THERMODYNAMICS APPLIED TO EARTH MATERIALS

James Connolly, NW/E/78.1, 2-7804
james.connolly@erdw.ethz.ch

These notes and other materials for this course are available at:
www.perplex.ethz.ch/thermo_course

SOME PRELIMINARIES

MAPLE TECHNICAL ISSUES

Installing Maple - Expand the Mac (OSX), LINUX or PC (Windows) zip archive in www.perplex.ethz.ch\thermo_course\maple. Follow the instructions in the Maple installation text file!

Display settings – if you wish to keep the format of your scripts similar to those on the course web-page and you are not using "Classic" Maple, then: under **Tools->Options->Display** set **Input display** to **Maple Notation** and **Typsetting level** to **Maple Standard**, these minimize complications caused by invisible formatting characters; and under **Tools->Options->Interface** set **Default format for new worksheets** to **Worksheet**.

Maple tutorial – this course does not require much skill with Maple and I will attempt to provide you with the essential syntax. However, if you want a better understanding of its syntax and capabilities, then the tutorial present in www.perplex.ethz.ch\thermo_course\maple may be useful.

Classic vs Java scripts – the Maple scripts prepared for this course were prepared in the Classic Maple version (file type *.mws). These scripts can be used in the Java version of Maple, but if you do so please save them as Java version files (file type *.mw), Classic version files that have been manipulated in the Java version become illegible if saved as Classic version files.

A word to the wise – Save your work frequently; do not rely on the auto-backup function.

PROBLEM SETS

The problem sets may be solved as a group effort. If you solve a problem set as a group, then please submit one copy of the solved problems for the entire group. In the first half of the semester, the problem sets are due within two weeks of their assignment.

If you do a problem with Maple, then I am happy to accept an e-mail copy of your Maple script rather than a hand-written answer. However, be sure that the script can be executed sequentially, to verify this, type "restart;" or press the Maple menu restart button and then step through the script. Just as in a handwritten problem set, maple scripts should be documented by explanatory comments, preferably inserted as text (the "T" menu button). In particular, it is essential that the units be given for any dimensional results. Some firewalls do not allow Maple scripts as attachments; therefore, it is best to enclose the Maple script in a zip file.

If necessary, then I will offer a tutorial for the more complicated problem sets, probably on Thursday's, 14:15-16:15. The penalty for solving problems in the tutorial is that the note for a perfect solution is 5. If you attend a tutorial, then please indicate this on your problem set.

THE FIRST LECTURE AND THE CORRESPONDING PROBLEM SET

To illustrate the purpose and goals of this course, in the first lecture I will begin at the end by considering how phase diagrams are constructed from thermodynamic models. There is no script for this lecture, but a short review of the basic concepts is in p 12-16 of www.perplex.ethz.ch\thermo_course\chapter_0\potenza.pdf. The problem set for this lecture consists of the four problems outlined in the maple scripts at ...\thermo_course\chapter_0.

1: THERMODYNAMIC PROCESSES AND LAWS

"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.

Chemical thermodynamics is a theory developed to predict and understand the consequences of processes. In principle it can be used to predict any process, but it is mainly used to understand the processes of **heat** and **mass transfer** and **isostatic dilation** (i.e., a change of **volume** (*V*) in an isotropic stress field). This restriction is implicit in the remainder of these notes. In this context, energy is referred to as the **internal energy** (***U***) to emphasize that it is only the energy accessible through the processes of interest. For a body of matter, i.e., a system, composed of ***k*** independently variable **kinds of mass** ($\boldsymbol{M}_1$, …, $\boldsymbol{M}_k$), there are thus *k*+2 independent processes. Intuitively one expects that any of these processes will change the energy of a system on which they operate. The **first law of thermodynamics** is a formal statement of this intuition. Specifically, the first law states that energy of a system may only change if the system does work on its environment. Moreover, the first law states that energy (*U*) is conservative, i.e.,

$$\mathrm{d}U - \text{đ}Q + \sum_{i=2}^{k+2} \text{đ}W_i = 0 \tag{1.1}$$

where *Q* is the heat gained by the system and W_i is the work done by the system in the i^{th} process, where đ is used to indicate an **inexact** (path dependent) **differential**. The sign convention in Eq 1.1 is by no means universal; in particular, in many textbooks *W* represents work done on the system in which case the work and heat differentials have the same sign.

Properties that are not path dependent are said to be **state functions** and the importance of the first law is that it establishes energy as a state function. It follows that the integral of a state function along a closed path, i.e., a path that returns the system to its initial state must be zero. Thus an alternative statement of the first law is

$$\oint \mathrm{d}U = 0\,. \tag{1.2}$$

But to define a closed path you must first define state. Early thermodynamicists understood that a system could only do work by changing its volume or mass, therefore the properties ***V***, $\boldsymbol{M}_1$, …, $\boldsymbol{M}_k$ are state functions that define mechanical and chemical state. Furthermore, **temperature** (***T***) was assumed to be a state function although the relationship between temperature and heat was not entirely clear.

If a system loses heat, it can be considered to have done positive thermal work, accordingly Eq 1.1 can be written more compactly

$$\mathrm{d}U + \sum_{i=1}^{k+2} \text{đ}W_i = 0\,.$$

Early thermodynamicists were concerned primarily with the construction of steam engines, which convert heat to mechanical work; thus they had the prejudiced view that mechanical work was useful and that thermal work was useless except to the extent that it could be converted to useful work. While this attitude is no longer appropriate, it is sometimes useful to isolate heat as a special kind of work in order to understand the perspective of the early thermodynamicists who were responsible for thermodynamic theory.

A MECHANICAL ANALOGY

Although mechanics is more complex than chemical thermodynamics in that it involves kinetic energy and vectors, it is familiar via elementary physics. Therefore it is helpful to introduce a mechanical analogy to Eq 1.1, specifically the potential energy *U* of a stationary ball as a function of its horizontal position *x* along a frictionless 1-dimensional surface with height *H*(*x*) in a gravitational field (Fig 1.1). The potential energy of the ball is proportional to the height *H* of the surface, i.e., $U \propto H(x)$ and by the first law (Eq 1.1)

$$\mathrm{d}U + \mathrm{d}W = 0 \tag{1.3}$$

the ball can do work if it lowers its potential energy by moving. In mechanics this work is

$$\mathrm{d}W = f\mathrm{d}x \tag{1.4}$$

where *f* is the force resisting the movement d*x*, thus

$$dU = -f dx \qquad 1.5$$

In this particular case, the work differential happens to be exact because there is only one process (path) possible.

Eqs 1.3 and 1.4 can be considered, although it is not conventional, to define force as the negative spatial gradient in potential energy

$$f \equiv -\frac{dU}{dx}. \qquad 1.6$$

The ball will have no tendency to move if this gradient is zero, thus the gradient can be viewed as the potential for the only process (displacement of the ball) possible in the system in the absence of external influence. For this reason spatial gradients in energy are often referred to as **potentials** for work

$$\theta \equiv \frac{dU}{dx}$$

thus forces may be regarded as the negative of potentials for work and 1.5 may also be written

$$dU = \theta dx. \qquad 1.7$$

The topographic highs and lows of the surface (Fig 1.1) are the only points at which a stationary ball is in mechanical equilibrium, i.e., in force balance. We may further characterize these equilibria as being stable or unstable if they correspond to maxima or minima, it being apparent that an equilibrium at a maximum is unstable with respect to small perturbations.

For the case of a single ball we have the trivial result that the condition for equilibrium, i.e., a state where no processes are possible is that θ = 0. At this point the example is not especially relevant to thermodynamics because no processes are possible within the system. Therefore, consider now a system consisting of two balls that are constrained to remain in contact. In this system, we have the possibility of an internal process in that one ball can push the other. In this case, the condition for equilibrium is not that the balls are at the same height, but rather that the potentials of the balls must be equal in magnitude and opposite in sign. The necessity for the opposing signs is that in mechanics forces have direction and this is the only real distinction to thermodynamics where the forces or potentials are scalar. Thus in thermodynamics a requirement for equilibrium with respect to a process that changes a property Ψ, is that the potential

$$\theta \equiv \frac{\partial U}{\partial \Psi} \qquad 1.8$$

for the process is uniform throughout the system.

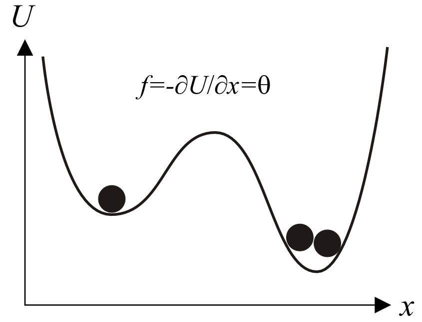


Fig 1.1 Energy of a stationary ball along a 1-d surface, the force that would induce the ball to roll is the negative of the gradient in the energy along the surface. A spatial gradient in energy is usually referred to as a potential. The potential is a measure of the amount of work that can be extracted from the ball by a displacement (d*x*) in the along the surface. If the system consists of only one ball it can be in equilibrium only if the potential of the ball is zero. However, if the system of interest consists of two balls, it will be in mechanical equilibrium when the potential of each ball is equal in magnitude (but opposite in sign).

Integrating Eq 1.5 at constant force

$$U = \theta x \qquad 1.9$$

and the differential of Eq 1.9 is then

$$dU = \theta dx + x d\theta. \qquad 1.10$$

Comparison of 1.5 and 1.10, leads to the conclusion that the exactness of 1.5 requires

$$x d\theta = 0, \qquad 1.11$$

which is the mathematical statement that changing the potential of a system does not affect the systems energy if the system does no work.

THERMODYNAMIC WORK

Just as in the foregoing mechanical example where the work differential can be written variously

$$dW = -\frac{dU}{dx}dx = -\theta dx = f dx.$$

The work differentials in Eq 1.1 can be written

$$\sum_{i=2}^{k+2} đW_i = -\sum_{i=2}^{k+2}\left(\frac{\partial U}{\partial \Psi_i}\right)_{Q,\Psi_{j\neq i}} d\Psi_i = -\sum_{i=2}^{k+2}\theta_i d\Psi_i \qquad 1.12$$

where the work differentials are now inexact because more than one process is possible and the thermodynamic potential θ_i is defined as the partial derivative of energy with respect to property Ψ_i for an adiabatic system ($\text{đ}Q = 0$) at constant $\Psi_{j\neq i}$. In Eq 1.13 the potentials are differential coefficients defined, at least in the adiabatic case, entirely in terms of state functions, therefore it follows that the potentials are also state functions. Using explicit notation, the differential coefficient on volume is known from mechanics to be pressure, i.e., the "force" that resists dilational work, thus

$$\text{đ}W_V = PdV \qquad 1.14$$

and pressure can be defined thermodynamically as the negative of the potential for volume

$$P \equiv -\left(\frac{\partial U}{\partial V}\right)_{Q,M_i \ldots M_k} .$$

In contrast, chemical work is entirely a thermodynamic concept and defined in terms of a potential for chemical work

$$\mu_i \equiv \left(\frac{\partial U}{\partial M_i}\right)_{Q,V,M_{j\neq i}}$$

such that

$$\text{đ}W_{M_i} = \mu dM_i .$$

Making use of these definitions, Eq 1.1 is

$$\mathrm{d}U = \text{đ}Q - P\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}M_i \qquad 1.15$$

The peculiar mixture of forces and potentials reflects the historical fact the dilational work term had been defined in mechanics in terms of pressure, whereas chemical work was not defined prior to the work of Gibbs on chemical thermodynamics.

EXACT DIFFERENTIALS

After reading thermodynamic textbooks one could easily be forgiven for concluding that the true statement of the 1st law is that energy is an exact first order homogeneous differential, rather than that these mathematical qualities are a consequence of energy conservation. I suspect this confusion, of which I was a victim, results from emphasis on mathematical rather than physical concepts, so to allay this confusion here let us consider illustrations of the inexactness (i.e., path dependence) of heat and work and the mathematical requirement for exactness (we leave an explanation of "first order homogeneity" for later).

For the first illustration (Fig 1.2), consider a system composed of a constant amount of a pure monatomic ideal gas for which

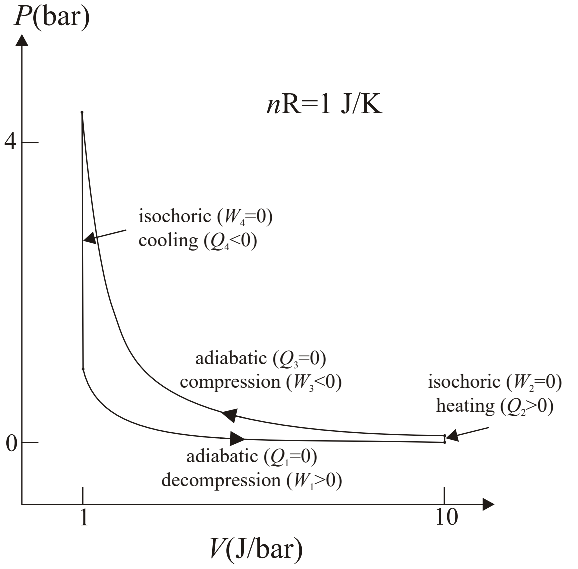


Fig 1.2 Illustration of a closed path for a fixed mass of an ideal gas initially at V_0=1 J/bar and T_0=1 K (P_0=1 bar). The path consists of 4 segments: adiabatic decompression to V_1=10 J/bar, isochoric (constant volume) heating back to T_0, adiabatic compression back to V_0, and isochoric cooling back to T_0. The mechanical work done along any segment is the area under the path from its initial to its final volume coordinate, thus the gas does no work in the isochoric segments and the amount of work done in the adiabatic segments is not equal. This partitioning demonstrates that work and heat are path dependent functions, however the first law requires that these functions sum to zero for closed path as the total energy of the gas must be conserved.

$$PV = n\mathrm{R}T. \qquad 1.16$$

Since the system is pure and at constant mass, its energy is a function of two inexact functions, heat and dilational work

$$\mathrm{d}U = \text{đ}Q - \text{đ}W_V .$$

Now let us devise a set of paths involving work and heat that ultimately leave the gas in its original state. First, we thermally insulate the system and allow it to expand. During this part of the cycle the system can neither gain nor lose heat (i.e., it is adiabatic, $\text{đ}Q \equiv 0$) and the pressure of the gas at any point can be shown to be

$$P = P_0\left(V_0/V\right)^{5/3}, \qquad 1.17$$

where the zero subscripts denote initial conditions. From Eqs 1.14 and 1.17, the change in energy and work done in this segment is

$$\Delta U_1 = -W_1 = -\int_{V_0}^{V_1} P_0\left(V_0/V\right)^{5/3} \mathrm{d}V \qquad 1.18$$

which is negative of the area under the path in a *V-P* diagram (Fig 1.2). From Eq 1.16 the gas must cool during this work to

$$T_1 = \frac{P_1 V_1}{nR}$$

as a consequence of its expansion. Next, we remove the insulation and heat the gas at constant volume back to its original temperature T_0. As the gas does not change its volume it does no mechanical work, but its pressure increases to

$$P_2 = \frac{nRT_0}{V_1}\,.$$

We now adiabatically compress the gas back to its original volume and restore the gas to its original state by isochoric (constant volume) cooling. Thus, we have a closed path for which energy conservation requires

$$\Delta U = \oint \mathrm{d}U = 0$$

yet because the *V-P* paths during compression and decompression are different it is evident that

$$\Delta W = \oint \text{đ}W_V = W_1 + W_2 \neq 0\,,$$

i.e., that work is not a state function in that the net amount of work done is dependent on the amount of heating done during the isochoric segments of the path.

The path independence of exact differentials attracted much attention in science and mathematics during the 1700's because the existence of such perfection was construed as evidence for the hand of god. To illustrate the mathematical requirement for exactness, consider the **total differential** of *f*(*x*,*y*)

$$\mathrm{d}f = \frac{\partial f}{\partial x}\mathrm{d}x + \frac{\partial f}{\partial y}\mathrm{d}y\,. \qquad 1.19$$

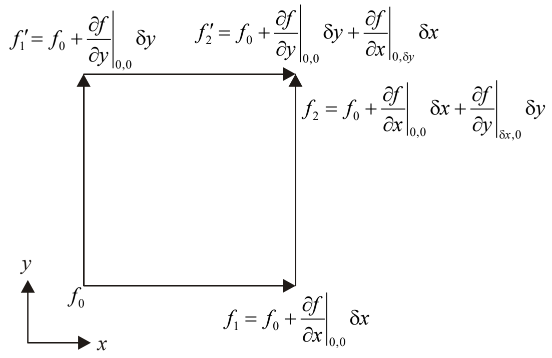
If this differential is exact, its integral must be the same regardless of path, so let us consider the two alternate paths defined by small, but finite, increments δ*x* and δ*y* (Fig 1.2). Because the increments are small, we approximate *f* by a first order Taylor series as

$$f_{\delta x,0} = f_{0,0} + \left.\frac{\partial f}{\partial x}\right|_{0,0}\delta x$$

or

$$f_{0,\delta y} = f_{0,0} + \left.\frac{\partial f}{\partial y}\right|_{0,0}\delta y$$

where the subscripts indicate the *x-y* coordinates at which the function, or its derivatives are evaluated.



if $f_2 = f_2'$ then

$$f_0 + \left.\frac{\partial f}{\partial x}\right|_{0,0}\delta x + \left.\frac{\partial f}{\partial y}\right|_{\delta x,0}\delta y = f_0 + \left.\frac{\partial f}{\partial y}\right|_{0,0}\delta y + \left.\frac{\partial f}{\partial x}\right|_{0,\delta y}\delta x$$

$$\frac{\left.\frac{\partial f}{\partial y}\right|_{\delta x,0} - \left.\frac{\partial f}{\partial y}\right|_{0,0}}{\delta x} = \frac{\left.\frac{\partial f}{\partial x}\right|_{0,\delta y} - \left.\frac{\partial f}{\partial x}\right|_{0,0}}{\delta y}$$

$$\lim_{\delta x,\delta y\to 0}\left(\frac{\left.\frac{\partial f}{\partial y}\right|_{\delta x,0} - \left.\frac{\partial f}{\partial y}\right|_{0,0}}{\delta x} = \frac{\left.\frac{\partial f}{\partial x}\right|_{0,\delta y} - \left.\frac{\partial f}{\partial x}\right|_{0,0}}{\delta y}\right) = \frac{\partial^2 f}{\partial y\partial x} = \frac{\partial^2 f}{\partial x\partial y}$$

Fig 1.3 Proof that the cross derivatives of two variable function *f*(*x*,*y*) must be equal if the differential of the function is exact. If the differential is exact, then the value of the function must be independent of path, therefore consider two alternative paths involving finite increments of *x* and *y*. The value of the function after each increment is approximated by a first order Taylor series. If the value of the function is the same at path endpoints, then variation in the *x*-derivative with a finite *y* increment must equal the change in the *y*-derivative with a finite *x* increment; in the limit of infinitesimal increments this equality reduces to Euler's Criterion.

Applying this approximation successively for the two possible paths, the result can only be independent of path if

$$\frac{\left.\frac{\partial f}{\partial y}\right|_{\delta x,0} - \left.\frac{\partial f}{\partial y}\right|_{0,0}}{\delta x} = \frac{\left.\frac{\partial f}{\partial x}\right|_{0,\delta y} - \left.\frac{\partial f}{\partial x}\right|_{0,0}}{\delta y}\,.$$

The Taylor series approximation is exact in the infinitesimal limit (δ*x*, δy → 0) in which case we obtain the result

$$\frac{\partial^2 f}{\partial y\partial x} = \frac{\partial^2 f}{\partial x\partial y}$$

that the cross derivatives of an exact function must be independent of the order of differentiation. This result is known **Euler's criterion** (the Euler formerly on the 10 CHF note) for exactness.

Ordinarily in thermodynamics the partial derivatives that are differential coefficients of a differential equation are given special names, e.g., $\partial U/\partial M = \mu$ or $\partial U/\partial V = -P$ as in Eq 1.15. Adopting this shorthand Eq 1.19 is

$$\mathrm{d}f = p\mathrm{d}x + q\mathrm{d}y$$

and **Euler's criterion** yields

$$\frac{\partial p}{\partial y} = \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial q}{\partial x} . \qquad 1.20$$

if f is exact.

From a thermodynamic perspective, the important feature of an exact differential is that its integrals can be evaluated given only knowledge of initial and final states, i.e.,

$$\int_{x_i,y_i}^{x_f,y_f} \mathrm{d}f = f_f - f_i \equiv \Delta f$$

$$= \left(p_f x_f + q_f y_f\right) - \left(p_i x_i + q_i y_i\right)$$

Where, if necessary, the differential coefficients may be evaluated as explicit functions of x and y, e.g.,

$$p_i = \left.\frac{\partial f}{\partial x}\right|_{x_i,y_i} .$$

From the foregoing considerations, it is apparent that it would be desirable to decompose the inexact heat differential in Eq 1.15 into the product of an exact differential and a differential coefficient, just as the work differentials were decomposed into the product of the differential of a state function and an integrating factor. The decomposition of the heat differential was accomplished by Rudolf Clausius while he was a professor at the ETH.

THE SECOND LAW

In the mid-19th century it was realized that heat flow occurs as a consequence of a gradient in temperature T. However, the property in heat transfer analogous to mass or volume for chemical and mechanical work was not understood. This problem was resolved by Clausius' (1850, 1865) formulation of the **second law of thermodynamics**, which introduced the state function **entropy** S as

$$\mathrm{d}S \geq \frac{\text{đ}Q}{T} . \qquad 1.21$$

and substituting 1.21 into 1.15 a combined statement of the first and second laws is

$$\mathrm{d}U \leq T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}M_i \qquad 1.22$$

The equalities in 1.21 and 1.22 apply for any real process and the equalities correspond to the theoretical limit that the processes of are non-dissipative, in thermodynamics this type of behavior is said to be **reversible**.

Unlike the macroscopic properties energy, mass and volume, entropy is unique to thermodynamics and therefore non-intuitive. Entropy is best understood as a macroscopic measure of disorder. In the specific case of heat transfer this disorder may simply be an increase in atomic vibrational energy. From the first law, dissipation cannot affect the energy of a system, rather it is a lowering of the quality of the energy. This reduction in quality is manifest by an increase in disorder. In this regard, the second law is pessimistic in that it implies that any real process increases the net disorder of the universe. A simple illustration is the heating of a system at constant mass and volume, if the heating is reversible

$$\Delta Q = T_{f,rev} S_{f,rev} - T_i S_i$$

where the subscripts i and f designate the initial and final states; if instead the same amount of heat is added irreversibly

$$\Delta Q < T_{f,irrev} S_{f,irrev} - T_i S_i$$

and subtracting the equality from the inequality and rearranging the result

$$T_{f,rev} S_{f,rev} < T_{f,irrev} S_{f,irrev} .$$

However, as the energy in both cases is identical

$$T_{f,rev} S_{f,rev} - P_{f,rev} V_i + \mu_{f,rev} M_i =$$

$$T_{f,irrev} S_{f,irrev} - P_{f,irrev} V_i + \mu_{f,irrev} M_i$$

ergo

$$-P_{f,rev} V_i + \mu_{f,rev} M_i > -P_{f,irrev} V_i + \mu_{f,irrev} M_i .$$

Thus, the irreversible heat exchange causes a net lowering in the capacity of the system to do work by mechanical and chemical processes, should the constant mass and volume constraints be relaxed. In other words, the capacity of the system to do useful work has been dissipated by irreversible processes. It may be noted that this attitude is prejudicial with regard to what processes constitute useful work, i.e., it neglects the fact that the irreversible process has increased the amount of energy that can be drawn out of the system as heat.

Another illustration of dissipation is provided by the mechanical analogy mentioned earlier (Fig 1.1). Previously we discounted the fact that the "work" the ball does is translation (a process that is not usually considered in thermodynamics), i.e., the balls potential energy (U) is converted into kinetic energy in which case the total energy of the ball is

$$E = U + v^2/2\ . \tag{1.23}$$

Taking 1.23 as truth together with the first law, implies that if we place a ball above a minimum, then the ball will oscillate back and forth across the minimum forever (a perpetual motion machine). The second law says that this, and therefore 1.23 cannot be true. Rather Eq 1.23 but must be extended to

$$E = U + v^2/2 + TS \tag{1.24}$$

and that every motion of the ball must increase its entropy (temperature), an effect usually attributed to friction but which may also arise as a consequence of deformation. Consequently the potentials for potential (height) and kinetic (velocity) processes will dissipate until the ball settles to the minimum. Of course, this process heats the ball raising the potential for thermal work.

Although the designation of energy derivatives as potentials follows Gibbs, it is nonetheless unconventional in thermodynamic literature. More commonly U itself, and free energy functions derived from U that will be introduced later, are referred to as **thermodynamic potential functions**. The logic of this usage is that the functions measure the total energy that can be extracted from a system. For example, in the previous mechanical analogy (Fig 1.1) U is a direct measure of the height of the ball, and the possible variation in the height along the surface is therefore a direct measure of the potential of the ball to do work. In contrast, potentials as defined here (1.8) are a measure of the potential for individual processes within a system.

The **thermodynamic potentials** $\{T, -P, \mu_1, \ldots, \mu_k\}$ corresponding to the differential coefficients of 1.22 can only be defined for a system in a non-arbitrary way if they are uniform in all parts of the system. For example, imagine a two part system with distinct temperatures. What is the temperature of the entire system? There are numerous ways we may compute an average temperature, and thus there is no unique answer. In contrast, if the temperature is uniform, it is defined by a reversible variation in entropy at constant mass and volume, i.e.,

$$T \equiv \frac{\partial U}{\partial S}\ .$$

As the same argument can be made for any of the potentials in 1.22, it follows that for any **reversible process** the potentials must be uniform throughout the system. Thus, for a system to be heated reversibly it is necessary that temperature remain uniform during heating. Since rates of heat conduction, mass transport and dilation are finite, this requirement leads to the conclusion that reversible processes must be infinitely slow and manifest by infinitesimal potential gradients. In this regard, the form of 1.22 is deceptive as the coefficients cannot be defined for an irreversible process. For this reason, a restricted statement of the first and second laws known as **the Gibbs differential**

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}M_i \tag{1.25}$$

is preferred for reversible processes.

The Gibbs differential defines the fundamental variables of thermodynamics as entropy, volume and mass, i.e., $U(S, V, M_1, \ldots, M_k)$. Knowledge of these variables must provide a complete definition of any thermodynamic system; in other words, any attribute of a system that cannot be defined from these variables is not a thermodynamic attribute of the system. All other thermodynamic properties are derived, and specifically

$$\begin{aligned} T &\equiv \frac{\partial U}{\partial S} \\ -P &\equiv \frac{\partial U}{\partial V} \\ \mu_i &\equiv \frac{\partial U}{\partial M_i} \end{aligned} \tag{1.26}$$

Thus, the thermodynamic potentials that we are accustomed to thinking of as independent variables are dependent parameters in the context of the Gibbs differential, i.e., $T(S, V, M_1, \ldots, M_k)$, etc. As the Gibbs differential is simply a summation of reversible work differentials, it is analogous to the mechanical system discussed earlier. This analogy can be made more succinct by introducing the general notation

$$\mathrm{d}U = \sum_{i=1}^{k+2} \theta_i \mathrm{d}\Psi_i \qquad 1.27$$

where

$$\theta_i \equiv \frac{\partial U}{\partial \Psi_i}\,. \qquad 1.28$$

Eq 1.28 defines a special relationship between each fundamental variable and its potentials, properties related in this manner are said to be **conjugate**, e.g., T is conjugate to S, θ_i is conjugate Ψ_i. Just as in mechanical systems, where force balance defines the conditions of a mechanical equilibrium, the uniformity of thermodynamic potentials define conditions of **thermodynamic equilibrium**, a state in which no reversible processes may take place in a system without external influence. **Equilibrium processes** are thus processes that occur entirely in response to external influence since any system described by 1.25 must be in **internal equilibrium** (Fig 1.2).

As in the case of the mechanical system (1.9), 1.25 may be integrated holding the potentials constant to obtain

$$U = TS - PV + \sum_{i=1}^{k} \mu_i M_i \qquad 1.29$$

or

$$U = \sum_{i=1}^{k+2} \theta_i \Psi_i \qquad 1.30$$

and as the total differential of 1.30 is

$$\mathrm{d}U = \sum_{i=1}^{k+2} \theta_i \mathrm{d}\Psi_i + \sum_{i=1}^{k+2} \Psi_i \mathrm{d}\theta_i \qquad 1.31$$

comparison of 1.31 and 1.27, requires

$$\sum_{i=1}^{k+2} \Psi_i \mathrm{d}\theta_i = 0 \qquad 1.32$$

or in non-general form

$$S\mathrm{d}T - V\mathrm{d}P + \sum_{i=1}^{k} M_i \mathrm{d}\mu_i = 0 \qquad 1.33$$

Eq 1.33 is known as **the Gibbs-Duhem relation** and has the profound implication that only k+1 potentials of an equilibrium system are capable of independent variation. Thus the variation of one thermodynamic potential during a reversible process can always be expressed as a function of the remaining potentials.

SECOND THOUGHTS: THE 0TH AND 3RD LAWS

It is often difficult to distinguish what is assumed in thermodynamics from what is axiomatic. The 0th law is an example of this, as it was only realized by Caratheodory (1909) after the second law was postulated that temperature was not formally defined. Caratheodory's statement of the **0th law**, which was designated as such by Fowler (1956), was that if two bodies are in thermal equilibrium with a third body, then they are in thermal equilibrium with each other. The 0th law is necessary for legalistic arguments about temperature, but of little practical importance because it is usually implicitly assumed.

The **third law**, or **Nernst's Law**, is of greater practical importance because it establishes an absolute scale for entropy. A weak form of this law is the statement that the entropy of a system at zero Kelvin is zero. This form is "weak" because it is strictly correct only for a perfect crystal, but the statement is adequate for present purposes. A more robust statement is that no real processes are possible at absolute zero. Ergo, from the second law if no real processes are possible, the entropy change of any process must be zero at absolute zero.

ALTERNATIVE STATEMENTS

http://en.wikiquote.org/wiki/Thermodynamics

READING MATERIAL

I do not recommend any particular text for this course because I have only been able to convince myself that I understand anything of thermodynamics by looking at many different texts. In this regard, texts can be broadly categorized as theoretical books that explain principles but presume practical applications are trivial; or as "how to" books that explain the "trivia" but neglect or restrict theory in a way that hinders a general understanding. A few examples of each genre are:

Basic principles

Thermodynamics. N. A. Gokcen, R. G. Reddy

Thermodynamics and an introduction to thermostatistics. H. B. Callen

Thermodynamics : an advanced treatment for chemists and physicists. E. A. Guggenheim

Twenty lectures on thermodynamics. H.A. Buchdahl

How to

Applied mineralogical thermodynamics: selected topics. N. D. Chatterjee

The elements of physical chemistry. Peter Atkins (an excellent P-Chem text)

The Principles of chemical equilibrium: with applications in chemistry and chemical engineering. Kenneth George Denbigh

Thermodynamics of natural systems. Greg Anderson (this book is geologically oriented, but best for hydrothermal geochemistry)

Geochemical thermodynamics. Darrell Kirk Nordstrom, James L. Munoz (easy reader text)

PROBLEMS

In this course, if you do a problem with Maple, then I am happy to accept an e-mail copy of your Maple script rather than a hand-written answer. Because some firewalls do not allow Maple scripts, it is best to enclose scripts in a zip file or send a pdf of the script.

1.1) For the function $f(x) = ax^2 + bx + c$ use Maple (preferably the classic version) to a) solve for the roots of the function with the **solve** command, b) integrate and differentiate the function using the **int** and **diff** commands, and c) plot the function, its definite integral from zero to x, and its derivative in a single plot with the **plot** and **subs** commands for a=1, b=2, c=3.

1.2) Evaluate the amount of work done by the ideal gas during the closed cycle illustrated by Fig 1.2. Use the First Law to compute the heat gained by the gas. **Note:** to evaluate a definite integral in Maple use the command "int(1/x,x=x0..x1);". In some cases Maple will tell you that it cannot evaluate the integral because it is unable to determine if 0 is between x0 and x1, in such cases modify the command using the **assuming** qualifier as in: "int(1/x,x=x0..x1) assuming x0>0, x1>0;". **Beware:** variable ranges are indicated in Maple by two values separated by two periods, e.g., x0..x1, if you use actual rather than symbolic numbers for such a range and inadvertently separate the numbers by an ellipsis ("…") Maple interprets the third dot as a decimal point, e.g., Maple interprets the range 1…10 to be from 1 to 0.1.

1.3) **a)** Use Euler's criterion (Eq 1.20) to determine which of the differentials $\mathrm{d}f_1 = P\mathrm{d}V - V\mathrm{d}P$ and $\mathrm{d}f_2 = P\mathrm{d}V + V\mathrm{d}P$ are exact. **b)** If $\mathrm{d}f_3 = P^2\mathrm{d}V + V^{1/2}\mathrm{d}P$ is exact, then how does V depend on P? **c)** Write the total differential (Eq 1.19) of $f_4 = y^2x + y^3$, is it exact? **d)** $f(x,y)$ is single-valued (i.e., formally a function of x and y), is its differential exact? **Note:** it is easiest to solve **a**-**c** analytically; it is possible, but exceedingly painful, to solve the problems as outlined in Fig 1.3; and it is nearly impossible to solve the problems in Maple (i.e., do not waste your time trying).

1.4) A constant mass system is composed of an ideal gas ($P = M\mathrm{R}T/V$) and is in thermal equilibrium with an infinite heat reservoir at temperature T. If the system does work by expanding, then heat must flow into the system (in response to infinitesimal temperature gradients) to maintain thermal equilibrium with the reservoir. For this process we may define the differential of a function known as the Helmholtz free energy A, such that $\mathrm{d}A \equiv \mathrm{d}U - \mathrm{d}Q = -P\mathrm{d}V + \mu\mathrm{d}M$, which represents the maximum amount of work that can be extracted from the system. Evaluate the change in the Helmholtz energy of the system if it expands isothermally from V_0 to 10 V_0 by integrating $-P\mathrm{d}V + \mu\mathrm{d}M$. Is this result identical to ΔA the obtained by evaluating the difference in the integrated form of the Helmoltz energy ($A = -PV + \mu M$) between the initial and final state of system (the Gibbs-Duhem relation, Eq 1.33, may be helpful in this regard)?

NOTE: a dimensional numerical result is not an answer without units. You should always indicate appropriate units for answers to problems in this course. You can make Maple work with units, but unless you are fanatical I do not recommend this.

2: THERMODYNAMIC VARIABLES AND HETEROGENEOUS SYSTEMS

The variables of the Gibbs differential $\{S, V, M_1, \ldots, M_k\}$ characterize all thermodynamic processes of interest. As such they are the determinative parameters of any real system, i.e., the parameters that we, as masters of the universe, control. Any one of these properties may be used as a measure of the size of a system. It follows that the properties $\{U, S, V, M_1, \ldots, M_k\}$ must vary linearly with the size or extent, such properties are said to be **extensive**. Thus, if the size of the system is changed by a factor q, then

$$qU = U\left(qS, qV, qM_1, \ldots, qM_k\right). \qquad 2.1$$

A function with this character is a first order **homogeneous function** in all its variables. Euler's theorem on homogeneous functions states that if f is a homogeneous function of order o in $\mathbf{x} = \{x_1, \ldots, x_n\}$ then

$$f = o\mathbf{x} \cdot \nabla f\left(\mathbf{x}\right). \qquad 2.2$$

Thus for $U(S, V, M_1, \ldots, M_k)$ and

$$\begin{aligned} U &= \frac{\partial U}{\partial S}S + \frac{\partial U}{\partial V}V + \sum_{i=1}^{k}\frac{\partial U}{\partial M_i}M_i \\ &= TS - PV + \sum_{i=1}^{k}\mu_i M_i \end{aligned} \qquad 2.3$$

a result previously obtained by integration with the unstated assumption that U, S, V and M are extensive properties. That U and M must be extensive follows from the fact that they are **conservative properties** by the first law and conservation of mass (an implicit law in thermodynamics due to Lomonosov, 1747). The second law defines entropy as a conservative property for reversible processes. Thus it must be conservative in the absence of any processes. Oddly, volume is not conservative. Therefore that volume is extensive follows only from the unstated assumption that matter is continuous within any system. In mechanics this assumption is referred to as the **continuity constraint**.

