# Phase Diagram Principles and Computations: A Review*

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The purpose of these notes is to provide a brief (?) discussion of how computer programs for the calculation of multidimensional phase diagrams work. The notes are divided into 2 parts. Part I is a review of phase diagram principles that I wrote for an earlier lecture, it is included here to provide background for Part II. The focus of Part II is computer strategies specifically developed for the calculation of the phase diagram projections used in metamorphic petrology. At the end of Part I, there is also a discussion of computational methods. Although this overlaps with the discussion in Part II, I have left it in because it is more lucid and more general than Part II, though less complete.

## 1. PHASE DIAGRAM PRINCIPLES

*A scientific communication from Bowen to Gilluly on equilibrium:*

"*Having had occasion some years ago to learn the art of lip-reading I noticed yesterday when I was giving my paper that at the end of each of my sentences you said, 'Horse shit.' Evidently you had made special note of the word 'equilibria' in the title of my paper and were from time to time reminding yourself and your neighbors of the gist of the discussion. You are, however, under a misapprehension as to the derivation of the word 'equilibria.' It does not come from equus = horse and libria = things liberated or discharged, but is from quite different roots. If you will consult a chemist you will be able to learn the real significance of the word and I may add that I feel one so highly placed in geological circles as you should make it a point to acquire some familiarity with the exact significance of common terms used in collateral sciences.*

*Trusting that you will not resent my corrections and suggestions I am, yours sincerely,*" /s/ *Norman L. Bowen, April 29, 1948.*

The thermodynamics of chemical equilibrium owes its origin to Gibbs' treatment of thermodynamic surfaces, but unfortunately this way of thinking about thermodynamics is largely neglected in teaching. This method is particularly useful for understanding phase equilibria involving phases of variable composition (solutions). In this part several familiar thermodynamic concepts in the context of Gibbs energy surfaces.

### 1.1. $\overline{\mathrm{G}}$–X Diagrams

The basis of equilibrium thermodynamics is the Gibbs stability criterion, which states that an isobaric-isothermal system is in stable equilibrium when its Gibbs energy (G) is a minimum.

To understand this criterion begin by considering a 2-component phase of variable composition, i.e. a solution. If the molar Gibbs energy is plotted (the Gibbs energy of the phase per mole of components, $\overline{\mathrm{G}}$) vs. composition (X) (at constant P and T), a curve such as that shown by the heavy curve in Fig 1.1a will be obtained. Let us consider a system in which this phase is the only possible phase, but ignore the stability criterion, in this case the system may consist of any number of parts each of which will be described by a point on the $\overline{\mathrm{G}}$–X curve of the phase. The only constraints on the system and its parts are that the mean (mole weighted) composition and Gibbs energy of the parts must be equal to the bulk composition and Gibbs energy of the system. Suppose the system has a composition $X_s$, and consists of 2 equal parts a and b, the Gibbs energy of the system will be given by the point on the line connecting the $\overline{\mathrm{G}}$–X coordinates of

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a and b at $X_s$ ($\overline{G}_s$ in Fig 1.1). Now, considering the Gibbs' stability criterion, it is clear that this is not the lowest Gibbs energy for the system, for example if we change the composition of the parts to a' and b', we can lower the Gibbs energy of the system. In fact, we can keep lowering the Gibbs energy of the system by making the composition of the 2 parts of the system approach the bulk composition of the system $X_s$, and the minimum Gibbs energy will be attained when both parts are of composition $X_s$. In other words, the system will only be in stable equilibrium if the phase has the same composition in all parts of the system. It is noteworthy that this would be true for any bulk composition of the system because the $\overline{G}$–X surface** of the phase is concave with respect to the $\overline{G}$ ordinate. Solutions which have this property are known as continuous solutions, olivine (fo-fa) and most Mg-Fe mineral solutions are examples of continuous solutions.

There is no reason to expect that the $\overline{G}$–X surface of all phases should be concave, and indeed they are not; however, for regions of composition in which the $\overline{G}$–X surface of a phase is convex the phase (with the corresponding composition) is always unstable. This is illustrated in Fig 1.1b, consider that a system consists initially of a homogeneous phase a, the system can lower its Gibbs energy if the phase unmixes into 2 parts with compositions on either side of a, and it will minimize its Gibbs energy if the parts have the compositions a' and b'. This would be true for any bulk composition between a' and b'. Such solutions are said to exhibit immiscibility, and the compositions a' and b' locate the limbs of the solutions solvus at constant P and T, Orthoclase (Or-Ab) and Muscovite (Mu-Pa) are mineral solutions with immiscibility (at least at low temperature).

It is also conceivable that the $\overline{G}$–X surface of a solution is always convex as in Fig 1.1c. In this case, a mechanical mixture of the solution endmembers is always more stable than any solution composition, and so, for practical purposes, there is no solution. In principle the $\overline{G}$–X surface of any solution cannot be always convex, that is, on a fine enough scale, the surface must be concave near the endmember compositions (e.g. there is some solubility of Zr in forsterite, and likewise some solubility of Mg in Zircon). In the limit that these concave regions are small they can be ignored and the endmembers regarded as phases with fixed compositions, i.e. compounds (e.g. zircon and forsterite, or $\alpha$ and $\beta$ in Fig 1.1c). The $\overline{G}$–X surface of a compound is actually a point rather than a surface.

Remember that in general the shape of the $\overline{G}$–X surface will vary as a function of both P and T; thus, a solution maybe continuous at one P-T condition and immiscible at another.

### 1.2. The Gibbs Energy

The Gibbs energy of a c-component system or phase is defined by the summation:

$$G \equiv \sum_{i=1}^{c} \mu_i n_i \tag{1.1}$$

where $n_i$ is the number of moles of component i, and $\mu_i$ is the chemical potential of the component defined as:

$$\mu_i \equiv \left( \frac{\partial G}{\partial n_i} \right)_{p,T,n_{j,j\neq i}} . \tag{1.2}$$

The mathematical significance $\mu_i$ is that it tells us how the Gibbs energy will change if we change $n_i$ by an infinitesimal amount, holding all the other independently variable properties (p, T, $n_{j,j\neq i}$) of the system or phase constant. The physical importance of $\mu$'s will be considered in the next section.

Eq 1.1 enables us to calculate G for a system of arbitrary size, as defined by the number of moles of each component, but in the study of phase relations we are only concerned with the state of the system which is determined by its pressure, temperature, and composition. Thus it is convenient to define a property which gives the G as a function of composition, this property is known as the molar Gibbs energy and is related to G by:

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*Throughout these notes the terms surface and plane are used in a general geometric sense, i.e. in an n-dimensional space these are n-dimensional nonlinear and linear geometric elements. Thus, in the context of a 2-dimensional (c=2) $\overline{G}$–X diagram, a curve is a surface and a line is a plane.

$$\overline{G} = \frac{G}{\sum_{i=1}^{c} n_i}. \tag{1.3}$$

If the composition (or "mole fraction") of component i is defined as:

$$X_i \equiv \frac{n_i}{\sum_{i=1}^{c} n_i}, \tag{1.4}$$

then by substituting Eq 1.1 into Eq 1.3 we obtain:

$$\overline{G} = \sum_{i=1}^{c} \mu_i X_i. \tag{1.5}$$

Any expression in terms of the integral properties ($G$ and $n_i \cdots n_c$) is equally valid in terms of ($\overline{G}$ and $X_i \cdots X_c$), but the advantage of the second form is that it involves one less independent variable because of the constraint:

$$\sum_{i=1}^{c} X_i = 1. \tag{1.6}$$

Thus Eq 1.1 is a linear equation in c-dimensional space, whereas Eq 1.5 is a linear equation in (c-1)-dimensional space.

If you are already familiar with thermodynamics, you may be thinking that there is something missing in Eqs 1.1 & 1.5, namely p and T, in which case you are confusing the differential form of the Gibbs energy:

$$dG = V\,dP - S\,dT + \sum_{i=1}^{c} \mu_i\, dn_i, \tag{1.7}$$

with the integrated forms given here, in which the P, T dependence of G or $\overline{G}$ is hidden in the $\mu$'s. Eq 1.7 is the basis for calculating the change in G from one condition to another through the use of complicated sounding things like heat capacity, isobaric expansivity, isothermal compressibility, Margules expansions, and enthalpy. Although such calculations can be mathematically complex, they are unimportant for understanding thermodynamics, and can be summarized by the simple statement:

$$G = f(P, T, n_i \cdots n_c). \tag{1.8}$$

In practice, it is rarely even necessary to know the actual form of this function, one simply looks up the value at the desired at the $P, T,$ and $n_i \cdots n_c$ of interest, or calculates them with a computer program such as FRENDLY. There is a trick though, the values one looks up, or calculates, are the Gibbs energy per molar formula unit of the phase ($G^m$) in question. A molar formula unit contains $\nu_i$ moles of component i (i=1 $\cdots$ c), therefore from Eq 1.4:

$$\overline{G} = \frac{G^m}{\sum_{i=1}^{c} \nu_i}. \tag{1.9}$$

Suppose we have calculated $G^m$ of Enstatite ($MgSiO_3$). If we are interested in a system (c=2) with the components MgO and $SiO_2$, then $\nu_{En,MgO}=1$, $\nu_{En,SiO2} = 1$, and $\overline{G}_{En} = G^m_{En}/2$. Note that if we choose a different set of components for our problem $\overline{G}_{En}$ will also change, e.g. if we choose $Mg_2SiO_4$ and $SiO_2$ then $\overline{G}_{En} = G^m_{En}$.

