization or modification by users; however, under certain circumstances users may wish to create their own lists. Accordingly, the format of the read statements used to read data on N5 is described below:

Read 1 - IIPCT - format-free - I -

the number of (pseudo-) invariant phase fields stored in the list on N5. For each invariant phase field, i.e., I= 1,IIPCT:

Read 2 - IPV(I) - format-free - I -

the number of phases in the I<sup>th</sup> invariant field.

Read 3 - (IPNMS(I,J), J= 1,IPV(I)) - 8(A8,1X) -

the names of the phases which define the I<sup>th</sup> phase field.

Read 4 - IIRCT - format-free - I -

the number of (pseudo-) univariant phase fields stored in the list on N5. For each univariant phase field, i.e., I= 1,IIRCT.

Read 5 - IRV(I) - format-free - I -

the number of phases in the I<sup>th</sup> univariant reaction.

Read 6 - (IRNMS(I,J), J= 1,IRV(I)) - 8(A8,1X) -

the names of the phases which define the I<sup>th</sup> univariant reaction.

Note that the numeric codes IP1 and IP2 used to identify invariant phase fields (refer to write statements 8 and 11 for LUN N4) are determined by the index J in read statements 2 and 3, above. Similarly, the numeric codes IRD and J used to identify univariant reactions (refer to write statements 4 and 13 for LUN N4) are determined by the index J in read statements 5 and 6, above. Figure C.15 shows the permanent lists created with the calculation summarized in Figure C.10.

## **8. THE SCRATCH FILE**

The scratch file assigned to N6 is used only to maintain a list of invariant conditions identified in the course a Schreinemakers or stability field diagram calculation. This file is used to generate the graphics file written to N4 and therefore must be assigned only if IO4=0 and ICOPT=1 or 3. The physical device corresponding to the logical assignment must be rewindable, i.e., either a disk or tape drive. Only two write statements and one read statement address LUN N6. The write statements are executed from routine OUTIER and are described above as write statements 13-14 addressed to LUN N4. The read statement is executed from the MAIN program segment, this statement reads the C\*80 variable RECORD with an A-mask, i.e., A80.

## **9. BUGS AND ERRATA**

This section is interactive, you write down bugs and errata, and then send them to me. Then i think about it and send something back to you.

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