Since all extensive properties are proportional to the size of a system, **size** is defined by any extensive property. However, for practical purposes it is preferable to choose properties that are conservative, i.e., for which

$$\mathrm{d}\Psi = 0 \qquad 2.4$$

for all processes that are possible in the system other than a change in size.

Thermodynamic Variables

	Extensive	Intensive	
		Potentials/ –forces	Specific/ Molar/ Compositional
Thermal	S	T	s
Mechanical	V	$-P$	v
Chemical	M_i	μ_i	m
General	Ψ_i	θ_i	ψ_i

A process that changes only the size of a system, changes all the systems extensive attributes by a common factor. Any other process must change the relative proportions of the extensive attributes; such a process changes the **state** of the system. Thus state is defined by the relative proportions of extensive properties and is independent of extent. An attribute of matter that is independent of size is said to be **intensive**. As it is only possible to form k+1 independent ratios from the k+2 independent extensive properties of a system, e.g.,

$$\frac{V}{M} = \frac{S}{M}\frac{V}{S} \qquad 2.5$$

it is evident that a thermodynamic system can have only k+1 independent intensive properties.

Thermodynamic potentials, the ratio of two differentials of extensive properties, are, of course, also intensive.

UGLY REALITY: COMPOSITIONAL, SPECIFIC AND MOLARVARIABLES

In practice it is often desired to separate variations in extent from variations in state, where the latter are usually the variations subject of interest, e.g., phase diagrams show phase relations only as a function of state. This separation is accomplished by defining **specific variables**

$$\psi_i \equiv \frac{\Psi_i}{\alpha}, \quad u = \frac{U}{\alpha} \qquad 2.6$$

where α is an arbitrary linear combination of extensive properties chosen to define the extent or **amount** of matter (e.g., total mass or volume). In other words, α is an arbitrarily defined extensive property. As 2.6 is a linear transformation, 1.29 yields the integral form of the specific energy

$$u = Ts - Pv + \sum\nolimits_{i=1}^{k}\mu_i m_i \qquad 2.7$$

such that

$$U\left(S,V,M\right)=\alpha u \tag{2.8}$$

The desired separation of state and extent is then obtained from the differential of 2.8

$$\mathrm{d}U=\alpha\mathrm{d}u+u\mathrm{d}\alpha \tag{2.9}$$

as α is solely a function of extent and u solely a function of state. The ugliness alluded to in the section title arises because only k+1 of the k+2 specific variables on the right hand side of 2.7 are independent; but unfortunately without prior knowledge of the definition of α, the explicit dependence of the specific energy can only be written in general form as $u\left(\psi_1 ... \psi_{k+1}\right)$, i.e., by making use of a relation such as 2.5 to obtain $\psi_{k+2}=f\left(\psi_1 ... \psi_{k+1}\right)$. This form is not only ugly because of its vagueness, but also for its asymmetry with respect to the extensive properties.
For the sake of clarity equations for specific properties are written here in terms of k+2 variables, with the implicit understanding that only k+1 of these variables are independent, e.g., $u\left(s,v,m\right)$.

To illustrate the difficulties arising from the definition of specific variables, three explicit formulations for $u\left(\psi_1 ... \psi_{k+1}\right)$ are outlined below.

Gibbs' Form

Not surprisingly, the most logical form is due to Gibbs, who defined amount

$$\alpha \equiv M_k$$

Noting that differential of a specific property ψ_i is

$$\mathrm{d}\psi_i=\frac{\mathrm{d}\Psi_i}{\alpha}-\Psi_i\frac{\mathrm{d}\alpha}{\alpha^2}, \tag{2.10}$$

then the variation in the specific internal energy of a system due to a change in state at constant amount is

$$\mathrm{d}u=T\mathrm{d}s-P\mathrm{d}v+\sum_{i=1}^{k-1}\mu_i\mathrm{d}m_i \tag{2.11}$$

in only k+1 differentials. The disadvantage of this form is that in graphical analysis (e.g., phase diagrams), the specific variables of a state in which $M_k = 0$ are infinite.

Molar Specific Variables

For historical reasons, in applied chemical thermodynamics an indirect measure of mass, known as a mole, is used in place of mass. A **mole** of any consists of Avogadro's number ($\mathrm{N_A}$) of the constituent entities of that substance and is thus directly proportional to the mass of the constituent entity (m_i). Any equation written in terms of mass may be written equivalently in terms of moles via

$$N_i={}^{M_i}\!\big/_{\mathrm{N}_A\mathrm{m}_i}$$

where roman face font is used to denote constants. Thus, in terms of moles 1.29 is

$$U=TS-PV+\sum_{i=1}^{k}\mu_i N_i\ . \tag{2.12}$$

Molar variables are specific variables formed by defining amount as the total number of moles

$$\alpha\equiv\sum_{i=1}^{k}N_i\big/\mathrm{e}_{N_i} \tag{2.13}$$

where e_{N_i} is a unit quantity of N_i, introduced so that the molar variables remain dimensionally consistent with the chemical potentials of 2.12. The resulting molar variables n_1, …, n_k are the **mole fractions** of the different kinds of mass and subject to the constraint

$$\sum_{i=1}^{k}n_i\big/\mathrm{e}_{N_i}=1,$$

which implies

$$\mathrm{d}n_k=-e_{n_k}\sum_{i}^{k-1}\mathrm{d}n_i\big/e_{n_i} \tag{2.14}$$

As 2.10 requires that for a variation in state at constant extent (dα=0)

$$\mathrm{d}u=T\mathrm{d}s-P\mathrm{d}v+\sum_{i=1}^{k}\mu_i\mathrm{d}n_i \tag{2.15}$$

substitution of 2.14 into 2.15 yields $u\left(s,v,n_1,...,n_{k-1}\right)$, i.e.,

$$\mathrm{d}u=T\mathrm{d}s-P\mathrm{d}v+\sum_{i=1}^{k-1}\left(\mu_i-\frac{e_{n_k}}{e_{n_i}}\mu_k\right)\mathrm{d}n_i\ . \tag{2.16}$$

Thus

$$\begin{aligned}\frac{\partial u}{\partial s}&=T\\ \frac{\partial u}{\partial v}&=-P\\ \frac{\partial u}{\partial n_i}&=\mu_i-\frac{e_{n_i}}{e_{n_k}}\mu_k\end{aligned} \tag{2.17}$$

from which it is apparent, that unlike Gibbs' form (2.11), 2.16 does not maintain the relationships between specific variables and potentials present in the Gibbs differential. The virtue of molar variables is that it is always possible to choose mass variables so that

$$0\le m_i\le 1$$

is true for all possible chemical compositions. Consequently, the chemical states of the system can be represented within k–1 dimensional **simplex** (a polygon with k vertices in k–1 dimensions), the triangular (k=3) and tetrahedral (k=4) representations of which are familiar to petrologists.

General Compositional Variables

The definition of molar variables treats mass differently than volume or entropy, however there is no fundamental reason for such a distinction. Indeed for certain types of systems it is desirable to define specific variables that define the complete physicochemical composition of a system. To this end, amount is defined

$$\alpha \equiv \sum_{i}^{k+2} \Psi_i \big/ e_{\Psi_i} \qquad 2.18$$

so that it is symmetric with respect to all the extensive properties. All the specific variables are then analogous to mass fractions, as used in chemistry, in that

$$0 \le \psi_i \le 1$$

and

$$\sum_{i}^{k+2} \psi_i \big/ e_{\psi_i} = 1 \, . \qquad 2.19$$

As in the case of molar variables, from 2.19, the dependent differential in can be expressed as

$$d\psi_{k+2} = -e_{\psi_{k+2}} \sum_{i}^{k+1} d\psi_i \big/ e_{\psi_i} \qquad 2.20$$

so that the total differential of the specific energy becomes

$$\mathrm{d}u = \sum_{i=1}^{k+1} \left(\theta_i - \frac{e_{\psi_k}}{e_{\psi_i}} \theta_k \right) \mathrm{d}\psi_i \, . \qquad 2.21$$

The virtue of this form is that all possible states of a system can be represented within k + 1 dimensional simplex, the vertices of which represent limiting states. Although specific properties defined in this was may seem exotic, their physical significance is not difficult to understand. For example, for a system containing only one kind of mass, dropping the unit factors for transparency, 2.6 in combination with 2.18 yields

$$u = \frac{U}{S+V+M}$$

$$s = \frac{S}{S+V+M}$$

$$v = \frac{V}{S+V+M}$$

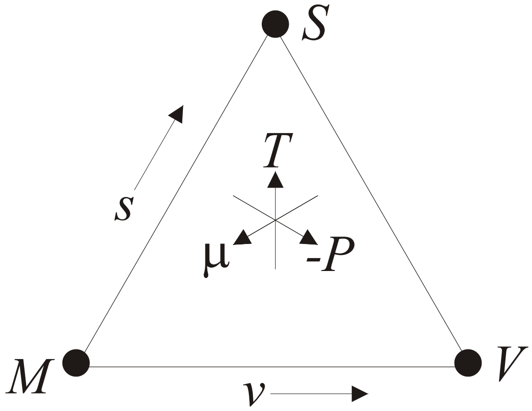


Fig 2.1 Ternary composition space for an isolated system composed of one kind of mass.

$$m = \frac{M}{S+V+M}$$

and from 2.19

$$v = 1 - s - m$$

For this system, all states can be plotted within a ternary simplex (Fig 2.1). If the system has a composition such that m = 1 the system is infinitely dense (v = 0) and infinitely cold (s = 0). By varying entropy or volume from this state we can achieve all possible thermal and mechanical states (i.e., states of lower pressure or higher temperature).

HETEROGENEOUS SYSTEMS

A system is **heterogeneous** if it consists of matter in two or more states (e.g., vapor and liquid). Although a heterogeneous system may be composed of many parts (e.g., liquid droplets dispersed in a vapor) thermodynamics is only concerned with those parts of the system that differ in state. All the parts of a system that are in the same state are grouped together and considered to comprise a **phase** of the system. A heterogeneous system is in **internal equilibrium** if there is no process possible among the existing phases of the system (Fig 1.1). Since potentials are the thermodynamic forces that enable a process, it follows that a system is in internal equilibrium if each potential has the same value in all $\boldsymbol{p}$ phases of the system, i.e.,

$$\theta_i^1 = \ldots = \theta_i^p \quad i = 1 \ldots k+2$$

$$T^1 = \ldots = T^p$$

$$P^1 = \ldots = P^p$$

$$\mu_i^1 = \ldots = \mu_i^p \quad i = 1 \ldots k$$

Thus, in contrast to specific properties, in equilibrium, systems potentials do not distinguish phase states and are only characteristic of a system as a whole. The extensive attributes of the system are

$$\begin{aligned}
&\Psi_i^{\mathrm{sys}} = \sum\nolimits_{j=1}^{p} \Psi_i^j = \sum\nolimits_{j=1}^{p} \alpha^j \psi_i^j = \alpha^{\mathrm{sys}} \psi_i^{\mathrm{sys}} \\
&U^{\mathrm{sys}} = \sum\nolimits_{j=1}^{p} U^j = \sum\nolimits_{j=1}^{p} \alpha^j u^j = \alpha^{\mathrm{sys}} u^{\mathrm{sys}} \\
&S^{\mathrm{sys}} = \sum\nolimits_{j=1}^{p} S^j = \sum\nolimits_{j=1}^{p} \alpha^j s^j = \alpha^{\mathrm{sys}} s^{\mathrm{sys}} \qquad 2.22 \\
&V^{\mathrm{sys}} = \sum\nolimits_{j=1}^{p} V^j = \sum\nolimits_{j=1}^{p} \alpha^j v^j = \alpha^{\mathrm{sys}} v^{\mathrm{sys}} \\
&M_i^{\mathrm{sys}} = \sum\nolimits_{j=1}^{p} M_i^j = \sum\nolimits_{j=1}^{p} \alpha^j m_i^j = \alpha^{\mathrm{sys}} m_i^{\mathrm{sys}}
\end{aligned}$$

where α^j is the absolute amount of the phase. Given that

$$\sum\nolimits_{j=1}^{p} \alpha^j = \alpha^{\mathrm{sys}}$$

the left-most equality in 2.22 can be rearranged as

$$\begin{aligned}
&\sum\nolimits_{j=1}^{p} x^j \psi_i^j = \psi_i^{\mathrm{sys}} \\
&\sum\nolimits_{j=1}^{p} x^j u^j = u^{\mathrm{sys}} \\
&\sum\nolimits_{j=1}^{p} x^j s^j = s^{\mathrm{sys}} \qquad 2.23 \\
&\sum\nolimits_{j=1}^{p} x^j v^j = v^{\mathrm{sys}} \\
&\sum\nolimits_{j=1}^{p} x^j m_i^j = m_i^{\mathrm{sys}}
\end{aligned}$$

where x^j is the relative or fractional amount of the j^{th} phase

$$x^j = \alpha^j / \alpha^{\mathrm{sys}} \qquad 2.24$$

subject to the constraint

$$\sum\nolimits_{j=1}^{p} x^j = 1 \, . \qquad 2.25$$

THE PHASE RULE

Ordinarily the phase equilibrium problem is to find the relative amounts and specific properties of the phases in an equilibrium system. However, if the specific properties of the phases are known in advance, then the equations of state for each phase provide p equations of the form

$$u^j = Ts^j - Pv^j + \sum_{i=1}^{k} \mu_i m_i^j \qquad 2.26$$

Viewed from this perspective the equations comprise a system of p equations in k+2 unknown potentials, i.e. in matrix form

$$\begin{vmatrix} s^1 & v^1 & \cdots & m_k^1 \\ \vdots & \vdots & \ddots & \vdots \\ s^p & v^p & \cdots & m_k^p \end{vmatrix} \begin{vmatrix} T \\ -P \\ \vdots \\ \mu_k \end{vmatrix} = \begin{vmatrix} u^1 \\ \vdots \\ u^p \end{vmatrix} \qquad 2.27$$

or

$$\begin{vmatrix} \psi_1^1 & \cdots & \psi_{k+2}^1 \\ \vdots & \ddots & \vdots \\ \psi_1^p & \cdots & \psi_{k+2}^p \end{vmatrix} \begin{vmatrix} \theta_1 \\ \vdots \\ \theta_{k+2} \end{vmatrix} = \begin{vmatrix} u^1 \\ \vdots \\ u^p \end{vmatrix} . \qquad 2.28$$

While the system of equations need not be of full rank (i.e., $p = k$+2), it is evident that it cannot have a solution if $p > k$+2. It follows that in an equilibrium system

$$p \le k+2, \qquad 2.29$$

a deduction known as the **phase rule**. Phase equilibria are often characterized by the number of potentials that can be varied without causing a change of phase, i.e., the **variance** of an equilibrium. In a system consisting of one phase there are thus k+1 independent variables of state. Since the equation of state of each phase adds one constraint (i.e., 2.26), it follows that the variance of a system or equilibrium is

$$f = k + 2 - p \, , \qquad 2.30$$

which is the most common expression of the phase rule.

PHASE PROPORTIONS: THE LEVER RULE

The constraints of 2.23 are simply a statement that the parts of the system must sum to the whole. If the equilibrium compositions of a system and its constituent phases are known, these statements furnish k+2 constraints on the $p \le k$+2 relative amounts $x^1, \ldots, x^p$ of the phases. Thus it is always possible to determine the relative amounts of the phases, by making use of any subset of p of the k+2 constraints, e.g., if $p \le k$+2 then

$$\begin{vmatrix} s^1 & \cdots & s^p \\ v^1 & \cdots & v^p \\ \vdots & \ddots & \vdots \\ m_k^1 & \cdots & m_k^p \end{vmatrix} \begin{vmatrix} x^1 \\ \vdots \\ x^p \end{vmatrix} = \begin{vmatrix} s^{sys} \\ v^{sys} \\ \vdots \\ m_k^{sys} \end{vmatrix} \qquad 2.31$$

can be solved for $x^1, \ldots, x^p$. The geometric expression of this logic is referred to as the **lever rule** in the analysis of phase diagrams.

PROBLEMS

2.1) **a)** Given the following properties for molar quantities of the aluminosilicate polymorphs

	andalusite	kyanite	sillimanite
u(J)	-2330280	-2334497	-2327357
s(J/K)	251.065	241.994	253.916
v(J/bar)	5.19585	4.45214	5.01131
n(mol)	1	1	1

use Eq 2.27 compute the *P*-*T*-μ condition at which all 3 polymorphs coexist. **b)** The 3 polymorphs coexist in an isolated system that contains 1 mol of Al_2SiO_5, and has an entropy of 246 J/K and a volume of 4.7 J/bar, use Eq 2.31to compute the molar and volume fractions of the polymorphs [**hint:** the easiest way to get the volume proportions is to express the specific properties of the system and its phases per unit volume, rather than as per mole Al_2SiO_5 as in the above table]. **c)** Eq 2.31 can be used for either absolute or relative proportions. The relative proportions sum to unity, use this constraint to formulate the previous problem as a system of two equations in two unknowns. **d)** Construct an *s*-*v* phase diagram of the triple point, shade (or indicate) the physically accessible range of entropy and volume for this system [**hint:** if you wish to make the plot in Maple see "Plotting Points in Maple" below].

SOLVING MATRIX PROBLEMS IN MAPLE

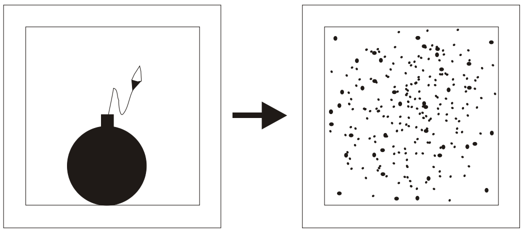
The Maple commands listed below may be helpful (a template for these commands is in ../chapter_2/problems_chapter_2_setup.zip):
a) Load the linear algebra package by typing: "with(linalg);".
b) Create an **n** x **n**-dimensional matrix **A** by typing: "A := matrix (n, n, [a_{11}, a_{12},…, a_{1m},…, a_{n1}…, a_{nm}]);" where the elements a_{ij} may be numeric or symbolic.
c) Create the transpose of **A** by typing: "At := transpose(A);".
c) Create an **n**-dimensional **b** vector by typing: "b := vector (n, [b_1,…, b_n]);".
d) Solve for the **n**-dimensional **x** vector by typing: "linsolve (a, x);"
e) Concatenate 3 vectors **a**, **b**, **c** by typing: "d := concat (a,b,c);"

POINT PLOTS IN MAPLE

To plot an array of points in Maple the following commands may be helpful:
a) To create an array of pairs of x-y points: "pts := [[x_1,y_1],...,[x_n,y_n]];".
b) To make the default plot (points connected by lines): "plot(pts);"
c) To make a fancier plot in which the individual points are marked and connected by lines and the axes are labeled and bound the entire range of points: "plot ([pts,pts], style=[line,point], color=[blue,red], symbol=cross, axes=boxed, thickness=2, labels=["X-axis","Y-axis"]);"
d) To overlay two, or more, plots assign them "handles" and use the "display" command, e.g., "a_plot := plot(y,x); b_plot := plot(z,x); display({a_plot,b_plot});"

3: STABILITY AND SPONTANEOUS PROCESSES

Thermodynamics admits a special class of processes known as **spontaneous processes** that occur without any external influence. In an equilibrium system no internal processes are possible between the phases of the system, therefore the only possible spontaneous process is the formation of a new phase. If the state of a system is such that no spontaneous processes are possible, then the system is in a **stable equilibrium** state.



$$\Delta U = \Delta V = \Delta M = 0$$

$$\Delta S > 0$$

Fig 3.1 A spontaneous process in an isolated system, i.e., a bomb exploding to form a gas (or plasma). Experience suggests that the reverse process will not occur. From the first law the energy of the system must be unchanged by the process, but by the second law the specific entropy must increase after the process. The second law is simply the formal statement of the experience that the if the bomb has exploded spontaneously, the gas will never condense back into its bomb-like form, i.e., that all spontaneous processes are unidirectional (i.e., irreversible) and proceed in the direction that increases the net entropy of the universe.

In the event of a spontaneous process, entropy can no longer be equated with heat (Q), because the spontaneous process may also create entropy. Explicitly the second law states that for any real process system

$$\mathrm{d}S > \frac{\mathrm{d}Q}{T}. \qquad 3.1$$

It follows that a spontaneous process may occur in an **isolated system** (i.e., $\mathrm{d}Q = \mathrm{d}U = \mathrm{d}V = \mathrm{d}M = 0$) if there is a state of greater entropy possible for the system (Fig 3.1). Thus a system is in a state of **stable equilibrium**, i.e., no internal or spontaneous processes may occur, if its entropy is a maximum. For any variation from a stable equilibrium, which is by definition impossible,

$$\mathrm{d}S_{U,V,M} < 0 \qquad 3.2$$

where the subscripts are added to emphasize that the variation is constrained to occur at constant U, V and M.

An odd feature, resulting from the historical development of thermodynamics, is that 3.2 is rarely used as a stability criteria, rather 3.1 is substituted into 1.25 to obtain

$$\mathrm{d}U < T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}M_i \,. \qquad 3.3$$

Condition 3.3 can be viewed as a general criterion for possible processes, i.e., it must be true for any real process. It follows, that if a system is in stable equilibrium, then a variation, again by definition impossible, to any other real physical state must satisfy

$$\mathrm{d}U > T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}M_i \,, \qquad 3.4$$

which is therefore a general stability criterion. Taken literally, 3.4 implies Gibb’s second, and oft cited, second criterion for the stability of an isolated system

$$\mathrm{d}U_{S,V,M} > 0. \qquad 3.5$$

The problem (Fig 3.2) with this criterion is that there is no spontaneous process in an isolated system at constant entropy or, more importantly, at variable energy. The problem with employing the criterion 3.5 is somewhat metaphysical, if we have an isolated system and there is another state of the system such that $\mathrm{d}S_{U,V,M} > 0$, then it is apparent that the current state is metastable, and that the system would be more stable in this alternative state. However if we have an isolated system and there is another state of the system such that $\mathrm{d}U_{S,V,M} < 0$, then it is indeed true that the system cannot be stable, but the alternative state is not a possible state of the system since the energy of an isolated system must remain constant (i.e., the first law of thermodynamics).

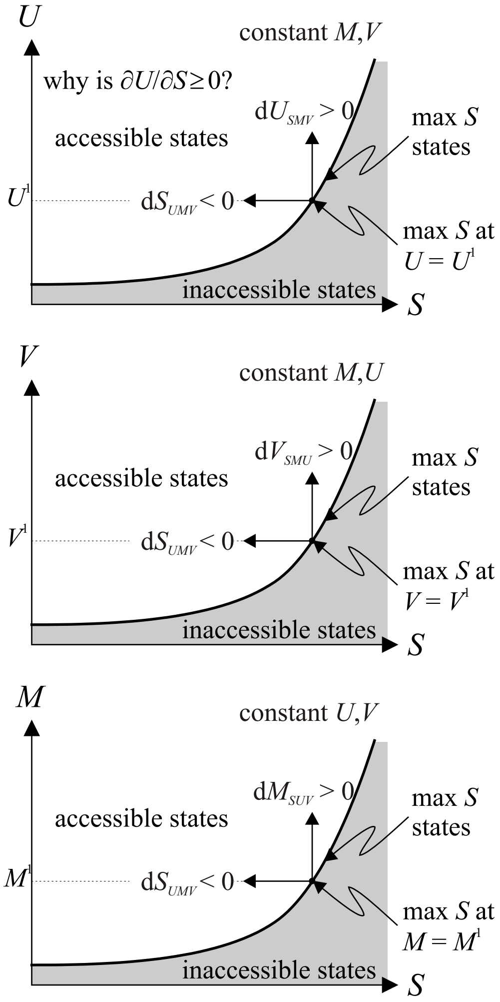


Fig 3.2 *S-U, S-V, S-M* diagrams illustrating the extremal character of entropy for a stable system. Accessible states correspond to physically real states, inaccessible states are states that cannot be achieved by any real process. If a system is on the boundary between the these regions, then the system has the maximum entropy consistent with its energy and the minimum energy consistent with its entropy, i.e., the system is in a stable equilibrium state. This argument generalizes to any extensive property Ψ_i as: for a stable system, any Ψ_i property will be at a minimum if θ_i/T is < 0 and at a maximum if θ_i/T is > 0.

Condition 3.5 has had the unfortunate consequence that people often think of spontaneous processes as processes that minimize the energy of a system, which is, of course, nonsense. The same logic used to derive 3.5, can be used to derive any number of equally valid, and misleading, criteria, e.g.:

	"real" process	stability crit.
	$dU<TdS-PdV+\mu dM$	$dS<0$
const. S,V,M	$dU<0$	$dU>0$
const. U,S,M	$0<-PdV$ or $dV<0$	$dV>0$
const. U,S,V	$0<\mu dM$ or $dM<0$	$dM>0$

4: OPEN SYSTEMS: RULES OF THE GAME

In general isolated systems, with a few minor exceptions such as the universe, are not of interest, so it would be useful to be able to apply our stability criteria to systems that are able to interact with their environment in some limited way. The problem is that in thermodynamics we are only allowed (or, more accurately, we only want to) observe the system. This means that we can only derive a stability criterion for a specified system if all the interactions between the system and its environment are reversible. If this were not the case, it would always be possible for a spontaneous process to alter the entropy of the system in some way that we cannot predict without looking at the environment as well.

ISOTHERMAL-ISOBARIC CHEMICALLY CLOSED SYSTEMS

Given these rules consider a system that can exchange entropy and volume with its surroundings, but is closed with respect to mass ($\mathrm{d}M = 0$, Fig 4.1). From the Gibbs differential (1.25), if the exchange of volume and entropy with the environment is reversible we have:

$$\mathrm{dU} = T\mathrm{d}S^{\text{external}} - P\,\mathrm{d}V \tag{4.1}$$

and from Eqs 3.1 and 2.16:

$$\mathrm{dU} - T\mathrm{d}S^{\text{external}} + P\,\mathrm{d}V \leq T\mathrm{d}S^{\text{internal}} \tag{4.2}$$

where $\mathrm{d}S^{\text{external}}$ is the entropy derived by reversible heat exchange with the environment, and $\mathrm{d}S^{\text{internal}}$ is the positive S production due to a spontaneous internal process. Technically, the assumption that heat exchange and dilation are reversible requires that the system is perfectly transparent to heat and has no viscous resistance to deformation. A system with these attributes is **diathermal** (infinite thermal conductivity) and **inviscid** (lacking viscosity). No such system exists (with the possible exception of superfluid Helium), but the model is a reasonable approximation for systems where the time scale for chemical equilibration is long compared to the time-scales for changes in pressure and temperature. The occurrence of high-pressure-temperature minerals on the earth's surface demonstrates that such a model is often appropriate for geological processes.

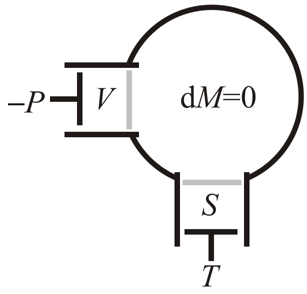


Fig 4.1 Schematic isobaric-isothermal closed chemical system. If a (spontaneous) process occurs within the system, the pressure and temperature of the system are buffered by the transfer of volume and entropy from (infinite) reservoirs at the temperature and pressure of the system.

Rearrangement of 4.1 yields the differential of a function G, such that

$$\begin{aligned}\mathrm{d}G &= \mathrm{d}U - T\left(\mathrm{d}S^{\text{external}} + \mathrm{d}S^{\text{internal}}\right) + P\mathrm{d}V \\ &= \mathrm{d}U - T\mathrm{d}S + P\mathrm{d}V\end{aligned} \tag{4.3}$$

Integrating 4.3 yields

$$G = U - TS + PV \tag{4.4}$$

and combining 4.4 and 1.29

$$G = \sum\nolimits_{i=1}^{k} \mu_i M_i \tag{4.5}$$

The total differential of G is obtained by taking the differential of 4.4 and combining this with the Gibbs differential (1.25)

$$\begin{aligned}\mathrm{d}G &= \mathrm{d}U - \mathrm{d}(TS) + \mathrm{d}(PV) + \sum\nolimits_{i=1}^{k} \mu_i \mathrm{d}M_i \\ &= \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T + P\mathrm{d}V + V\mathrm{d}P \\ &= \sum\nolimits_{i=1}^{k} \mu_i \mathrm{d}M_i - S\mathrm{d}T + V\mathrm{d}P\end{aligned} \tag{4.6}$$

From which we deduce the independent variables for G, the well-known Gibbs function, are $\{M_1 ... M_k, -P, T\}$. Since 4.6 is an exact differential

$$\left(\frac{\partial G}{\partial M_i}\right)_{P,T,M_{j\neq i}} = \mu_i \tag{4.7}$$

$$\left(\frac{\partial G}{\partial T}\right)_{P,M} = -S \tag{4.8}$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,M} = V \tag{4.9}$$

the variables held constant during differentiation are indicated by subscripts to emphasize that they are not the same as when the Gibbs differential is differentiated. G may either increase or decrease with changes in the environmental P-T conditions, but if the P and T of our system are kept constant, then for any real process, from 4.2 and 4.6

$$\mathrm{d}G_{P,T,M} = -T\mathrm{d}S^{\text{internal}} < 0 \tag{4.10}$$

So if an isobaric-isothermal chemically closed system is in stable equilibrium, then for any variation in the state of the system

$$\mathrm{d}G_{P,T,M} > 0 \tag{4.11}$$

A change in Gibbs "energy" as described by 4.10 does not arise through a change in the energy of the system, but rather in an internal change in the entropy of the system. However, such a change does lower the potentials for useful work in the system, and thus it would be more difficult to extract energy from a system with lower G. It may be worth noting that the condition

$$\Delta G_{P,T,M} = 0 \tag{4.12}$$

is **NOT** a stability criterion, but rather a criterion for equilibrium, specifically that of a reaction.

The Gibbs energy is often referred to as a **free energy** because it is a measure of the fraction of the internal energy of a system that is available to do work if the work occurs at constant pressure and temperature.

Heterogeneous Closed Systems

In an isobaric-isothermal heterogeneous closed chemical system consisting of p phases, the specific gibbs energy of each phase provides an equation of the form

$$g^j = \sum_{i=1}^{k} \mu_i m_i^j \tag{4.13}$$

and must satisfy

$$\begin{vmatrix} m_1^1 & \cdots & m_k^1 \\ \vdots & \ddots & \vdots \\ m_1^p & \cdots & m_k^p \end{vmatrix} \begin{vmatrix} \mu_1 \\ \vdots \\ \mu_k \end{vmatrix} = \begin{vmatrix} g^1 \\ \vdots \\ g^p \end{vmatrix}. \tag{4.14}$$

Taken at face value, 4.14 implies that the maximum number of phases in a closed chemical system is $p \leq k$ at an arbitrarily chosen pressure temperature condition. Goldschmidt (1911) combined this observation with the observation that the many minerals, particularly in skarns, have such restricted compositions that they can be regarded as stoichiometric compounds (i.e., that the specific masses are constants) to postulate that in closed chemical systems $p = k$. This restricted statement of the phase rule (2.29) is known as Goldschmidt's mineralogical phase rule.

In principle, it is possible to vary the pressure and temperature of an isochemical system to obtain a condition at which $p > k$ phases coexist. However such a variation is not arbitrary and in fact the probability of observing such an equilibrium is zero for a perfectly diathermal and inviscid system, as would be required if the variations in pressure and temperature is to be truly reversible, which of course they are never. The reason for the vanishing probability is that in a pressure-temperature coordinate frame the dimension of the stability field of $p > k$ phases is equal to the variance (2.30) of the equilibrium. Thus, univariant and invariant equilibria are geometrically degenerate 1- and 0-dimensional fields in the 2-dimensional P-T field. As such they occupy zero area of the 2-d field and as the probability of encountering a given field is proportional to its area (e.g., see the P-T diagram of Fig 4.2).

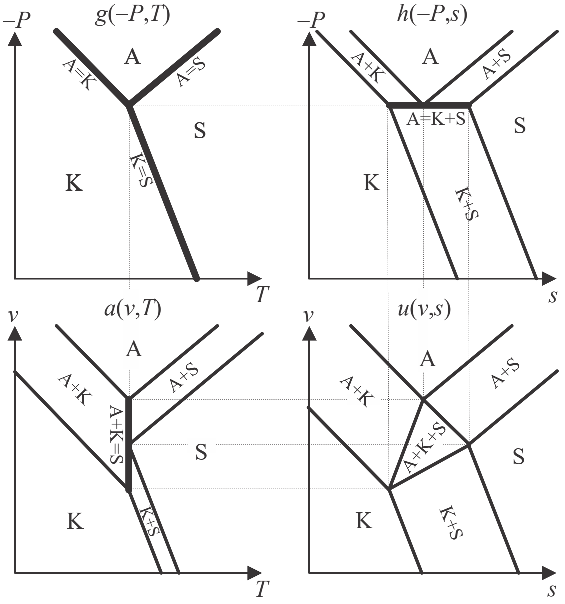


Fig 4.2 Phase diagrams for the aluminosilicate (k=1) system (A-andalusite, K-kyanite, S-sillimanite) as a function of the variables of the Gibbs (g, c=1), enthalpy (u, c=2), Helmholtz (a, c=2) and Internal (u, c=3) specific free energy functions. Phase fields of $p > c$ degenerate to singularities (heavy solid lines) at which the state of the system cannot be determined from the state function for the phase diagram variables. These singularities are referred to as reactions. Constant pressure-temperature-mass reactions (A=K, A=S, K=S) conserve mass and Gibbs energy, constant pressure-entropy-mass reactions conserve entropy, mass and enthalpy (A=K+S), constant temperature-volume-mass reactions conserve volume, mass and Helmholtz energy. Only the internal energy (c=k+2) is capable of resolving all the phase relations of a thermodynamic system. For this reason the internal energy provides the only general equation of state for heterogeneous systems.

The Stefan Problem

The geometric degeneracy of univariant and invariant phase fields as a function has profound consequences, known as the Stefan problem, for modeling heat and deformation in real systems. These arise because although g is an equation of state for a single phase, it is not an equation of state for an equilibrium system consisting of $p > k$ phases (Fig 4.2). This failing can be understood by observing that for such an assemblage, 4.14 must be true for any permutation of k of the $p > k$ phases. Therefore, in an invariant equilibrium, the chemical potentials cannot depend on the proportions of the phases and the specific Gibbs energy of the system

$$g^{sys} = \sum_{i=1}^{k} \mu_i m_i^{sys}$$

must remain constant during heating or compression, which is constrained to occur at constant pressure and temperature. However, if g does not vary as a function of the proportions of the phases it cannot define the state of the system; ergo it is not an equation of state. Likewise, for a univariant equilibrium, g must remain constant for isobaric heating or isothermal compression and therefore cannot resolve either process. In contrast, the natural variables of the specific internal energy resolve equilibria of any variance.