Eq 1.5 has the interesting implication that if a tangent to the $\overline{G}$–X surface of a phase is drawn, the intersection of the tangent with the $\overline{G}$ axes of a $\overline{G}$–X diagram gives the value of the $\mu$'s in the phase when its composition corresponds to the point of tangency (Fig 1.1). This can be demonstrated mathematically by expanding Eq 1.5 for a 2-component (c=2) system:

$$\overline{G} = X_1 \mu_1 + X_2 \mu_2. \tag{1.10}$$

If $X_1 = 1 - X_2$ is substituted into Eq 1.10, and the result rearranged, one obtains:

$$\overline{G} = \mu_1 + X_2 (\mu_2 - \mu_1). \tag{1.11}$$

which is the equation of a line for which $\overline{G} = \mu_1$ at $X_2 = 0$ and $\overline{G} = \mu_2$ at $X_2 = 1$.

### 1.3. Chemical Potentials

To understand the physical significance of μ's, it is useful to draw an analogy between μ's and temperature or pressure. There are 3 kinds of thermodynamic processes, heat (entropy) transfer, mechanical work (volume transfer), and mass transfer. A system is in stable equilibrium when no thermodynamic processes are possible. Intuitively, you will probably accept that heat transfer will only occur between 2 parts of a system if there is a temperature difference between the parts of the system (Fig 1.2). Moreover you know from experience that the heat will be transferred from the high-T part to the low-T part. Likewise 1 part of the system will only do mechanical work on the other if there is a pressure difference within the system. This work is done by the high pressure part of the system compressing the low pressure part (i.e. negative volume transfer) In these cases, we can think of temperature and pressure, respectively, as the thermal and mechanical potentials for the system, and if these potentials are uniform then no thermal or mechanical processes can occur. Chemical potentials are exactly analogous, that is, they are a measure of the potential for chemical processes (mass transfer) in a system, and in the absence of a μ difference no chemical process will occur. These process will always occur such that mass is transferred from an area where its μ is high to one in which it is low (so-called "uphill" processes, which may occur when more than 1 thermodynamic process occurs at the same time, are not considered here).

For those familiar with elementary mechanics it may be useful to note that work in mechanics is defined as:

$$W \equiv \int F\,dx \tag{1.12}$$

where dx is the displacement of an object, and F is the opposing force. The only difference between mechanics and thermodynamics is that in thermodynamics we consider 3 kinds of work:

$$W_{mechanical} \equiv \int p\,d(-V), \quad W_{thermal} \equiv \int T\,dS, \quad \text{and} \quad W_{chemical} \equiv \int \mu_i\,dn_i. \tag{1.13}$$

Comparison of eqs (12) and (13) suggests that p, T, and μ can be thought of as the thermodynamic forces against which mechanical, thermal, and chemical work are done. If these forces are equal in all parts of a system, then no work will be done by any part of the system.

Returning to the 2 part system of Fig 1.2, it is now easy to see why Gibbs' criterion works, as the μ's in different parts of the system can only be the same if all parts of the system have the same composition. This will always be true for a system in which the only possible phase is a continuous solution.

### 1.4. Heterogeneous Systems

In the previous section it has been argued that Gibbs' stability criterion requires that the μ of each component must be uniform in all parts of a stable equilibrium system. For a system composed of a single continuous solution, this implies that all parts of the system must have the same composition because the values of the μ's are different for every composition. In systems where more than 1 phase may occur there will be a separate $\overline{G}$–X curve corresponding to every possible phase (e.g. α, β, γ, and δ in Fig 1.3). As the μ's of the components can be determined for any composition of any phase by drawing a tangent line or plane if c>2) at the composition of interest, it is evident that the μ's of the components must be equal in phases which are tangent to a common line in $\overline{G}$–X space. In general, such phases will not have the same composition, but because the μ's are uniform no thermodynamic process may occur and the phases will be in equilibrium. Thus for a c-component heterogeneous system composed of p coexisting phases, the Gibbs stability criterion requires:

$$\mu_{1i} = \cdots = \mu_{pi} \quad \text{for} \quad i = 1 \cdots c. \tag{1.14}$$

The foregoing discussion has been a little oversimplified, in addition to thermal, mechanical, and chemical processes, thermodynamics has spontaneous processes which occur (in theory) in the absence of any potential gradients (in reality, or in statistical mechanics, which is at least closer to reality, they occur because of microscopic gradients). Thus, the equality of potentials at equilibrium is considered a necessary, but not sufficient criterion for stable equilibrium, and it becomes necessary to distinguish stable, metastable, and unstable equilibria. In unstable equilibria, there are no potential gradients in the system, but the composition of at least 1 phase is in a convex region of the $\overline{G}$–X surface of the phase (e.g. point a in Fig 1.1b). In metastable equilibria, all the phases have compositions along the concave portions of their $\overline{G}$–X surfaces, but there is an accessible state (involving at least 1 additional phase) of lower Gibbs energy (e.g. the equilibrium of phases $\delta$ and $\gamma$, tangent to the dashed line in Fig 1.3b, is metastable with respect to phases $\beta$ and $\alpha$).

The fundamental problem in equilibrium thermodynamics is the determination of the stable state of a system in which there is more than 1 phase possible. In fact, there is no analytical solution to this problem and there are several journals (e.g. CALPHAD and the Bull. of Alloy Phase Diagrams) devoted to trying to find one, but it is easy to answer graphically. As an example, consider the system illustrated in Fig 1.3a. We can determine all the possible stable equilibrium by draping a rope under the $\overline{G}$–X surfaces of all the phases and then pulling upwards on the ends of the rope (Fig 1.3a). When the rope is taut it will define the minimum Gibbs energy surface (MFES) of the system, that is, it will define all possible stable states of the system (at constant P and T). Along this surface we can distinguish 2 different kinds of regions, linear regions in which the surface spans the surfaces of 2 phases and nonlinear one-phase regions in which the surface overlaps the surface of a single phase.

This diagram demonstrates 3 important points:

1) Linear regions of the surface define the composition interval over which a particular 2-phase assemblage is stable, and in such a region the compositions of the phases and the $\mu$'s of the system are independent of the composition of the system.

2) Because the MFES surface of the system is never convex, the $\mu$ of any component will always increase if the composition of the component in the system is increased.

3) If the surfaces of the phases are independent (and they are) and the P-T condition arbitrarily specified, the probability that more than 2 phases will ever be stable in a 2-component system is zero.

These arguments can easily be made more general, for example in a 3-component system the $\overline{G}$–X space is 3-dimensional and we can expect the maximum number of phases tangent to a 3-dimensional plane to be 3. This is just a graphical statement of "Goldschmidts mineralogical phase rule," $p \le c$ (this rule is valid if the P and T are independent of the system in question; however in many geologic systems the systems buffer T and/or P). More importantly, it implies that in any c-component system, if c-phases are in equilibrium their composition is a uniquely determined at any P and T.

### 1.4.1. Heterogeneous Systems Composed Entirely of Compounds

Many minerals can be regarded to a good approximation as stoichiometric compounds. This approximation has the interesting consequence that all the phase regions of the system are defined by c-phases (Fig 1.3c) and the $\mu$'s in any region can be determined by linear algebraic solution of Eqs 1.1 or 1.5.

### 1.5. Thermobarometry

Mineral thermobarometry makes use of the thermodynamic fact that we have just deduced, namely, that in a c-component system the compositions of the phases in a c-phase equilibrium are uniquely determined at any pressure and temperature (in practice, mineral thermobarometry is applied to a subset of a rocks real components, with the supposition that the only significant variation occurs in this subsystem, e.g. the Fe-Mg subsystem is used for garnet-biotite thermometry). Because the position of the $\overline{G}$–X surface of each phase is an independent function of pressure and temperature, if the pressure and temperature of a system is changed, the $\overline{G}$–X surfaces of the phases will shift relative to each other and hence the compositions of coexistent phases will also change as illustrated by Fig 1.4a.

In the foregoing discussion we have been using thermodynamics to tell us what composition phases will have at a given P-T, mineral thermobarometry turns the problem around, that is we observe certain mineral compositions and try to find the P-T at which the minerals were in equilibrium. To demonstrate how this is done consider our simple 2-component system. If we have observed 2 phases together, $\alpha$ and $\beta$, then at the pressure and temperature of their equilibrium the chemical potential of each component must be equal in both phases, i.e. $\mu_a^\alpha=\mu_a^\beta$ and $\mu_b^\alpha=\mu_b^\beta$. Each $\mu$ can be expressed as a function of pressure and temperature of the form $\mu_a^\alpha = \bar{G}_a^\alpha + RT \ln a_a^\alpha$, where $\bar{G}_a^\alpha$ is the molar Gibbs energy of the pure a endmember of $\alpha$ (a function of P and T), and $a_a^\alpha$ is the thermodynamic activity of the a endmember of $\alpha$ (a function of composition and generally also a function of P and T). Thus, each equality of $\mu$'s gives us 2 equations in 2 unknowns (the X's are known, P and T are the unknowns), which can be solved simultaneously for the "equilibrium" T, if P is known, or P, if T is known.