GENERALIZATION OF OPEN SYSTEMS

The foregoing derivation of a criterion for the stability of an isobaric-isothermal-isochemical system can be made general for a system that is closed with respect to the c-extensive properties $\Psi_1 ... \Psi_c$, i.e., $d\Psi_1 = ... = d\Psi_c = 0$ (Fig 4.3). From the Gibbs differential (1.25) and Gibbs' minimum energy criterion (3.5), if the exchange of $\Psi_{c+1} ... \Psi_{k+2}$ with the environment is reversible

$$dU - \sum\nolimits_{i=c+1}^{k+2} \theta_i d\Psi_i \le 0 \qquad 4.15$$

From which we can define the differential of a function Ω, such that

$$d\Omega = dU - \sum\nolimits_{i=c+1}^{k+2} \theta_i d\Psi_i \qquad 4.16$$

Integrating 4.16 at constant yields

$$\Omega \equiv U - \sum\nolimits_{i=c+1}^{k+2} \theta_i \Psi_i \qquad 4.17$$

and combining 4.17 and the integrated form of the Gibbs differential (1.6)

$$\Omega = \sum\nolimits_{i=1}^{c} \theta_i \Psi_i \ . \qquad 4.18$$

The exact differential of Ω is obtained from the differential of 4.17 combined with the Gibbs differential (1.25)

$$\begin{aligned} d\Omega &= dU - \sum\nolimits_{i=c+1}^{k+2} d(\Psi_i \theta_i) \\ &= \sum\nolimits_{i=1}^{c} \theta_i d\Psi_i - \sum\nolimits_{i=c+1}^{k+2} \Psi_i d\theta_i \end{aligned} , \qquad 4.19$$

from which we deduce the independent variables for Ω are $\Psi_1 ... \Psi_c$, $\theta_{c+1} ... \theta_{k+2}$. Since 4.19 is exact

$$\left(\frac{\partial \Omega}{\partial \Psi_i} \right)_{\Psi_{j \ne i}, \theta_{c+1} \cdots \theta_{k+2}} = \theta_i \quad i = 1 \ldots c \qquad 4.20$$

$$\left(\frac{\partial \Omega}{\partial \theta_i} \right)_{\Psi_1 \cdots \Psi_c, \theta_{j \ne i}} = -\Psi_i \quad i = c+1 \ldots k+2 \qquad 4.21$$

The function Ω measures the maximum amount of energy that can be extracted from a system if the extraction is constrained to occur at constant $\theta_{c+1} ... \theta_{k+2}$. As such it may be viewed as an extremal work function or a general free energy function.

The free energy function Ω may either increase or decrease with changes in the environmental variables $\theta_{c+1} ... \theta_{k+2}$, but if these variables are kept constant, then from 4.15, for any real process

$$d\Omega_{\Psi_1 \cdots \Psi_c, \theta_{c+1} \cdots \theta_{k+2}} < 0 \qquad 4.22$$

So for a system subject to the constraints $d\Psi_1 = ... = d\Psi_c = d\theta_{c+1} = \ldots = d\theta_{k+2} = 0$ at stable equilibrium, then for any variation in the state of the system

$$d\Omega_{\Psi_1 \cdots \Psi_c, \theta_{c+1} \cdots \theta_{k+2}} > 0 \qquad 4.23$$

which is a general criterion for stability.

The foregoing may be stated more succinctly: If a system is closed with respect to the properties $\{\Psi_1 ... \Psi_c\}$, then we may derive a function $\Omega(\Psi_1 ... \Psi_c, \theta_{c+1} ... \theta_{k+2})$

$$\begin{aligned} \Omega &= U - \sum\nolimits_{i=c+1}^{k+2} \theta_i \Psi_i \\ &= \sum\nolimits_{i=1}^{c} \theta_i \Psi_i \end{aligned} \qquad 4.24$$

and

$$d\Omega = \sum\nolimits_{i=1}^{c} \theta_i d\Psi_i - \sum\nolimits_{i=c+1}^{k+2} \Psi_i d\theta_i \qquad 4.25$$

such that for any variation from a stable equilibrium at constant $\theta_{c+1} ... \theta_{k+2}$

$$d\Omega_{\Psi_1 \cdots \Psi_c, \theta_{c+1} \cdots \theta_{k+2}} > 0 \ . \qquad 4.26$$

The transformation of U to Ω is known as a **Legendre transformation**, such transformations are commutative, i.e., it is possible to change any potential with its extensive conjugate (as defined by 1.28), or any extensity with its intensive conjugate.

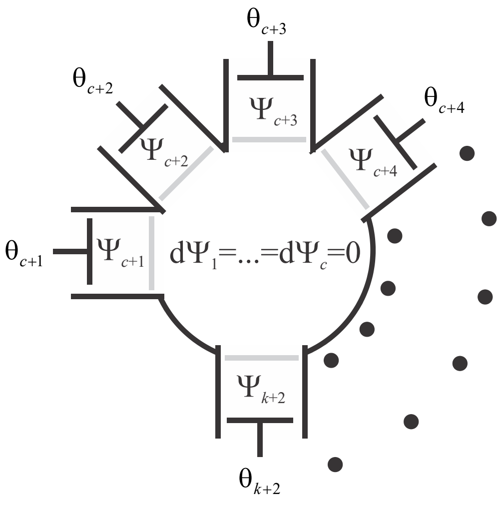


Fig 4.3 A schematic system closed with respect to $\{\Psi_1,..., \Psi_c\}$ and open with respect to $\{\Psi_{c+1},..., \Psi_{k+2}\}$ at constant $\{\theta_{c+1},..., \theta_{k+2}\}$. If a (spontaneous) process occurs within the system, the values of $\{\theta_{c+1},..., \theta_{k+2}\}$ within the system are buffered by the transfer of $\{\Psi_{c+1},..., \Psi_{k+2}\}$ from (infinite) reservoirs into the system.

Natural Variables and Partial Differential Notation

The Gibbs differential and its Legendre transforms define state functions each of which has a specific set of independent variables. These variables are referred to **natural variables** of the function, e.g., the natural variables of the Gibbs function are $-P$, T, M_1, …, M_k. However, there is no fundamental reason that the resulting function cannot be expressed in terms of any arbitrary choice of independent state functions. For example, the specific internal energy, can be expressed legitimately as $u(T,v)$, i.e.,

$$du = \left(\partial u/\partial T\right)_v dT - Pdv \; ; \qquad 4.27$$

where the partial derivative is a quantity that is often measured experimentally known as the isochoric heat capacity

$$c_v \equiv \left(\partial u/\partial T\right)_v .$$

Comparing 4.27 to the form of specific energy derived from the Gibbs differential

$$du = Tds - Pdv$$

at constant volume yields

$$\mathrm{d}s_v = \frac{c_v}{T}\mathrm{d}T_v$$

from which it follows

$$\left(\partial u/\partial v\right)_T \neq \left(\partial u/\partial v\right)_S .$$

Thus in thermodynamics it is important to distinguish the variables that are held constant during partial differentiation. Throughout the remainder of this text, partial differential notation is made compact by dropping the subscripts on partial derivatives and differential of thermodynamic functions, if the differential or partial derivative is taken with respect to a natural variable of the function holding all other natural variables constant. Thus, it is to be understood that

$$\partial U/\partial V = \left(\partial U/\partial V\right)_{S,M}$$

or

$$\partial\Omega/\partial\Psi_i = \left(\partial\Omega/\partial\Psi_i\right)_{\Psi_{j,j\neq i},\theta_{c+1},...,\theta_{k+2}}$$

and

$$\mathrm{d}\Omega = \mathrm{d}\Omega_{\Psi_1...\Psi_c,\theta_{c+1}...\theta_{k+2}} \; .$$

Although the choice of variables used to express a given free energy function is in principle arbitrary, thermodynamic stability criteria (4.23) are only valid for spontaneous processes that occur at constant values of the natural variables for the free energy function, i.e., it is not possible to formulate a stability criterion in terms of differentials such as $\mathrm{d}U_{T,V,M}$ or $\mathrm{d}G_{S,P,M}$.

Common Free Energy Functions

There are several well-known thermodynamic functions that were derived by Gibbs from the Gibbs differential (1.25) for closed chemical systems by Legendre transformations. The most important of these is the Gibbs energy for isobaric-isothermal chemically closed systems that we have derived previously (4.1-4.11). The additional functions are: the **enthalpy** function $H(S, -P, M)$ for **adiabatic**-isobaric systems

$$H \equiv U - \left(-PV\right) = TS + \sum\nolimits_{i=1}^{k} \mu_i M_i \qquad 4.28$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P + \sum\nolimits_{i=1}^{k} \mu_i \mathrm{d}M_i \qquad 4.29$$

and the **Helmholtz** energy $A(T, V, M)$ for **diathermal** isochoric systems

$$A \equiv U - TS = -PV + \sum\nolimits_{i=1}^{k} \mu_i M_i \qquad 4.30$$

$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V + \sum\nolimits_{i=1}^{k} \mu_i \mathrm{d}M_i \qquad 4.31$$

For adiabatic systems, the optimal stability criterion is always the maximum entropy criterion

$$dS_{\Omega,\Psi_{1,...,}\Psi_{c-1},\theta_{c+1,...,}\theta_{k+2}} > 0 \qquad 4.32$$

whereas for diathermal systems the optimal stability criterion (4.26) provided by minimizing the appropriate free energy function.

KORZHINSKII'S PHASE RULE

We have established that for a system closed with respect to $\Psi_1 \ldots \Psi_c$ at constant $\theta_{c+1} \ldots \theta_{k+2}$ we minimize the function Ω to determine the stable phase assemblages. In such a system consisting, the specific free energy of each phase provides an equation of the form

$$\omega^j = \sum_{i=1}^{c} \theta_i \psi_i^j$$

and must satisfy

$$\begin{vmatrix} \psi_1^1 & \cdots & \psi_c^1 \\ \vdots & \ddots & \vdots \\ \psi_1^p & \cdots & \psi_c^p \end{vmatrix} \begin{vmatrix} \theta_1 \\ \vdots \\ \theta_c \end{vmatrix} = \begin{vmatrix} \omega^1 \\ \vdots \\ \omega^p \end{vmatrix} \qquad 4.33$$

or in matrix notation

$$\boldsymbol{\psi}_{p\times c}\, \boldsymbol{\theta}_c = \omega_c \qquad 4.34$$

from which we deduce that in a system that is closed with respect to c extensive properties the maximum number of phases is $p \le c$. Various authors have made similar observations and suggested restricted statements of the phase rule. Notably, Korzhinskii (1957) states (among other variations) that for an isobaric-isothermal system open to q kinds of matter (designated **mobile components**) the phase rule should be $p \le k - q$. Such statements are subject to qualifications and obscure the fundamental meaning of the phase rule as originally formulated by Gibbs.

PARTIAL DIFFERENTIAL RELATIONS

In a variety of problems it is necessary or, at least, useful to relate thermodynamic function to properties that are not measured as a function of the natural variables for the function. To this end, the following rules are useful. For an exact differential

$$df = \left(\partial f/\partial x\right)_y dx + \left(\partial f/\partial y\right)_x dy \qquad 4.35$$

subsequent differentiation is independent of the order of differentiation, i.e. Euler's criterion,

$$\left(\partial\left(\partial f/\partial x\right)_y/\partial y\right)_x = \left(\partial\left(\partial f/\partial y\right)_x/\partial x\right)_y \qquad 4.36$$

Given a third variable z that is a function of x and y, as in e.g., $P = g(V,T)$, the total differential of z is

$$dz = \left(\partial z/\partial x\right)_y dx + \left(\partial z/\partial y\right)_x dy\,. \qquad 4.37$$

Therefore at constant z (dz=0), 4.37 requires

$$\left(\partial z/\partial x\right)_y dx_z = -\left(\partial z/\partial y\right)_x dy_z$$

or

$$\left(\partial x/\partial y\right)_z = -\left(\partial z/\partial y\right)_x \big/ \left(\partial z/\partial x\right)_y \qquad 4.38$$

and making use of the identity

$$\left(\partial x/\partial y\right)_z = 1\big/\left(\partial y/\partial x\right)_z \qquad 4.39$$

equation 4.38 is rearranged to obtain **Euler's chain rule** for differentiation

$$\left(\partial x/\partial z\right)_y \left(\partial z/\partial y\right)_x \left(\partial y/\partial x\right)_z = -1\,. \qquad 4.40$$

Given $f(x,y)$ and $z(x,y)$, the partial derivatives of f at constant z are obtained by differentiation of 4.35 as

$$\left(\partial f/\partial x\right)_z = \left(\partial f/\partial x\right)_y + \left(\partial f/\partial y\right)_x \left(\partial y/\partial x\right)_z\,. \qquad 4.41$$

These derivatives can be expressed entirely as derivatives at constant x and y, by substituting 4.38 into 4.41 to obtain

$$\left(\partial f/\partial x\right)_z = \left(\partial f/\partial x\right)_y - \left(\partial f/\partial y\right)_x \left(\partial y/\partial z\right)_x \left(\partial z/\partial x\right)_y \qquad 4.42$$

Finally, it may be useful to recollect that

$$\left(\partial f/\partial x\right)_z \big/ \left(\partial g/\partial x\right)_z = \left(\partial f/\partial g\right)_z \qquad 4.43$$

therefore

$$\left(\partial s/\partial P\right)_T \big/ \left(\partial v/\partial P\right)_T = \left(\partial s/\partial v\right)_T$$

but

$$\left(\partial s/\partial P\right)_T \big/ \left(\partial v/\partial P\right)_S \ne \left(\partial s/\partial v\right)_T\,.$$

This result reemphasizes the importance of keeping track of the variables that are held constant in thermodynamic partial derivatives.

To illustrate the utility of 4.42, suppose we know the isochemical specific Gibbs energy as a function of pressure and temperature, $g(P,T)$ and we require $\left(\partial g/\partial P\right)_v$. Since we can only differentiate $g(P,T)$ with respect to P and T, we cannot obtain $\left(\partial g/\partial P\right)_v$ directly, however given that $v(P,T)$, 4.42 allows us to write

$$\left(\partial g/\partial P\right)_v = \left(\partial g/\partial P\right)_T - \left(\partial g/\partial T\right)_P \left(\partial T/\partial v\right)_P \left(\partial v/\partial P\right)_T$$

where the derivatives of g on the right hand side are entirely involve only P and T.

Applying 4.36 to the Gibbs Differential at constant mass yields

$$\left(\partial T/\partial V\right)_S = -\left(\partial P/\partial S\right)_V \qquad 4.44$$

the first of four relations known as the **Maxwell relations**. The remaining three Maxwell relations are obtained in the same manner from dA (4.31), dH (4.29), and dG (4.6).

PROBLEMS

4.1) Eq 4.44 is the first Maxwell relation, derive the three additional Maxwell relations from dA (4.31), dH (4.29), and dG (4.6).

4.2) Use the Legendre transform (4.24-4.26) to obtain the thermodynamic stability criterion for the chemical system Fe-O at constant pressure, temperature and chemical potential of oxygen. How many phases would you expect to be stable in this system at an arbitrary P-T-μ_{O2} condition? List 4 minerals that might occur in this system.

4.3) Compute specific molar a-v diagrams for the aluminosilicate system at 500 and 1000 K (using the data for problem 2.1 and the definition of A, 4.30). What phases are the possible stable phase assemblages in each diagram? Use 4.33 to calculate the pressure for each of the stable assemblages. Use your results (together with invariant point conditions obtained in problem 2.1) to sketch P-T and v-T phase diagrams for the aluminosilicate system. Balance the reaction that occurs in the v-T phase diagram.

4.4) Thermodynamics deals with all reversible processes, elastic deformation is reversible and therefore described by thermodynamics. In the elastic limit, acoustic (sound) velocities through a crystal are entirely a function of thermodynamic properties, e.g., sound velocity is

$$\sqrt{K_S/\rho} \tag{4.45}$$

where K_S is the adiabatic bulk modulus

$$K_S \equiv -v\left(\frac{\partial P}{\partial v}\right)_S, \tag{4.46}$$

ρ is density

$$\rho = \mathrm{N}/v, \tag{4.47}$$

and N is the molar mass. In geophysics texts K_S is usually expressed in terms of the isobaric expansivity α and heat capacity c_P, the isothermal compressibility K_T, and the Gruneisen thermal parameter γ_T as

$$K_S = K_T\left(1 + T\alpha\gamma_T\right) \tag{4.48}$$

where

$$K_T \equiv -v\frac{\partial P}{\partial v} \tag{4.49}$$

$$\alpha \equiv \frac{1}{v}\frac{\partial v}{\partial T}$$

$$\gamma_T = \frac{\alpha K_T v}{c_P - T\alpha^2 K_T v}$$

$$c_P \equiv \frac{\partial h}{\partial T}.$$

Derive an expression for the sound velocity through a crystal in terms of the N, P, T, and $g(P, T)$ and its pressure-temperature derivatives given the above relations. To express c_P in terms of g observe that as $h \equiv u - (-Pv)$ and $g \equiv u - Ts - (-Pv)$ then $h = g + Ts$ (and $s = -\partial g/\partial T$). This is problem is most easily done in Maple. See the paragraph "Using Derivatives in Maple" for additional hints.

4.5) The danger in using derived expressions from the literature, such as Eq 4.48, is that they may have typographical errors or may assume secondary definitions that are different from what you expect. To avoid this danger, derive sound velocity as a function of N (molar mass), P, T, and $g(P,T)$ and its pressure-temperature derivatives from Eqs 4.45-4.47 without making use of Eq 4.48; i.e., use one or more of the rules given by Eqs 4.40-4.43 to derive an expression for $(\partial P/\partial v)_s$. This problem is partially solved in Maple script ../thermo_course /chapter4/problem_4_5 _setup.zip).

4.6) The heat capacity of a material is the amount of heat that must be added to it to raise its temperature 1 K. The isobaric (constant pressure) heat capacity $c_P = (\partial h/\partial T)_P$ is different from the isochoric (constant volume) heat capacity $c_v = (\partial u/\partial T)_v$ because in the isobaric case the system can do work (expand) during heating. **a)** Beginning from the relations $\mathrm{d}u = T\mathrm{d}s - P\mathrm{d}v$ and $\mathrm{d}h = T\mathrm{d}s + v\mathrm{d}P$ derive $c_P - c_V$ as a function of P, T, and $g(P,T)$ and its pressure-temperature derivatives. **b)** Do you expect c_V to be larger or smaller than c_P? Why? The Maple setup script for problem 4.5 is useful for this problem as well.

4.7) The convecting portion of the Earth's mantle is, to a good approximation, adiabatic (i.e., isentropic). Consequently, given the temperature of the mantle at the base of the lithosphere, where convection begins, the mantle temperature at greater depth can be obtained by integrating the adiabatic gradient $(\partial T/\partial z)_s = (\partial T/\partial P)_s\,\rho\mathbf{g}$, where z is depth, the $\rho\mathbf{g}$ term is the hydrostatic pressure gradient $\partial P/\partial z$, ρ is the density (Eq 4.47), and a bold-faced **g** is used to distinguish gravitational acceleration from the specific Gibbs energy. Derive the adiabatic gradient $(\partial T/\partial z)_s$ as a function of N, P, T, and $g(P, T)$ and its pressure-temperature derivatives. The Maple setup script for problem 4.5 is useful for this problem as well.

4.8) In Chapter 3 we deduced that for an equation of state of the form *u*(*s*), a requirement for stability is that *u*(*s*) has positive curvature, i.e., $\partial^2 u/\partial s^2 = \partial T/\partial s > 0$. Likewise, states of matter represented by a two-dimensional equation of state *u*(*s,v*) are stable only if *u*(*s,v*) has positive curvature. It can be shown that this is true if the determinant of the "Stiffness" matrix (Tisza, 1977)

$$\mathbf{C} = \begin{pmatrix} \partial^2 u/\partial s^2 & \partial(\partial u/\partial v)/\partial s \\ \partial(\partial u/\partial s)/\partial v & \partial^2 u/\partial v^2 \end{pmatrix}$$

is greater than or equal to zero. Use this condition, i.e., $\det|\mathbf{C}| \geq 0$, to deduce a relationship between the pressure-temperature derivatives of *g*(*P*, *T*) for stable states of matter. Although not required for this problem, it is possible to simplify the relationship to constrain the relationship between the isobaric expansivity,

$$\alpha \equiv \frac{1}{v}\frac{\partial v}{\partial T} = \frac{1}{\partial g/\partial P}\frac{\partial g}{\partial P \partial T},$$

the isobaric heat capacity,

$$c_P \equiv \frac{\partial h}{\partial T} = -T\frac{\partial^2 g}{\partial T^2},$$

and the isothermal bulk modulus

$$K_T \equiv -v\frac{\partial P}{\partial v} = -\frac{\partial g}{\partial P}\frac{1}{\partial^2 g/\partial P^2}$$

of the material.

DERIVATIVES IN MAPLE

In problem 4.4 and 4.5 you do not know the functional form of *g*, therefore to indicate that *g* is a function of *P* and *T* in maple you must type *g*(*P*, *T*). You can then indicate a derivative of *g*(*P*, *T*) by typing "diff(*g*(*P*, *T*),*v1,v2…*)" where *v1*, *v2* are, in sequence, the variables of differentiation (i.e., *P* or *T*). For example,

$$\frac{\partial g}{\partial P} = \mathrm{diff}(g(P,T),P);$$

and since

$$\frac{\partial g}{\partial P} = v$$

the thermal expansivity

$$\alpha \equiv \frac{1}{v}\frac{\partial v}{\partial T}$$

can be written in maple as

```
alpha := 1/diff(g(P,T),P)*diff(g(P,T),P,T);
```

The resulting expression can be simplified with

```
alpha := simplify(alpha);
```

5: CALCULATION OF $G(P, T)$ FOR AN ISOCHEMICAL SOLID

For various reasons, most prominently that P and T are the variables most commonly controlled in experimental systems, empirical thermodynamic data bases are designed for computation of the specific (molar) Gibbs free energy g (3.4, 3.5). To this end, the differential

$$\mathrm{d}g = -s\mathrm{d}T + v\mathrm{d}P \qquad 5.1$$

must be integrated from a reference condition P_r, T_r (normally 1 bar, 298.15 K) at which g, s and v is tabulated to the condition of interest. Here we are concerned with the properties of an isochemical phase, i.e., a phase with fixed composition, therefore the μdn differentials are zero by definition. By splitting the integration into an isothermal and an isobaric component it is possible to reduce the amount of empirical information on the pressure or temperature dependence of either s or v. Since calorimetric measurements are more complicated the integration path

$$g(P,T) = g(P_r,T_r) - \int_{P_r,T_r}^{P_r,T} s(P_r,T)dT + \int_{P_r,T}^{P,T} v(P,T)dP \qquad 5.2$$

which requires only s as a function of T, but v as a function of both P and T is invariably preferred. The immediate problem is to choose the empirical functions used to represent $v(P, T)$ and $s(T)$.

$v(P,T)$

Experimental measurements, e.g., X-ray diffraction, provide a direct means of extracting absolute volumes (e.g., $v(P_r, T_r)$) as well as the temperature and pressure derivatives

$$K_T \equiv -v\left(\frac{\partial P}{\partial v}\right)_T \qquad 5.3$$

$$\alpha \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \qquad 5.4$$

which are known, respectively as the **isothermal bulk modulus** and the **isobaric expansivity**. In some older tabulations the K_T is replaced by its inverse

$$\beta_T \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

the **isothermal compressibility**. Because K_T and α for minerals are relatively small, to a good first approximation at pressures below 10^4 bar, mineral volumes can be considered constant.

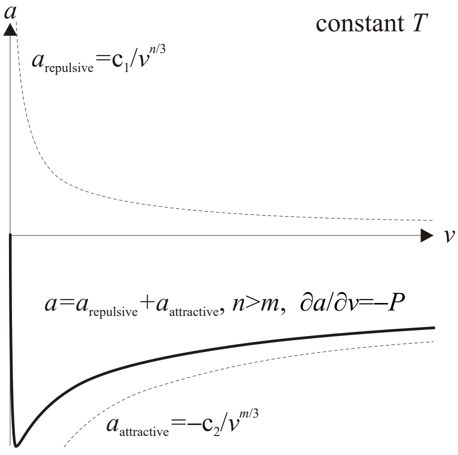


Fig 5.1 Schematic of the Mie-Grueneisen model of the specific isothermal Helmholtz free energy. The model assumes the energy can be expressed as the sum of a long-range (i.e., weak dependence on volume, $m \to 0$) attractive term and a short range repulsive term (i.e., strong dependence on volume, $n>m$). The derivative of the net function with respect to volume is the pressure, thus physically real states correspond to specific volumes less than the volume at the minimum value of a (i.e., at higher volumes $P<0$).

For high pressure, or precise calculations, K_T and α are given in tabulations as polynomial functions of pressure and temperature. Given these functions it is thus possible to formulate an equation of state (**EoS**), i.e.,

$$\alpha \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \left(\frac{\partial \ln v}{\partial T}\right)_P$$

ergo

$$\frac{v(P_r,T)}{v(P_r,T_r)} = \exp\left(\int_{P_r,T_r}^{P_r,T} \alpha(P_r,T)dT\right) \qquad 5.5$$

and likewise

$$\frac{v(P,T)}{v(P_r,T)} = \exp\left(\int_{P_r,T}^{P,T} \frac{-dP}{K_T(P,T)}\right). \qquad 5.6$$

However, as the integrals in 5.5 and 5.6 are small numbers, in which case a Taylor series expansion gives $\exp(x) \approx 1 + x$, the combined integral is usually approximated (where it is also assumed that as each integral is small, the product of the two integrals is negligible) as

$$v(P,T) \approx v(P_r,T_r)\left(1 + \int_{P_r,T_r}^{P_r,T} \alpha(P_r,T)dT - \int_{P_r,T}^{P,T} \frac{dP}{K_T(P,T)}\right) \qquad 5.7$$

In practice it is difficult to fit K_T and α to arbitrary polynomials without leading to an EoS that violates the Maxwell relations. This difficulty can be avoided, or at least minimized, by adopting the structure of a theoretical equation of state. Such equations were a major focus of solid state physics in the early part of the 20th century. The formulation used in Geoscience follows **Mie-Grueneisen theory**, which assumes that the energy of a solid at constant T (the specific Helmholtz energy a, 4.30) can be expressed as the sum of an attractive potential that holds the atoms together and repulsive potential that prevents the solid from collapsing

$$a = -\frac{c_1}{v^{m/3}} + \frac{c_2}{v^{n/3}} \tag{5.8}$$

where c_1 and c_2 are, respectively, constants characteristic of the attractive and repulsive potentials (Fig 5.1). Because the attractive forces are expected to be long range in comparison to the repulsive forces and interatomic distances are proportional to $v^{1/3}$, we expect $n > m$. Thus, as pressure is

$$P = -\left(\frac{\partial a}{\partial v}\right)_T \tag{5.9}$$

and, from 5.9 and 5.3, differentiation of 5.8 yields

$$P = \frac{3K_T(P_r,T)}{m-n}\left[f^{(m+3)/3} - f^{(n+3)/3}\right] \tag{5.10}$$

$$K_T(P,T) = \frac{K_T(P_r,T)}{m-n}\left[(m+3)f^{(m+3)/3} - (n+3)f^{(n+3)/3}\right] \tag{5.11}$$

where

$$f = v(P,T)/v(P_r,T)$$

is volumetric strain. Additionally differentiation of 4.9 with respect to pressure at P_r (i.e., for $f = 1$) gives

$$K'(P_r) = \left(\frac{\partial K_T(P_r)}{\partial P}\right)_T = (m+n+6)/3 \tag{5.12}$$

Experimentally it is found that for solids K' is, for practical purposes (i.e., for $P < 10^6$ bar), a constant which is usually near 4; thus for $n > m$, $3 < n < 6$. For various choices of the exponents m and n, 5.10 has the same low pressure limiting behavior as semi-empirical equations of state derived from finite-strain theory. In particular, for $m = 2$ and $n = 4$

$$P = \frac{3}{8}K_T(P_r,T)f^{5/3}\left(f^{2/3}-1\right)\left(\left(3K'f^{2/3}-12\right)+16-3K'\right) \tag{5.13}$$

is identical to the widely used (truncated) form of the **Birch-Murnaghan EoS**. A complication with 5.13 is that is not explicit in volume, therefore to evaluate the integral it is necessary to change variables as in

$$\int_{P_r,T}^{P,T} v(P,T)dP = \int_{v_r,T}^{v,T} P(v,T)dv - Pv\Big|_{P_r v_r}^{P,v} \tag{5.14}$$

The complication in evaluating the in this form is it first necessary to solve (by iteration) for the volume at the pressure and temperature of interest, before the integral can be evaluated. This is, in fact, what is done for high pressure calculations, but for m=–3 5.10 gives a volume explicit form

$$V(P,T) = V(P_r,T)\bullet \left[1 - \frac{K'(P_r,T_r)P}{K_T(P_r,T) + K'(P_r,T_r)P}\right]^{\frac{1}{K'(P_r,T_r)}} \tag{5.15}$$

that is adequate at pressures below about 10^5 bar and is identical to **Murnaghan equation**. To use 5.15, it is necessary to have K_T and v as functions of T, the former is usually supplied as a polynomial, whereas the latter is obtained by integration, i.e.,

$$V(P_r,T) \approx V(P_r,T_r)\left(1 + \int_{P_r,T_r}^{P_r,T} \alpha(P_r,T)dT\right) \tag{5.16}$$

s(*T*)

The experiment used to obtain $s(T)$ is to measure the energy required to raise the temperature of the material of interest as a function of temperature. Such calorimetric experiments may be done constant volume or constant pressure; the latter case is of direct relevance. Reversible heat at constant pressure is enthalpy (4.28), therefore the isobaric experiment yields the temperature dependence of the enthalpy which is known as the **isobaric heat capacity**, i.e.,

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_P \tag{5.17}$$

[1]

which is usually provided as a polynomial in T. The isochemical differential of enthalpy is

$$dh = Tds - vdP \tag{5.18}$$

therefore at constant pressure

$$ds = \frac{dh}{T} \tag{5.19}$$

---

[1] Heat capacity (specific heat) is formally defined as an intensive, i.e., molar or specific (e.g., per unit mass or volume) property.

and

$$\frac{\partial s}{\partial T} = \frac{1}{T}\frac{\partial h}{\partial T} = \frac{c_P}{T} \qquad 5.20$$

The **third law of thermodynamics** (also known as **Nernst's law**) states that at 0 K the entropy of a perfect crystal is zero, thus the absolute or "third law" entropy of a solid is, in principle, obtained as

$$s^0(P_r,T) = \int_{P_r,0}^{P_r,T} \frac{c_P}{T} dT \qquad 5.21$$

where the superscript 0 is used to denote specifically the "third law" entropy obtained by this integration. Unfortunately, crystals are not perfect and often are not perfectly ordered at 0 K because the kinetics of ordering (particularly **displacive transformations** that involve moving atoms within the crystal structure) is too slow to occur on the time scale of experimental observation so that at 0 K the crystal contains residual entropy (disorder). Moreover some potentially important ordering transformations occur near 0 K, where it is not possible to make heat capacity measurements. Thus the true entropy of a crystal is

$$s(P_r,T) = s^{conf} + \int_{P_r,0}^{P_r,T} \frac{c_P}{T} dT \qquad 5.22$$

where s^{conf} represents the contribution from irreversible disorder, a subject we will return to later. Eq 5.2 requires only integration from the reference temperature, i.e.,

$$s(P_r,T) = s(P_r,T_r) + \int_{P_r,T_r}^{P_r,T} \frac{c_P}{T} dT \qquad 5.23$$

and therefore it is to be hoped that $s(P_r, T_r)$ includes any non-third law contributions to the entropy. Sadly, this pious hope is not always justified, thus configurational entropy represents a potential source of inaccuracy in thermodynamic calculations.

We have treated entropy without regard to microscopic Mie-Grueneisen theory which has many interesting implications for temperature dependent properties. In particular, in combination with Debye (an enthusiastic Nazi) theory, it justifies the **Dulong-Petit limiting law** that states that the isochoric heat capacity

$$c_V \equiv \left(\frac{\partial u}{\partial T}\right)_V \qquad 5.24$$

reaches a limiting value of $3N_oR$ at high temperatures. Debye theory defines high temperature in this context as what is now known as the **Debye temperature** Θ, which for most minerals is on the order of 1000 K. While this greatly simplifies calculations for the inner portions of the earth, the isobaric heat capacity which is related to c_V by

$$c_p = c_V + \alpha^2 v K_T T \qquad 5.25$$

does not have a limiting value, although for the conditions likely within the earth it is unlikely to exceed $3N_oR$ by more than 10%. Eq 5.25 has the important consequence that the calorimetric component of an EoS is not independent of the volumetric component. An interdependence that is often neglected in low pressure geological data bases.

PERVERSE FORMULATIONS OF 5.2

For traditional reasons, in the geosciences the isobaric portion of 5.2

$$g(P_r,T) = g(P_r,T_r) - \int_{P_r,T_r}^{P_r,T} s(P_r,T)dT \qquad 5.26$$

is often perversely written by making use of the identity $g = h - Ts$ as

$$g(P_r,T) = h(P_r,T_r) + \int_{P_r,T_r}^{P_r,T} c_P \mathrm{d}T - Ts(P_r,T)$$

which, in combination with 5.17 and 5.23, becomes:

$$g(P_r,T) = h(P_r,T_r) - Ts(P_r,T_r) + \int_{P_r,T_r}^{P_r,T} c_P \mathrm{d}T - T\int_{P_r,T_r}^{P_r,T} \frac{c_P}{T}\mathrm{d}T \qquad 5.27$$

Both 5.26 and 5.27 are valid, but depending on the conventions (see section 4.5) used to define the reference state constants $g(P_r, T_r)$, $h(P_r, T_r)$ and $s(P_r, T_r)$ they may yield different values for $g(P_r, T)$, therefore the two integration schemes should not be mixed.

NON-DISPLACIVE PHASE TRANSFORMATIONS

Crystalline phases may undergo subtle phase transformations that involve only slight distortions of the crystal lattice, most notably the α/β transformation in quartz. These transformations may be gradational, i.e., occur over a range of *P-T* conditions, but are kinetically so fast that their effects cannot be isolated experimentally. Thus, it is essentially impossible to measure the properties of α-quartz in the stability field of β-quartz, and worse still, near the "transition" α-quartz consists of a microscopic mixture of α- and β-quartz like domains. There is a vast literature devoted to such transformations in solid-state physics; however in geological data bases there are only two types of treatment. The first, and most common, is to approximate such transformations as discontinuous. The second, more elegant, approach consists of adding a term to the base function 5.2, that accounts for the local effects of the phase transformation. For example, for the stable state of quartz at any pressure and temperature Holland & Powell (1998) use

$$g'(P,T) = g(P,T) + \lambda(P,T)$$

where λ accounts for the rapid, but continuous effects of the α/β transformation. Because λ involves conditionals, and is relatively small, we will not incorporate the term in the exercises of this course, but the term should be incorporated for real applications of this database, which is currently the most widely used thermodynamic database for minerals at pressures below 10^5 bar.

G(*P_R*, *T_R*) - CONVENTION

The final issue to be resolved for the evaluation of 5.2 is reference state energy. In thermodynamic calculations, absolute energies are never used (or almost never, a possible exception being first principles calculations in mineral physics). Thus, in practice energies are always relative energies defined via an arbitrary convention. The most widely used convention is the "**Gibbs energy of formation from the elements**" g_f in this convention the stable forms of the pure elements are assigned a *g* of zero at all pressures and temperatures. The molar g_f for a phase is thus in reality the change in *g* for the stoichiometric reaction between 1 mol of the phase and its constituent elements in their stable states at the pressure and temperature of interest, e.g., for enstatite ($MgSiO_3$)

$$g_\mathrm{f}^\mathrm{enstatite} = g^\mathrm{enstatite} - g^\mathrm{Mg} - g^\mathrm{Si} - \frac{3}{2} g^{\mathrm{O}_2} \qquad 5.28$$

Such conventions always involve the arbitrary assignment of energies to a set of *c* phases (or entities) the compositions of which are capable of forming a basis for the chemical composition space of interest. That these assignments have no influence on the computational results is apparent by considering the energy change for the reaction of enstatite to clinoenstatite

$$\begin{aligned}\Delta g &= g_\mathrm{f}^\mathrm{clinoenstatite} - g_\mathrm{f}^\mathrm{enstatite} \\ &= g^\mathrm{clinoenstatite} - g^\mathrm{enstatite}\end{aligned}$$

Because databases may have different conventions (e.g., *g* of formation from oxides vs elements) it is wise to be cautious when mixing data from different sources.

The "Gibbs energy of formation from the elements" convention does not imply that the entropies and volumes of the elements are arbitrary. Thus, to obtain $g_\mathrm{f}(P,T)$ for a phase from 5.2 it would be necessary to integrate the volume and entropy changes for the reaction forming the phase from its constituent elements, rather than the intrinsic volume and entropy of the phase. There is no reason to add this complexity and therefore, provided it is done consistently, 5.2 leads to consistent relative energies. To emphasize that such relative energies are not equivalent to $g_\mathrm{f}(P,T)$, even if they are computed from the integration constant $g_\mathrm{f}(P_r,T_r)$, the molar Gibbs energy obtained from is sometimes referred to as an "**apparent Gibbs energy of formation from the elements**".

G(*P_R*, *T_R*) – EXPERIMENTAL BASIS I

The classical experiment for direct determination of relative energies involves the measurement of the amount of energy required to decompose the phase to its constituent elements. Because such calorimeric experiments often require extreme conditions they are usually done adiabatically rather than isothermally, consequently the property obtained is the enthalpy of formation, which is then related to the Gibbs energy via

$$g_f = h_f - Ts_f$$

For geological materials, calorimetric measurements are extremely difficult to make with any accuracy and instead indirect measurements from phase equilibrium experiments are preferred. A subject reserved for the next chapter.

EXTRACTING OTHER FUNCTIONS FROM *G*(*P,T*)

Although 5.2 is based solely on $s(P_r, T)$ and $v(P, T)$ it is valid for all *P-T* conditions. Thus, properties that we do not know as general functions (e.g., $s(P, T)$, $\alpha(P, T)$) which we do not "know" from our calibration are readily obtained from elementary thermodynamic relations, e.g.,

$$s(P,T) = -\left(\frac{\partial g(P,T)}{\partial T}\right)_P \qquad 5.29$$

$$\alpha(P,T) = \frac{1}{v(P,T)}\left(\frac{\partial v(P,T)}{\partial T}\right)_P$$

$$= \left(\frac{\partial g(P,T)}{\partial P}\right)_T^{-1}\left(\partial\left(\frac{\partial g(P,T)}{\partial P}\right)_T \Big/ \partial T\right)_P \qquad 5.30$$

indeed a useful trick for testing the correctness of the integrations in 5.2 is to verify that the values for $s(P_r, T_r)$ and $v(P_r, T_r)$ derived by differentiation of $g(P, T)$ are in fact identical to the values used as input for the calculation.

Additionally, the values of any state function derived by Legendre transformations are trivially obtained as, e.g.,

$$u = g + Ts - Pv$$

$$= g(P,T) - T\left(\frac{\partial g(P,T)}{\partial T}\right)_P - P\left(\frac{\partial g(P,T)}{\partial P}\right)_T \qquad 5.31$$

Such constructions are perfectly valid, but have the unfortunate consequence that they yield explicit functions in terms of the natural variables of G, i.e., $\{P, T\}$. Thus, to obtain the value of the derived functions in terms of its own natural variables iteration is required. For example, 5.31 gives us $u(P, T)$, so to obtain u at a specific value of s and v, it would be necessary to vary P and T to obtain the desired values of s and v at which u is required.

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PROBLEMS

5.1) Complete the Maple script provided in thermo_course/chapter5/problem_5_1_setup.mws to compute $g(P,T)$. Calculate the g of forsterite at P = 40000 bar, T = 1000 K; if your script is correct you should obtain a $g = -2{,}001{,}593.99$ J/mol. Use the script to compute the following thermodynamic properties for forsterite at P = 40000 bar, T = 1000 K: **a)** v, **b)** s (5.29), **c)** density (ρ, in kg/m^3, the molar mass of forsterite, N_{fo}, is 0.14073 kg/mol), **d)** isobaric heat capacity (c_P, 5.20), **e)** isobaric expansivity (α, 5.30), **f)** isothermal compressibility (β, i.e., the inverse of the isothermal bulk modulus K_T, 5.3).

5.2) Using your results from problems 5.1 and 4.5-8: **a)** Compute the isentropic and isothermal speed of sound through forsterite, whose properties are an excellent proxy for those of the upper mantle, at P = 40000 bar, T = 1000 K (the isothermal speed is computed using the isothermal bulk modulus, K_T, rather than the adiabatic modulus, K_S, in 4.45). **b)** The heat capacity ratio (c_P/c_V) of forsterite at P = 40000 bar, T = 1000 K. **c)** The adiabatic geothermal gradient in forsterite at P = 40000 bar, T = 1000 K. **d**) Use the relation derived in problem 4.8 to test whether the equation of state for forsterite from problem 5.1 is valid at 2800 K and 1400 kbar, conditions representative of the core-mantle boundary.

Be sure to indicate the units where appropriate. Maple can be made to assign and propagate units through calculations to give dimensional results. As I do not use this functionality myself, I certainly do not expect you to use it. However, you may find the convert/units commands helpful, e.g., convert(1, units, (kg/mol)*(m/s^2)/(J/K/mol), K/km) converts 1 (kg/mol)(m/s^2)/(J/K/mol) to K/km.

6: COMPONENTS, COMPOSITION, $\bar{\omega}-X$ DIAGRAMS AND FREE ENERGY MINIMIZATION

We have established that $\mathrm{d}\Omega > 0$ is a general condition for stability in a system in which the c extensive properties $\Psi_1...\Psi_c$ are conserved and the k+2–c environmental properties $\theta_{c+1}...\theta_{k+2}$ are held constant. Further, we have deduced that for an arbitrary choice of the environmental properties $\theta_{c+1}...\theta_{k+2}$ that p, the maximum number of phases possible in a system, is identical to c, the number of conservative independently variable extensive properties. Since $\Psi_1...\Psi_c$ are conservative properties they are the intrinsic physical attributes of the system and it is natural to regard these properties as the systems **components**. For example, we can imagine composing an isolated system by mixing a specific amount of S[2], V, and M (for simplicity consider chemically homogeneous matter). The stable state of the system (e.g., P and T) is determined entirely by the proportions of S, V, and M in the initial mixture, thus these properties are the components of the isolated system. In contrast, suppose we are interested in a system where P and T are determined by the environment (e.g., by the systems location in the lithosphere) but the masses $M_1...M_k$ are conserved by all processes that occur in the system. In this case $M_1...M_k$ are components, but S and V are determined by the amounts of the components and the environmental parameters P and T. S and V are thus no longer intrinsic properties of the system. It is apparent that a logical definition of components depends upon the character of the system of interest. Moreover, since the concept of composition is useful only if the composition defines the intrinsic attributes of a system (i.e., those attributes that do not depend upon environmental conditions), a useful composition must be defined in terms of these attributes.

The foregoing suggests the following thermodynamically rigorous definitions of components and composition in the context of phase equilibria: **Thermodynamic components** are the c independent extensive properties of a system $\Psi_1...\Psi_c$ that are conserved for all processes that occur at constant $\theta_{c+1}...\theta_{k+2}$, where the c independent extensive properties of a system are those extensive properties that are capable of independent variation among the phases of the system. At a given environmental condition $\theta_{c+1}...\theta_{k+2}$ the stable state of the system is uniquely determined by the proportions of the components $X_1...X_c$. These proportions define the **thermodynamic composition** of the system. Recalling the definition of specific properties as discussed in Chapter 2, it is evident that the compositional variables $X_1...X_c$ are identical the specific variables $\psi_1...\psi_c$ defined by equation 2.8 provided the amount α is defined

$$\alpha \equiv \sum_i^c \Psi_i / e_{\Psi_i} \ . \qquad 6.1$$

MOLAR PROPERTIES AND COMPOSITIONS IN HETEROGENEOUS SYSTEMS

Until now, we have used molar properties to characterize the properties of a phase rather than the system itself. This makes sense because it is possible to define more or less rigorously what one mole of a phase is (i.e., Avogadro's number of molecules of the phase, though the definition of a molecule is not unambiguous when it comes to solids and liquids), but in a system where phase changes are possible this definition becomes impossible. Consider as an example the system H_2O, at low temperature most of the atoms are associated in H_2O molecules, but at high temperature an appreciable amount of the H_2O is dissociated to O_2 and H_2, what then is a mole of the system?

A simple, but arbitrary, definition of a mole of system is that it the amount of a system that contains one mole of its thermodynamic components. Regardless of whether this definition is adopted a mole of phase may not contain a mole of the systems components. This creates an annoying

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[2] In chapter 2, for isolated systems, we identified $\Psi_1...\Psi_c$ with S, V, M_1, …, M_k because conventionally the Gibbs differential is written with U as the dependent variable. This formulation is unfortunate from a logical point of view because S is not conserved in an isolated system, but U is. However in practice we are primarily concerned with reversible processes and in an adiabatic system reversible processes are isentropic.

inconsistency because the molar properties depend on the choice of components. For example, suppose that the molar formula unit of enstatite is chosen to be $MgSiO_3$, then (neglecting the unit quantity divisors e_{Ψ_i} in the formal definition of amount, Eq 6.1, for brevity)

$$g^{\mathrm{en}} = G^{\mathrm{en}} / N^{\mathrm{en}} \qquad 6.2$$

corresponds to G^{en} at $N_{\mathrm{MgSiO3}} = 1$ (Fig 6.1), but if we choose N_{MgO} and N_{SiO2} as the components of a system composed entirely of enstatite, then

$$g^{\mathrm{en}} = G^{\mathrm{en}} / \left(N^{\mathrm{en}}_{\mathrm{MgO}} + N^{\mathrm{en}}_{\mathrm{SiO_2}}\right) \qquad 6.3$$

corresponds to G^{en} at $N_{\mathrm{MgO}} + N_{\mathrm{SiO2}} = 1$, which is evidently half the value obtained by Eq 6.2. This inconsistency is inescapable because it is impossible to know in advance what components will be chosen to describe a particular system. In view of this difficulty, a bar character is introduced to denote specific properties and amount defined in terms of a systems components, i.e.,

$$\overline{\psi}_i \equiv \frac{\Psi_i}{\overline{\alpha}}, \quad \overline{\varpi} = \frac{U}{\overline{\alpha}} \qquad 6.4$$

Specific properties defined for one definition of amount (α) to another ($\overline{\alpha}$), by observing that

$$\overline{\psi}_i = \psi_i \frac{\alpha}{\overline{\alpha}}. \qquad 6.5$$

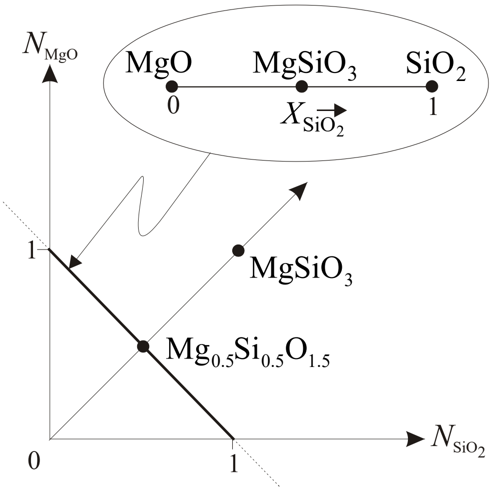

Fig 6.1 Relationship between 2-dimensional component space N_{MgO}-N_{SiO2} and 1-dimensional composition space for an isobaric-isothermal system. For such a system $\overline{\varpi} = \overline{g}$ and if specific phase properties are defined for an arbitrary molar unit, then $\overline{g} = g/(n_{\mathrm{MgO}} + n_{\mathrm{SiO_2}})$, where n_{MgO} and $n_{\mathrm{SiO_2}}$ are the specific quantities of the components. Thus if the molar quantity of Enstatite is $MgSiO_3$, then $\overline{g}^{\mathrm{En}} = g^{\mathrm{En}}/2$.

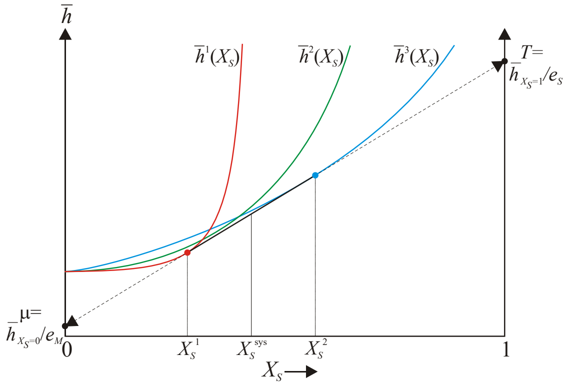

Fig 6.2 $\overline{\varpi} - X$ diagram for the states of an isobaric-adiabatic system with one chemical kind of matter (i.e., k=1, c=2) and three states of matter described by the equations of state $\overline{h}^1(X_S)$, $\overline{h}^2(X_S)$ and $\overline{h}^3(X_S)$. For this system $\overline{\varpi} - X$ and the thermodynamic components correspond to S and M. The 3rd law requires that all states degenerate at X_S=0 (i.e., at T=0 K), but otherwise the illustration is generic to c=2 systems. If a tangent to the $\overline{\varpi} - X$ surface for any state of interest is extrapolated to the X_i=1, the $\overline{\varpi}$ coordinate of the tangent is identical to the value of the dependent potential θ_i. At $X_S \le X_S^1$, the stable (minimum enthalpy) state of the system a single phase described by the equation of state $\overline{h}^1(X_S)$ in which T increases continuously with X_S. For $X_S^1 \le X_S \le X_S^2$, the system consists of 2 phases with fixed specific entropies (i.e., X_S^1 and X_S^2) whose proportions vary according to the lever rule, but whose T is independent of X_S as indicated graphically by the tangent construction.

In view of the fact that $\overline{\psi}_1 .... \overline{\psi}_c$ represent thermodynamic composition, it is helpful to distinguish these properties with the notation

$$X_i = \overline{\psi}_i, \quad i = 1 ... c. \qquad 6.6$$

Thus, the integral and differentials of the specific form of Eqs 4.24 and 4.19 are, respectively,

$$\overline{\varpi} = \sum_{i=1}^{c} \theta_i X_i \qquad 6.7$$

$$\mathrm{d}\overline{\varpi} = \sum_{i=1}^{c} \theta_i \, \mathrm{d} X_i - \sum_{i=c+1}^{k+2} \overline{\psi}_i \, \mathrm{d}\theta_i \qquad 6.8$$

or, making use of the constraint (Eq 2.19)

$$\sum_{i=1}^{c} X_i / e_{\Psi_i} = 1,$$

$$\overline{\varpi} = \sum_{i=1}^{c-1} \left(\theta_i - \frac{e_{\Psi_c}}{e_{\Psi_i}} \theta_c \right) X_i + \frac{\theta_c}{e_{\Psi_c}} \qquad 6.9$$

$$\mathrm{d}\overline{\varpi} = \sum_{i=1}^{c-1} \left(\theta_i - \frac{e_{\Psi_c}}{e_{\Psi_i}} \theta_c \right) \mathrm{d}X_i + \sum_{i=c+1}^{k+2} \overline{\psi}_i \mathrm{d}\theta_i . \qquad 6.10$$

For completeness, in terms of this notation the dependent potentials of a system composed of $p = c$ phases satisfy

$$\left|\begin{matrix} X_1^1 & \cdots & X_c^1 \\ \vdots & \ddots & \vdots \\ X_1^p & \cdots & X_c^p \end{matrix}\right| \left|\begin{matrix} \theta_1 \\ \vdots \\ \theta_c \end{matrix}\right| = \left|\begin{matrix} \overline{\omega}^1 \\ \vdots \\ \overline{\omega}^p \end{matrix}\right| \qquad 6.11$$

and the lever rule for the fractions of the phase is

$$\left|\begin{matrix} X_1^1 & \cdots & X_1^p \\ \vdots & \ddots & \vdots \\ X_c^1 & \cdots & X_c^p \end{matrix}\right| \left|\begin{matrix} x_1 \\ \vdots \\ x_p \end{matrix}\right| = \left|\begin{matrix} X_1^{\mathrm{sys}} \\ \vdots \\ X_c^{\mathrm{sys}} \end{matrix}\right| . \qquad 6.12$$

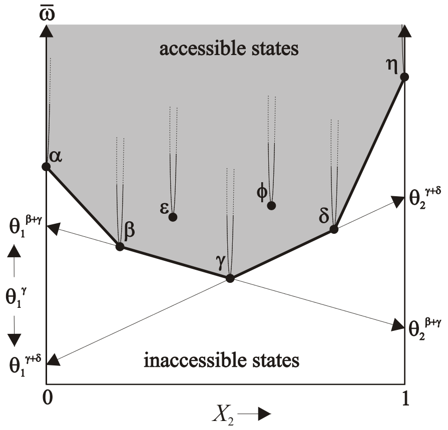

Fig 6.3 $\overline{\omega}-X$ diagram for a system in which all possible phases are stoichiometric compounds, i.e., $\overline{\omega}-X$ points. Whether true compounds exist is a metaphysical issue, but many phases have such strongly curved $\overline{\omega}-X$ surfaces, a behavior illustrated by the thin solid curves, that they can be regarded has having fixed compositions. The minimum free energy surface separates the accessible states of the system from inaccessible states and defines the stable states of the system. Because the surface of the system is a *c*-dimensional piecewise linear hull, the potentials of the system vary discontinuously and the state of the system is undefined for $p<c$ phases, this is illustrated by the range of values for θ_1 possible for the system when it consists entirely of γ (of course it can be argued that a system that consists of pure γ is a one component system or that γ is not a true compound).

$\overline{\omega}-X$ DIAGRAMS

A unique virtue of using specific properties defined from Eq 6.1, is that in an $\overline{\omega}-X$ diagram if a tangent to $\overline{\omega}(X_1 ... X_{c-1})$ is extrapolated to $X_i = 1$, then the $\overline{\omega}$ coordinate of the tangent is numerically identical to the value of θ_i for the state represented by the point of tangency. This follows, by observing the derivatives of the tangent and $\overline{\omega}(X_1 ... X_{c-1})$ are by definition identical at the point of tangency, thus the tangent is also described by Eq 6.9 and substituting X_i=1 (ergo, $X_{j\neq i} = 0$) into 6.9 yields

$$\overline{\omega} = \left.\frac{\theta_i}{e_{\Psi i}}\right|_{X_i=1} \qquad 6.13$$

For the remainder of this chapter we restrict consideration to phases that cannot change their thermodynamic composition, i.e., **compounds**. It is doubtful that true compounds exist, but the energy of many phases rises so rapidly away from a particular composition that these alternative compositions are not observed, thus such phases are well approximated as phases with fixed compositions and specific free energies. Quartz and aluminosilicates are examples of phases that are commonly regarded as compounds in chemical systems (i.e., as "pure" phases), but via problems 2.1 and 4.3 that they can be treated as compounds in systems that are described in terms of physical components (*S*, *V*) as well.

The accessible states of a system composed entirely of compounds are those defined by positive linear combination of the $\overline{\omega}-X$ states of the compounds possible in the system. It follows that the accessible states will be separated from inaccessible states by a piecewise linear *c*-dimensional hull, the **minimum free energy surface** of the system as a function of its composition (Fig 6.3). Each facet of the hull is defined the $\overline{\omega}-X$ coordinates of *c* compounds that may stably coexist. From the tangent construction (Eq 6.13) and the lever rule, or formally from Eqs 6.11 and 6.12, the state of the system is completely defined for any assemblage of $p=c$ phases. A peculiarity of systems composed entirely of compounds is that the state of the system is undefined for an equilibrium of $p<c$ phases, since such equilibria correspond to the discontinuities on the minimum energy surface of the system. For example, in the binary (c=2) $\overline{\omega}-X$ diagram of Fig 6.3, and if the system has the composition of pure γ, an infinitesimal variations in X_2^{sys} may cause the potentials to vary anywhere between their values in the assemblages β+γ and γ+δ. While there is no theoretical argument against such behavior, in reality compounds are invariably an approximation for phases that show extremely limited solution. So at high enough resolution compositional, the two phase linear regions of the $\overline{\omega}-X$ surface of Fig 6.2 would be separated by non-linear one phase regions. Regardless of whether or not true compounds exist in nature, the problem is of practical

relevance because many phases are assumed to be true compounds in phase equilibrium calculations.

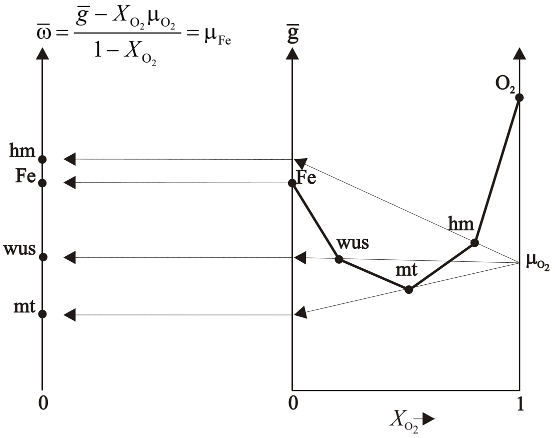

Fig 6.4 Graphical illustration that the Legendre transform of $\overline{g}(X_{O_2}, P, T)$ (c=2) for the Fe-O_2 (k=2) system to $\overline{\omega}(\mu_{O_2}, P, T)$ (c=1) is analogous to the petrologic projection of phase relations through the chemical component O_2. For an externally imposed μ_{O2}, the stable phase is that which minimizes $\overline{\omega}$, ergo for the illustrated condition mt is the stable phase. If μ_{O2} was varied continuously, the reactions in the projected system would involve c+1=2 phases and correspond to the assemblages along the faces if the minimum $\overline{g} - X_{O_2}$ surface. The unit quantity divisors are omitted for clarity.

Petrologic Projections and the Legendre Transform

While the notion that the thermodynamic composition of a system may not be identical to its chemical composition may seem unfamiliar, such distinctions are entirely commonplace in petrology. For example, if quartz is present in excess (i.e., saturated) in a rock, the compositional phase relations are often simplified by “projection” through the chemical component SiO_2. Such projections consist of nothing more than simply removing SiO_2 from the composition space. Similarly it is commonly assumed that the redox state of isobaric-isothermal geological systems is externally controlled, implying that the system is open with respect to O_2. This external control is usually specified by derived thermodynamic quantities redox potential (*Eh*) or oxygen fugacity (f_{O2}) that are simply alternative expressions for oxygen chemical potential (μ_{O2}). Consider then the problem of identifying the stable phase assemblage in the Fe-O2 system at constant pressure, temperature and μ_{O2} as illustrated by Fig 6.4. For this system, the Legendre transform of

$$\overline{g} = X_{Fe}\mu_{Fe} + X_{O_2}\mu_{O_2} \qquad 6.14$$

where I neglect the unit divisors e_{Fe} and e_{O2} to make the equations easier to follow, yields the function to be minimized at constant μ_{O2}

$$\omega' = \overline{g} - X_{O_2}\mu_{O_2} \qquad 6.15$$

but ω' is for a specific amount of each phase containing X_{Fe} moles (or mass units) of iron, thus to obtain the free energy per mole of iron, ω' must be divided by X_{Fe} = 1-X_{O2}, i.e.,

$$\overline{\omega} = \frac{\omega'}{X_{Fe}} = \frac{\overline{g} - X_{O_2}\mu_{O_2}}{1 - X_{O_2}} \qquad 6.16$$

However, rearrangement of 6.14, shows that

$$\mu_{Fe} = \frac{\overline{g} - X_{O_2}\mu_{O_2}}{1 - X_{O_2}}.$$

Therefore the function $\overline{\omega}$ obtained by the Legendre transform is identical to the μ_{Fe} (neglecting the unit divisor) obtained for each phase in a $\overline{g} - X$ diagram (Fig 6.4) by the petrologic projection of its $\overline{g} - X$ coordinate from the imposed μ_{O2} onto the X_{Fe} = 1 axis. Thus, for an imposed μ_{O2} the stable phase (mt, in Fig 6.4) can be found equivalently by finding the phase (or more generally the phase assemblage) that minimizes $\overline{\omega}$, or doing the graphical projection to find the phase with the lowest μ_{Fe}. Since the minimization of $\overline{\omega}$ is a 1-dimensional problem, and the projection is a 2-dimensional problem, from a computational perspective the Legendre transform is advantageous.

FREE ENERGY MINIMIZATION FOR SYSTEMS COMPOSED ENTIRELY OF COMPOUNDS

In a c-component system in which the only possible phases are compounds the stable phases assemblages always consist of p=c phases. Thus, the stability of any non-degenerate assemblage can be determined by first computing the potentials $\theta_1 ... \theta_c$ from Eq 6.11, and then testing that the inequality

$$\omega^j - \sum_{i=1}^{c} \theta_i \psi_i^j > 0 \qquad 6.17$$

for all phases that are not in the original assemblage. Graphically, this procedure corresponds to determining the $\overline{\omega} - X$ plane defined by an assemblage of p=c phases and then checking that the $\overline{\omega} - X$ plane lies below the coordinates of all other phases in the system. This latter requirement follows from the convex geometry of the minimum free energy surface. This procedure establishes the stability of an assemblage, but does not establish whether the assemblage is possible for a given composition. Thus, given an assemblage of known stability and a bulk composition, it is necessary to esatablish that amounts $\alpha_1 \ldots \alpha_p$ of the phases are greater than zero by solving

$$\begin{vmatrix} \psi_1^1 & \cdots & \psi_1^p \\ \vdots & \ddots & \vdots \\ \psi_c^1 & \cdots & \psi_c^p \end{vmatrix} \begin{vmatrix} \alpha_1 \\ \vdots \\ \alpha_p \end{vmatrix} = \begin{vmatrix} \psi_1^{\text{sys}} \\ \vdots \\ \psi_c^{\text{sys}} \end{vmatrix} \qquad 6.18$$

before concluding that the assemblage is possible for the bulk composition of interest.

The strategy outlined above for determining the stable phases for a system of specified composition is a trial and error method that is cumbersome in complex systems. Fortunately, the free energy minimization problem belongs to a category of problems known generally as **optimization** problems that are studied intensively in fields such as operations research (industrial engineering) and economics. In essence, optimization problems consist of finding the values of a set of variables that optimize (i.e., minimize or maximize) a function subject to a set of constraints, which may themselves be functions of the variables. The function to be optimized is referred to as the **objective function**. For the phase equilibrium version of the optimization problem, the variables are the amounts (α^j) of the phases and the objective function is the free energy of the system expressed as

$$\Omega^{\text{system}} = \sum_{j=1}^{\Pi} \alpha^j \omega^j \qquad 6.19$$

where Π is the total number of compounds that may occur in the system, as opposed to those which are actually stable. From thermodynamic argumentation we know that of these Π compounds only $p=c$ can be stable and if a compound is stable its amount must be greater than zero, while the amounts of the unstable compounds must be zero. Thus the for the optimization problem the variables α^j are subject to the linear inequality constraints

$$\alpha^j \geq 0, \quad j = 1 \ldots \Pi . \qquad 6.20$$

Additionally, as the amounts of the components in the stable phases must sum to the amounts of the components in the system, the optimization is subject to linear equality constraints

$$\Psi_i^{\text{system}} = \sum_{j=1}^{\Pi} \alpha^j \psi_i^j, \quad i = 1 \ldots c . \qquad 6.21$$

As formulated here by Eqs 6.19, 6.20 and 6.21, the phase equilibrium problem is a linear optimization or **linear programming** (**LP**) problem. The LP problem was famously solved by **George Dantzig** with the **Simplex algorithm** in 1947, which is widely used for resource allocation problems and is considered by many to the most important mathematical advances of the twentieth century. From our perspective, this has the advantage that LP programming routines are available even in primitive (e.g., Excel) mathematical computer packages. Thus, we have no need to understand the details of the algorithm in order to use it.

Up to this point in this section, free energy minimization problem has been formulated in terms of arbitrarily defined specific properties. This is possible we are merely concerned with the amounts of the compounds that add up to make the properties of the system. Thus amounts in Eqs 6.18-6.21 need not be defined consistently. It is of course possible to use specific amounts defined consistently in terms of the amounts of a systems components. In this case, the minimization variables are the fractional amounts x^j of the compounds subject to the constraint

$$\sum_{j=1}^{\Pi} x^j = 1 , \qquad 6.22$$

and Eqs 6.19-6.21 become

$$\overline{\omega}^{\text{system}} = \sum_{j=1}^{\Pi} x^j \overline{\omega}^j \qquad 6.23$$

$$0 \leq x^j \leq 1, \quad j = 1 \ldots \Pi \qquad 6.24$$

$$X_i^{\text{system}} = \sum_{j=1}^{\Pi} x^j X_i^j, \quad i = 1 \ldots c . \qquad 6.25$$

If all c constraints from Eq 6.25 are imposed explicitly for optimization then Eq 6.22 is satisfied automatically, but if only $c-1$ constraints from Eq 6.25 are implemented, then Eq 6.22 must be implemented as an explicit constraint. Thus, either formulation (Eqs 6.19-6.21 or 6.22-6.25) involve $\Pi+c$ explicit constraints, and the only reason to favor one over the other is whether relative or absolute amounts are of greater interest.

The free energy minimization strategy outlined here is strictly applicable only to systems composed entirely of compounds, in which case $\omega \neq f(\psi_1 ... \psi_c)$ and the optimization problem is truly linear. In general, the thermodynamic composition of a phase may vary in which case it is a **solution** phase for which $\omega = f(\psi_1 ... \psi_c)$. In this case, Eqs 6.19-6.21 (or 6.22-6.25) still hold but the compositions of the phases must also be determined by optimization. Optimizations of this type are non-linear, a subject we will return to later after consideration of the thermodynamics of solutions.

PROBLEM

6.1) Use the maple script at thermo_course/ chapter6/problem_6_1_setup.zip to construct the phase diagram for the CaO-Al_2O_3-SiO_2 system (i.e., the ternary chemography) at 1000 bar and 1073 K considering the phases quartz, gehlinite, grossular, sillimanite, anorthite, rankinite, larnite, corundum, lime, and wollastonite. The script loads the requisite thermodynamic data into the function for $g(P,T)$ that you should have obtained from Problem 5.1. It then solves the optimization problem as expressed by Eqs 6.19-6.21.

I will accept a qualitative sketch of the phase diagram for this exercise, i.e., you do not need to plot the diagram in maple (but you are welcome to do so).

If you want to prove to yourself that you actually understand the script you might try modifying the script to solve Eqs 6.22-6.25.

7: REACTIONS

Having just gone to great lengths to argue that the only meaningful statement of the phase rule is $p = c$, we will now consider violations of this rule that may occur when the environmental variables are not arbitrarily fixed, but rather chosen or varied in a special way. For illustration imagine that for the system shown in Fig 6.3 the only phase whose energy depends on θ_{c+1} is phase ε. Clearly then, if θ_{c+1} is decreased or increased eventually the $\overline{\omega}-X$ coordinate of ε will become co-linear with the $\beta-\gamma$ $\overline{\omega}-X$ line, this co-linearity defines a singularity in which the system has an infinite number of possible states that are energetically indistinguishable. In the special case that the singularity is defined by $c + 1$ phases, as in the present illustration, all the states are related by a reaction equation. The reaction equation is deduced from the consideration that the formation of new phase from the existing phases of a system by a phase transformation must satisfy the conservation constraints on the components. It follows that the composition vector of the new phase must be a linear combination of the composition vectors of the existing phases

$$-v^1\phi^1 - \ldots - v^c\phi^c - v^{c+1}\phi^{c+1} = 0 \qquad 7.1$$

where

$$\phi^j = \begin{bmatrix} \psi_1^j \\ \vdots \\ \psi_c^j \end{bmatrix} \qquad 7.2$$

and ν^j is the **reaction coefficient** of phase j. Since 7.1 remains valid if multiplied by an arbitrary constant, one coefficient in 7.1 may be arbitrarily specified. Thus, setting $\nu^{c+1} = 1$, Eq 7.1 may be written

$$\begin{bmatrix} \psi_1^1 \cdots \psi_1^c \\ \vdots \ \ddots \ \vdots \\ \psi_c^1 \cdots \psi_c^c \end{bmatrix} \begin{bmatrix} -\nu_1 \\ \vdots \\ -\nu_c \end{bmatrix} = \begin{bmatrix} \psi_1^{c+1} \\ \vdots \\ \psi_c^{c+1} \end{bmatrix} \qquad 7.3$$

and solved for the unknown reaction coefficients.

Conventionally in chemical thermodynamics Eq 7.1 is not written in the form of a conservation equation, but is rearranged to obtain a **balanced** reaction, where phases with positive coefficients (the **products** of the reaction) are moved to the right of the equals sign. This form results in an equation in which all the coefficients are positive (i.e., the coefficients of the reactants are negative and when multiplied by –1 become positive quantities, while the coefficients of the products are defined convention to be positive). This convention is of little value in geoscience and in essence amounts to defining the products of a reaction as those phases that have positive coefficients in Eq 7.1.

The change in any extensive property of the system as a consequence of forming ν_{c+1} moles of the c+1th phase is

$$-\sum_{j=1}^{c+1} v^j \psi_i^j = \Delta\psi_i \qquad 7.4$$

where, by definition, $\Delta\psi_j = 0$ for $j = 1\ldots c$, but, in general, the $\Delta\psi_j$ for $j = c+1\ldots k+2$ are finite. The reaction equation relates two possible states of the system that are compositionally and energetically indistinguishable at the equilibrium condition for the reaction. It follows that equilibrium is defined by the condition

$$-\sum_{j=1}^{c+1} v^j \omega_i^j = \Delta\omega = 0 \qquad 7.5$$

and that if $\Delta\omega$ is computed at any other condition, then $\Delta\omega < 0$ if the reaction products are stable, and greater than zero otherwise.