Now there are always at least 2 $\mu$ equalities, and either of these can be solved for P or T, but in mineral thermobarometry only 1 equality, e.g. $\mu_a^\alpha = \mu_a^\beta$, is solved, this is the root of all evil in thermobarometry. The reason for this is illustrated in Fig 1.4b which shows that if we solve only 1 equality for P or T (and it is always possible to find a solution to just one), it is quite probable that the second equality will not be satisfied. In other words, either the mineral compositions are not the equilibrium compositions (very probable), or the thermodynamic formulation of the thermobarometer is incorrect (even more probable). The only way to test for consistency is to solve all the chemical potential equalities, unfortunately the thermodynamic data is often not available (although this is done in a few cases, such as feldspar thermometry). An interesting observation which follows from this discussion, is that if one has the thermodynamic data to solve all the $\mu$ equalities, then any mineral assemblage of variable composition provides enough information to obtain a unique solution for both P and T.

This is not intended as an indictment of mineral thermobarometry, but rather merely a warning that mineral thermobarometry does not (as applied in petrology) provide any test for the validity of the measured compositions, nor even whether or not the observed phase assemblage was stable. In contrast, phase diagram, or equilibrium, calculations have the merit of being thermodynamically consistent in that they show (or they should, when done correctly with correct data) the stability fields and equilibrium compositions of all phases in a system. In defense of thermobarometry, it must be remarked that most thermobarometers are based on careful empirical observations, and that phase diagrams calculations are based on thermodynamic databases which have a much weaker link to the stark reality posed by real data.

### 1.6. What is a phase diagram?

A phase diagram is a diagram which indicates the relative amount and state of every phase in a stable equilibrium system. The most basic kind of phase diagram is an isobaric-isothermal diagram which shows the phase relations of a system as a function of composition, i.e. a composition diagram (the chemographic diagrams of petrography). Such diagrams are simply the projections of the MFES onto composition space as illustrated by the vertical projection of Fig 1.5. By projecting the tangents of the MFES onto the $\bar{G}$ axis of a $\bar{G}$–X diagram we can derive a second kind of phase diagram which tells us how the system would respond if we could control $\mu_1$.

There is an interesting distinction (see Hillert 1985 for a good discussion of this) between the diagrams, in the composition diagram if we arbitrarily specify the composition of the system we have about the same probability of being in a 1-phase region as in a 2-phase region. In contrast, in the $\mu_1$ diagram we have zero probability of landing in a 2-phase region (if $\mu_1$ is arbitrarily specified, i.e. it is a true independent variable). Recognition of this difference led Korzhinskii (1959) to restate the mineralogic phase rule as $p \le c - m$, where m is the number of independent potentials for a system.

#### 1.6.1. Phase diagrams as a function of P and T

More complex phase diagrams are derived by looking at the changes in the MFES as a function of variables like P and T, such phase diagrams are known as mixed-variable phase diagrams. To illustrate how mixed variable diagrams can be computed consider a system with 3 phases, $\alpha$, $\beta$, and $\gamma$, such that at low T, only $\alpha$ and $\gamma$ are on the MFES. Then we have 3 phase fields, $\alpha$, $\alpha$+$\gamma$, and $\gamma$. Now, if the Gibbs energy of $\beta$ decreases relative to the other phases as temperature increases, then eventually the system will reach a condition ($T_2$) at which all 3 (c+1) phases, alpha, beta, and $\gamma$ are simultaneously tangent to a $\bar{G}$–X plane. This condition is a c+1-phase equilibrium, if we cross the equilibrium condition $\alpha$+$\gamma$ will react to form $\beta$. Any c+1 phase equilibrium can be described by a mass balance reaction, the stoichiometry of which will depend on the compositions of the phases as given by their points of tangency with the MFES. When the $\bar{G}$–X surface of $\beta$ crosses the $\alpha$+$\gamma$ $\bar{G}$–X plane, $\alpha$+$\gamma$ becomes metastable with respect to the assemblages $\alpha$+$\beta$ and $\beta$+$\gamma$. If temperature is increased still further, the system will reach a point (>$T_3$) at which the $\bar{G}$–X surface of pure $\beta$ crosses that of pure $\alpha$ in the component 1 subsystem (i.e. at X = 0). This corresponds to the reaction $\alpha$=$\beta$, which would never be observed in a true binary system (i.e. $0 < X < 1$), and marks the thermal limit of the assemblage $\alpha$+$\beta$, a similar reaction, $\gamma$=$\beta$, will limit the stability of $\gamma$+$\beta$.

You probably have seen many diagrams like these for melt systems (eutectic-peritectic diagrams), but exactly the same kinds of diagrams exist for solid solutions (but they have been generally ignored by petrologists, an exception to this is Thompson 1981, yes, our very own).

You may also be wondering why this diagram looks so much different than the T-$X^f_{CO2}$ diagrams of petrologic fame, the reason is that the X here is a composition variable of the system, whereas $X^f_{CO2}$ is the composition of a phase (which is assumed to be stable). When used as a phase diagram variable $X_{CO2}$ determines the potential of $H_2O$ and $CO_2$ and is therefore not really a compositional variable at all, but more like a potential. For this reason, the petrologists habit of calling P-T-$X^f_{CO2}$ diagrams simply P-T-X diagrams is sloppy and misleading.

The foregoing procedure could be repeated for other pressures, and if the pressures were reasonably close, the resulting diagrams could be stacked upon each other, and the phase relations interpolated between the diagrams, to obtain a 3-dimensional P-T-X phase diagram. For simplicity, let us construct such a diagram assuming that the phase equilibria of our T-X diagram are only shifted to higher temperature with increasing pressure.

### 1.6.2. P-T-X phase diagrams

Given that phase diagram shown in Fig 1.7a is only for a binary system, and that each additional component to be treated would add another dimension to the diagram, the complexity of the phase diagram problem is apparent. In fact, multidimensional phase diagrams are in themselves to complex to be of any value and they must be simplified for our use. In this respect, there are 2 methods by which the phase relations of a multicomponent system may be represented in the P-T plane, sectioning or projection.

### 1.6.3. P-T Phase Diagram Sections

The P-T phase diagram section is conceptually simple, it is a 2-dimensional slice at constant composition through the multidimensional phase diagram (Fig 1.7b). The resulting section consists of regions of $\le$ c phases, which represent regions of homogeneous reaction, i.e. regions where the amount and compositions of the phase. The boundaries of such regions can be distinguished from true univariant equilibria by the number of phases represented, for example in Fig 1.7b, the boundary between the $\beta$ and $\beta$+$\alpha$ field involves only 2 (=c) phases and therefore is not a univariant equilibrium. The section in Fig 1.7b includes only phase regions of $\le$ c phases; however, it is possible to obtain sections which represent equilibria of c+1 and c+2 phases. For example, if a section of Fig 1.7a were constructed, at constant composition, so as to intersect the $\beta$ eutectic, a c+1 phase equilibrium, then the section would include a line representing the eutectic reaction.

Phase diagram sections can be very useful for interpreting the phase relations of systems in which the bulk composition of the system is fixed, for example, as in isochemical metamorphism of a subducted basalt or in mantle phase relations (Saxena and Erickson 1986, Wood and Holloway 1986). There are 2 major disadvantages to using phase diagram sections: (i) the boundaries in sections can be extremely sensitive to the bulk composition chosen; and (ii) their application requires bulk equilibrium, however, in many crustal metamorphic rocks mineral zonation indicates that this cannot be assumed. Phase diagram sections can contain some unusual topologic features and these, as well as topologic rules for such sections are discussed in great detail by Palatnik and Landau (1963, also Hillert 1985)

### 1.6.4. P-T Phase Diagram Projections

By far the most widely used type of petrologic diagram is the P-T phase diagram projection. Phase diagram projections are obtained by projecting the phase fields of a multidimensional phase diagram onto a P-T coordinate frame. In principle, it is possible to project all the phase fields, however, because phase fields of fewer than c+1 phases project as overlapping fields (e.g. $\alpha$+$\beta$ and $\beta$+$\gamma$ in Fig 1.7d), as a result complete projections are so complex as to be almost meaningless. As an alternative, in the conventional Schreinemakers projection (with which you are probably quite familiar), only the geometric elements of the phase diagram which project as lines (univariant curves) and points (invariant points) are shown. A feature of Fig 1.7d which may be confusing, is that there are 3 univariant curves which limit the stability of the $\beta$. The reason this is not a violation of Schreinemakers rules is that 2 of the curves, $\alpha$=$\beta$ and $\gamma$=$\beta$, represent reactions which would only be observed in the pure component 1 or component 2 subsystems. In systems with more phases it is possible to get even more curves, for example consider what would happen if $\beta$ had 2 eutectoids separated by a thermal maximum for the phase $\delta$ as in Fig 1.7e. Then we would have five univariant curves $\alpha$=$\beta$, $\beta$=$\alpha$+$\delta$, $\delta$=$\beta$, $\beta$=$\delta$+$\gamma$, and $\gamma$=$\beta$. In this case, each 2-phase curve represents the equilibrium, and P-T limit of a special composition of $\beta$, such curves are known as singular curves (in systems with more components this gets even more complex). It is a general rule that if there are 2 c+1-phase reactions limiting the stability of a phase then there is a c-phase singular reaction limiting the stability of the phase as well. This c-phase reaction will be for a composition of the phase between the compositions of the phase in the 2 c+1-phase reactions. Singular reactions do not occur in systems in which there are no solutions.