Because $\Delta\psi_1 \ldots \Delta\psi_c$ are zero by definition the complete differential of $\Delta\omega$ is

$$\mathrm{d}\Delta\omega = -\sum_{i=c+1}^{k+2} \Delta\psi_i \mathrm{d}\theta_i \,. \qquad 7.6$$

Eq 7.6 has two special uses. The first is that if we are at a condition at which we do not have equilibrium we can estimate the amount we need to change a particular potential by to attain equilibrium as

$$\Delta\theta_i \approx -\frac{\Delta\omega}{\Delta\psi_i}\,, \qquad 7.7$$

which is exact if $\Delta\psi_i \neq f(\theta_i)$ and approximate otherwise. Alternatively, if we consider an assemblage at equilibrium, if $\Delta\psi_i > 0$, then we know that an increase in θ_i will stabilize the phases characterized by positive reaction coefficients. The second use of 7.6 is to predict the trajectory of the equilibrium of a reaction as a function of two variables. Along this trajectory $\mathrm{d}\Delta\omega = 0$, therefore 7.6 implies

$$\frac{\mathrm{d}\theta_{c+1}}{\mathrm{d}\theta_{c+2}} = -\frac{\Delta\psi_{c+2}}{\Delta\psi_{c+1}} \qquad 7.8$$

which is the general form of the **Clausius-Clapeyron relation**.

PROBLEMS

The Maple script in thermo_course/chapter7/problem_7_1_2_setup.zip may be helpful for the problems listed below.

7.1) At a prestigious mineralogical institute hidden high in the Swiss Alps, a brilliant, but mysterious, experimental petrologist named Elena Melekhova makes the following observations:

P(bar)	*T*(K)	Stable minerals
8000	825	forsterite + phase-A
8000	840	phase-A + chondrodite
18000	860	forsterite + phase-A
18000	880	phase-A + chondrodite

Sadly, before she can analyze her results she succumbs to Po-210 poisoning. **a)** Use her observations to estimate the Gibbs energy of formation and third law entropy of chondrodite from the thermodynamic data in ../chapter5/thermo_data_comma_delimited.txt (in this file the abbreviations for Chondrodite, phase-A, and forsterite are, respectively, chond, phaseA, and fo. **b)** Calculate the temperature of the reaction between forsterite, phase-A and chondrodite at 1000 bar. **Hint #1:** The compositions of forsterite (Mg_2SiO_4), chondrodite ($Mg_5Si_2O_8(OH)_2$), and phase-A ($Mg_7Si_2O_8(OH)_6$) lie along a line in the MgO-SiO_2-H_2O composition space (i.e., they are compositionally degenerate) such that they can be described by 2 independent chemical components. If you do not want to reformulate their compositions in terms of 2 components, then you can balance the reaction between these phases by considering only the MgO and SiO_2 components. **Hint #2:** If you evaluate Δg for the reaction of chondrodite to forsterite + phase-A) you obtain an expression of the form:

$$\Delta g = f(P,T)$$

$$+\nu_{\text{chond}}\left[g_{\text{chond}}\left(P_r,T_r\right)-\left(T-T_r\right)s_{\text{chond}}\left(P_r,T_r\right)\right]$$

which must be zero at the equilibrium conditions of the reaction, where ν_{chond} is the reaction coefficient of chondrodite. Thus each pair of isobaric experimental observations constrains the equilibrium temperature and gives you a linear equation in the unknown parameters $g_{\text{chond}}\left(P_r,T_r\right)$, $s_{\text{chond}}\left(P_r,T_r\right)$.

7.2) Sketch the $\varpi - X$ diagram topology for each of the eight sectors of the Schreinemakers projection (Fig 7.1) of the univariant fields about an invariant field for a two component system (c = 2) in which the α, β, γ and δ are possible compounds. To solve this problem you must first deduce the relative compositions of the compounds. Which univariant equilibria can occur in a system that has a bulk composition intermediate between β and δ?

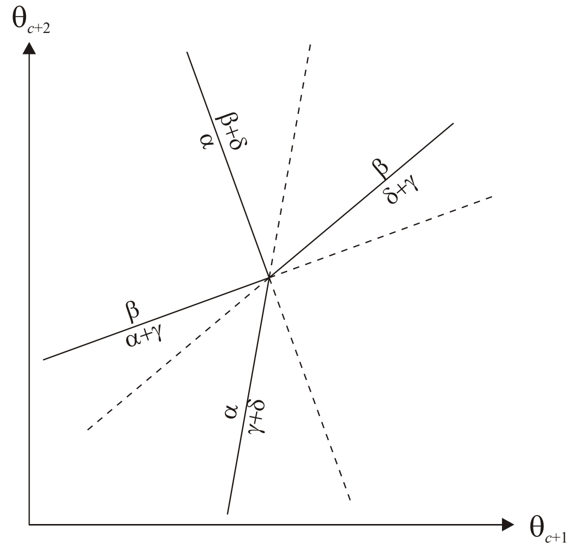

Fig 7.1 Schreinemakers projection of univariant (c+1) phase fields, labeled by their associated reactions, about a c+2 phase invariant point in a θ_{c+1}–θ_{c+2} coordinate frame for a system with c=2 components. The stable and metastable portions of the univariant fields are indicated, respectively, by solid and dashed lines.

7.3) **a)** Compute and plot the univariant curves emanating from the sapphirine (spr7) + enstatite (en) + sillimanite (sill) + pyrope (pyr) invariant point in the MgO-Al_2O_3-SiO_2 system as a function of pressure and temperature assuming that the system is saturated with respect to quartz (i.e., μ_{SiO2} = $g^{\text{quartz}}\left(P,T\right)$). **b)** These curves divide the pressure temperature diagram into 8 sectors, sketch qualitatively (or plot quantitatively if you prefer) the $\varpi - X$ diagram for each sector, where $\omega(n_{\text{MgO}}, n_{\text{Al}_2\text{O}_3}, P, T, \mu_{\text{SiO}_2})$. **c)** Sketch the (3) stable univariant curves of the pressure-temperature phase diagram section for this system if $X_{\text{MgO}} = n_{\text{MgO}}/(n_{\text{MgO}} + n_{\text{Al}_2\text{O}_3}) = 0.8$ and compute the amounts of the phases that are stable in each of the three sectors.

8: SIMPLE SOLUTION MODELS

Phases of variable composition, i.e., **solution phases**, are invariably described as a mixture of s real or hypothetical **endmembers**, for which data is tabulated (i.e., as in the Holland & Powell '98 data base). The problem is then to formulate a **solution model** that describes the Gibbs energy of such a solution phase in terms of these endmembers. Such models consist of three components

$$g = g^{\text{mech}} + g^{\text{conf}} + g^{\text{ex}} \tag{8.1}$$

where g^{mech} is the energy arising from mechanically mixing of the endmembers, g^{conf} is the energy expected to arise from theoretical entropic considerations, and g^{ex} is a component that accounts for the energetic effects caused by distortions of the atomic structure (e.g., strain) of the chemical mixing process or, in some cases, simply error in g^{conf}.

NOTATION

In general, we can expect that there may be several potentially stable solution phases in any given system. Additionally the possible compositions of these solutions may not span the entire range of compositions possible for the system, i.e., the t endmember compositions chosen to represent a particular solution may not be the same as the c components chosen to represent the systems composition. To avoid ambiguity from these formalities we adopt notation to discriminate between properties of a system in general and a specific solution. To wit, for systems we have written

$$\bar{g}^{\text{sys}} = \sum_{i=1}^{c} \mu_i X_i, \quad \mu_i \equiv \frac{\partial G^{\text{sys}}}{\partial N_i} \tag{8.2}$$

whereas for a solution we will write

$$g^{\text{sol}} = \sum_{i=1}^{t} g_i^{\text{sol}} y_i, \quad g_i^{\text{sol}} \equiv \frac{\partial G^{\text{sol}}}{\partial N_i} \tag{8.3}$$

thus y_i is the mole fraction of the i^{th} endmember and g_i^{sol} is its specific Gibbs energy defined relative to a mole of its endmembers. As it is always possible to define a system so that it consists of a single solution, any relationship that can be written in terms of the $\bar{g} - \mu - X$ coordinates of 8.2 remains valid in the $g - g_i - y$ coordinates of 8.3. In particular, it is pertinent to observe that in considering the phase relations of a single solution, which may nonetheless involve more than one phase (i.e., an immiscible solution), that the equality of g_i^{sol} in all phases is an auxiliary condition of Gibbs' stability criterion.

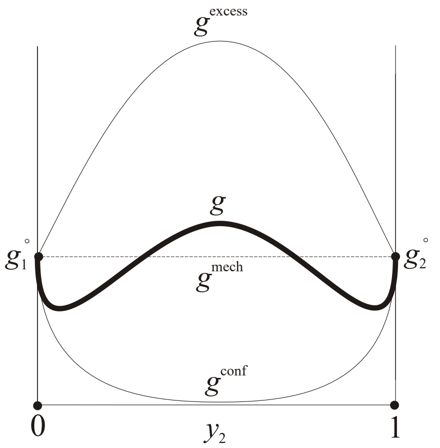

Fig 8.1. Schematic g–y diagram illustrating the three components of the specific Gibbs energy of a binary solution, the diagram is constructed with the assumption that the Gibbs energies of the endmembers are zero.

THE GIBBS ENERGY OF MECHANICAL MIXING

The Gibbs energy of mechanical mixing for a solution with t endmembers is

$$g^{\text{mech}} = \sum_{i=1}^{t} y_i g_i^{\circ} \tag{8.4}$$

where the superscript $^{\circ}$ denotes a property of the pure endmember.

For a binary (t=2) solution, Eq 8.4 defines a line (and for t>2 a plane) connecting the Gibbs energies of the endmembers in a ***g*–*y* diagram** (Fig 8.1). Such a diagram is the exact analogy of a $\bar{g} - X$ diagram. As the mechanical mixing process is energetically neutral (i.e., there is no gain or loss in energy caused by mechanical mixing), if we are only concerned with the internal phase relations of a solution we may arbitrarily assign the Gibbs energies of the endmembers to be zero, in which case g^{mech} is likewise zero.

CONFIGURATIONAL GIBBS ENERGY/ENTROPY

The loss of order, and hence increase in entropy, arising from mixing two or more chemically distinct endmembers is responsible for stabilizing solution phases. Because the configurational component by definition does not account for any distortions of the endmember structures during mixing it can be expressed as

$$g^{\mathrm{conf}} = -T\Delta s^{\mathrm{conf}} . \qquad 8.5$$

Classical thermodynamics does not provide a means for quantifying the entropy arising from mixing, but from statistical mechanics it can be shown that configurational entropy associated with a distinguishable object is

$$S^{\mathrm{conf}} = \mathrm{k} \ln W \qquad 8.6$$

where W is the number of distinguishable configurations created by mixing a total of $\mathbb{N}$ objects and k is named **Boltzman's constant** in honor of the Austrian physicist Ludwig E. Boltzman (1844-1906), who was the student of Josef Stefan and Arrehenius and Nernst where among his many famous students. Boltzman suffered from bouts of extreme depression and hung himself in 1906, equation 8.6, Boltzman's equation, is engraved on his tombstone in Vienna.

If there are t kinds of distinguishable objects, so that

$$\mathbb{N} = \mathbb{N}_1 + \ldots + \mathbb{N}_t$$

the number of distinguishable configurations is

$$W = \frac{\mathbb{N}!}{\mathbb{N}_1! \ldots \mathbb{N}_t!} . \qquad 8.7$$

In thermodynamics, we are concerned with ensembles involving large numbers of objects (e.g., atoms or molecules), in which case substituting Eq 8.7 in Eq 8.6 and applying **Stirling's approximation**

$$\ln x! \approx x \ln x - x \qquad 8.8$$

yields

$$S^{\mathrm{conf}} = -\mathrm{k} \sum_{i=1}^{t} \frac{\mathbb{N}_i}{\mathbb{N}} \ln \frac{\mathbb{N}_i}{\mathbb{N}}$$

where $\mathbb{N}_i/\mathbb{N}$ is the mole fraction y_i of the i^{th} object. Thus, in the simplistic limit of mixing between molecular endmembers, the molar entropy ($\mathbb{N} = \mathrm{N_A}$, Avogadro's number, and $\mathrm{kN_A=R}$, the Universal gas constant) of mixing is

$$s^{\mathrm{conf}} = -\mathrm{R} \sum_{i=1}^{t} y_i \ln y_i \qquad 8.9$$

Since $0 \le y_i \le 1$ it is apparent from 8.9 that $\overline{s}^{\mathrm{conf}}$ is always greater than zero and therefore that for any finite temperature g^{conf} stabilizes mixing (Fig 8.1). Eq 8.9 is appropriate for truly molecular solutions (e.g., some gases and liquids), but crystals tend to be somewhat more complex. To illustrate this complexity let us consider plagioclase as a binary mixture between albite $(\mathrm{Na})^{\mathrm{M}}(\mathrm{AlSi})^{\mathrm{T2}}(\mathrm{Si_2})^{\mathrm{T1}}\mathrm{O_8}$ and anorthite $(\mathrm{Ca})^{\mathrm{M}}(\mathrm{Al_2})^{\mathrm{T2}}(\mathrm{Si_2})^{\mathrm{T1}}\mathrm{O_8}$ endmembers, where the superscripts indicate the identsites on which the various elements occur. Three complications resulting from this complexity are: i) mixing may occur independently on different identisites, i.e., Ca and Na mix on the octahedral M-site, whereas Al and Si mix on the tetrahedral T2-sites; ii) there may be more (or less) than one identisite of any given type for the formula unit chosen to define the endmember, i.e., the standard 8-oxygen formula unit for plagioclase has 1 M-site, but 2 T2 sites; iii) the endmembers may themselves have configurational entropy, i.e., in albite Al and Si are disordered on T2. To account for these complications we need only recognize that the entropy arising from independent mixing the n identisites of a solution, by the same logic used to derive 8.9, is

$$s^{\mathrm{conf}} = -\mathrm{R} \sum_{i=1}^{n} \sum_{j=1}^{m_i} q_i z_{ij} \ln z_{ij} \qquad 8.10$$

where q_i is the number of sites of the i^{th} type, m_i is the number of kinds of atoms mixing on the i^{th} type, and z_{ij} is the atomic fraction of the j^{th} type of atom mixing on the i^{th} identisite. The only difficulty in applying 8.10 is that it is necessary to express the atomic site fractions (z_{ij}) as a function of the independent compositional variables of the solution, i.e., the endmember mole fractions (y_i). In plagioclase, taking y_{ab} as the independent compositional variable (i.e., $y_{\mathrm{an}} = 1 - y_{\mathrm{ab}}$), these site fractions are

$$z_{\mathrm{M,Na}} = y_{\mathrm{ab}}$$

$$z_{\mathrm{M,Ca}} = 1 - y_{\mathrm{ab}}$$

$$z_{\mathrm{T2,Si}} = y_{\mathrm{ab}}/2$$

$$z_{\mathrm{T2,Al}} = 1 - y_{\mathrm{ab}}/2$$

and $n = 2, m_{\mathrm{M}} = 2, m_{\mathrm{T2}} = 2, q_{\mathrm{M}} = 1, q_{\mathrm{T2}} = 2$, thus 8.10 simplifies to

$$\begin{aligned} s^{\mathrm{conf}}_{\mathrm{plag}} &= -\mathrm{R}[2y_{\mathrm{ab}} \ln y_{\mathrm{ab}} + (1 - y_{\mathrm{ab}}) \ln (1 - y_{\mathrm{ab}}) \\ &\quad + (2 - y_{\mathrm{ab}}) \ln (2 - y_{\mathrm{ab}}) - \ln 4] \end{aligned} . \qquad 8.11$$

Eqs 8.10 and 8.11 yield the total configurational entropy of a solution, but our concern is the entropy change from the unmixed to the mixed state. To obtain this change we compute the configurational entropy that is present in a mechanical mixture of the endmembers

$$s^{\mathrm{mech}} = \sum_{i=1}^{t} y_i s_i^{\mathrm{conf}} \qquad 8.12$$

and subtract this from the total entropy to obtain

$$\Delta s^{\mathrm{conf}} = -\mathrm{R}\sum_{i=1}^{n}\sum_{j=1}^{m_i} q_i z_{ij} \ln z_{ij} - \sum_{i=1}^{t} y_i s_i^{\mathrm{conf}} \qquad 8.13$$

where s_i^{conf} is the configurational entropy of pure endmember *i*, which is computed from 8.10 for the endmember composition. In plagioclase, this procedure yields $s_{\mathrm{an}}^{\mathrm{conf}} = 0$ and $s_{\mathrm{ab}}^{\mathrm{conf}} = R\ln 4$, thus 8.13 evaluates to

$$\begin{aligned}\Delta s_{\mathrm{plag}}^{\mathrm{conf}} &= -\mathrm{R}[2y_{\mathrm{ab}}\ln(y_{\mathrm{ab}}) + (1-y_{\mathrm{ab}})\ln(1-y_{\mathrm{ab}}) \\ &\quad + (2-y_{\mathrm{ab}})\ln(2-y_{\mathrm{ab}}) - (1-y_{\mathrm{ab}})\ln 4]\end{aligned} \qquad 8.14$$

The g^{conf} component of solution models is sometimes referred to as the "ideal" component, this terminology, while appropriate when the solution is a simple mixture of non-interacting molecules, is grotesquely misleading when applied to crystals because the assumptions regarding individual site populations are so uncertain as to be, in some cases, almost arbitrary. Taking plagioclase as an example, at low temperatures Al preferentially occupies only one of the T2 sites (low-albite), whereas at high temperatures Al may be present on all four of the tetrahedral sites (i.e., both the T1 and T2 sites, as in analbite). Moreover the transitions between these ordering schemes may be continuous. Worse still, in the low-plagioclase scenario, it is conceivable that Si on the T2 site is always located near an M-site Na so as to maintain local (ionic) charge balance. In this scenario, the "ideal" plagioclase model, there is no independent tetrahedral disorder and the model reduces to the molecular model 8.9

$$\Delta s_{\mathrm{plag}}^{\mathrm{conf}} = -\mathrm{R}\left[y_{\mathrm{ab}}\ln y_{\mathrm{ab}} + (1-y_{\mathrm{ab}})\ln(1-y_{\mathrm{ab}})\right], \qquad 8.15$$

which is drastically different from 8.11. It is also important to recognize that the endmembers chosen for a given solution model are derived using the same ordering scheme as assumed for the solution model. Thus, e.g., Holland and Powell (1998) provide three different endmembers for the albite composition, "ab" which is fully ordered, "abh" which has Al-Si disorder on T2 and "hab" in which Al and Si are disordered over both T1 and T2.

THE EXCESS GIBBS ENERGY

In theory the excess Gibbs energy term of a crystalline solution model accounts for strain induced by of foreign cations into an endmember crystal lattice. Intuitively, it is to be expected that this strain will be proportional to the difference in the foreign and endmember cation radii and that the strain energy will destabilize the solution. Both these expectations are often, but not invariably, met. Thus, it is to be expected, for example, that Mg^{2+} and Fe^{2+}, which have comparable radii, mix nearly ideally; and that in general the excess energy component of a solution model is positive as illustrated in Fig 8.1. However, in liquids and gases atomic interactions tend to be more complex and negative excess energies are commonplace (e.g., H_2O-NaCl). This complexity leads to yet another type of solution model formulation known as speciation models, which we will consider later. However for present purposes, we will confine ourselves to a macroscopic formulation appropriate for solids and simple fluids. While there are primitive theoretical models to predict the excess properties of trace-element solutions (e.g., Blundy & Wood, 1994), by and large, models for g^{ex} are empirically calibrated and expressed as polynomials in the endmember fractions y_i. There is an enormous variety of polynomial forms (cf. Ganguly 2001), but for most purposes the simplest possible model, known as the **regular model** is adequate. The regular model expresses g^{ex} as

$$g^{\mathrm{ex}} = \sum_{i}^{t-1}\sum_{j=i+1}^{t} W_{ij} y_i y_j \qquad 8.16$$

the sum of pair-wise interactions between the endmembers, where the interactions are characterized by the W_{ij} coefficients (**Margules parameters**), which are usually taken to be constants, but in some cases are allowed to vary as a function of pressure and temperature. For a binary solution, such as our plagioclase model, Eq 8.16 yields a symmetric excess function (i.e., $g^{\mathrm{ex}} = W_{\text{ab-an}} y_{\mathrm{ab}} y_{\mathrm{an}}$ as depicted in Fig 8.1) that is too simple to explain phase equilibrium observations. In such cases, higher order (**subregular**) expansions such as

$$g^{\mathrm{ex}} = W_{\text{ab-an-an}} y_{\mathrm{ab}} y_{\mathrm{an}} y_{\mathrm{an}} + W_{\text{ab-ab-an}} y_{\mathrm{ab}} y_{\mathrm{ab}} y_{\mathrm{an}} \qquad 8.17$$

are desirable. The necessity for high order excess functions is often an indication of a poor model for g^{conf} and because high order models may extrapolate poorly they are best avoided whenever possible.

SOLVII

We have shown previously that the condition for the stability of a homogeneous isobaric-isothermal system is that its $\bar{g} - X$ surface must be convex or linear with respect to the $\bar{g}$ coordinate, i.e.,

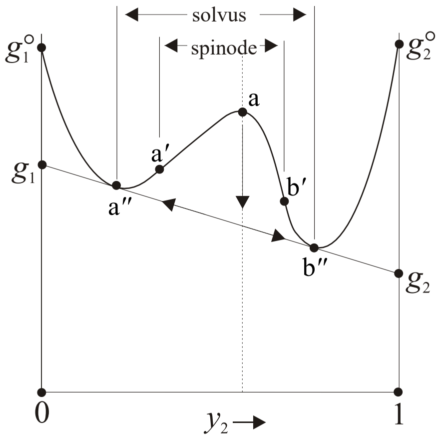

Fig 8.2 *g*–y diagram for a binary system with a partially miscible solution. Any composition of the solution between **a''** and **b''** is metastable with respect to a mixture of **a''** and **b''**, these compositions define the limbs of the solvus of the solution. The *g*–y surface is only convex between **a'** and **b'**, these points (or, in multidimensional solutions, curves or surfaces) are the **spinodes** of the solvus.

$$\frac{\partial^2 g}{\partial X_i^2} \geq 0, \quad i = 1 \ldots t-1$$

where, the equality applies when the system is heterogeneous (i.e., consists of more than one phase). For the three components of the Gibbs energy of a solution in 8.1, for any general (i.e., not pure) composition by definition

$$\frac{\partial^2 g^{\text{mech}}}{\partial y_i^2} \equiv 0$$

and

$$\frac{\partial^2 g^{\text{conf}}}{\partial y_i^2} \geq 0 \propto T$$

where the equality applies only at $T = 0$ K. There is no rigorous constraint on g^{ex}, but to a first approximation for many solutions

$$\frac{\partial^2 g^{\text{ex}}}{\partial y_i^2} < 0 \approx \text{constant}.$$

Additionally, g^{conf} is a weak logarithmic function of composition, whereas g^{ex} varies as at least a quadratic function of composition. Thus we can expect that at non-zero temperature, g^{conf} will dominate (and stabilize) dilute solution behavior, but that the destabilizing role of g^{ex} will become more significant at intermediate solution compositions. Since the stabilizing effect of g^{conf} vanishes at $T = 0$ K, but must be infinite at $T = \infty$ K, then if temperature is reduced continuously from a high value there must be a finite temperature at which

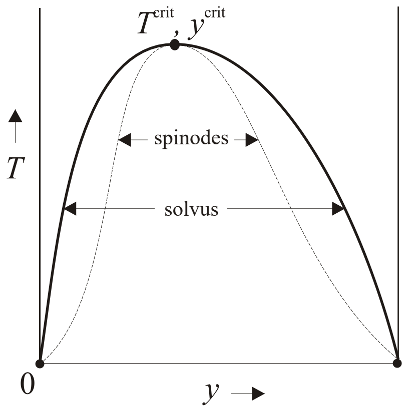

Fig 8.3 Temperature-composition diagram for an immiscible binary solution. The spinodes and the solvus coincide only at the critical point and at 0 K.

$$\frac{\partial^2 g}{\partial y_i^2} = 0$$

at exactly one composition. This composition and temperature are the **critical composition and temperature** of the solutions **solvus**. Determinations of the critical conditions for a solvus are the most accurate method of constraining the parameters and structure of a solution model, because at this condition all the high order derivatives must vanish, i.e.,

$$\frac{\partial^n g}{\partial y_i^n} = 0 \quad \text{for } n \geq 2 \text{ at } T = T^{\text{crit}}, y_i = y_i^{\text{crit}} \qquad 8.18$$

Thus critical conditions provide a set of equations that can be solved for the unknown parameters of a model.

Above the critical temperature the *g*–*y* surface is always concave and all compositions of the solution are stable. Below the critical temperature the surface is convex in the vicinity of the critical composition, and such compositions are metastable with respect to a mixture of compositions that can be determined from the stability criterion, these compositions are said to define the **limbs** of the solvus (Fig 8.2–3). The stable compositions of a solvus are always on the convex portion of the *g*–*y* surface of the solution and therefore include the conditions for which the surface is concave. The points (or curves or planes for multidimensional solutions) at which the surface changes from convex to concave are referred to as **spinodes**. There is no reason to ascribe spinodes any special significance from classical thermodynamics, but in statistical mechanics it is argued that between the spinodes any microscopic fluctuations within a homogeneous phase will lower the bulk G and hence favor exsolution of immiscible phases. In contrast, such fluctuations for compositions between the spinodes and the solvus raise the bulk energy and inhibit exsolution. This argument has been confirmed experimentally, in that phases within a spinode decompose rapidly to the spinodal compositions, but equilibration beyond the spinode to the solvus compositions is often extraordinarily slow.

By analogy with $\bar{g}-X$ diagrams, a tangent to the g–y surface of a solution extrapolated to the pure endmember composition defines the partial molar Gibbs energy of the endmember in the solution (Fig 8.2). Thus if A and B are two phases of a solution that coexist across a solvus the equalities

$$g_i^{\mathrm{A}} = g_i^{\mathrm{B}} \quad i = 1 \ldots t \tag{8.19}$$

can also be used to constrain the parameterization and/or structure of a solution model. Alternatively, if the solution model is known, then the numerical solution of 8.19 offers a means of computing the solvus, although for our purposes graphical methods may be preferable, and in the case of heterogeneous systems Gibbs energy minimization is always superior for this purpose.

PARTIAL MOLAR ENERGY AND ACTIVITY

The partial molar Gibbs energy of an endmember increases monotonically with the endmembers concentration for any stable composition (i.e., not within a solvus), and can thought of as a measure of the thermodynamic "concentration" of the endmember. Thus, if it is possible to write a reaction between the endmembers of various solutions, e.g.,

grossular + 2 kyanite + quartz = 3 anorthite 8.20

a necessary condition for the equilibrium of this reaction is that the change in the partial molar energies for the reaction is zero, i.e.,

$$\Delta g = 0 = 3g_{\mathrm{an}}^{\mathrm{Plag}} - g_{\mathrm{gr}}^{\mathrm{Grt}} - 2g_{\mathrm{ky}}^{\mathrm{Ky}} - g_{\mathrm{qtz}}^{\mathrm{Qtz}}, \tag{8.21}$$

or in general

$$\Delta g = 0 = \sum \nu_i g_i \tag{8.22}$$

Recognition of this fact in the geosciences led to the idea that, under the assumption of equilibrium, measurements of the composition of impure phases could be used to establish P-T the conditions of equilibration for the rock containing the phases. From 8.3, for any given composition of a solution, g_i for an endmember is obtained by extrapolating the tangent to the g–y surface at the solutions composition to the endmember composition (Fig 8.2). Thus for a solution with two endmembers

$$\begin{aligned} g_1 &= g + \left(1 - y_1\right)\frac{\partial g}{\partial y_1} \\ g_2 &= g + \left(1 - y_2\right)\frac{\partial g}{\partial y_2} \end{aligned} \tag{8.23}$$

where

$$\frac{\partial g}{\partial y_1} = -\frac{\partial g}{\partial y_2}$$

and more generally for a solution with t endmembers

$$g_i = g - \sum_{j \neq i}^{t} y_j \frac{\partial g}{\partial y_j}. \tag{8.24}$$

Given that

$$g_i^{sol} \equiv \frac{\partial G^{\mathrm{sol}}}{\partial N_i} \tag{8.25}$$

8.23 and 8.24 may seem unnecessarily complex, however because solution models are formulated in terms of constrained compositional variables y_i differentiation with respect to the general variable N_i is not at all straightforward.

The concept of **thermodynamic activity** separates the thermodynamics of the pure endmember from that of the solution model by defining the activity of an endmember as

$$a_i \equiv \exp\left(\frac{g_i - g_i^{\circ}}{\mathrm{R}T}\right) \tag{8.26}$$

Activity is often closely to the endmember concentration y_i, and in the limit of a pure phase $g_i - g_i^{\circ} = 0$ and $a_i = y_i = 1$. Activity models can thus be derived from a complete solution model by substituting 8.24 into 8.26, e.g., in the case of the plagioclase solution model (8.14, 8.17) derived earlier this procedure yields the activity of albite as

$$\begin{aligned} a_{\mathrm{ab}} = y_{\mathrm{ab}}^2\left(2 - y_{\mathrm{ab}}\right) \cdot \exp\left(\frac{\left(1 - y_{\mathrm{ab}}\right)^2 W_{\text{an-an-ab}}}{\mathrm{R}T}\right) \cdot \\ \exp\left(\frac{2y_{\mathrm{ab}}\left(1 - y_{\mathrm{ab}}\right)^2\left(W_{\text{an-ab-ab}} - W_{\text{an-an-ab}}\right)}{\mathrm{R}T}\right) \end{aligned} \tag{8.27}$$

Rearranging 8.26, the partial molar energies in Eq 8.22 are

$$g_i = g_i^{\circ} + \mathrm{R}T \ln a_i \tag{8.28}$$

Thus 8.22 is formulated in terms of activities as

$$\Delta g = 0 = \sum \nu_i \left(g_i^\circ + \mathrm{R}T \ln a_i \right) \qquad 8.29$$

or

$$\Delta g = 0 = \Delta g^\circ + \mathrm{R}T \ln K \qquad 8.30$$

where the **equilibrium constant** K is defined as

$$K \equiv \prod a_i^{\nu_i} \ , \qquad 8.31$$

which in the specific case of reaction 8.21 is

$$K = \frac{a_{\mathrm{an}}^{3}}{a_{\mathrm{gr}} a_{\mathrm{ky}}^{2} a_{\mathrm{qtz}}} \qquad 8.32$$

where given that quartz and kyanite are likely to be very nearly pure we may reasonably assume $a_{ky} = a_{qtz} \approx 1$.

PROBLEMS

8.1) An experimentalist establishes that the critical point of the Na-Ca plagioclase solvus is at y_{ab} = 1/3 and T = 900 K. **a)** Use this observation to determine $W_{\text{ab-ab-an}}$ and $W_{\text{an-an-ab}}$ for a subregular excess function (8.17) in combination with the configurational entropy model of 8.14 (the 2nd and 3rd derivatives of the solution model must be zero at the critical condition. **b)** Use these parameters to compute and plot the plagioclase solvus from 900 to 400 K. **c)** As a petrographer, you observe anorthite rich plagioclase (y_{ab}=1/10) coexisting with a more albite-rich plagioclase in a metapelite, what temperature did the metapelite equilibrate at?

Hint 1: use conditions 8.18 to determine $W_{\text{ab-ab-an}}$ and $W_{\text{an-an-ab}}$, but be sure to express g_{plag} entirely as a function of y_{ab}.

Hint 2: you can solve for the solvus conditions by at least four methods: i) plotting the g–y surface; ii) solving for the conditions at which $g_{\mathrm{an}}^{\text{Ab-Plag}} = g_{\mathrm{an}}^{\text{An-Plag}}$ and $g_{\mathrm{ab}}^{\text{Ab-Plag}} = g_{\mathrm{ab}}^{\text{An-Plag}}$; or iii) constructing a plot of $a_{\mathrm{an}}^{\mathrm{Plag}}$ vs $a_{\mathrm{ab}}^{\mathrm{Plag}}$, although in this case you'll have to figure out for yourself how to interpret the plot.

8.2) A rock contains garnet ($y_{\mathrm{almandine}}$=0.67, y_{pyrope}=0.16, $y_{\mathrm{grossular}}$=0.17), plagioclase (y_{ab}= 0.64) and pure kyanite, sillimanite and quartz. **a)** Derive activity models for anorthite in plagioclase and grossular in garnet from 8.26. For plagioclase use the solution model from problem 8.1, for garnet assume a regular model (8.16) with only one non-zero term $W_{\text{py-gr}}$ = 33000 J/mol and assume that mixing occurs only on the A-site (i.e., $\left(\mathrm{Ca,Mg,Fe}\right)_3^{\mathrm{A}} \mathrm{Al_2Si_3O_{12}}$). **b)** Assuming that the temperature of equilibration for the rock is known to be 1000 K by some independent means (for example, coexistence of kyanite+sillimanite), use these activity models to compute the pressure for the grossular-kyanite-anorthite-quartz equilibrium (i.e., the conditions for which 8.30 is true for the observed plagioclase and garnet compositions). **NOTE:** The thermodynamic data for the pure phases are loaded for you in the maple script thermo_course/ chapter8/problem_8_2_setup.zip.

9: THE EVIL OF THERMOBAROMETRY AND THE TRUE PATH TO WISDOM

"Phase diagrams are the beginning of wisdom..."
– Sir William Hume-Rothery (1899-1969)

For historical reasons (a euphemism for irrational reasons) thermodynamic formalisms in the geoscience focus more on activity models, then the solution models from which activities are derived. Because of this, albeit unwarranted, attention the present chapter enlarges on the activity concept as introduced in chapter 8.

A PHYSICAL MODEL FOR ACTIVITY/FUGACITY

To obtain a more intuitive understanding of activity as introduced in the previous chapter, consider the osmotic system of Fig 9.1. Here the main portion of the system contains a 2-component solution such as biotite (endmembers annite and phlogopite), which is separated from two, initially empty, chambers by rigid membranes that are permeable with respect to only one of the endmembers, i.e., osmotic membranes. Since the pressures in these chambers is independent of the pressure on the main portion of the system, we can arrive at an equilibrium condition in which the chambers are filled with pure endmembers at pressures dictated by the constraint that the partial molar Gibbs energy of the endmembers must be equal in all parts of the system where they are possible, e.g.,

$$g^{\mathbf{Bio}}_{\mathbf{phl}}\left(P,T,y\right)=g^{\circ}_{\mathbf{phl}}\left(P_{\mathbf{phl}},T\right) \tag{9.1}$$

where although $P \neq P_{\mathbf{phl}}$, the partial pressure P_{phl} is a function of the total P on biotite through 9.1. Activities are simply a means of accounting for this difference, this can be done explicitly in terms of pressure in which case the activity is referred to as a **fugacity** as in

$$\begin{aligned} g^{\mathbf{Bio}}_{\mathbf{phl}}\left(P,T,y\right)&=g^{\circ}_{\mathbf{phl}}\left(P_{\mathbf{phl}},T\right)\\ &=g^{\circ}_{\mathbf{phl}}\left(P_{\mathrm{r}},T\right)+\mathbf{R}T\ln f_{\mathbf{phl}}\end{aligned}$$

where P_{r} is the arbitrary reference pressure, i.e.,

$$f_i \equiv \exp\left(\frac{g_i\left(P,T,y\right)-g_i^{\circ}\left(P_{\mathrm{r}},T\right)}{\mathrm{R}T}\right) \tag{9.2}$$

a convention often used for fluids. This convention corresponds to the activity of the endmember defined relative to a standard state for the pure endmember at the reference pressure and the temperature of interest. For solids it is conventional to define the properties of the pure endmember at the pressure and temperature of interest, i.e.

$$\begin{aligned} g^{\mathbf{Bio}}_{\mathbf{phl}}\left(P,T,y\right)&=g^{\circ}_{\mathbf{phl}}\left(P,T\right)\\ &=g^{\circ}_{\mathbf{phl}}\left(P,T\right)+\mathbf{R}T\ln a_{\mathbf{phl}}\end{aligned}$$

i.e.,

$$a_i \equiv \exp\left(\frac{g_i\left(P,T,y\right)-g_i^{\circ}\left(P,T\right)}{\mathrm{R}T}\right)$$

Such definitions are arbitrary and introduce artificial complexity into thermodynamic theory.

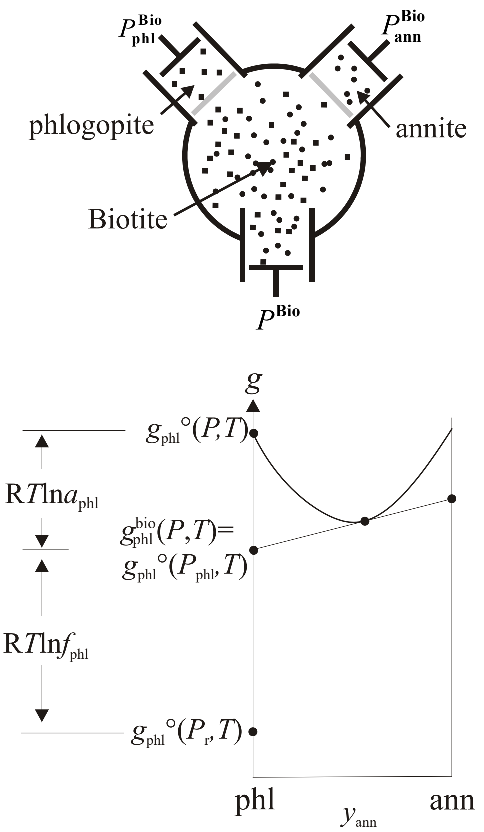

Fig 9.1. An isothermal system consisting of biotite with endmembers phlogopite and annite. The system is connected to 2 compartments by rigid osmotic membranes that are permeable with respect to only one endmember. In each compartment pressure is dictated by the constraint that the partial molar energy of the pure endmember in the compartment must be equal to that of the endmember in biotite. It follows that only 1 of the 3 pressures is independent. The conventional definition of the activity of a solution endmember is related to the difference in the partial molar energy of the endmember in the solution and in its pure state at the same P and T. Alternatively, activities may be defined relative to the partial molar energy of the pure endmember at a different pressure, in which case the activity is usually referred to as a **fugacity**.

MORE TECHNICALITIES ON ACTIVITY

The Gibbs energy of a solution can be expressed in terms of activities as:

$$g^{\mathrm{sol}} = \sum_{i=1}^{t} y_i g_i^{\circ} + \sum_{i=1}^{t} y_i \mathrm{R}T \ln a_i$$

where comparison with 6.4 identifies the first term to be g^{mech} term of a solution model. The relationship of the second summation to the remaining components of a solution model ($g^{\mathrm{conf}} + g^{\mathrm{ex}}$) is made clear splitting the activity into an “ideal” factor (a^{ideal}) related to the configurational entropy and non-ideal factor known as the **activity coefficient**, γ, related to the excess energy, in which case

$$g^{\mathrm{sol}} = \sum_{i=1}^{t} y_i g_i^{\circ} + \sum_{i=1}^{t} y_i \mathrm{R}T \ln a_i^{\mathrm{ideal}} + \sum_{i=1}^{t} y_i \mathrm{R}T \ln \gamma_i \qquad 9.3$$

where, in the special case of a molecular solution model (6.9) $a_i^{\mathrm{ideal}} = y_i$. Comparison of 6.1, 6.24 and 9.3 requires

$$\mathrm{R}T \ln a_i^{\mathrm{ideal}} = g^{\mathrm{conf}} - \sum_{j \neq i}^{t} y_j \frac{\partial g^{\mathrm{conf}}}{\partial y_j} \qquad 9.4$$

$$\mathrm{R}T \ln \gamma_i = g^{\mathrm{ex}} - \sum_{j \neq i}^{t} y_j \frac{\partial g^{\mathrm{ex}}}{\partial y_j}\,. \qquad 9.5$$

The geometry of g–y diagrams (Fig 9.2), or alternatively a Taylor series expansion of 9.4 and 9.5, suggests two important limiting behaviors for actvities

$$\begin{matrix} y_i \to 1 & a_i \to a_i^{\mathrm{ideal}} \\ y_i \to 0 & \gamma_i \to k_{\mathrm{H}} \end{matrix} \qquad 9.6$$

known respectively the **Raoult’s** and **Henry’s limiting laws**, where k_{H} is the **Henry’s law constant**. From application of the Gibbs-Duhem relation (1.9) it can be shown that if one endmember of a solution obeys Raoult’s law, then the other endmembers must behave according to Henry’s law. Henry’s law behavior is sometimes used, particularly in aqueous chemistry, to formulate a standard state for a **pure endmember at infinite dilution**, also known as a **solute standard state**, that is derived from the pure endmember, or **solvent standard state,** as

$$g_i^{*} \equiv g_i^{\circ} + \mathrm{R}T \ln k_{\mathrm{H}}\,. \qquad 9.7$$

The virtue of adopting the Henry’s law standard state for a dilute solute is that the contribution of the excess (“non-ideal”) component of the solution model becomes implicit and the energy of the solution has the pseudo-ideal form

$$g_i = g_i^{*} + \mathrm{R}T \ln a^{\mathrm{ideal}} \left(y_i \to 0\right). \qquad 9.8$$

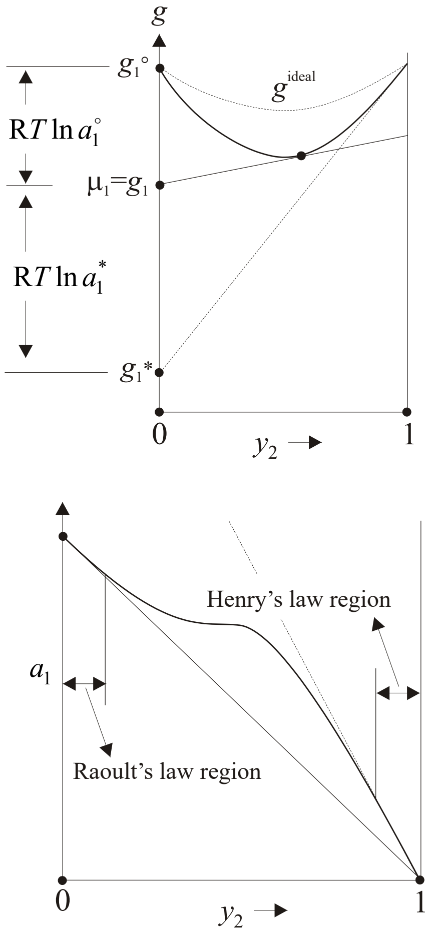

Fig 9.2 g–y diagram showing the difference between the activity of endmember 1 for an intermediate solution composition measured relative to the solvent (g°) and solute (g*) reference states. The **solvent reference state** is the pure endmember (or species) at P and T. The **solute standard state** is the (hypothetical) pure species at infinite dilution and the P and T of interest. The lower diagram shows the activity of component 1 in the solution as a function of y_2. There are 2 limiting behaviors, in the Raoult’s law region the activity is ideal if measured relative to the solvent standard state, in the Henry’s law region the activity is ideal if measured relative to the solute

The application of this model to melts and solid-solutions has been popularized by Holland & Powell (1998), who essentially refer to the solute standard state as a standard state that has been corrected according to **Darken’s quadratic formalism (DQF)**, and the term $\mathrm{R}T \ln k_{\mathrm{H}}$ as a **DQF-correction**. For any stable solution it is evident that $k_{\mathrm{H}} > 0$ must be positive and therefore $g_i^{*} > g_i^{\circ}$.

THERMOBAROMETRY AND ACTIVITY-CORRECTED EQUILIBRIA

The use of activities in thermobarometric calculations as briefly outlined in chapter 6 is seductively simple. One merely measures the compositions of the minerals in some rock, identifies equilibria involving endmember compositions of the mineral, and computes the *P*-*T* location of the equilibria. In many cases, the equilibria are constrained for the pure endmembers by experimental measurements so that the free energy change of the pure endmember reaction is a known function of pressure and temperature, i.e.,

$$\Delta g^{\circ} = f\left(P,T\right)$$

and therefore it is only necessary to compute the equilibrium constant for activity models for each equilibrium and solve

$$0 = f\left(P,T\right) + \mathrm{R}T\ln K$$

for the conditions of equilibrium. Unfortunately, this method, while simple, can lead to solutions that are in fact totally inconsistent with equilibrium. The origin of this problem is that while the condition $\Delta g = 0$ is a necessary condition for equilibrium it is not a sufficient condition. Moreover even if a system is in equilibrium, it is not necessarily stable.

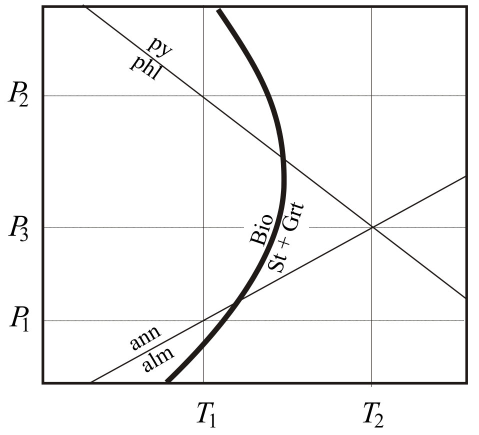

Fig 9.3 *P*-*T* diagram projection for phase relations in the system K_2O-FeO-MgO-Al_2O_3-SiO_2 with μ_{SiO_2}, $\mu_{Al_2O_3}$, μ_{K_2O} and μ_{H_2O} determined by external (e.g., saturation constraints) so that the system has two thermodynamic components (FeO and MgO). The univariant equilibrium biotite (Bio) = Staurolite (St) + Garnet (Gt) defines the true limit for the stability of Bio. The two thin solid lines represent "activity corrected" univariant curves for specific (e.g., observed) compositions of garnet and biotite as depicted in the ω-*X* diagrams of Fig 9.4.

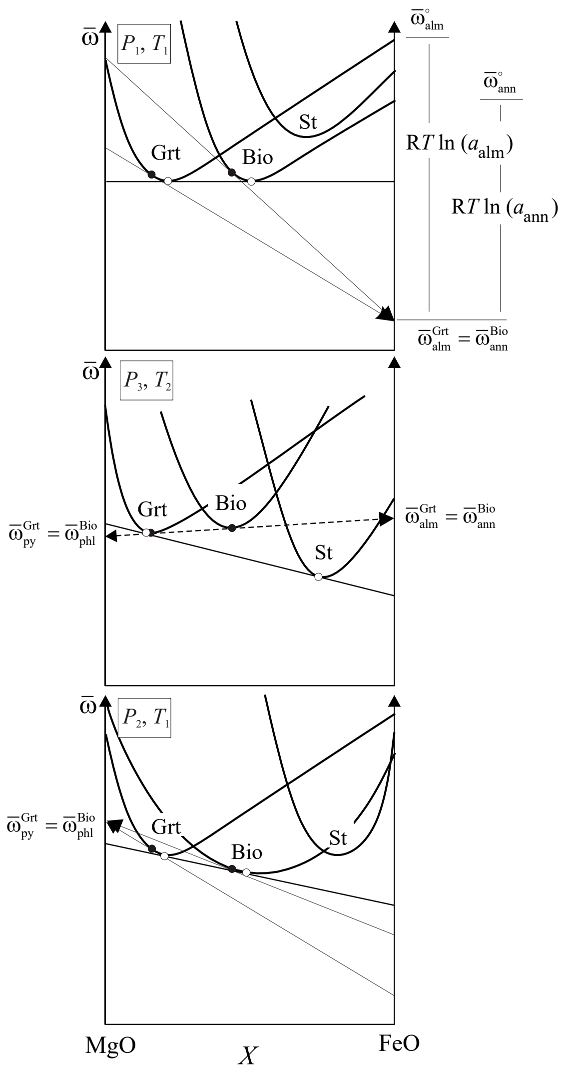

Fig 9.4 Free energy composition diagrams corresponding to conditions on Fig 9.3, the free energyhere is $\omega = g - n_{SiO_2}\mu_{SiO_2} - n_{Al_2O_3}\mu_{Al_2O_3} - n_{K_2O}\mu_{K_2O} - n_{H_2O}\mu_{H_2O}$. The "observed" compositions of Grt and Bio are indicated by filled black circles on the corresponding ω-*X* curves, the true equilibrium compositions of coexisting Grt+Bio are indicated by open circles.

To understand the consequences of using a necessary but not sufficient condition for equilibrium, consider the “GASP” barometer defined by reaction 6.20 in the CaO-Al_2O_3-SiO_2 system, the condition $\Delta g = 0$ for this reaction implies that activity corrected partial molar energies of anorthite, grossular, quartz and kyanite are coplanar in the CaO-Al_2O_3-SiO_2 $\bar{g} - X$ space and therefore that the chemical potentials of CaO, Al_2O_3 and SiO_2 are equal in the observed garnet, plagioclase, etc. However, both garnet and plagioclase contain other components as well and these are not constrained to be equal at the conditions of the GASP equilibrium;

indeed, in general they will not be equal. To illustrate this problem, consider garnet-biotite equilibrium in the K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O system. To reduce the dimension of the composition space, assume that the system contains water, quartz, kyanite and muscovite at all conditions of interest, thus we can make the Legendre transform

$$\omega = g - n_{\mathrm{H_2O}}\mu_{\mathrm{H_2O}} - n_{\mathrm{K_2O}}\mu_{\mathrm{K_2O}} - n_{\mathrm{SiO_2}}\mu_{\mathrm{SiO_2}} - n_{\mathrm{Al_2O_3}}\mu_{\mathrm{Al_2O_3}} \qquad 9.9$$

and we are left with MgO and FeO as thermodynamic components, so we can now analyze the phase relations in a two dimensional $\overline{\omega} - X$ diagram (Fig 9.4). Both biotite (a solution between annite and phlogopite) and garnet (a solution between almandine and pyrope) are continuous solutions in the reduced composition space. The necessary conditions for equilibrium are (assuming we have chosen the formula units of garnet and biotite so that each has a total of 1 mole of FeO+MgO, so that the stoichiometric coefficients are one)

$$\overline{\omega}^{\mathbf{Grt}}_{\mathbf{alm}} = \overline{\omega}^{\mathbf{Bio}}_{\mathbf{ann}} \text{ (i.e., } \mu^{\mathbf{Grt}}_{\mathbf{FeO}} = \mu^{\mathbf{Bio}}_{\mathbf{FeO}} \text{)} \qquad 9.10$$

$$\overline{\omega}^{\mathbf{Grt}}_{\mathbf{py}} = \overline{\omega}^{\mathbf{Bio}}_{\mathbf{phl}} \text{ (i.e, } \mu^{\mathbf{Grt}}_{\mathbf{FeO}} = \mu^{\mathbf{Bio}}_{\mathbf{FeO}} \text{)} \qquad 9.11$$

These equalities can be reformulated as the conditions for independent "activity corrected" univariant equilibrium in the MgO and FeO subsystems, i.e., from 9.10

$$\begin{aligned} \Delta\omega_1 &= \omega^{\mathbf{Gt}}_{\mathbf{alm}} - \omega^{\mathbf{Bio}}_{\mathbf{ann}} \\ &= \Delta\omega^{\circ}_1 + \mathbf{R}T \ln \frac{a^{\mathbf{Gt}}_{\mathbf{alm}}}{a^{\mathbf{Bio}}_{\mathbf{ann}}} \end{aligned} \qquad 9.12$$

and from 9.11

$$\begin{aligned} \Delta\omega_2 &= \omega^{\mathbf{Gt}}_{\mathbf{py}} - \omega^{\mathbf{Bio}}_{\mathbf{phl}} \\ &= \Delta\omega^{\circ}_2 + \mathbf{R}T \ln \frac{a^{\mathbf{Grt}}_{\mathbf{py}}}{a^{\mathbf{Bio}}_{\mathbf{phl}}} \end{aligned} \qquad 9.13$$

which for any arbitrary, e.g., observed compositions, can be solved to define the *P*-*T* conditions of activity-corrected univariant equilibria. Taken individually these curves do not define the equilibrium conditions for Grt+Bio, but rather the conditions at which the tangents of the $\overline{\omega} - X$ surfaces of each phase at the specified compositions extrapolate to the same intercept (Fig 9.4). Thus, in general the curves do not indicate equilibrium conditions, the only true equilibrium condition being the condition at which the two "activity-corrected" univariant curves intersect (Fig 9.3). Use of the activity corrected GASP barometer is exactly analogous to considering only one of these curves, it establishes a range of conditions that include the equilibrium condition, but which, in general, are not themselves possible conditions.

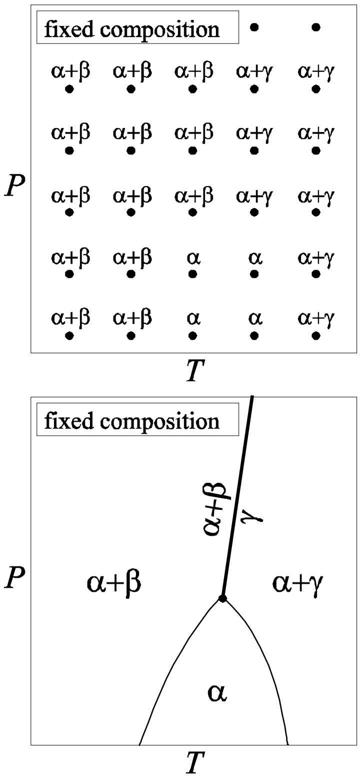

Fig 7.5 Construction of a phase diagram section as a mapping problem wih Gibbs energy minimization. Gibbs energy minimization can be used to "sample" the phase relations on, for example, a regular grid as in the upper diagram. The true phase relations (the lower diagram) can then be inferred by interpolating between the sample points.

A more insidious problem is that even if simple inverse thermobarometry is done in such a way as to establish the conditions of a true equilibrium, it cannot provide information about the stability of the observed phases relative to those that are not observed. In our Grt+Bio example, we have a system with c=2 components and 3 phases must coexist along any real univariant curve such as that corresponding to the equilibrium of Grt + Bio + Staurolite, which limits the stability of Biotite (Fig 9.3). Thus, in this example, the thermobarometric results are inconsistent with the phase relations predicted from essentially the same data. Often such inconsistencies are dismissed by statements such as "the assemblage is observed, therefore it must have been stable", but such casual argumentation belies the complexity of thermobarometry. The sad truth is that observed mineral compositions rarely represent anything approximating equilibrium conditions (after all, if they did thermobarometry would always yield ~298 K and 1 bar) and therefore it is not possible to find a single *P-T* condition at which all the observed phases of a rock are in equilibrium. In recent years, in recognition of this complexity petrologists have developed more sophisticated inverse methods such as WEBINVEQ (Gordon 1992) and "Average *P-T*" (Powell 1985, Holland & Powell 1998) that attempt to obtain identify the conditions at which an observed rock is closest to equilibrium. However, to date there are no inverse methods that also account for thermodynamic stability.

THE TRUE PATH: FREE ENERGY MINIMIZATION

The fundamental flaw in thermobarometry is that it involves prescribing mineral compositions and then asking what conditions yield the prescribed (observed) compositions. The flaw being that we cannot prescribe mineral compositions and expect to find a thermodynamically consistent solution. Given that thermodynamics provides us with a means of predicting all the properties of a rock as a unique function of its environmental variables, the alternative is to use such predictions (i.e., forward models) to find the closest match between observed and predicted phase relations. Phase diagrams embody thermodynamic these predictions and are themselves a consequence of the geometry of the minimum $\overline{\omega}-X$ for a system as function of its environmental variables. The method by which this surface is determined graphically is straightforward, but to compute such surfaces numerically is surprisingly difficult. Here we will only briefly outline the formulation of the simplest method, **constrained free energy minimization**, which enables us to predict the amounts and compositions of the stable phases of a system as a function of variables $\left\{X_1,\ldots,X_{\rm c},\theta_{\rm c+1},\ldots,\theta_{\rm k+2}\right\}$. The construction of a phase diagram using constrained free energy minimization, amounts essentially to a mapping program in which one samples the variable space, records the stable phases, and maps the fields in which the various phase assemblages are stable (Fig 9.5).

To simplify the formulation of Free energy minimization we will describe all the phases of the system as solutions in all the components of the system. If a phase has a fixed composition, or otherwise limited solution behavior, then it can be treated as a special case by imposing appropriate constraints. The problem can be stated as follows: minimize

$$\overline{\omega}^{\rm sys} = \sum_{j=1}^{\Pi} x^j \overline{\omega}^j \left(y_1^j \ldots y_{c-1}^j\right) \qquad 9.14$$

subject to the physical constraints

$$X_i^{\rm sys} = \sum_{j=1}^{\Pi} x^j y_i^j \quad i = 1 \ldots c-1 \qquad 9.15$$

$$0 \le x^j \le 1 \qquad 9.16$$

$$0 \le y_i^j \le 1 \qquad 9.17$$

$$\sum_{j=1}^{\Pi-1} x^j \le 1 \qquad 9.18$$

$$\sum_{i=1}^{c-1} y_i^j \le 1 \qquad 9.19$$

where Π is the total number of phases that may occur in the system, as opposed to those which are actually stable; x^j is the molar proportion of the $j^{\rm th}$ phase and i indexes the c-components of the system and the c-endmembers of each solution. Constraint 9.15 is a restatement of the lever rule, which requires that the amounts of the components in the phases of the system must sum to the total amounts of the components in the system; and constraints 9.16-9.19 are necessary to ensure all amounts and compositions remain positive. As formulated the Free energy minimization problem is the classical non-linear minimization problem, wherein 9.14 is the **objective function** to be minimized, subject to the **linear constraints** 9.15, 9.18 and 9.19; and the **linear inequalities** 9.16 and 9.17; to solve for the amounts (x^j) and compositions (y_i^j) of the stable phases. In the context of the optimization problem, the $p \le c$ stable phases are those phases with non-zero amounts. A maple script to solve the general non-linear problem is provided in the course notes for the solution of problem 9.1. Drawbacks of non-linear optimization strategies are that they often require initial guesses for the phase compositions. In contrast, the case in which the possible phases all have fixed compositions can be solved by linear optimization methods that are numerically robust. The robustness of the linear optimization, suggests a third method in which the non-linear problem is linearized by replacing approximating each possible solution phase by a series of stoichiometric compounds. The linearized problems is illustrated by the maple script at www.perplex.ethz.ch/simplex.html.

PROBLEMS

9.1 The maple script in ../problem_9_setup.zip derives $\varpi - X$ functions, where $X = n_K/(n_K+n_{Na})$, for white mica and alkali-feldspar for a system in which these phases coexist with water, kyanite and quartz (i.e., the Legendre transform is equivalent to a petrological “projection” through water, kyanite and quartz. **a)** Use the $\varpi - X$ functions to construct a T-X phase diagram (at P = 3000 bar, as set in the scrupt) for temperatures from 800-980 K. The topology of the diagram is determined entirely by the location of: two 2-phase reactions (pure albite reacting to pure paragonite, pure sanidine reacting to pure muscovite), two 3-phase reactions, and the sanidine critical condition (at T = 961 K, X = 1/3). Locate univariant equilibria and critical points within +/-1 K, the rest of the diagram can be sketched qualitatively. **b)** Balance the 3-phase reactions, do you expect the reaction stoichiometries to vary as a function of pressure?

Hint: you can do this problem graphically by plotting the $\varpi - X$ or by making use of the optimization command in the script, the latter is more practical for determining the phase relations in the vicinity of the 3-phase reactions (to use the script for this purpose you will need to vary the constraint on bulk composition specified in the NLPSOLVE command).

10: MOLECULAR FLUIDS

There is nothing unique to the thermodynamics of fluids (or, for that matter, any phase), but fluids, and in particular gases, are microscopically simpler than solids and therefore have a longer experimental and theoretical history. This history has led to a situation in which, from a practical perspective, fluids are treated differently than solids in two distinct ways: fluid equations of state tend to incorporate more theory and the thermodynamic reference state for fluid species is defined differently than for solids.

WHAT IS A FLUID?

Fluids are defined by concepts that are themselves poorly defined, but a reasonable starting point is to define a **fluid** as any phase that lacks long-range order on an atomistic scale. Thus, fluids are clearly distinguished from crystals in which atoms are arranged periodically on an effectively infinite structure, excepting the occasional defect. By this definition, glasses qualify as fluids, which may be a little counterintuitive, but is certainly less troubling than the rheological definition of a fluid, which is anything that has time-dependent deformation, e.g., the earth's mantle. The only legitimate definition of a **gas** (or **vapor**) is that it is a fluid that may undergo a discontinuous transformation to a fluid with higher density, which is thereby defined to be a **liquid** fluid. Ignoring the complexities introduced by impure fluids, the necessity for this unsatisfying definition is that the pressure-temperature trajectory of the liquid-gas equilibrium phase boundary of any one-component system terminates at a point at which the properties of gas and liquid become indistinguishable, i.e., a **critical point**. For example, the critical point of water is at 647 K and 220 bar, at a temperature below this point if the pressure of a water gas is continuously increased at some point the gas will undergo a discontinuous transformation to liquid water (Figs 10.1 and 10.2). However, because of the existence of the water critical point, it is possible to vary pressure and temperature in such a way as to go from the gaseous to the liquid state continuously, thereby making the distinction between liquid and gas meaningless.

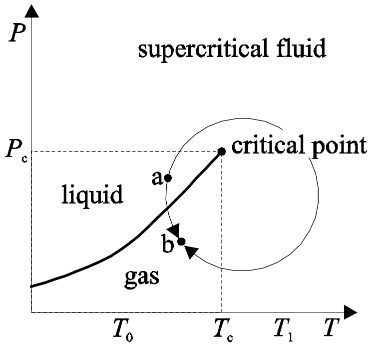

Fig 10.1 Phase diagram for a pure fluid. At pressure and temperature below the critical point of the fluid, the liquid field is separated from the gas field by a univariant curve (sometimes called the boiling curve). At pressure or temperature greater than the critical point conditions, the fluid is said to be supercritical. The circle illustrates two paths from a (liquid) to b (gas). On the counterclockwise path the liquid undergoes a discontinuous transition to gas (boiling), whereas for the clockwise path the transition from liquid to gas is continuous.

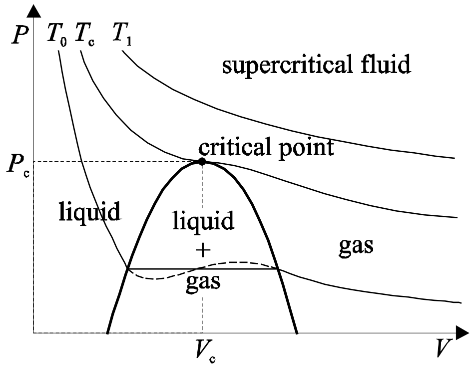

Fig 10.2 *P-V* diagram corresponding to the phase diagram for a pure fluid in Fig 10.1. The 2-phase field liquid+gas is equivalent of the boiling curve in the phase diagram. On the $T=T_1$(supercritcal) isotherm *P* varies continuously with *V*. On the critical isotherm ($T=T_c$), the pressure derivative vanishes at the critical point. Lower *T* isotherms (e.g.,$T=T_0$) intersect the 2-phase field at 2 isobaric points, at any point between these points the amount of gas and liquid are determined by the lever rule. It is impossible for a continuous function to reproduce the linear portion of a sub-critical isotherm. However a cubic EoS (illustrated by the dashed curve) can reproduce the liquid and gas densities on the limbs of the 2-phase field. In conventional terminology the 2-phase field is not a solvus because a *P-V* diagram is not a phase diagram. However its features are analagous to a solvus. In fact, it can be shown that the equivalent phase field in *T-V* diagram is technically a solvus (although the terminology is non-conventional).

Another vague non-thermodynamic distinction is that of **molecular** and **ionic** fluids. The former supposedly being composed entirely of covalently bonded molecular species, and the latter consisting of ionized species. To a first approximation, fluids composed of volatile elements (i.e., gaseous elements at room pressure and temperature) tend to be molecular, whereas fluids composed of non-volatile elements tend to be ionic. Thus, C-O-H-N-S-Cl-F fluids are dominantly molecular, while aqueous fluids with dissolved solids (e.g., **electrolytes**) or melts tend to be ionic. Unfortunately, the validity of these generalizations is limited, in that pressure tends to decrease the ionic character of both electrolytes and melts. The critical points of molecular fluids are rarely at more extreme conditions than the critical point of water, thus within the earth molecular fluids are typically **supercritical**.

ELEMENTARY THEORY

The basis for the early theoretical treatments of fluids was Clapeyron's (1834) combination of Boyle's (1662) and Charles's (1787) laws as the **ideal gas law**

$$PV = n\mathrm{R}T \qquad 10.1$$

or

$$Pv = \mathrm{R}T \qquad 10.2$$

the first complete equation of state (**EoS**). This equation of state is theoretically justified in the limit that the phase of interest is composed of zero-dimensional non-interacting particles, which is not an entirely unreasonable approximation for low-pressure gases. However, at higher pressure the condensation of the gas to a liquid provides evidence of both attractive intermolecular forces and that gases cannot be compressed to zero volume, i.e., the existence of short range repulsive intermolecular forces.

Van der Waals (1873) improved on the ideal gas model by postulating the molar volume of a gas should approach a limiting value at 0 K, i.e.,

$$b = v - \frac{RT}{p} \qquad 10.3$$

where b is a positive constant characterizing the size of the gas molecules, i.e., the molar **covolume**. Further, van der Waals postulated that intermolecular attractive forces should vary as $1/r^6$, where r is intermolecular distance. As the pressure of a gas is the manifestation of these forces and the average intermolecular distance in a gas is $V^{1/3}$, Van der Waals argued that the pressure predicted by 10.3 could be corrected for the effect of intermolecular forces as

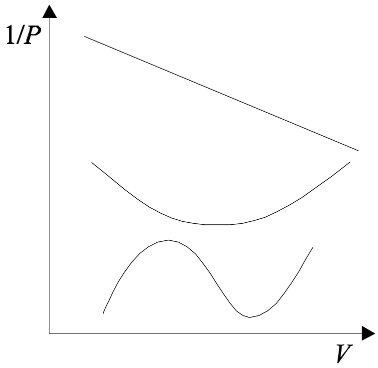

Fig 10.3 Necessity of a cubic equation of state to describe boiling. At the boiling pressure the equation must describe both the volume of both gas and liquid. The ideal gas law gives a linear relation (upper curve) between volume and 1/P and therefore can have only 1 value at any pressure. Quadratic functions are parabolic (middle curve), therefore they have 2 values for volume at a given value of pressure, but the compressibility of one phase must be negative, which is physically impossible. A cubic function (lower curve) is thus the simplest functional form of the EoS. When all roots are real, the minimum and maximum roots are the physically meaningful roots. The illustration shows that both roots have positive compressibilities. The integral $V\mathrm{d}P$ between these roots must be zero.

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \qquad 10.4$$

where a is a constant characteristic of the gas, which must be positive if the force are attractive. I do not know enough history to know if Van der Waals motivation for the $1/r^6$ (i.e., $1/v^2$) dependence for interatomic forces was physical or mathematical, but I do know he was interested in obtaining an equation of state that could reproduce boiling. The mathematical requirement for such an equation is that for a given isotherm: i) it must be able to predict two states with different molar volumes at a single pressure, and ii) on either side of this pressure the molar volume must decrease with pressure $(\partial v/\partial P < 0)$. The ideal gas is linear in volume (Fig 10.3) and therefore cannot meet the first condition. A quadratic equation in volume could meet the first condition in that it may have two real roots, but $\partial v/\partial P$ would be opposite in sign for each root and therefore violate the second requirement. Thus an equation of state must be at least third order in volume to predict boiling, and this is exactly what results from Van der Waals a/v^2 term, as by rearrangement of 10.4

$$av-(Pb+\mathrm{R}T)v^2+Pv^3=ab. \qquad 10.5$$

With suitable parameters 10.4 (or 10.5) has 1 real root for $T > T_c$, and 3 real roots at $T < T_c$. Of the 3 roots, only the minimum and the maximum have $\partial v/\partial P < 0$, and therefore meet the second requirement for the equation of state, the intermediate root has no physical significance.

Experimental and theoretical models have shown that the there are 4 major categories of intermolecular forces in fluids: **nuclear repulsion** ~ $1/r^n$, n = 6-12, short range; **electrostatic** (or **Coulombic**) due to permanent polar moments, net attractive forces, ~ $1/r^2$, comparatively long range; **inductive,** induced by interaction of polar and nonpolar molecules, attractive, ~ $1/r^6$; and **dispersive**, (or **London**) caused by fluctuations by in nonpolar molecules, attractive, ~ $1/r^6$. Thus, as electrostatic forces are absent in true molecular fluids, dispersive and inductive forces are indeed consistent with van der Waals' model. Moreover, because all the intermolecular forces decay rapidly with intermolecular distance, all gases must behave as ideal gases in limit $P \to 0$ (this is a law named after some dead physicist).

The choice of the covolume b and dispersion a term in the Van der Waals equation of state are easily derived by differentiation of 10.4

$$\frac{\partial P}{\partial v}=-\frac{\mathrm{R}T}{v-b}+\frac{2a}{v^3} \qquad 10.6$$

$$\frac{\partial^2 P}{\partial v^2}=\frac{2\mathrm{R}T}{(v-b)^3}-\frac{6a}{v^4} \qquad 10.7$$

Equating these derivatives to zero at the critical condition (Fig 10.2) and solving for the constants in terms of the critical temperature (T_c), pressure (P_c) and volume (v_c) gives

$$b=\frac{v_c}{3},\quad a=\frac{9}{8}\mathrm{R}T_c v_c,\quad P_c=\frac{3}{8}\frac{\mathrm{R}T_c}{v_c}. \qquad 10.8$$

Van der Waals realized that by scaling the pressure, temperature and volume of a gas relative to the respective critical properties, 10.4 yields a "universal" equation of state

$$P^*=\frac{T^*}{3v^*-1}-\frac{3}{v^{*2}} \qquad 10.9$$

where the scaled or "reduced" variables are

$$v^*=\frac{v}{v_c},\quad P^*=\frac{P}{P_c},\quad T^*=\frac{T}{T_c}.$$

This realization was the origin of the **theory of corresponding states**, which essentially postulates that all gasses in the same reduced state have the same reduced properties (reduced compressibility, etc.). There is nothing wrong with this theory in principle, but in practice, it requires an equation of state with perfect accuracy. In this regard, the Van der Waals EoS has been found wanting.

Although the van der Waals equation is not accurate, its formulation established the importance of cubic equations of state for the prediction of phase transitions and it has served as a basis for virtually all subsequent theoretical and semi-empirical equations of state. In earth science, empirical modifications of the **Redlich-Kwong** (1941) EoS

$$P=\frac{\mathrm{R}T}{v-b}-\frac{a}{\sqrt{T}(v+b)v} \qquad 10.10$$

are the most popular descendent of the van der Waals equation. Typically these modifications are to the covolume (b) and/or dispersion term (a) is taken to be a function of pressure and/or temperature.