As a result of projection we lose a lot of information, but the projection has the advantage of telling us the absolute P-T stability field of the stable phase assemblages of the system. For example, the curve $\alpha$+$\gamma$=$\beta$ tells us the lowest temperature that $\beta$ can be stable, however, $\beta$ will only appear in the system if the bulk composition of the system is between the eutectoidal compositions of $\alpha$ and $\beta$. Likewise from the position of the singular curves, we may deduce that the assemblages $\alpha$+$\beta$ and $\gamma$+$\beta$ will only occur at temperatures between the curve $\alpha$+$\gamma$=$\beta$ and the curves $\alpha$=$\beta$the curve $\gamma$=$\beta$, respectively.

In this example we have an unfair advantage in that we have seen the complete phase diagram, but consider what would happen if you only had the projection. In this situation, if someone were to ask you if 2 phases coexist, say $\delta$ and $\varepsilon$, you would have no way of answering from the projection alone, which only tells you there is no reaction involving $\delta$ and $\varepsilon$ over the P-T range of the projection. In essence, Schreinemakers projections tell you the changes in the topology of the compositional phase relations for a system; thus, you must have some idea of the compositional phase relations (or better still, a composition diagram) at some P-T point within the projection coordinate frame.

### 1.7. COMPUTATIONAL METHODS

There are 2 broad approaches to computing phase diagrams or projections and sections of phase diagrams, Gibbs energy minimization, and combinatorial enumeration. The following sections briefly describe each method and discuss the applications and limitations of the methods with respect to geologic problems.

#### 1.7.1. Free Energy Minimization.

The oldest and most basic computational method is numerical Gibbs energy minimization, by this method the user specifies a P-T-X coordinate for a system and the stable phase assemblage at this coordinate is determined. For example, the user might specify the system is at pressure P, temperature T, and composition $X_1$ as in Fig 1.8a. A minimization method would then determine the stable phases for these condition and the amount and composition of each phase (i.e. phases b and d, Fig 1.8a). If this procedure were repeated for a number of different compositions at the same P-T condition, the results could be used to map out the compositional phase relations of the system. This would be a 1-dimensional composition diagram, the problem with this method for calculating phase diagrams becomes apparent if we consider the effect of adding variables like P and T or additional components. For the sake of argument let us suppose that we decide to divide our P-T-X space into a grid by spacing the points so that we will have 10 points along each axis (this would in fact be a rather coarse spacing). If we have a five component system, we will have 4 independent composition variables and P and T, thus our grid would consist of $10^6$ points. At each point we would have to do a minimization, and the number of operations for each minimization goes as $\pi c^2$, where $\pi$ is the total number of possible phases. Therefore, not only would the method involve an astronomical number of operations (even for a super computer), but we would be left with the job of interpolating between a million grid points in six-dimensional space. The difficulty with minimization techniques is that they require as input P-T-X conditions, but in a phase diagram there are an infinite number of possible P-T-X conditions and there is no a priori means of choosing the important ones. Basically, using minimization methods to determine a phase diagram of more than 2 dimensions is like trying to map the moon with a microscope.

Although minimization methods are not practical for multidimensional phase diagrams, they have proved useful for the calculation of phase diagram sections (Fig 1.7b). For example they have been used to calculate how the phase relations of a rock with fixed bulk composition (e.g. pyrolite) change as a function of P and T (e.g. Saxena and Eriksson 1983, Wood and Holloway 1986). More generally, minimization can be used to calculate any 2-dimensional section through a multidimensional space, thus it is possible to compute how a multicomponent system behaves if only 1 compositional variable is changed, i.e. the pseudobinary phase diagrams of igneous and mantle petrology fame. Minimization methods have the advantage that they are capable of treating complex solution behavior and systems with any number of components. Two recent examples of minimization programs designed specifically for geologic problems are given by DeCapitani and Brown (THERIAK, 1987) and Harvie et al. (1987). There is also a wealth of literature on minimization techniques in the engineering and metallurgical journals (see references) which has been largely ignored by the geoscientific community.

A major drawback of minimization methods applied to crustal metamorphism problems is that the methods assume bulk equilibrium. Thus, they are not applicable to systems where mineral zonation occurs or where the phase rule is violated. It also should be remembered that the phase relations of a multicomponent system can be extremely sensitive to the bulk composition of the system.

### 1.7.2. Combinatorial Methods for Computing Phase Diagram Projections

Combinatorial methods make use of the fact that although there are an infinite number of P-T-X conditions in a phase diagram there are only a finite number of phase equilibria, or phase fields. Consider the system of Fig 1.8a, there are a total of 4 phases possible in the system, thus there are a total of 4 1-phase and 6 2-phase equilibria. The composition of the phases in the 2-phase equilibria are fixed, so the phase diagram can be determined in a 3 step process, first a 2-phase assemblage is chosen, say a+c, then equilibrium composition of a and c is determined (i.e. the plane tangent to the $\overline{G}$–X surface of both a and c is located), and lastly the stability of a+c is evaluated by testing whether any phases lie below the a+c $\overline{G}$–X plane (in Fig 1.8a a+c is metastable with respect to phases b and d). If this were repeated for all the 2-phase assemblages then all the 2-phase fields of the composition diagram would be known, and the identity of the 1-phase fields which fill the gaps between the 2-phase fields could be determined from the 2-phase fields. Strategies of this sort are used in a number of metallurgical programs, they become a little more complicated for multicomponent systems, but they are generally quite efficient and reliable (e.g. Sundman et al. 1985, Lukas et al. 1982).

#### 1.7.2.1. Schreinemakers Projections, GEO-CALC and THERMOCALC

For phase diagrams as a function of P-T combinatorial methods become less efficient because c-phase assemblages are stable over regions in P-T space, and these regions can only be determined by incremental or grid mapping. However, the combinatorial method is still feasible for the calculation of Schreinemakers projections, because in this case it is only necessary to determine the stability of c+1-phase assemblages. A simple combinatorial method algorithm for this is: (i) a c+1 phase assemblage is selected, (ii) temperature (or pressure) is specified, (iii) the equilibrium pressure and the equilibrium compositions of the phases are determined (i.e. the $\overline{G}$–X plane), and (iv) the stability of the equilibrium is tested. The temperature is then incremented and steps (ii)-(iv) repeated until the stability of equilibrium has been determined over the entire temperature range of the diagram (Fig 9b). This process is repeated for every possible permutation of c+1 phases. This method has been implemented by Perkins et al. (1986) in a computer program now called GEO-CALC for calculating Schreinemakers projections as a function of P-T-$X^f_{CO2}$* In the computer program THERMOCALC, Powell & Holland (1990) have used a similar but more efficient strategy. Neither THERMOCALC nor GEO-CALC are capable of treating solution phases in a fully automated mode (all the programs are capable of making activity corrections; however, fixed activity corrections are almost

*In geologic literature the variable $X^f_{CO2}$ and T-$X^f_{CO2}$ phase diagram projections are often incorrectly referred to as a composition variable and temperature-composition phase diagrams, respectively. In contrast to the variable X as used here to represent the composition of a thermodynamic system, $X^f_{CO2}$ is a variable that represents the composition of a phase which is assumed to be stable. With this restriction, $X^f_{CO2}$ is basically equivalent to a complex $\mu$ variable. Thus, T-$X^f_{CO2}$ phase diagram projections are of the same class as P-T projections, and should not be confused with composition or mixed-variable phase diagrams, as noted earlier (sections 1.5 and 1.6).

always thermodynamically inconsistent and should be avoided, see section 1.1.4), but THERMOCALC can be used to calculate solution phase equilibria (although it will not tell you if they are stable).

A drawback of combinatorial methods is that they become inefficient as the number components and possible phases for a system, because the number of c+1-phase permutations rapidly becomes very large. For example in the system $CaO$-$SiO_2$-$Al_2O_3$-$CO_2$-$H_2O$ there are a total of about 80 phases possible and the number of c+1 phase permutations is $3.2\times10^8$, each of which must be tested for stability.

#### 1.7.2.2. PeRpLeX

The necessity for combinatorial methods arises from the difficulties involved in evaluating and keeping track of all the changes that occur on the MFES of a system as a function of P and T. These difficulties have been overcome by a relatively simple linear algorithm for evaluating thermodynamic surfaces (Connolly and Kerrick 1987) used in the PeRpLeX program (Connolly 1990). Through this algorithm it is possible to calculate composition diagrams, i.e. chemographies, for systems with up to ten components. It is then a relatively simple matter to monitor the changes in such chemographies as a function of variables like pressure and temperature in order to obtain mixed-variable phase diagrams or Schreinemakers-type phase diagram projections. The advantages of this method are twofold; it can be used to calculate any kind of phase diagram; and, in contrast to pure combinatorial methods, it is extremely efficient and virtually independent of the number of phases considered in a calculation. In addition the program can be used to treat highly non-ideal solutions.

The PeRpLeX algorithm is numerically exact only for phases with fixed composition. For problems in which it is necessary to consider phases of variable composition, PeRpLeX approximates the continuous $\overline{G}$–X surface of solutions by a series of arbitrarily defined compounds, designated *pseudocompounds.* As a result, the $\overline{G}$–X surface of each phase is approximated as a polyhedra, the vertices of which are the pseudocompounds (Fig 2.4). The user controls the number and positions of the pseudocompounds, and thereby the accuracy of the approximation. The primary weakness of the pseudocompound approximation is that it becomes impractical for solutions with more than 3 species mixing on a single lattice site.

## 2. PETROLOGICAL PHASE DIAGRAM CALCULATORS

"*Thermodynamics is the science of the impossible. It enables you to tell with certainty what cannot happen. Thermodynamics is noncommittal about the things that are possible. Thermodynamics is at its best when nothing can happen, a condition called equilibrium. The concept of equilibrium has been fruitfully extended to reversible processes. Here everything is impossible except one very specific process and even this process is on the verge of being impossible.*" -- *An anonymous, slightly inaccurate, wit.*

The purpose of this chapter is to provide a more detailed overview of the software packages, GEO-CALC, THERMOCALC and PeRpLeX, for petrological phase diagram calculations. As the author of PeRpLeX, I will use PeRpLeX as a vehicle for explaining how these computer programs work in general. Thereafter I will briefly outline how the other programs work and some of their special capabilities. Both THERMOCALC and PeRpLeX can be used to calculate equilibria involving solution phases, and I will begin by trying to demonstrate why this is preferable to "activity corrections".

### 2.1. Why Consider Solution Phases?

Very commonly petrologists treat the effects of mineral solution by making activity-corrections. Basically, this approach consists of identifying a subcomposition of the system in which no solution behavior occurs, but in which 1 or more of the minerals has an endmember component. For specified compositions of the solutions it is then possible to determine activity corrected endmember properties, and the "stable" equilibria between these endmembers are then computed. Problems with this approach are twofold: (i) activity corrected reactions may bear little resemblance to the actual metamorphic process; and (ii) computation begins with the assumption that the equilibrium solution compositions are known, as often in thermobarometry (Sect 1.6), but provides no test for the validity of the assumption.

As an example consider a 2-component system with 3 solution phases (G-X diagram of Fig 2.1), all of which have an A-endmember and a B-endmember. Suppose that our friend Joe-petrologist observes solution $\alpha$ and $\beta$ with compositions indicated by the dots in Fig 2.1. He now makes activity corrections to the

A-endmembers of these solutions:

$$G_B^{\alpha} = G_B^{o,\alpha} + R\,T \ln a_B^{\alpha}$$

and

$$G_B^{\beta} = G_B^{o,\beta} + R\,T \ln a_B^{\beta}$$

where $G_B^{o,\alpha}$ is the G of the B endmember of $\alpha$ at the P-T condition of interest, etc.; and computes the activity corrected equilibrium by finding P-T conditions such that $G_B^{\alpha} = G_B^{\beta}$, as is the case for the P-T condition illustrated in the G-X diagram of Fig 2.1. Regardless of anything to do with equilibrium conditions he will always find a P-T curve where $G_B^{\alpha} = G_B^{\beta}$ (Fig 2.1), but as can be seem in the G-X diagram the conditions of this curve will not necessarily be those of a true equilibrium. In general, at best, only 1 point along such curves will represent a true equilibrium, but Joe has no way of knowing this. There are few constraints on the relation of the true univariant equilibrium $\beta = \gamma + \alpha$ (in the A–B system) to the activity corrected "univariant" equilibrium $\alpha = \beta$ (in the A subsystem); thus a configuration such as in Fig 2.1 is perfectly possible. Clearly in this case, admittedly a worst case scenario, the activity corrected reaction bears no relation to the actual reaction that limits the stability of $\beta$. Moreover, because $\beta$ becomes metastable in the A-B system the loci of the activity corrected $\alpha = \beta$ equilibrium is not even possible over much of its extent.

### 2.2. PeRpLeX

The independent variables of greatest geological interest are P, T, and chemical composition so the most useful thermodynamic state function is the Gibbs function which I will use as a vehicle for discussion here. The discussion (and PeRpLeX), is however completely general if one replaces G by a general free energy function, $\Omega$, P & T by potential variables, and chemical composition by physical composition (Hillert 1985, Connolly 1990). There are 2 basic kinds of phase diagrams, phase diagrams as a function of composition, and phase diagrams that show the changes in the composition diagram as a function of environmental variables like P & T. Because of this relationship a natural computational scheme is to first calculate the composition diagram of the system of interest, and then to monitor the phase relations in this diagram as pressure and temperature are varied. The immediate problem is thus one of finding the isobaric-isothermal stable phase assemblages, i.e. the phase assemblages that minimize G as a function of composition.

#### 2.2.1. Calculating the Minimum G Surface and Composition Diagrams

Determining assemblages of minimum free energy is not as straightforward as one might expect because of 2 problems illustrated by the schematic G-X diagram for a system with solution phases $\alpha, \beta, \gamma$, etc. The first is that the Gibbs energy of each phase is a nonlinear function of composition. Thus determining the equilibrium compositions of the phases will involve numerical methods that are costly and unstable. A more important problem, though, is that the stable equilibrium G–X surface for the system (the heavy solid curve in Fig 2.2) is difficult to describe analytically since its geometry is a composite of nonlinear surfaces in 1-phase regions (or generally in $p < c$ phase regions) and linear surfaces in two (or $p = c$) phase regions. These complications combine to make numerically exact calculations of multidimensional phase diagrams impractical for many systems unless some simplification is made. One simplification is that the phases of the system can be assumed to be stoichiometric, i.e. compounds. This simplification provides an adequate model for many metamorphic phase systems and was the starting point for PeRpLeX.

If a system includes only compounds, 1-phase fields degenerate to points and each phase region of the system must be comprised of $p = c$ phases (i.e. invariant at fixed P-T, or divariant as a function of P and T) as illustrated in Fig 2.3. Consequently the minimum G surface of the system becomes linear. This has 2 advantages: (i) the $\mu$'s for any phase assemblage can now be determined efficiently by analytic methods; and (ii) because the stable compounds define the vertices on the polygonal or polyhedral minimum G surface of the system, the geometry of this surface can be described by simply specifying the G–X coordinates of the stable compounds.

The stable compound assemblages can be identified by an abbreviated combinatorial algorithm that consists essentially of 3 steps discussed with reference to Fig 2.3: (i) The stable 1-component compound $\alpha$ is identified by simply determining the 1-component phase with the lowest G. (ii) Multicomponent compounds are then tested for compatibility with this phase. For example, as a first guess it is assumed $\varepsilon$ is compatible with $\alpha$, the assemblage $\alpha+\varepsilon$ is then used to define a G–X plane. The assemblage must be metastable if another compound lies below the G–X plane, as does $\beta$ in Fig 2.3. As it is known that $\alpha$ is stable, then $\beta$ must be more stable with $\alpha$ than $\varepsilon$ is; therefore, a new G–X plane can be defined by $\alpha+\beta$. If the G–X coordinates of the compounds are tested relative to this plane it is found that the assemblage $\alpha+\beta$ is stable, i.e. no compounds lie below the $\alpha+\beta$ G–X plane. (iii) It is now known that $\beta$ is stable, and therefore an additional compound compatible with $\beta$ is sought. The search is simpler than before, because this additional phase must lie at $X > X_\beta$. In this example, this phase would be $\gamma$ and the G–X surface would be completely defined, more generally the compound might be binary, in which case step (iii) is repeated. Arithmetically, the G–X planes are determined by solving the equation:

$$\begin{pmatrix} n_1^1 & . & . & n_c^1 \\ . & . & . & . \\ . & . & . & . \\ n_1^p & . & . & n_c^p \end{pmatrix} \begin{pmatrix} \mu_1 \\ . \\ . \\ \mu_c \end{pmatrix} = \begin{pmatrix} G^1 \\ . \\ . \\ G^p \end{pmatrix} \qquad (2.1)$$

where $n_c^p$ is the amount of component c in phase p. Given the $\mu$'s from Eq 1, a phase p lies below the G–X plane defined by these $\mu$'s if:

$$G^p < \sum_{i=1}^{c} n_i^p \mu_i \qquad (2.2)$$

As one might anticipate, this procedure gets more complicated for hyperdimensional composition spaces (Connolly & Kerrick 1987), but despite this, the algorithm is so efficient that it is possible to model solutions by series of stoichiometric compounds.

In effect this is equivalent to modeling nonlinear surfaces by inscribed polyhedra. For instance, a hypothetical solution B can be modeled by a series of arbitrarily defined compounds $B_1$–$B_8$ (Fig 2.4). To emphasize the fact that these compounds are arbitrarily chosen they are called pseudocompounds. Although all regions of the thermodynamic surface become linear as a result of this polyhedral approximation, it is still possible to recognize the true phase regions; e.g. in Fig 2.4, it is apparent that regions such as $A+B_2$ represent a heterogeneous 2-phase region, whereas the $B_3+B_4$ is a portion of the true homogeneous region of B. It is not difficult for a computer program to distinguish such regions; thus, as far as users are concerned both input and output to PeRpLeX is expressed in terms of solutions, rather than the pseudocompounds actually used in the calculations. As in Fig 2.4, the true and approximated regions of a given solution will not coincide, the maximum error of the approximation being equal to the spacing of the pseudocompounds. The approximation can be made as accurate as necessary by simply increasing the number of pseudocompounds.