GIBBS ENERGY AND FUGACITY OF PURE FLUIDS

The typical reference state used for solids is the Gibbs energy of the pure solid at the pressure and temperature of interest. In contrast, for molecular fluid species, the reference state is the temperature of interest and an arbitrary reference pressure (P_r). Thus, the Gibbs energy of a pure fluid at the pressure and temperature of interest must be evaluated from

$$g^\circ(P,T)=g^\circ(P_r,T)+\int_{P_r}^{P} v^\circ dP \qquad 10.11$$

For an ideal gas, substituting 10.2 into 10.11yields

$$g^{\circ,\mathrm{ideal}}(P,T)=g^\circ(P_r,T)+\mathrm{R}T\ln\left(\frac{P}{P_r}\right). \qquad 10.12$$

Historically, because non-ideal fluids are described by complex equations of state, for practical applications the value of the integral in 10.11 was tabulated. However, rather than tabulate the volume integral directly a proportional function known as **fugacity** was defined

$$f \equiv \exp\left[\int_0^P v dP \Big/ \mathrm{R}T\right] \qquad 10.13$$

the virtue of this function is that it parallels that for the ideal gas, in that the Gibbs energy of a pure real gas is then

$$g^\circ(P,T) = g^\circ(P_r,T) + \mathrm{R}T \ln \frac{f^\circ(P,T)}{f^\circ(P_r,T)}. \qquad 10.14$$

Such manipulations are anachronistic in that the integral

$$\int_{P_r}^{P} v^\circ dP = \mathrm{R}T \ln \frac{f^\circ(P,T)}{f^\circ(P_r,T)} = g^\circ(P,T) - g^\circ(P_r,T)$$

can be evaluated analytically and efficiently by computer. Nonetheless, as fugacities persist in geoscientific literature as relicts of the past, it is worthwhile to clarify a complication in explicitly evaluating 10.13, namely that the volume of a gas tends to infinity in the limit $P \to 0$. To avoid this difficulty a simple trick is to evaluate integral of the difference real gas volume from its ideal volume

$$\int_0^P \left(v^\circ - v^{\circ,\mathrm{ideal}}\right) dP = \mathrm{R}T \ln \frac{f^\circ(P,T)}{P}. \qquad 10.15$$

From the dead-physicist limiting law, the volume of a real fluid must approach that of an ideal gas in the limit $P \to 0$, thus the integrand of 10.15 is finite for any real pressure. This formulation suggests an alternative expression for fugacity as

$$f^\circ = P\varphi^\circ \qquad 10.16$$

where φ is known as the **fugacity coefficient**, and subject to the limiting law $\varphi \to 1, P \to 0$, thus 10.15 is

$$\int_0^P \left(v^\circ - v^{\circ,\mathrm{ideal}}\right) dP = \mathrm{R}T \ln \varphi^\circ \qquad 10.17$$

A potential complication that arises using complex equations of the general form *P*=*f*(*v*), is that it may not be possible to obtain the equivalent volume explicit form, i.e., *v*=*h*(*P*), which is necessary to evaluate 10.17 analytically. This complication can be circumvented by the rule of **integration by parts** (Fig 10.4), which states that if *b* is a continuous function of *a*, then

$$\int_{a_0}^{a} b\mathrm{d}a = ab - a_0 b_0 - \int_{b_0}^{b} a\mathrm{d}b. \qquad 10.18$$

Applying this rule to the volume integral in 10.17

$$\int_0^P \left(v^\circ - v^{\circ,\mathrm{ideal}}\right) dP = -P\left(v^\circ - \frac{\mathrm{R}T}{P}\right) - \int_\infty^{v^\circ} \left[P(v^\circ) - \frac{\mathrm{R}T}{P}\right] dv^\circ. \qquad 10.19$$

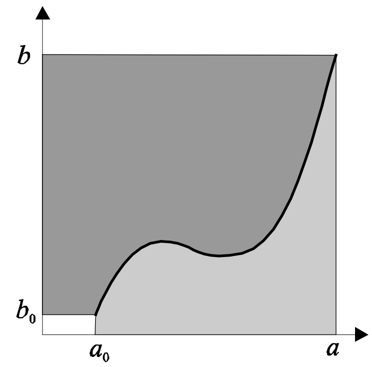

Fig 10.4 Graphical illustration of integration by parts for the integral *b*d*a* from a_0 to *a* (the lightly shaded area. Function *b*(*a*) is the heavy curve, the integral *a*d*b* from b_0 to *b* is the heavily shaded area. Therefore, the integral *b*d*a* is equal to the total area *ab* minus the area of the white rectangle, a_0b_0, minus the integral *a*d*b*.

A minor complication in evaluating 10.19 is that it is necessary to compute the volume at the pressure of interest to obtain the integration limit v°.

Another seemingly peculiar feature in the thermodynamic treatment of molecular fluids is that the reference state provided in virtually all tabulations of thermodynamic data for gaseous species is not for a pure real gas, but rather for a hypothetical pure ideal gas consisting entirely of the species of interest. The reasons for this convention are two-fold: i) the thermodynamic properties of an ideal gas can be computed from theory and ii) the properties of the corresponding real gas are dependent on the particular equation of state used to evaluate the pressure dependence of the fluid. Combining 10.12 and 10.14

$$g^\circ(P_r,T) - g^{\circ,\mathrm{ideal}}(P_r,T) = \mathrm{R}T \ln\left(\frac{f^\circ(P_r,T)}{P_r}\right), \qquad 10.20$$

where the superscript "ideal" denotes the hypothetical ideal gas standard state and using 10.20 to eliminate $g^\circ(P_r,T)$ from 10.14, the Gibbs energy of a real gas is

$$g^\circ(P,T) = g^{\circ,\mathrm{ideal}}(P_r,T) + \mathrm{R}T \ln \frac{f^\circ(P,T)}{P_r}. \qquad 10.21$$

IMPURE FLUIDS

With ever greater frequency in recent literature, impure fluids are treated identically to solid solutions as outlined in chapter 6, with the minor technical difference that the partial molar energy of pure species or endmembers are computed from 10.14 (or its approximation 10.21). However, many fluid equations of state include empirical mixing rules that relate the parameters of an impure gas to the parameters of the pure constituent species. For example, in the case of van der Waals and the unmodified Redlich-Kwong equations, the following mixing rules are considered appropriate

$$a_{mix} = \left(\sum y_i \sqrt{a_i}\right)^2, b_{mix} = \sum y_i b_i$$

Given such a rule, it can be shown by the same type of graphical argumentation as we used to define activities, that the fugacity of a species in an impure fluid is

$$\mathrm{R}T \ln f_i = \int_v^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,v,n_j} - \frac{\mathrm{R}T}{v} \right] dv - \mathrm{R}T \ln \left(\frac{v}{\mathrm{R}T} \right)$$

Algebraically, the thermodynamic activity of an impure molecular species is

$$a_i = y_i \gamma_i = \frac{f_i}{f_i^\circ} = \frac{P_i \varphi_i}{P \varphi_i^\circ} \qquad 10.22$$

which leads to a bewildering variety of ways in which equilibrium constants may be expressed for reactions involving both fluids and solids.

PROBLEMS

10.1 The critical temperature, pressure and molar volume for water are, respectively, 647 K, 220 bar, 9.16 J/bar (the critical volume has been faked here to make the van der Waals EoS give the correct critical pressure and temperature, the real critical volume is 4.787 J/bar). Calculate the covolume (*b*) and dispersion (*a*) terms for water in the van der Waals EoS (10.8). Evaluate the molar volume and fugacity of water 700 K and 2000 bar.

Hint: after determining which of the three roots of the van der Waals equation for volume is real at the conditions of interest, this root (i.e., $v^\circ(P)$) can be used explicitly in 10.17 to obtain the fugacity coefficient of water.: **Error! Bookmark not defined.**

11: SPECIATION AND ORDER-DISORDER SOLUTION MODELS

Solution models as discussed in the previous chapter are “simple” in that the models have as many endmembers as the solution has independently variable chemical components. It is, however, possible to formulate a solution model as a mixture of t chemical “entities” where $t > c$, the number of components necessary to describe the chemistry of the mixture. By definition, $t - c$ of the entities are compositionally dependent as it must be possible to write $t - c$ reactions among these “entities”. There are two distinct limiting model types: pure **speciation models** in which the thermodynamic properties of all t entities are independent and pure **reciprocal models** in which the thermodynamic properties of $t - c$ of the entities are described in terms of the remaining c independent entities. Such models combine as reciprocal solution models with speciation. Reciprocal and combined solution models involve more complex bookkeeping and are described in chapter 12.

SPECIATION MODELS

Thermodynamic theory neither requires nor treats species within a solution. Such models are simply a means of introducing atomistic models to explain macroscopic behavior. The success of such a model depends on the accuracy of the atomistic model. Suppose as an example we wish to model macroscopic H-O fluids (Fig 11.1). If we recognize that on the atomistic scale H-O mixtures consist dominantly of H_2O, H_2, and O_2 molecules, we may succeed in predicting the macroscopic properties of the fluid as a nearly ideal mixture of three molecules. However if we describe the fluid as a mixture of only H_2 and O_2 molecules we can expect that the model will need a large excess term to account for the special stability of the fluid at the H_2O composition (Fig 11.2).

Once we have a macroscopic model we can of course calculate the thermodynamic properties of any species k in phase j through the relation

$$g_k^j = \sum_{i=1}^{c} \mu_i n_i^k \; . \qquad 11.1$$

Thus in our example we can calculate the partial molar free energy of H_2O_2 in our macroscopic H_2-O_2 mixture as

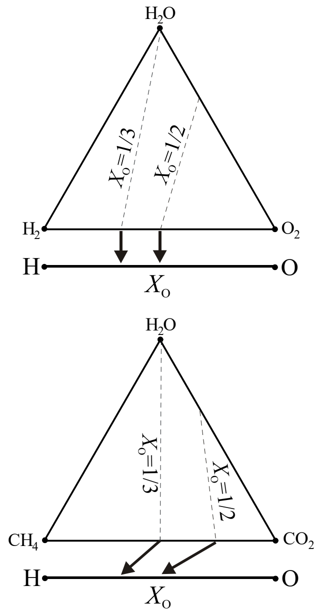

Fig 11.1 Relation between the ternary speciation composition space for H_2-O_2-H_2O and CH_4-CO_2-H_2O mixtures and the macroscopic H-O composition space. The dashed lines in the speciation composition space are lines of constant bulk composition. The speciation problem amounts to identifying the speciation that yields the lowest free energy for a given bulk composition. For CH_4-CO_2-H_2O these speciations are not at constant C-content, but the dimensionality of the true C-O-H composition space can be reduced by projection through carbon (as would be possible for graphite-saturated fluids).

$$\begin{aligned} g_{H_2O_2}^{\text{fluid}} &= 1 \cdot \mu_{H_2} + 1 \cdot \mu_{O_2} \\ &= g_{H_2}^{\text{fluid}} + g_{O_2}^{\text{fluid}} \\ &= g_{H_2}^{\circ} + g_{O_2}^{\circ} + \mathrm{R}T \ln\left(a_{H_2} a_{O_2}\right) \end{aligned}$$

The activity of H_2O_2 is then

$$a_{H_2O_2}^{\text{fluid}} \equiv e^{\left(g_{H_2O_2}^{\text{fluid}} - g_{H_2O_2}^{\circ}\right)} \Big/ \mathrm{R}T$$

and if the relation between H_2O_2 activity and composition is known we can obtain the concentration of H_2O_2, e.g., in the ideal limit we equate activity with concentration. If we find that this concentration is significant, then we may expect that the ideality of our macroscopic model will improve if we model the macroscopic H-O mixture as consisting of four species: H_2O, H_2, O_2, and H_2O_2. Thus, the success of a speciation model, i.e., its ability to explain macroscopic behavior without invoking non-ideal interactions, is critically dependent on the choice of species; models that incorporate insignificant species are unnecessarily complex.

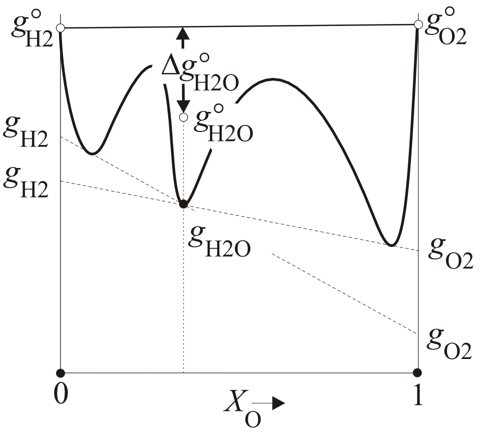

Fig 11.2 g–X_O diagram for an H-O fluid at a temperature and pressure at which a water-rich phase may coexist with hydrogen- and oxygen- rich fluids. The equilibrium free energy of the fluid as a function of bulk composition would be determined by solving for the stable speciation of the fluid at each bulk composition. The g–X_O surface lies below the free energy of pure H2O because the fluid at the water composition (X_O =1/3) is a mixture of all three species. Because speciation models often predict a strong stabilization of the solution when the bulk composition is coincident with a species, such models are often referred to as "compound formation"

There little new about the formulation of speciation models; the models consist of three components

$$g' = g^{\text{mech}} + g^{\text{conf}} + g^{\text{ex}} \qquad 11.2$$

where the prime is used to indicate the formulation as in chapter 8. However, in speciation models there are $t - c$ independent reactions between the species of the form

$$v_k^1\phi^1 + \ldots + v_k^c\phi^c + v_k^k\phi^k = 0 \quad k = c+1 \ldots t \qquad 11.3$$

for which the free energy change of reaction

$$\Delta g_k^{\circ} \neq 0 . \qquad 11.4$$

Therefore for purposes of computing homogeneous phase equilibria, in contrast to the simple solution models of chapter 8, we cannot assign all t species arbitrary energies; although, as before, we can arbitrarily assign c chemically independent species energies of zero, in which case 8.4 simplifies to

$$g^{\text{mech}} = \sum_{k=c+1}^{t} y_k \Delta g_k^{\circ} . \qquad 11.5$$

A more subtle problem is that the molar mass of the solution may vary as a function of speciation, e.g., for the H_2O bulk composition, if the fluid consists entirely of H_2O molecules ($y_{H2O} = 1$) if molar mas is ~18 g/mol, whereas when it is composed entirely of H_2 and O_2 molecules ($y_{H2} = 2/3$ $y_{O2} = 1/3$) its molar mass is ~12 g/mol. Anticipating that we will want to separate the effects of variation in speciation from the variation in mass it is desirable to define a normalization function that keeps the mass of the solution constant for a given bulk composition as a function of its speciation. For any speciation the molar mass of the solution is

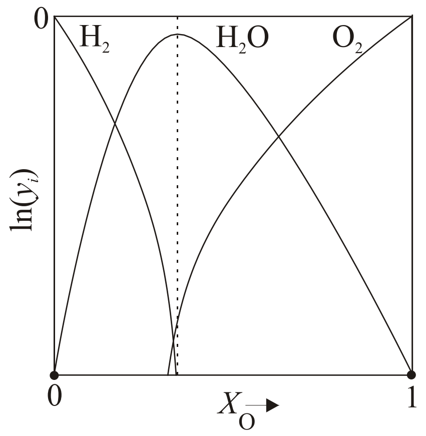

Fig 11.3 Schematic H-O speciation as a function of bulk composition. It can be shown by application of the Gibbs-Duhem relation that the maximum in the activity of any species must occur when the fluid and the species have the same composition (Connolly, 1995). There is no thermodynamic requirement that the maximum in the species concentration occurs at this composition, but generally maxima in species concentration and activity are in close proximity to each other.

$$\mathrm{N} = \sum_{i=1}^{c} y_i \mathrm{N}_i \qquad 11.6$$

where N_i is the molar mass of species i. Defining a reference mass

$$\mathrm{N}^0 = \sum_{i=1}^{c} y_i^0 \mathrm{N}_i \qquad 11.7$$

where $y_1^0, \ldots, y_c^0$ are the mole fractions of c chemically independent species when the mole fractions of the chemically dependent species are zero (i.e., $y_{c+1} = \ldots = y_t = 0$). Observing that $v_k^1 / v_k^k = \partial n_1 / \partial n_k$ is the change in the number of moles of species 1 per mole of species k formed by speciation reaction k; Eq 11.3 requires that a variation at both constant mass and composition must satisfy

$$n_i = y_i^0 + \sum_{k=c+1}^{t} \frac{\nu_k^i}{\nu_k^k} n_k$$

where n_i is the un-normalized molar amount of species i. The total number of moles of the species after this variation is then

$$n = \sum_{i=1}^{t} n_i = 1 + \sum_{k=c+1}^{t} \left(n_k \sum_{i=1}^{t} \frac{\nu_i}{\nu_k} \right)$$

and defining

$$\delta v_k \equiv \sum_{i=1}^{t} \frac{v_k^i}{v_k^k}$$

the normalized compositions of the solution are

$$y_i = \frac{n_i}{n} = \frac{y_i^0 + \sum\limits_{k=c+1}^{t} \frac{v_k^i}{v_k^k} n_k}{1 + \sum\limits_{k=c+1}^{t} n_k \delta v_k}.$$

Substituting these normalized compositions into 11.6 and rearranging the order of summation

$$\mathrm{N} = \frac{\sum\limits_{i=1}^{t} \mathrm{N}_i y_i^0 + \sum\limits_{k=c+1}^{t} n_k \sum\limits_{i}^{t} \frac{v_k^i}{v_k^k} \mathrm{N}_i}{1 + \sum\limits_{k=c+1}^{t} n_k \delta v_k}. \qquad 11.8$$

As the first summation in the denominator of 11.8 is N^0 (11.7) and the final summation in 11.8 is the change in mass caused by speciation reaction k, which is zero by definition, 11.8 simplifies to

$$\mathrm{N} = \mathrm{N}^0 \Big/ \left(1 + \sum_{k=c+1}^{t} n_k \delta v_k \right). \qquad 11.9$$

Thus, g', the specific free energy per mole of species, can be renormalized to the specific free energy of the mass of a mole of the reference speciation as

$$g = g'/\Xi \qquad 11.10$$

Where the normalization factor

$$\Xi = \frac{\mathrm{N}^0}{\mathrm{N}} = 1 \Big/ \left(1 + \sum_{k=c+1}^{t} n_k \delta v_k \right) \qquad 11.11$$

is commonly referred to as the Helffrich-Green Stuffed moles normalization factor. Although the derivation of Ξ is notationally impenetrable, it is not a complicated term. For example, in the present case of the three species H-O fluid, taking $y_{\mathrm{H_2}}^0 = 2/3$, $y_{\mathrm{O_2}}^0 = 1/3$, $v_{\mathrm{H_2}}/v_{\mathrm{H_2O}} = -1$, $v_{\mathrm{O_2}}/v_{\mathrm{H_2O}} = -1/2$, and $\Xi = 1/\left(1 - n_{\mathrm{H_2O}}/2\right)$. In fact, in solid solutions, speciation reactions typically conserve the number of moles of the species, in which case $\Xi = 1$.

Returning to our 3-species water model (c=2, t=3), in general 11.4 is

$$\begin{aligned} g^{\mathrm{mech}} &= \sum_{i=1}^{t} y_i g_i^\circ \\ &= y_{\mathrm{H_2}} g_{\mathrm{H_2}}^\circ + y_{\mathrm{O_2}} g_{\mathrm{O_2}}^\circ + y_{\mathrm{H_2O}} g_{\mathrm{H_2O}}^\circ \end{aligned} \qquad 11.12$$

Choosing H_2O as the c+1th species, there is one independent speciation reaction

$-H_2 - ½\, O_2 + H_2O = 0$

and assigning H_2 and O_2 energies of zero, 11.5 becomes

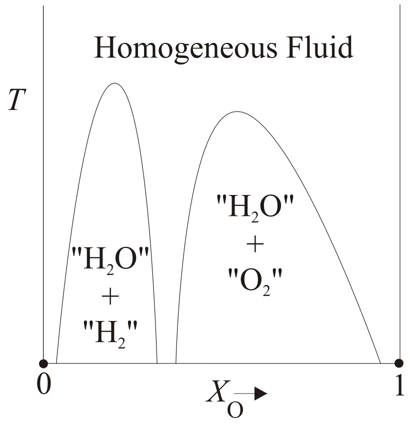

Fig 11.4 Schematic isobaric phase diagram illustrating paired solvi around the H_2O composition (X_O=1/3). The species names indicate the dominant species in the coexisting fluids. Aqueous molecular fluids typically show this type of behavior at temperatures in the vicinity of the water critical point (647 K).

$$g^{\mathrm{mech}} = y_{\mathrm{H_2O}} \Delta g_{\mathrm{H_2O}}^\circ. \qquad 11.13$$

If the fluid is truly a molecular mixture, then from 8.9

$$g^{\mathrm{conf}} = \mathrm{R}T\left(y_{\mathrm{H_2}} \ln y_{\mathrm{H_2}} + y_{\mathrm{O_2}} \ln y_{\mathrm{O_2}} + y_{\mathrm{H_2O}} \ln y_{\mathrm{H_2O}} \right). \qquad 11.14$$

As in simple solution models, the excess component of speciation models is largely ad-hoc. In H-O fluids at temperatures below ~650 K paired solvi separate the H_2O-rich fluids from both H_2- and O_2-rich fluids (Fig 11.4). This behavior is reproduced with an excess function of the form

$$g^{\mathrm{ex}} = W_{\mathrm{H_2O\text{-}H_2}} y_{\mathrm{H_2O}} y_{\mathrm{H_2}} + W_{\mathrm{H_2O\text{-}O_2}} y_{\mathrm{H_2O}} y_{\mathrm{O_2}} \qquad 11.15$$

if the interaction energies $W_{\mathrm{H_2O\text{-}H_2}}$ and $W_{\mathrm{H_2O\text{-}O_2}}$ are assigned positive values to counteract the stabilizing entropic effects of 11.14. It is noteworthy, that if H-O fluids were treated as a simple binary mixture the existence of paired solvi would require, at least, a fifth order excess function. Thus, the ease with which complex behavior such as paired solvi are explained by speciation models is a virtue. Although the formulation of speciation models involves no new features, they introduce additional degrees of freedom in that for any general bulk composition the species fractions are not uniquely determined. From thermodynamics, the stable speciation must be that which minimizes the energy of the phase for the bulk composition of interest. To determine this speciation it is necessary to convert the solution model in terms of the independent species fractions $g\left(y_1, ..., y_{c-1}, y_{c+1}, ..., y_t\right)$ (where y_c

has been eliminated by the closure constraint) to a function of the bulk solution composition $\{X_1,...,X_{c-1}\}$ and the fraction of $t-c$ chemically dependent species, i.e., $g\left(X_1,...,X_{c-1},y_{c+1},...,y_t\right)$. This trivial, albeit sometimes messy, conversion is accomplished by noting that the total amount of any chemical component in a phase must be the sum of that component in the species present in the phase weighted by the species fractions, i.e.

$$X_i = \sum_j^t y_j n_i^j \Big/ \sum_j^t y_j n_{\text{total}}^j, \quad i = 1\ldots c \qquad 11.16$$

where n_i^j is the number of moles of component i in species j, n_{total}^j is the total number of moles of the components in species j, and

$$y_c = 1 - \sum_{i \neq c}^t y_i\,. \qquad 11.17$$

Returning again to our H-O fluid model and taking the atomic fraction of oxygen as the independent bulk compositional variable, 11.16 and 11.17 are

$$X_{\text{O}} = \frac{n_{\text{O}}}{n_{\text{O}} + n_{\text{H}}} = \frac{y_{\text{H}_2\text{O}} + 2y_{\text{O}_2}}{2y_{\text{H}_2} + 3y_{\text{H}_2\text{O}} + 2y_{\text{O}_2}} \qquad 11.18$$

$$y_{\text{O}_2} = 1 - y_{\text{H}_2} - y_{\text{H}_2\text{O}}\,. \qquad 11.19$$

Eqs 11.18 and 11.19 can be rearranged as

$$y_{\text{H}_2} = 1 - \left(1 + X_{\text{O}}\right) y_{\text{H}_2\text{O}} \big/ 2 - X_{\text{O}} \qquad 11.20$$

$$y_{\text{O}_2} = \left(1 + X_{\text{O}}\right) y_{\text{H}_2\text{O}} \big/ 2 + X_{\text{O}} - y_{\text{H}_2\text{O}} \qquad 11.21$$

and substituted into 11.13–11.15 to obtain $g\left(X_{\text{O}}, y_{\text{H}_2\text{O}}\right)$, which is minimized at constant X_{O} to determine the equilibrium concentration $y_{\text{H}_2\text{O}}$, the remaining species concentrations are then obtained from 11.20-11.21 (Fig 11.3). In this simple case, the minimization can be done graphically by plotting $g\left(X_{\text{O}}, y_{\text{H}_2\text{O}}\right)$ vs $y_{\text{H}_2\text{O}}$ at constant X_{O}.

ANALYTIC SOLUTIONS OF THE SPECIATION PROBLEM

The speciation problem can be formulated analytically to avoid the necessity of numerical or graphical energy minimization. Such a formulation exploits the fact that derivative of a function must vanish at the functions minimum. Thus given $g\left(X_1,...,X_{c-1},y_{c+1},...,y_s\right)$, the stability criterion provides $t-c$ additional constraints of the form

$$\left(\frac{\partial g}{\partial y_j}\right)_{X_1\ldots X_{c-1}} = 0 \qquad j = c+1\ldots t\,, \qquad 11.22$$

which comprise a system of $t-c$ simultaneous non-linear equations that can be solved, usually numerically, for the unknown species concentrations. The disadvantage of such an approach is that 11.22 is a necessary, but not sufficient condition, for a global minimum, i.e., 11.22 may have more than one solution, thus in general it is not certain that a particular speciation is the speciation with the lowest possible free energy. Indeed, 11.22 may also correspond to maxima.

A Less Rational Analytical Solution:

The **equilibrium constant** method is a less rational means of solving the speciation problem. It is therefore perhaps unsurprising that this method is widely applied in earth sciences. The method exploits the fact that the equilibrium condition requires that the free energy change of any reaction between the species of a solution must be zero at equilibrium. Thus from 11.3 we have

$$\Delta g^j = 0 \qquad j = c+1\ldots t \qquad 11.23$$

and expanding 11.23 as in 8.30

$$\Delta g^{\circ,j} + \text{R}T \ln K_j = 0 \qquad j = c+1,...,t. \qquad 11.24$$

The activities that comprise the equilibrium constants K_j are then derived from 6.24 and, with 11.16 and 11.17, recast as functions of $X_1,...,X_{c-1}$, $y_{c+1},...,y_t$ so that, as in 11.22, a system of $t-c$ simultaneous non-linear equations in the unknown species concentrations is obtained. The reason this method is “less” rational is that it has all the disadvantages of the direct solution of 11.22, but involves many more mathematical operations.

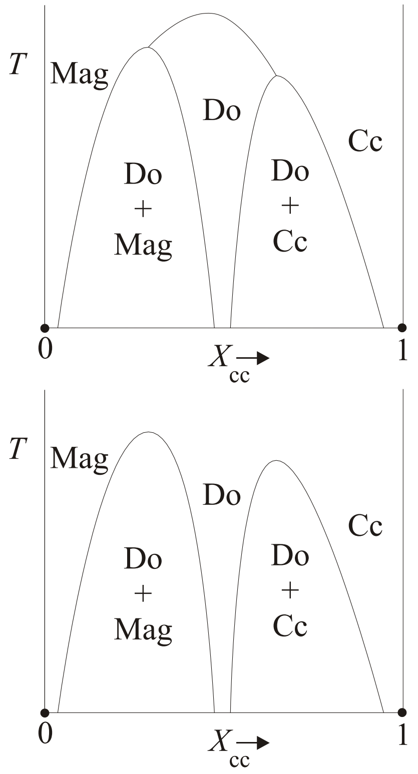

Fig 11.5 Schematic isobaric phase diagrams illustrating the two types of paired solvi that may result from a speciation model of calcite-magnesite solutions with an ordered dolomite species. In the upper diagram the solvi connected by a "tricritical" line, which marks a discontinuous ordering transition between dolomite and fully disordered calcite-magnesite solution. Solutions with that exhibit this type of behavior are said to have "convergent" ordering. In such solutions the distinction between an ordered and disordered phase is legitimate. In the non-convergent case (lower diagram) there is a continuous transition between ordered and disordered states. The nature of the transition is controlled by the parameter values for the speciation

COMPOUND FORMATION AND ORDER-DISORDER MODELS

Speciation models are widely applied in the description of mineral solutions, but because people seem to be uncomfortable with the idea of a "species" in the context of a solid phase, these models often referred to as **compound formation** or **order-disorder** models. The origin of this terminology arises from the fact that in some solutions it is possible to achieve particularly favorable energetics if different cations can be regularly ordered on a particular crystallographic site. A famous example of this is dolomite, which has two octahedral identisites, M1 and M2, per $\mathrm{Ca}_{0.5}^{\mathrm{M2}}\mathrm{Mg}_{0.5}^{\mathrm{M1}}\mathrm{CO}_3$ formula unit. At low temperature, the energy of stoichiometric dolomite is minimized if Ca is entirely on M2 and Mg on M1. Any deviation from this perfectly ordered scheme causes a rapid increase in the energy, but such a deviation is inescapable if there is solution of either magnesite, $\mathrm{Mg}_{0.5}^{\mathrm{M2}}\mathrm{Mg}_{0.5}^{\mathrm{M1}}\mathrm{CO}_3$, or calcite, $\mathrm{Ca}_{0.5}^{\mathrm{M2}}\mathrm{Ca}_{0.5}^{\mathrm{M1}}\mathrm{CO}_3$, in dolomite. This effect destabilizes calcite and magnesite solution, or viewed from another perspective, stabilizes the formation of stoichiometric dolomite, i.e., compound formation. With increasing temperature dolomite structure expands so the energetic penalty of putting Ca on the M1 site decreases and, as there is an entropic benefit to disordering, the extent of solution between stoichiometric dolomite and both calcite and magnesite increases and ultimately becomes complete, at which point there is no distinction between dolomite and a calcite-magnesite solution $(\mathrm{Ca,Mg})_{0.5}^{\mathrm{M2}}(\mathrm{Ca,Mg})_{0.5}^{\mathrm{M1}}\mathrm{CO}_3$.

Chemically the dolomite solution is analagous to the H-O fluid speciation discussed earlier, in that we can write a reaction between calcite (cc) and magnesite (mag), in both of which no octahedral site order-disorder is possible, and ordered dolomite (odo)

½ mag + ½ cc = odo

Thus, we can formulate a speciation model of calcite-magnesite solution that accounts for dolomite formation with cc, mag and odo as species. However, in contrast to the H-O fluid, where our atomistic model of the fluid consisted of true H_2O, H_2, O_2 molecules, in a crystal structure the species influence individual identisite populations. In the case of calcite magnesite, mixing occurs on M1 and M2 with site fractions

$$\begin{aligned} z_{\mathrm{M1,Ca}} &= y_{\mathrm{cc}} \\ z_{\mathrm{M1,Mg}} &= y_{\mathrm{mag}} + y_{\mathrm{odo}} \\ z_{\mathrm{M2,Ca}} &= y_{\mathrm{cc}} + y_{\mathrm{odo}} \\ z_{\mathrm{M2,Mg}} &= y_{\mathrm{mag}} \end{aligned} \qquad 11.25$$

required by the species site populations, deduced as previously for plagioclase (chapter 8). From Eqs 8.31 and 11.25, the change in configurational entropy of our calcite-magnesite model (n=2, $m_{\mathrm{M2}} = m_{\mathrm{M1}} = 2,\ q_{\mathrm{M2}} = q_{\mathrm{M1}} = 1/2$) is

$$\begin{aligned} s^{\mathrm{conf}} = -\mathrm{R}/2[&y_{\mathrm{cc}} \ln y_{\mathrm{cc}} + (1-y_{\mathrm{cc}})\ln(1-y_{\mathrm{cc}}) \\ &+ y_{\mathrm{mag}} \ln y_{\mathrm{mag}} + (1-y_{\mathrm{mag}})\ln(1-y_{\mathrm{mag}})] \end{aligned} \qquad 11.26$$

note that in this case the configurational entropies of the endmembers are zero, since in cc and mag there is only one octahedral cation, and in odo, although there are two cations, they are perfectly ordered onto M1 and M2 (i.e., $s^{\text{mech}}=0$). As in the H-O fluid, the species fractions of calcite and magnesite can be expressed from 11.16 and 11.17 in terms of bulk composition and the fraction of the ordered dolomite species

$$X_{\text{cc}} = \frac{n_{\text{Ca}}}{n_{\text{Ca}} + n_{\text{Mg}}} = y_{\text{cc}} + y_{\text{odo}}/2$$

$$y_{\text{mag}} = 1 - y_{\text{cc}} - y_{\text{odo}}$$

and rearranged to obtain

$$\begin{aligned} y_{\text{cc}} &= X_{\text{cc}} - y_{\text{odo}}/2 \\ y_{\text{mag}} &= 1 - X_{\text{cc}} - y_{\text{odo}}/2. \end{aligned} \qquad 11.27$$

Combining suitable expressions for g^{mech} and g^{ex} with 11.26 and substituting 11.27 in the result would yield $g\left(X_{\text{cc}}, y_{\text{odo}}\right)$ which is minimized at constant X_{cc} (and, of course, P and T) to determine the equilibrium free energy and speciation of the solution phase. As discussed previously, this may be done by free energy minimization, or, as is more common, by solving 11.22 or 11.24.

In effect speciation models are temperature (and in some cases pressure) dependent models for the configurational entropy of a solution. Recognition of this aspect of speciation models had led to alternative formulations of the speciation problem in which the free energy of solutions are expressed in terms of bulk composition and microscopic **order parameters** that specify crystallographic site populations. For example, in our calcite-magnesite-ordered-dolomite model, we may define a microscopic order parameter

$$Q = z_{\text{M1,Mg}} - z_{\text{M2,Mg}} \qquad 11.28$$

that describes the degree to which Mg is ordered between the M1 and M2 sites. For the endmember site populations, Q is 0 for calcite and magnesite species and 1 for ordered dolomite. Since the microscopic site fractions of a speciation model are completely determined by the macroscopic fractions of the independent species, it is mathematically evident that the number of independent ordering parameters in an order-disorder solution model $r = t - c$ the number of independent reactions that can be written between the species of the solution. Thus, in the order-disorder formulation $g\left(X_1, ..., X_{c-1}, Q_1, ..., Q_r\right)$, whereas with speciation $g\left(X_1, ..., X_{c-1}, y_{c+1}, ..., y_t\right)$. The relation between the independent order parameters and species concentrations is recovered by substituting the site fraction definitions in terms of species fractions into the definition of the order parameters (or vice versa). Thus, for calcite-magnesite from 11.25 and 11.28 we have the trivial result

$$Q = y_{\text{mag}} + y_{\text{odo}} - y_{\text{mag}} = y_{\text{odo}}.$$

Not uncommonly, the relationship between order-parameters and species fractions is more complex, but in essence order parameters are species fractions, and just as in a speciation model, the equilibrium state of order in an order-disorder model is determined by finding values of the order parameters that minimize the free energy of the solution at a given bulk composition. Or analogously to 11.22

$$\left(\frac{\partial g}{\partial Q_j}\right)_{X_1 \ldots X_{c-1}} = 0 \qquad j = 1, \ldots, r. \qquad 11.29$$

Mathematically there is no distinction between speciation models and order-disorder models, but the latter formulations are more popular in the geological literature. I personally prefer the speciation formulation because mass balance constraints and the physical meaning of terms, such as

$$W_{\text{cc-odo}} y_{\text{cc}} y_{\text{odo}},$$

are relatively transparent. In contrast, in the order-disorder formulation the solution model must be expressed as a function of macroscopic compositional variables and microscopic ordering parameters, e.g., the above term is

$$W_{\text{cc-odo}} \left(X_{cc} - Q\right) Q,$$

and as there is no closure constraint on microscopic ordering parameters, mass balance constraints tend to be less straightforward than in speciation models.