The pseudocompound approximation is not a particularly profound method, but it makes PeRpLeX a remarkably stable and general program. Three features of the algorithm are particularly noteworthy: (i) it is independent of assumptions about the stable phase configurations of the system in question; (ii) the algorithm defines the entire thermodynamic surface of the system, ensuring that all stable equilibria will be identified; and (iii) the algorithm is independent of the analytical form of the compositional equations of state.

Fig 2.5 shows a composition phase diagram for the system $CaO$–$Al_2O_3$–$SiO_2$ at 1 bar and 1673 K, calculated with the pseudocompound approximation. Three types of phase regions may be distinguished within the diagram; homogeneous melt regions are shaded; 2-phase regions such as pW + melt are shown by dashed tielines; and invariant 3-phase regions such as An + Co + melt are drawn with heavy solid lines. Within the melt regions smaller triangular regions are visible, each of these is defined by 3 of the roughly 700 pseudocompounds used to represent the melt phase. Total time for the calculation was 0.26 s on a Sun Sparc 2 computer.

### 2.2.2. Mixed-Variable Phase Diagrams

If the minimum G–X surface of a system modeled by pseudocompounds, then all assemblages will consist of p = c compositionally nondegenerate (i.e. all p phases have linearly independent compositions) compounds $\{\phi_1 \cdots \phi_c\}$. An assemblage of c-phases can only become metastable with respect to an additional phase $\{\phi_{c+1}\}$ and because the c-phases are nondegenerate it must be possible to write a mass balance reaction:

$$\sum_{i=1}^{c+1} \alpha_i \phi_i = 0 \tag{2.3}$$

between the assemblage and this additional phase. The signed (i.e. products + and reactants −) stoichiometric coefficients, $\alpha_i$, in Eq 2.3 can be determined by solving:

$$\begin{pmatrix} n_1^1 & . & . & n_1^p \\ . & . & . & . \\ . & . & . & . \\ n_c^1 & . & . & n_c^p \end{pmatrix} \begin{pmatrix} \alpha_1 \\ . \\ . \\ \alpha_c \end{pmatrix} = - \begin{pmatrix} n_1^{c+1} \\ . \\ . \\ n_c^{c+1} \end{pmatrix} \tag{2.4}$$

where $\alpha_{c+1} \equiv 1$. If the assemblage $\{\phi_1 \cdots \phi_c\}$ is metastable with respect to only 1 phase (Eqs 2.1 & 2.2), then the equilibrium of the reaction must also be stable. The P or T condition for this equilibrium can be found by solving:

$$\sum_{i=1}^{c+1} \alpha_i G_i(p, T) = \Delta G = 0 \tag{2.5}$$

by a numerical method. The stable p=c-phase assemblages at conditions beyond the c+1-phase equilibrium can be deduced from the reaction stoichiometry. The phases with null or positive coefficients must coexist in every c-phase assemblage generated by the reaction; thus there will be c+1−k new c-phase assemblages, consisting of each unique permutation of c−k phase with negative stoichiometric coefficients plus the k phases with null or positive coefficients.

The foregoing logic suggests a simple algorithm for calculating mixed-variable diagrams that is described here with reference to the hypothetical T-X diagram for a binary system as in Fig 2.6: Once the stable c-phase assemblages are determined at the minimum T for the diagram, then 1 of these assemblages, $\alpha+\beta$, is selected and its stability tested as T is varied (Eqs 2.1 & 2.2). Eventually a condition is reached at which $\alpha+\beta$ become metastable with respect to $\delta$; it follows that a stable reaction involving $\alpha+\beta+\gamma$ must occur at lower T. The reaction is determined from Eq 2.4 to be $\delta - ½\alpha + ½\beta = 0$ (or $½\alpha + ½\beta = \delta$, eutectoidal) and located exactly by Eq 2.5. There are now 2 new c-phase assemblages, $\alpha+\delta$ and $\delta+\beta$, and the stability of each of these is tested as T is varied from the $\alpha+\beta=\delta$ eutectoid. $\alpha+\delta$ is stable at all higher temperatures, but $\delta+\beta$ eventually becomes metastable with respect to $\gamma$ beyond the peritectoidal reaction $\beta=\delta+\gamma$. The assemblage $\delta+\gamma$ generated by the peritectoid remains stable at all higher temperatures. There is no reason to expect that any single one of the original c-phase assemblages will be affected by every possible reaction, so this procedure must be repeated for each of the original c-phase assemblages identified at the outset of the calculation. In this case there is only 1 additional assemblage, $\beta+\gamma$ and it is only affected by the $\beta$–peritectoid, and therefore does not lead to the identification of any new equilibria.

If a system is comprised entirely of true compound phases, all the reactions identified by this procedure will be true invariant eutectoidal or peritectoidal reactions (variance of a p–phase assemblage is defined here in the context of a phase diagram n−p where n−1 is the dimension of the diagram). More generally it is possible to distinguish 2 categories of equilibrium reactions that manifest changes in mixed-variable diagrams, discontinuous invariant reactions (as for compounds) and continuous high-variance reactions that cannot be written stoichiometrically. As a result of the pseudocompound approximation, all changes are modeled by discontinuous reactions among c+1 pseudocompounds; but some of the reactions are only pseudoinvariant in that 1 or more pseudocompounds represents a single homogeneous phase. Pseudoinvariant reactions approximate the continuous variations of a phase field by a discrete step. Three basic types of reactions that result from the pseudocompound approximation, and there "real" meaning are illustrated in Fig 2.7. PeRpLeX can (usually) distinguish the different types of reactions, with the result that the true mixed-variable diagram can be reconstructed from its output. Fig 2.8 shows a mixed-variable diagram calculated by PeRpLeX for the system $K_2O$–$Na_2O$–$Al_2O_3$–$SiO_2$–$H_2O$ after projection through water, quartz and the stable aluminosilicate. Two immiscible solutions are stable in this system, Mica (paragonite-muscovite solution) and K-feldspar (albite- sanidine). This system is of considerable importance in metamorphic petrology, because the Muscovite (+ quartz) decomposition reaction is easily recognized in the field (the famous "second sillimanite isograd"). It is interesting to observe that although this reaction is usually modeled by the discontinuous pure KASH equilibrium, if any Na is present (and it invariably is), the reaction will be continuous commencing at temperatures as low as the Or-eutectoid (ca. 20 K below the KASH equilibrium). The steps in the phase field boundaries in Fig 2.8 locate pseudoinvariant reactions. This calculation was done with each solution represented by 35 pseudocompounds, the spacing of which decreases toward the compositional limits of the diagram. Time for the calculation was 17 s.

### 2.2.3. Schreinemakers Diagrams

PeRpLeX's algorithm for calculating Schreinemakers diagrams is basically the same as that for mixed-variable diagrams; this should not be too surprising because a Schreinemakers diagram is simply the projection of a the univariant fields of a mixed-variable diagram with 2 independent potential variables (P & T) onto the P-T coordinate frame. The algorithm may be summarized as follows with reference to the Schreinemakers diagram for a hypothetical binary system in Fig 2.9. The stable c-phase assemblages are determined at 1 corner of the P-T coordinate frame of interest. The stability of a stable c-phase assemblage, $\alpha+\beta$, is tested as P varied along the edge of the diagram, eventually it becomes metastable with respect to $\delta$. The stable reaction between $\alpha, \beta$ and $\delta$ is found to be $\beta=\delta$ by solving Eq 2.4, and the equilibrium conditions for the reaction are traced by solving Eq 2.5 as either independent variable is incremented. After each increment the stability of the univariant field* is tested, by scanning the G-X coordinates of all phases in the system relative to the G-X plane defined by Eq 2.1 for a non-degenerate subset of c-phases of the c+1 phase univariant assemblage (i.e. $\alpha+\beta$ or $\alpha+\delta$). Eventually a condition is reached at which an additional phase, $\gamma$ becomes tangent to the G-X plane. This condition corresponds to an invariant field at which all c+2 phases coexist. There are c+1 additional univariant fields emanating from the invariant field (the fields $\alpha+\beta+\delta$ and $\beta+\delta+\gamma$ overlap), and these may be established by enumerating the possible c+1 phase univariant assemblages. These fields are likewise traced until they intersect additional invariant fields or the boundaries of the diagram. Once this has been done the program returns to the condition at which it located the first univariant equilibrium, evaluates the stable divariant assemblages (as described for mixed-variable diagrams), and resumes testing their stability around the edge of the diagram to locate additional univariant fields. This procedure is repeated for each of the initial divariant assemblages and when completed successfully ensures all stable equilibria are identified.

Fig 2.10 shows of a Schreinemakers diagram for the system $CaO{-}FeO{-}Al_2O_3{-}SiO_2{-}H_2O{-}CO_2{-}O_2$ as a function of temperature and fluid composition at constant pressure (2 kbar) and $\mu_{O2}$ (−195 kJ). This system is relevant for interpreting skarn formation, but it is to be emphasized that the diagram is used mainly for purposes of demonstration, as the $\mu_{O2}$ constraint has no quantitative meaning (can you imagine a system in which $\mu_{O2}$ is independent of T?). To further simplify the example the system was assumed to be saturated with respect to quartz and the stable $CaO{-}SiO_2$ compound that coexists with quartz (either calcite or wollastonite, depending on $T{-}X^f_{CO2}$ conditions). The foregoing constraints determine the $\mu$'s of all the chemical components except FeO and $Al_2O_3$; thus the compositional phase relations can be projected into the $FeO{-}Al_2O_3$ subsystem. Because of the relatively high $\mu_{O2}$, only 2 binary solutions need be considered, epidote-zoisite and andradite-grossularite; the pseudocompounds of these solutions are designated by the abbreviation for the more aluminous endmember (cz or gr) followed by the mol % of that endmember; e.g. cz23 is an epidote with 23 mol % clinozoisite endmember. As in mixed-variable diagrams it is possible to distinguish to types of equilibria. Dashed curves correspond to the equilibrium loci of a pseudounivariant assemblage, in which 2 or more compounds represent the same solution. These curves contour homogeneous equilibria, e.g. the pseudounivariant curve cz50 = an + cz41 can be thought of as representing the continuous decomposition of epidote by a discrete step in which the epidote becomes depleted in zoisite component with increasing $X^f_{CO2}$. The loci actually defines conditions where anorthite is in equilibrium with

*Because $\beta$ and $\delta$ are compositionally degenerate the univariant assemblage should be distinguished from the univariant reaction. The assemblage $\beta + \delta$ cannot be a univariant assemblage of the 2-component system because it does not define a plane in G-X space, and therefore Eq 2.2 would be indeterminate. A univariant assemblage must always include c+1 phases, and because of the degeneracy between $\beta$ and $\delta$ there are 2 possible univariant assemblages in the system illustrated, $\alpha+\beta+\delta$ and $\beta+\delta+\gamma$. In this case the univariant fields of both assemblages are identical, although this is not generally true. At this point the program only "knows" about the assemblage $\alpha+\beta+\delta$, and hence this is the univariant assemblage discussed here.

both epidote pseudocompounds, and is best interpreted as indicating conditions where anorthite is in equilibrium with an epidote composition equal to the average of the pseudocompounds (i.e. ≈ cz45); more zoisite-rich compositions being confined to water-rich conditions. Solid lines define conditions of true univariant equilibria; ordinarily the stoichiometry of a univariant reaction involving a solution varies continuously as the composition of the solution changes; but as a consequence of the pseudocompound approximation this variation occurs discretely at pseudoinvariant points (small dots in Fig 2.10) where 1 or more pseudounivariant curves intersect the univariant curve. Thus, epidote stability is limited in $CO_2$-rich fluids by the univariant reaction epidote = hematite (hm) + anorthite, where the epidote becomes progressively less aluminous with increasing T.

Because it is possible to show continuous equilibria in Schreinemakers projections, as well as the univariant equilibria conventionally shown, there are 2 ways in which the projections can be used. If only true univariant equilibrium are shown, the diagrams define the maximum stability of the possible phase assemblages of a system. For example, the assemblage anorthite + epidote is only stable within the $T{-}X^{f}_{CO2}$ region bound by the univariant curves epidote = an + garnet (high T) and epidote = an + hm (high $X^{f}_{CO2}$). Alternatively, if the specific composition of the epidote solution is considered, then the pseudounivariant curves can be used to define a much narrower region for stability of the assemblage. This is basically a form of thermobarometry; it differs from the conventional approach in that one uses thermodynamic models to predict mineral compositions as a function of environmental variables.

Fig 2.10 is the projection of a mixed-variable diagram with the variables $T{-}X^{f}_{CO2}{-}X_{FeO}$ (where $X_{FeO} = n_{FeO}/(n_{FeO} + n_{Al2O3})$). Consequently it is possible to get a better understanding of the diagrams phase relations by computing mixed-variable diagrams at constant fluid composition as shown in Fig 2.11. Comparison of Figs 2.10 & 2.11 reveals that Fig 2.10 is simplified in that only pseudounivariant equilibria involving 1 solution are shown, thus the pseudounivariant curves that show the compositions of coexisting epidote and garnet (between the epidote-out reaction epidote = an + garnet and the garnet-out reaction garnet = epidote + epidote) are not shown. A peculiar feature of Fig 2.10 are the kinks in the univariant and pseudounivariant curves that occur along the faint dotted curve. This occurs because the phases that determine the chemical potentials of the saturated components CaO and $SiO_2$, change from calcite + quartz (at low T) to wollastonite (at high T) (the way in which PeRpLeX decides this is discussed below).

### 2.2.4. Saturation and Potential Constraints

In many geologic systems the dimension of the composition space that must be considered can be reduced because 1 or more μ's are constrained by the presence of relatively pure phases. Such constraints are known as saturation constraints. For example, if quartz, or 1 of the silica polymorphs, is known to be stable at all conditions of interest it can be assumed to a good approximation that $\mu_{SiO2} \approx G^{m}_{SiO2}$. If the $\mu_{SiO2}$ is known then it is no longer necessary to consider silica as a chemical component, and the composition space of the system can be reduced by 1 dimension. This follows because the μ of a component, c, must be the same in all coexisting phases; thus from Eq 1.1, for any composition of any phase, we can create a transformed G function:

$$G' = G - n_c\mu_c = \sum_{i=1}^{c-1}\mu_i n_i.$$

It is easily demonstrated that G′ must be a minimum at equilibrium, but G′ is only a function of c−1 components so instead of having to deal with a c−dimensional G−X space, we may solve the phase equilibrium problem in the c−1 dimensional G′−X space. The transformation from G to G′ is known as a Legendre transform, and by adding the total differential of $\mu_c n_c$ ($\mu_c dn_c$ + $n_c d\mu_c$) to Eq 1.7 the differential form of G' is:

$$dG' = V\,dP - S\,dT - n_c\,d\mu_c + \sum_{i=1}^{c-1}\mu_c\,dn_c.$$

Since $\mu_c$ is equal to $G^m$ of a pure phase, $\mu_c$ = f(P, T) and therefore G′ = f(P, T, $n_1 \cdots n_{c-1}$). The geometric equivalent of the transformation is illustrated in Fig 2.12.

In principle any number of saturation constraints can be applied simultaneously, but situations can easily arise where the constraints become inconsistent. Consider a system in which we assume a system is saturated with respect to the components $CO_2$-fluid, $SiO_2$, and CaO. Clearly such an assumption has extremely limited validity because components may react to form various multicomponent compounds, most notably wollastonite and calcite. To get around this problem PeRpLeX applies saturation constraints successively rather than simultaneously. Thus the user specifies a hierarchy listing the order in which saturation constraints are to be applied. At each condition of interest PeRpLeX determines the stable phase representing the first component and then projects the remaining phases through this component. After this projection, all phases consisting of only the first and second components will project onto the composition of the second component. Of these phases, the one with the lowest $\overline{G}'$ coordinate will be stable and the $\mu$ of the second component will be the $\overline{G}'$ of this phase. A projection can then be done through this component and the potential of the third component determined. This is repeated for each component until the chemical potential of every saturated component, and the saturated phases, are determined.

The advantage of this approach is that if the saturated phases are compounds they will always be compatible, and that under certain circumstances it is possible to project through the composition of solution phases. To understand how and when this is permitted consider the system $TiO_2$–FeO–$Fe_2O_3$ after projection through $O_2$ component into the $TiO_2$–FeO subcomposition (this first projection implies $\mu_{O2}$ is known from some constraint, such as the composition of a C-O-H fluid). If the only stable phases are an ilmenite solution (Il) and rutile (ru, essentially pure $TiO_2$) then the $G'$–X diagram of the system will be as in Fig 2.14. In this case at any P-T-$\mu_{O2}$ condition there is only 1 possible composition of ilmenite that coexists with rutile. If the system is rutile saturated ($\mu_{TiO2}=\overline{G}_{ru}$), we can find the rutile-saturated Ilmenite composition by making the transformation (shown graphically in Fig 2.14):

$$\mu_{FeO}=\overline{G}''_{Il}=\overline{G}'_{Il}-X^{Il}_{TiO2}\mu_{TiO2}.$$

The stable Il composition is that which minimizes $\overline{G}''_{Il}$, and this composition also gives $\mu_{FeO}$, so we could now project through FeO component. In PeRpLeX this is done with pseudocompounds, and at every P-T-$\mu_{O2}$ the program would determine the stable Ilmenite composition before projecting through FeO. Note that projection is not valid if made through FeO first because the FeO-ilmenite endmember (hematite) would be the stable FeO-saturated phase; however this composition cannot be stable if there is any $TiO_2$ component in the system. In general, projection through a solution phase is possible provided the $\mu$'s of all but 1 of the components of the solution have been determined by previous projections. Another way of putting this is that such projections are only possible if the solution is in an invariant composition diagram assemblage (i.e. an assemblage of c = p phases). Fig 2.15 illustrates valid saturated component hierarchies for the system CaO–$TiO_2$–FeO after projections though $O_2$, $CO_2$, and $SiO_2$.

### 2.3. PTX-PTAX-GEOCALC-TWEEQU

PTX-PTAX-GEOCALC are software packages for calculating phase equilibria. The basis of these packages is a program written by Perkins et al. (1986) for calculating Schreinemakers projections as a function of P–T–$X^f_{CO2}$–$a_i$ coordinates. The program works only for compound phases (or solution components with fixed-activity corrections) and uses a combinatorial algorithm. The algorithm consists of enumerating every possible univariant assemblage of p = c + 1 phases and then testing whether each assemblage is stable within the specified P–T–$X^f_{CO2}$–$a_i$ coordinate frame. The difficulty with this algorithm can be demonstrated by considering that in a 3 component system with 80 phases (e.g. CaO–$Al_2O_3$–$SiO_2$ after projection through $H_2O$–$CO_2$) there are 1,581,580 (p!/(p–c–1)!/(c+1)!) p=c+1-phase assemblages possible. The equilibrium conditions of each of these assemblages must be traced in the coordinate-frame of interest and at each point a test must be made to determine its stability. In practice, things are not as bleak as they may seem at first because degeneracy in geologic systems reduces the number of possible assemblages, and the stability of the univariant equilibrium can be tested at the corners of the diagram to determine if it occurs within the diagrams coordinate frame. Although this algorithm is nevertheless slow it is robust and the programs are easy to use and self-contained. The source of the original program is available from Perkins, subsequent modifications are generally available only as programs compiled for IBM PC's. The IBM PC versions also incorporate computer driven graphics. PTAX and GEOCALC are set up to use Berman's (1988) data base; however, data with the same heat-capacity and volumetric functions can be added to the data-base.

TWEEQU is a thermobarometry program developed by Berman (1990) and included in recent versions of GEO-CALC. TWEEQU is similar to the Average P-T calculation program in THERMOCALC, but in contrast to THERMOCALC, TWEEQU considers all possible mineral component equilibria rather than a set of p–c independent equilibria, where p is the number of compounds or solution endmembers in the assemblage of interest. All these equilibria are plotted in the $P–T–X^f_{CO2}–a_i$ coordinate frame of interest and in the ideal situation they will intersect at a single point representing the conditions of equilibration. Invariably equilibria will not do this because of flawed thermodynamic data (and solution models) and disequilibrium. The P-T condition is then determined by calculating a weighted average intersection point. There are 2 problems resulting from the use of all possible component equilibria: (i) Results are influenced by the number of reactions that it is possible to write, rather than the quality of the data. (ii) For unwary users TWEEQU can produce deceptive results because for any 2 independent equilibria involving p endmembers TWEEQU will generate up to $p!/(p–c–1)!/(c+1)!$ dependent equilibria. All these equilibria will intersect at a single $P–T–X^f_{CO2}–a_i$ regardless of whether the assemblage is in equilibrium or not. Thus, graphical assessment of TWEEQU's output is highly biased.

### 2.4. THERMOCALC(s)

There are 2 programs for calculating phase equilibria called THERMOCALC. The version of Sundman et al. (1985) uses Eriksson's (e.g. Saxena & Eriksson 1983) free energy minimization algorithm and is capable of treating solution phases. This program has been applied to geologic problems (e.g. Saxena & Erikkson 1983) and is very useful for situations where, but it is not well suited for computing multidimensional phase diagram projections. The petrological THERMOCALC program, discussed here was developed by Powell & Holland and is briefly described in their thermodynamic data base papers (e.g. Powell & Holland 1988). Compiled versions of the program are available for IBM PC's and MacIntosh computers from either author.

THERMOCALC has 3 computational modes, discussed below.

#### 2.4.1. Schreinemakers Projections ($P–T–X^f_{CO2}$ Diagrams)

For systems comprised entirely of compounds it calculates Schreinemakers projections by an algorithm that is roughly as outlined here:

i) Enumerate all possible divariant (p = c) assemblages.

ii) Test stability of every assemblage each of the 4 corners of the phase diagram projection coordinate frame. Saving the identity of any assemblage that changes stability within the coordinate frame in a list.

ii) Enumerate all possible univariant (p = c + 1) assemblages. Compare each univariant assemblage to the list of divariant assemblages. If the univariant assemblage includes 1 of the divariant assemblages then determine the stable equilibrium conditions for the univariant reaction.

This algorithm makes use of the facts that the maximum variance of any phase field in a system composed entirely of compounds is 2 (i.e. divariant), and that the stability of divariant field can only be affected by a univariant field. Thus if a univariant assemblage includes the phases of a divariant field that changes stability in the projection coordinate frame then the univariant field must be stable within the boundaries of the diagram. As univariant fields can only terminate at invariant fields (points), the invariant fields are also located by this method. By testing the stability of divariant assemblages, rather than univariant assemblages as in GEO-CALC, the THERMOCALC algorithm saves a considerable amount of computer time. Taking the ≈ 80 phase $CaO–Al_2O_3–SiO_2$ system (after projection through fluid components) as an example, the maximum number of divariant assemblages is 82,160; compared to 1,581,580 univariant assemblages.

#### 2.4.2. Solution Phase Equilibrium Calculator

THERMOCALC includes a sophisticated calculator that can be used to determine solution phase equilibria subject to a variety of different kinds constraints (Powell 1978). In this mode the user supplies thermocalc with a list of phases, and instructs the program to locate phase equilibria involving a specified number ($p \leq c + 2$) of phases. If the $p > c$, the program will determine the $P\text{-}T\text{-}X^f_{CO2}$ conditions for the equilibria as well as the phase compositions. If $p = c$, the phase compositions are determined as a function of $P\text{-}T\text{-}X^f_{CO2}$

conditions; and if $p < c$ they are determined as a function of P-T-$X^f_{CO2}$ conditions and an additional variable such as the composition of one phase. In all cases it is possible to have THERMOCALC determine whether a the calculated equilibria would be "seen" by a specified bulk composition, or range of bulk compositions. At present the program does not determine the stability of the equilibria; thus, it is necessary to determine the stable configuration of the equilibria in a phase diagram from Schreinemakers principles and geologic constraints. In many geologic systems this is not critical, because the stable equilibria are known, and the problem is primarily determining the compositions of the participating phases, as in the case of many important isograd equilibria. There are no restrictions on the types of solution models used for the calculations. A number of petrogenetic grids and phase diagram constant composition sections calculated by this method have been published in recent literature (e.g. Powell & Holland 1990)

### 2.4.3. Average P-T Calculations

Given minerals of known composition, THERMOCALC computes the independent (activity corrected) mineral component equilibria and then determines, by least squares, the P–T–$X^f_{CO2}$ conditions that minimize the discrepancies in the equilibria (Powell & Holland 1988). This is basically a slightly more advanced form of the TWEEQU analysis proposed by Berman (1990). In comparison to TWEEQU it has the advantage that THERMOCALC provides a statistical assessment of the error in the analysis.

## 2.5. A Practical Comparison of GEO-CALC, THERMOCALC and PeRpLeX

Each package has particular advantages that make it uniquely useful in certain situations. GEO-CALC and THERMOCALC are well managed by their authors and relatively easy to use; PeRpLeX offers more flexibility and is accordingly more difficult to use and easier to abuse, as well as being managed in an amateur manner. GEO-CALC and THERMOCALC are available only as compiled programs. THERMOCALC runs on IBM PC's or MacIntosh Computers, GEO-CALC runs on IBM PC's. The FORTRAN source of PeRpLeX is supplied to users, thus the program can be made to run on any computer on which it can be compiled, but the user has to compile it. GEO-CALC software includes computer graphics as an integral part of the package; PeRpLeX includes a separate program that generates PostScript plot information that can be printed and edited by many different computer systems; THERMOCALC is not currently supplied with graphics support. All 3 packages can do fully automated calculations of phase diagram projections of systems comprised entirely of compounds (or solution components with specified activities) as a function of P–T–$X^f_{CO2}$. GEO-CALC will also do phase diagram projections as a function of a components activity, and PeRpLeX will do calculations as a function of entropy, enthalpy, volume, $\mu$'s, and a composition variable, $X^f_O$, for C–O–H–S fluids. Both GEO-CALC and THERMOCALC are both designed to be used with the data bases of their respective authors, PeRpLeX runs with virtually all of the geologic data bases (a current exception being the high pressure data base of Saxena & Fei 1989). PeRpLeX is unique in that it can do automated calculations of composition and mixed-variable phase diagrams, and in that it can treat phases of variable composition, although it does this through an approximation. In contrast, THERMOCALC can determine, by numerically exact procedures, the equilibrium compositions of coexisting phases, but it cannot, at present, determine whether the equilibrium is stable. Thus in principle THERMOCALC can be used to calculate any kind of phase diagram, but the construction is not fully automated and requires user expertise. This is not necessarily a limitation because it requires a certain level of user understanding, whereas fully automated calculations lead users to generate diagrams that they cannot properly interpret.

Both GEO-CALC and THERMOCALC have special routines for thermobarometry, TWEEQU and Average P-T calculations. To my way of thinking, these routines are superceded by phase diagram or equilibrium calculations for the system in question. The distinction is equivalent to that between forward and and backward modeling. In thermobarometry one begins with observed mineral compositions and then attempts to deduce conditions of formation, in essence a backward modeling approach. The problem is that flaws in thermodynamic models employed and the complexities of natural equilibria (and disequilibria) virtually ensure inconsistency between natural and modeled equilibria. THERMOCALC attempts to resolve this by an objective (statistical) approach, but even so I dislike these methods because they encourage a "black box" attitude toward thermobarometry. In this respect, I favor classical thermobarometry where practitioners must carefully consider which phases are in equilibrium, and the causes for discrepancies. Phase diagram and equilibrium calculations for solution phases provide a preferable alternative to thermobarometry. Such calculations permit prediction, i.e. forward modeling, of both the composition and, in the case of phase diagrams, stability of coexisting phases as a function of pressure and temperature. This approach is thermodynamically consistent, by definition, and in attempting to match observed and predicted assemblages practitioners can easily assess the significance of discrepancies.

**3. ANNOTATED BIBLIOGRAPHY**

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