ORDER-DISORDER PHASE TRANSFORMATIONS

Order-disorder in solids is intimately associated with polymorphic phase transformations. This association arises because ordering may result in a lowering of point group symmetry. For example, in high temperature dolomite the M1 and M2 sites have the same average site populations and are thus chemically indistinguishable and do not constrain symmetry; whereas at lower temperatures the ordering of Ca and Mg onto M2 and M1, respectively, makes the sites chemically non-equivalent and distinguishable; an effect that can only decrease symmetry. The transformation from ordered to disordered point group may be smooth in that the order-parameter that characterizes the transition varies continuously towards zero (i.e., toward the disordered high symmetry state), in which case the phase is said to have **convergent ordering** (Fig 11.5). Alternatively, the ordering parameter may jump from finite values to zero across a boundary in pressure-temperature-composition space that is said to define the **critical line** of **non-convergent** ordering transformation (the boundary between low-symmetry dolomite and fully disordered calcite-magnesite solution in Fig 11.5). Speciation models are capable or reproducing both convergent and non-convergent phase transformations. The relationships between the model parameters necessary to produce a particular behavior is discussed in detail by Holland & Powell (1996ab).

Speciation Models for Pure Phases

As the speciation problem is solved at constant bulk composition, it may be self-evident that the thermodynamic properties of pure phases, i.e., phases that can have only one bulk composition, can be described by speciation models. A pure oxygen fluid is a trivial example of this application. Ordinarily we assume such an oxygen fluid to be composed of the dimer O_2, but spectroscopic measurements show that while O_2 is usually the dominant species, ozone O_3 and monatomic oxygen O can also be significant species if not dominant species in oxygen fluids. For such a system, minimization of the free energy of a speciation model analogous to our H-O fluid model would yield the equilibrium speciation and true free energy for oxygen.

A more geological example of the application of speciation models to pure phases is the prediction of order-disorder transformations in pure minerals. A prominent example is albite, where at high temperature Al and Si are disordered on the T2 site, $\mathrm{Na}\left(\mathrm{AlSi}\right)^{\mathrm{T2}}\left(\mathrm{Si}\right)_2^{\mathrm{T1}}\mathrm{O}_8$, while at low temperature the T2 site splits to T2a and T2b with Al and Si confined to a single site, i.e., $\mathrm{Na}\left(\mathrm{Al}\right)^{\mathrm{T2a}}\left(\mathrm{Si}\right)^{\mathrm{T2b}}\left(\mathrm{Si}\right)_2^{\mathrm{T1}}\mathrm{O}_8$. The α/β quartz transformation is an additional example of a transformation that is appropriately by speciation.

Problems

11.1) Holland & Powell (1996b) suggest a speciation model for omphacitic clinopyroxene $[(\mathrm{Ca,Na})^{\mathrm{M2}}(\mathrm{Al,Mg})^{\mathrm{M1}}\mathrm{Si_2O_6}]$ in which they propose that at low temperature the M2 and M1 sites split into four non-equivalent octahedral sites M2a, M2b, M1a, and M1a with the following species:

		Site			
		M2a	M2b	M1a	M1b
	q_i	1/2	1/2	1/2	1/2
	di	Ca	Ca	Mg	Mg
Species:	jd	Na	Na	Al	Al
	om	Na	Ca	Al	Mg

Additionally they specify that the free energy change for the speciation reaction om $-$ ½ jd – ½ di = 0 is –3500 J/mol and independent of pressure and temperature and specify the following interaction energies: $W_{\text{di-jd}} = 26000$ J/mol, $W_{\text{om-jd}} = 16000$ J/mol, $W_{\text{om-di}} = 16000$ J/mol. At 773 K, for a bulk composition identical to that of the om species, use the model to compute: **a**) the equilibrium speciation; **b**) Holland & Powell’s order parameter $Q = z_{\mathrm{M1a,Al}} - z_{\mathrm{M1b,Al}}$; and **c**) the thermodynamic activity of diopside.

12: RECIPROCAL SOLUTIONS

"*What is a reciprocal solution*?"

-R. Powell, 2006

"*The answer my friend is blowing in the wind*"

-Puff, the Magic Dragon, ca 1966

If a solution model is described in terms of $t > c$ chemical entities (e.g., endmembers or species), it is always possible to describe $t - c$ of these entities as a chemical mixture of c compositionally independent endmembers. In speciation models, although the compositions of $t - c$ entities are compositionally independent, the remaining thermodynamic properties of the entities are independent. Thus, the stable speciation can only be determined by finding the mixture of these entities that minimizes the total energy of the solution subject to mass balance constraints. Logically there can be only one other limiting case of a solution model with $t > c$ endmembers; to wit, **reciprocal solutions** in which the thermodynamic properties of $t - c$ of the endmembers are dependent. However, if the $t - c$ endmembers are both compositionally and thermodynamically dependent, then why not describe the solution in terms of c independent endmembers? The answer to this question is that a reciprocal formulation provides a simple means of relating real and model solution compositions. For this reason, reciprocal solution models are common in petrology. Unfortunately, the failure to recognize that the endmembers of reciprocal solutions cannot be independent is a widespread and fundamental thermodynamic error.

NOTE: as currently written, this chapter may not account for the possibility that the Helffrich Green Stuffed moles normalization factor Ξ is not constant (Eq 11.11).

WHAT IS A RECIPROCAL SOLUTION?

A reciprocal solution is a phase that exhibits more than one independent chemical exchange. The classical example being ionic salts such has halite, in which the exchange of alkali metal cations is, at least to a good approximation, independent of the exchange of halogen anions. Taking solution of K, Cs and Br in halite as an example, we may write any general halite composition as the sum of a basis composition (e.g., NaCl) and three **exchange operators**

$$Na_{1-x-y}K_xCs_yCl_{1-w}Br_w = NaCl + x\ KNa_{-1} + y\ CsNa_{-1} + w\ BrCl_{-1} \qquad 12.1$$

where the exchange operators, KNa_{-1}, $CsNa_{-1}$ and $BrCl_{-1}$, are imaginary chemical entities that combine linearly with a real composition to obtain another real composition, i.e., to affect an exchange.

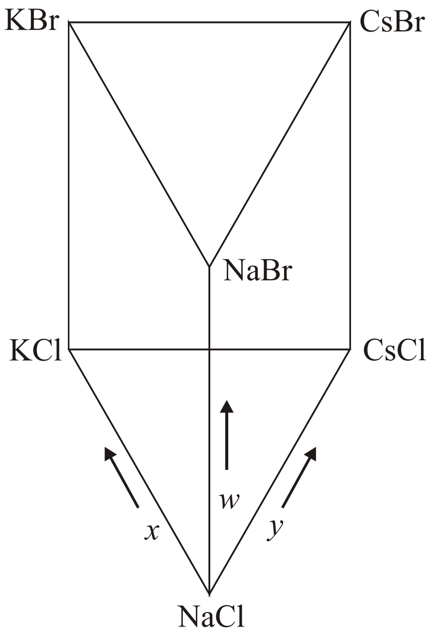

Fig 12.1 Triangular prismatic composition space of the reciprocal (Na,K,Cs)(Cl,Br) solution, formed by joining the 2-dimensional composition space of the cation site (i.e., the triangular faces) with the 1-dimensional composition space of the anion site (the vertical axes). Although the solution has 6 endmember compositions, only 4 of the endmembers are independent (i.e., the composition space is 3-dimensional and therefore can be defined by 4 components).

Exchanges are mutually dependent if the stoichiometric coefficients of the corresponding exchange operators are dependent. For halite solution 12.1, charge balance requires

$$0 \leq x + y \leq 1 \qquad 12.2$$

$$0 \leq w \leq 1 \qquad 12.3$$

thus, the exchanges of K and Cs for Na are mutually dependent, but independent of the $BrCl_{-1}$ exchange. Each group of dependent exchanges defines an orthogonal composition space, which may be thought of as defining the composition of a **chemical mixing site**. If the number of independent species mixing on the i^{th} chemical mixing is site is c_i, the dimension of the corresponding composition space must be a d_i-dimensional simplex, where d_i =

$c_i - 1$. The (orthogonal) conjunction of these composition spaces defines the **complete composition space** of a reciprocal solution which is a polygon with

$$t = \prod_i^M c_i \qquad 12.4$$

vertices and dimension

$$d = \sum_i^M d_i = c - 1, \qquad 12.5$$

where M is the number of mixing sites, corresponding to the endmember compositions of the reciprocal solution. In halite (Fig 12.1), taking the cation site as site 1, $c_1 = 3$, $c_2 = 2$, the number of endmembers is $t = 6$ from 12.4, and the dimension of the composition space (a triangular prism) is $d = 3$ and therefore $c = 4$, from 12.5. The result that

$$c < \sum_i^M c_i \qquad 12.6$$

is a peculiar consequence of the fact that the composition spaces share a common origin (e.g., 12.1).

Adopting the notation that the composition of independent species j on chemical mixing site i of a solution is Z_{ij}; and that $y_{klm\ldots}$ is the fraction of the endmember with species k on the mixing site 1, species l on mixing site 2, species m on site 3, and so forth, geometric argumentation gives

$$y_{klm\ldots} = Z_{1k} Z_{2l} Z_{3m} \cdots \qquad 12.7$$

For halite this is illustrated in Fig 12.2, in which it is seen that if a general point is placed in the interior of the composition space it is possible to fill the composition space with t non-overlapping triangular prisms that share this vertex. The volume of the triangular prism opposite the NaCl vertex is $Z_{1\mathrm{Na}} Z_{2\mathrm{Cl}}$ which, from 12.7, is y_{NaCl}. Eq 12.7 permits two equivalent expressions for any extensive or molar property ψ of a solution, i.e.,

$$\psi = \sum_k^{c_1} \sum_l^{c_2} \sum_m^{c_3} .. Z_{1k} Z_{2l} Z_{3m} \psi_{klm\ldots} \qquad 12.8$$

which, I think, is called a **Bragg-Williams summation**, or, dropping the multiple subscripts, the form employed previously for simple solutions

$$\psi = \sum_i^t y_i \psi_i \qquad 12.9$$

as in, e.g., 6.4

$$g^{\mathrm{mech}} = \sum_{i=1}^t y_i g_i^{\circ}$$

In combination Eqs 12.7 and 12.9 provided a perfectly admissible means of calculating the properties of a reciprocal solution in terms of $t > c$ endmembers that are defined by the stoichiometric limits of a reciprocal solution. However, in contrast, to speciation problems where the fractions of the chemically dependent species $y_{c+1}, \ldots, y_t$ are determined by thermodynamics, 12.7 implies the fractions of all species are determined by stoichiometry.

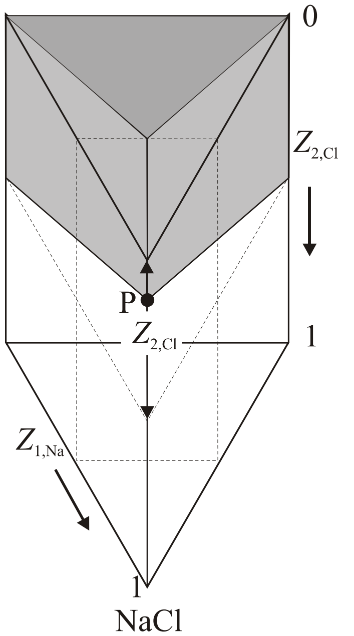

Fig 12.2 Reciprocal salt composition space as in Fig 12.1, showing the barycentric coordinates $Z_{1,\mathrm{Na}}$ and $Z_{2,\mathrm{Cl}}$ for the composition indicated by point P. The vertical projection of P onto the triangular face of the prism is $Z_{1,\mathrm{Na}}$ which is identical to the area of the heavily shaded triangle; the horizontal projection of P onto the vertical axis defines $Z_{2,\mathrm{Cl}}$; thus the shaded volume is identical to barycentric fraction y_{NaCl}, as given by eq 12.7, for the salt at composition P.

In petrology, it is not uncommon that this is where the story of reciprocal solutions ends, i.e., the properties of the t reciprocal endmembers are determined, and configurational entropy and excess energy models are formulated in terms of the fractions of these endmembers. Sadly, this simple ending is also an unhappy ending, because although 12.7 assigns endmember fractions that satisfy mass balance, the assignment is not unique, i.e., any general composition of the solution in an infinite number of ways from the t endmembers. This statement follows from the observation that we may vary the fractions of $t-c$ endmembers arbitrarily provided the remaining fractions conserve mass, i.e.,

$$\nu_i^1\phi^1+\ldots+\nu_i^c\phi^c+\phi^i=0 \quad i=c+1...t\,. \qquad 12.10$$

These variations are

$$\delta y_{1i}+\ldots+\delta y_{ci}+\delta y_i=0 \quad i=c+1...t \qquad 12.11$$

where δy_i is an arbitrary variation of the fraction y_i and δy_{ji} is the variation in the fraction of y_j required in response to δy_i by mass balance (12.10). Equating 12.10 and 12.11 gives

$$\delta y_{ji}=-\nu_i^j\delta y_i\,. \qquad 12.12$$

Since the variations $\delta y_{c+1},...,\delta y_t$ are arbitrary, any composition $y_1,...,y_t$ from 12.7, can be converted to a composition involving only c independent endmembers by setting

$$\delta y_i=-y_i \quad i=c+1...t\,. \qquad 12.13$$

Designating the fractions of these endmembers in this new composition p_i, 12.11-12.13, give

$$p_i=y_i-\sum_{j=c+1}^{t}\nu_i^j y_j \quad i=1\ldots c\,. \qquad 12.14$$

Thus if we have a reciprocal solution model $g\left(y_1,...,y_t\right)$, 12.14 provides a mathematically equivalent model $g\left(p_1,...,p_c\right)$. Furthermore, as the models are mathematically equivalent, it follows that the thermodynamic properties of the t dependent endmembers of the reciprocal solution must correspond to those of the model $g\left(p_1,...,p_c\right)$ at the endmember compositions.

Until now, we have implicitly assumed that compositions are positive, but there is no fundamental requirement for this. A simple demonstration of this follows from the choice of H_2O and O_2 as components for an H-O system. $H_2 = H_2O - ½\, O_2$, thus for H_2, $n_{H2O} = 1$ and $n_{O2} = -½$, and $X_{H2O} = 2\,X_{O2} = -1$. While, the fractions defined by 12.7 are positive, reciprocal solution compositions defined by $p_1,\ldots,p_c$ are negative over half the composition space of the reciprocal solution. The reason for these negative compositions are that the composition of the j^{th} dependent endmember, from 12.14, is

$$p_i=-\nu_i^j \quad i=1\ldots c\,. \qquad 12.15$$

As at least one stoichiometric coefficient in 12.10 must be positive, at least one composition from 12.15 must be negative. Other than this technicality, there is no difference between the formulation of reciprocal solution model as a function of independent endmembers and the formulation of simple solution models as outlined in chapter 8. Thus, the answer to Powell's introductory, and probably rhetorical question, question is that from a mathematical perspective there is no such thing as a reciprocal solution.

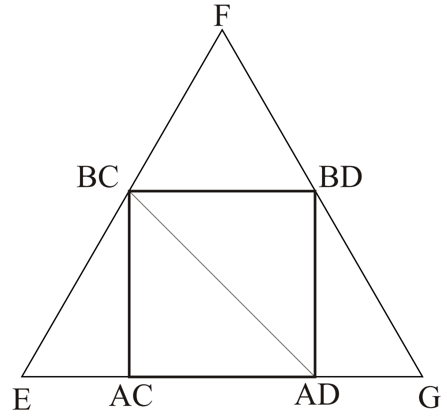

Fig 12.3. Possible representations of the composition space of a reciprocal solution $(A,B)_x(C,D)_y$. All possible compositions of the solution can be respresented as a positive linear combination of E, F, and G. Alternatively, compositions can be represented in terms of any three endmember compositions of the reciprocal solution if negative compositions are allowed. For example, taking AC, BC and BD as independent endmembers, then the composition of the AD endmember is $y_{AC}=-1$, $y_{BC}=1$, $y_{BD}=1$; and the thermodynamic properties of the dependent endmember AD must be given by the solution model at this

Before going on to consider the complexities that may arise in silicate solutions, it may be useful to make the algebra of 12.10-12.14 less abstract by revisiting the halite (c=4, t=6) example. Taking KBr and CsBr as dependent endmembers, 12.10 is

$NaCl - KCl - NaBr + KBr = 0$

$NaCl - CsCl - NaBr + CsBr = 0$.

For a composition $Na_{1-x-y}K_xCs_yCl_{1-y}Br_y$ with $x = y = ⅓$ and $w = ½$, from 12.7, each endmember has a fraction of $\frac{1}{6}$, thus 12.14 gives

$$p_{NaCl}=y_{NaCl}-y_{CsBr}-y_{KBr} \qquad =-\tfrac{1}{6}$$
$$p_{KCl}=y_{KCl}+y_{KBr} \qquad =\tfrac{1}{3}$$
$$p_{CsCl}=y_{CsCl}+y_{CsBr} \qquad =\tfrac{1}{3}$$
$$p_{NaBr}=y_{NaBr}+y_{CsBr}+y_{KBr} \qquad =\tfrac{1}{2}\,.$$

A SILICATE EXAMPLE: CHLORITE

An important chemical exchange in silicates is the coupled **Tschermaks exchange**

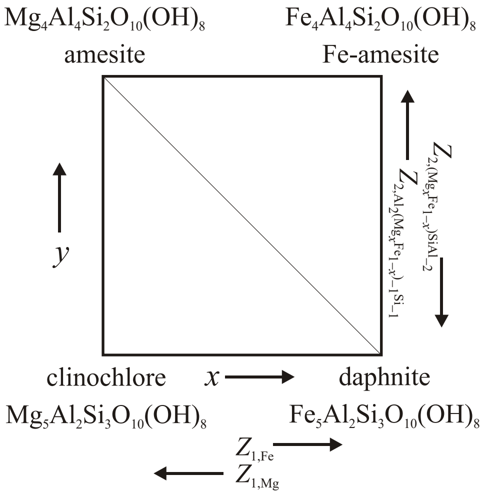

Fig 12.4 Reciprocal composition space of a chlorite model, although the solution can be described in terms of two independent exchanges, the chemical identity of the second (Tschermaks) exchange is dependent on the first. Moreoever, in contrast to the salt example of Figs 12.1-2, the chemical mixing sites do not correspond to crystallographic sites (Tab 12.1).

$Al^{VI}Al^{IV}M^{VI}_{-1}Si^{IV}_{-1}$ or simply $Al_2M_{-1}Si_{-1}$, in which Al^{3+} replaces a divalent cation M on an octahedral site and a tetrahedral Si. For a solution with more than one kind of divalent cation mixing on octahedral sites, the Tschermaks exchange is independent if the exchange does not alter the relative proportions of the divalent cations. Thus for an Fe-Mg-Al-silicate, the Tschermaks exchange is $Al_2(Fe_xMg_{1-x})_{-1}Si_{-1}$. As written, the Tschermaks exchange operator is only dependent on the number of divalent cations, i.e., 1+x–x, and as this number is constant, the Tschermaks exchange is independent. The combination of Tschermaks with $FeMg_{-1}$ exchange therefore results in a reciprocal solution, and as both exchanges are typical of Fe-Mg-Al-silicates, reciprocal solutions are an omnipresent feature of the petrologic landscape. To illustrate the complete formulation of a reciprocal silicate solution consider a chlorite model

$$(Fe_xMg_{1-x})_{5-y}Al_{2(1+y)}Si_{3-y}O_{10}(OH)_8 = Mg_5Al_2Si_3O_{10}(OH)_8 + x\ FeMg_{-1} + y\ Al_2(Fe_xMg_{1-x})_{-1}Si_{-1},$$
$$0 \le x \le 1, \quad 0 \le y \le 1 \qquad 12.16$$

where the basis endmember (x=0, y=0) $Mg_5Al_2Si_3O_{10}(OH)_8$ is known as clinochlore, as x and y are independent it is evident that the Chlorite is a reciprocal solution with two binary chemical mixing cites, therefore the composition space is the conjunction of two orthogonal 1-d simplexes at the clinochlore composition. The compositions of the remaining endmembers (Fig 12.4) can be deduced from 12.16 with {x=1, y=0}, {x=0, y=1}, {x=1, y=1}. Thus the chlorite has a quadrilateral composition space (c=3, t=4) and one dependent endmember.

Table 12.1 Endmember site populations for chlorite. The table shows only sites on which solution occurs, chlorite has two additional sites: one M4 occupied solely by Al, and two T1 sites occupied solely by Si.

	Site:	M	T
	q_i	5	2
Species:	Clin	Mg	$Al_{1/2}Si_{1/2}$
	Daph	Fe	$Al_{1/2}Si_{1/2}$
	Ames	$Mg_{4/5}Al_{1/5}$	Al
	fames	$Fe_{4/5}Al_{1/5}$	Al

Table 12.2 Endmember site populations for a chlorite model to depict the tendency of Al to order preferentially on one octahedral site (M1). This model is incorrect because the atomic site fraction of Al on the M1 site of ordered Fe-amesite (ofames) cannot be formed from a linear combination of the M1 site populations of ordered amesite (oames), daphnite, and clinochlore that satisifies conservation of mass (i.e., 12.18).

	Site:	M1	M2	T2
	q_i	1	4	2
Species:	Clin	Mg	Mg	$Al_{1/2}Si_{1/2}$
	Daph	Fe	Fe	$Al_{1/2}Si_{1/2}$
	Oames	Al	Mg	Al
	ofames	Al	Fe	Al

This example reveals a common complexity of silicate reciprocal solutions, in that the chemical mixing sites bear little or no relation the crystallographic sites (Table 12.1), a consequence of the fact that the Tschermaks substitution operates across sites. Additionally, although the exact chemical identity of the Tschermaks exchange cannot be specified without knowledge of the $FeMg_{-1}$ exchange, we can specifiy the composition of the chemical mixing sites representing Tschermaks solely as a function of the stoichiometric coefficient y deduced from the chlorite formula. Thus, we may express the species fractions on the two independent mixing sites as:

$$\begin{aligned} &Z_{\mathrm{M,Fe}} = x \\ &Z_{\mathrm{M,Mg}} = 1 - x \\ &Z_{\mathrm{T,Al_2(Fe_{\mathit{x}}Mg_{1-\mathit{x}})_{-1}Si_{-1}}} = y \\ &Z_{\mathrm{T,(Fe_{\mathit{x}}Mg_{1-\mathit{x}})SiAl_{-2}}} = 1 - y \end{aligned} \qquad 12.17$$

Given 12.17 and 12.7, the barycentric endmember fractions are

$$\begin{aligned} y_{\mathrm{clin}} &= Z_{\mathrm{M,Mg}} Z_{\mathrm{T,(Fe_{\mathit{x}}Mg_{1-\mathit{x}})SiAl_{-2}}} = (1-x)(1-y) \\ y_{\mathrm{daph}} &= Z_{\mathrm{M,Fe}} Z_{\mathrm{T,(Fe_{\mathit{x}}Mg_{1-\mathit{x}})SiAl_{-2}}} = x(1-y) \\ y_{\mathrm{ames}} &= Z_{\mathrm{M,Mg}} Z_{\mathrm{T,Al_2(Fe_{\mathit{x}}Mg_{1-\mathit{x}})_{-1}Si_{-1}}} = (1-x)y \\ y_{\mathrm{fames}} &= Z_{\mathrm{M,Fe}} Z_{\mathrm{T,Al_2(Fe_{\mathit{x}}Mg_{1-\mathit{x}})_{-1}Si_{-1}}} = xy \end{aligned}$$

Selecting Fe-amesite as the dependent endmember, and making use of the mass balance relation

$\tfrac{4}{5}$ clin $-\tfrac{4}{5}$ daph – ames + fames = 0. 12.18

The chemical difference

$\tfrac{4}{5}$ clin $-\tfrac{4}{5}$ daph = 4 $\mathrm{MgFe_{-1}}$

thus 12.18 can be rewritten

fames = ames – 4 $\mathrm{MgFe_{-1}}$ 12.19

where $\mathrm{MgFe_{-1}}$ is implicitly the Mg-Fe exchange operator for the octahedral site of chlorite. From 12.14, the independent endmember fractions are

$$\begin{aligned} p_{\mathrm{clin}} &= y_{\mathrm{clin}} - \tfrac{4}{5} y_{\mathrm{fames}} \\ p_{\mathrm{daph}} &= y_{\mathrm{daph}} + \tfrac{4}{5} y_{\mathrm{fames}} \\ p_{\mathrm{ames}} &= y_{\mathrm{ames}} + y_{\mathrm{fames}} \end{aligned} \qquad 12.20$$

For the sake of completeness, the components of a complete chlorite model, assuming a regular excess function are:

$$\begin{aligned} g^{\mathrm{mech}} &= p_{\mathrm{clin}} g^{\circ}_{\mathrm{clin}} + p_{\mathrm{daph}} g^{\circ}_{\mathrm{daph}} + p_{\mathrm{ames}} g^{\circ}_{\mathrm{ames}} \\ g^{\mathrm{ex}} &= W_{\text{clin-daph}} p_{\mathrm{clin}} p_{\mathrm{daph}} + W_{\text{clin-ames}} p_{\mathrm{clin}} p_{\mathrm{ames}} \\ &\quad + W_{\text{daph-ames}} p_{\mathrm{daph}} p_{\mathrm{ames}} \\ g^{\mathrm{conf}} &= -T \Delta s^{\mathrm{conf}} \end{aligned} \qquad 12.21$$

where Δs^{conf} is necessary because the clinochlore and daphnite endmembers have Al-Si disorder on the T2 site. From the site populations in Table 12.1 and 6.10

$$\begin{aligned} s^{\mathrm{conf}} = -\mathrm{R}[&5(z_{\mathrm{M,Mg}} \ln z_{\mathrm{M,Mg}} + z_{\mathrm{M,Fe}} \ln z_{\mathrm{M,Fe}} \\ &+ z_{\mathrm{M,Al}} \ln z_{\mathrm{M,Al}}) \\ &+ 2(z_{\mathrm{T,Al}} \ln z_{\mathrm{T,Al}} + z_{\mathrm{T,Si}} \ln z_{\mathrm{T,Si}})] \end{aligned}$$

where

$$\begin{aligned} z_{\mathrm{M,Mg}} &= p_{\mathrm{clin}} + \tfrac{4}{5} p_{\mathrm{ames}} \\ z_{\mathrm{M,Fe}} &= p_{\mathrm{daph}} \\ z_{\mathrm{M,Al}} &= \tfrac{1}{5} p_{\mathrm{ames}} + \tfrac{1}{5} p_{\mathrm{fames}} \\ z_{\mathrm{T,Al}} &= \tfrac{1}{2} p_{\mathrm{clin}} + \tfrac{1}{2} p_{\mathrm{daph}} + p_{\mathrm{ames}} \\ z_{\mathrm{T,Si}} &= \tfrac{1}{2} p_{\mathrm{clin}} + \tfrac{1}{2} p_{\mathrm{daph}} \end{aligned} \qquad 12.22$$

Evaluating 12.22 at the composition of pure daphnite and clinochlore yields $s^{\mathrm{conf}}_{\mathrm{clin}} = s^{\mathrm{conf}}_{\mathrm{daph}} = R \ln 4$ and for amesite $s^{\mathrm{conf}}_{\mathrm{ames}} = R \ln(3125/256)$. Thus, from 6.13,

$$\Delta s^{\mathrm{conf}} = s^{\mathrm{conf}} - p_{\mathrm{clin}} s^{\mathrm{conf}}_{\mathrm{clin}} - p_{\mathrm{daph}} s^{\mathrm{conf}}_{\mathrm{daph}} - p_{\mathrm{ames}} s^{\mathrm{conf}}_{\mathrm{ames}}.$$

Evaluating this model at the composition of Fe-amesite (i.e., $p_{\mathrm{clin}} = -\tfrac{4}{5}$, $p_{\mathrm{daph}} = \tfrac{4}{5}$, $p_{\mathrm{ames}} = 1$), the free energy of pure Fe-amesite is:

$$\begin{aligned} g^{\circ}_{\mathrm{fames}} &= -\tfrac{4}{5} g^{\circ}_{\mathrm{clin}} + \tfrac{4}{5} g^{\circ}_{\mathrm{daph}} + g^{\circ}_{\mathrm{ames}} \\ &\quad - \tfrac{16}{20} W_{\text{clin-daph}} - \tfrac{4}{5} W_{\text{clin-ames}} + \tfrac{4}{5} W_{\text{daph-ames}} \end{aligned}.$$

SPECIATION IN RECIPROCAL SOLUTIONS

A deficiency of the model just outlined is that in natural chlorites Al partitions preferentially, i.e., orders, into one of the five octahedral sites previously designated M (in addition to the M4 site, which was assumed to contain only Al). A first guess as to the model necessary to describe this behavior would logically be a reciprocal solution with endmember site populations as proposed in Table 12.2. Unfortunately, the model is incorrect because the site occupancy of the ordered Fe-amesite endmember cannot be formed by a linear combination of the site populations of the remaining endmembers that satisfies conservation of mass:

ofames = oames $-\tfrac{4}{5}$ clin $+\tfrac{4}{5}$ daph 12.23

This difficulty follows from the fact, that if the M1 and M2 sites are energetically distinct for Al, then they also must be energetically distinct for Fe and Mg. Microscopically, this means that chlorite is characterized by two thermodynamically independent $\mathrm{MgFe_{-1}}$ operators, one for M1 ($[\mathrm{MgFe_{-1}}]^{\mathrm{M1}}$) and another for M2 ($[\mathrm{MgFe_{-1}}]^{\mathrm{M1}}$), so the chemical difference $\tfrac{4}{5}$ clin $-\tfrac{4}{5}$ daph becomes

$\tfrac{4}{5}$ clin $-\tfrac{4}{5}$ daph = $\tfrac{4}{5}\,[\mathrm{MgFe_{-1}}]^{\mathrm{M1}}$ + $\tfrac{16}{5}\,[\mathrm{MgFe_{-1}}]^{\mathrm{M2}}$ 12.24

which cannot possibly yield the ofames site population in combination with the oames site populations because oames does not have Mg on the M1 site. The only means of resolving this dilemma is to introduce an additional endmember that allows us to discriminate between the energetics of the two substitutions. The anti-ordered amesite (aames) and Fe-amesite (afames) endmembers of our previous model serve this purpose (Table 12.3). In this case,

$$\text{aames} - \text{afames} = [\text{MgFe}_{-1}]^{\text{M1}} + 3\,[\text{MgFe}_{-1}]^{\text{M2}} \qquad 12.25$$

which can be combined with 12.24 to isolate $[\text{MgFe}_{-1}]^{\text{M2}}$ is possible to isolate the two octahedral exchanges as:

$$(\text{clin} - \text{daph}) - (\text{aames} - \text{afames}) = [\text{MgFe}_{-1}]^{\text{M2}}$$
$$\tfrac{4}{3}(\text{aames} - \text{afames}) - 3(\text{clin} - \text{daph}) = [\text{MgFe}_{-1}]^{\text{M1}} \qquad 12.26$$

Since aames and afames are chemically equivalent to oames and ofames, it is evident that the model must be a reciprocal solution with speciation. However the complete formulation of such a model is a little too much for these notes.

Table 12.3 Endmember site populations for a valid reciprocal chlorite model that accounts for Al-partitioning of Al preferentially on M1. The model is a reciprocal solution with speciation.

Site:	M1	M2	T2
q_i	1	4	2
clin	Mg	Mg	$\text{Al}_{0.5}\text{Si}_{0.5}$
daph	Fe	Fe	$\text{Al}_{0.5}\text{Si}_{0.5}$
oames	Al	Mg	Al
ofames	Al	Fe	Al
aames	Mg	$\text{Mg}_{3/4}\text{Al}_{1/4}$	Al
afames	Fe	$\text{Fe}_{3/4}\text{Al}_{1/4}$	Al

13:AN INDEX OF SORTS

EXAMPLE: C-O-H FLUID SPECIATION

For geological conditions, graphite-saturated fluids can to a good first approximation be considered mixtures of three molecular species water, carbon dioxide (CO_2) and methane (CH_4). Since the system is saturated in a pure carbon phase (graphite), the Legendre transform

$$\Omega = G - n_{\mathrm{C}} G^{\mathrm{o,graphite}}$$

allows us to eliminate carbon as a component with the result that the fluid has c=2 components (H,O) and t=3 species with the carbon-free compositions H_2O, O_2 (carbon dioxide) and H_4 (methane). Choosing X_{O} as the independent macroscopic variable, **EQ REF** yields

$$X_{\mathrm{O}} = \frac{\left(y_{\mathrm{H_2O}}\left[n_{\mathrm{H}}^{\mathrm{H_2O}} + n_{\mathrm{O}}^{\mathrm{H_2O}}\right] + y_{\mathrm{CO_2}} n_{\mathrm{O}}^{\mathrm{CO_2}}\right)}{\left(y_{\mathrm{CH_4}} n_{\mathrm{H}}^{\mathrm{CH_4}} + y_{\mathrm{H_2O}}\left[n_{\mathrm{H}}^{\mathrm{H_2O}} + n_{\mathrm{O}}^{\mathrm{H_2O}}\right] + y_{\mathrm{CO_2}} n_{\mathrm{O}}^{\mathrm{CO_2}}\right)} \qquad 12.27$$

and from **EQ REF**

$$y_{\mathrm{CO_2}} = 1 - y_{\mathrm{H_2O}} - y_{\mathrm{CH_4}}. \qquad 12.28$$

Substituting 12.28 into 12.27, and rearranging the result gives methane concentration

$$y_{\mathrm{CH_4}} = \frac{\left(\begin{array}{l}\left[\left(n_{\mathrm{O}}^{\mathrm{CO_2}} - n_{\mathrm{O}}^{\mathrm{H_2O}} - n_{\mathrm{H}}^{\mathrm{H_2O}}\right) y_{\mathrm{H_2O}} - n_{\mathrm{O}}^{\mathrm{CO_2}}\right] X_{\mathrm{O}} \\ + \left[n_{\mathrm{O}}^{\mathrm{H_2O}} - n_{\mathrm{O}}^{\mathrm{CO_2}}\right] y_{\mathrm{H_2O}} + n_{\mathrm{O}}^{\mathrm{CO_2}}\end{array}\right)}{n_{\mathrm{O}}^{\mathrm{CO_2}} - \left[n_{\mathrm{O}}^{\mathrm{CO_2}} - n_{\mathrm{H}}^{\mathrm{CH_4}}\right] X_{\mathrm{O}}} \qquad 12.29$$

as a function of the macroscopic composition X_{O} and y_{H2O}, the concentration of ordered species, a result can also be substituted into 12.28 to obtain CO_2 concentration as a function of X_{O} and y_{H2O}.

Since t–c = 1, there is only one independent reaction between the species of the form **EQ REF**!

$$\mathrm{CO_2 + CH_4 = 2H_2O} \qquad 12.30$$

(after projection through carbon); thus

$$\Omega^{\mathrm{mech}} = y_{\mathrm{H_2O}} \Delta\Omega \qquad 12.31$$

where $\Delta\Omega$ is the free energy change of 12.30. Given that the model is for a molecular fluid, a simple molecular configurational entropy model (6.9) is appropriate in which case

$$S^{\mathrm{conf}} = -R\left[y_{\mathrm{H_2O}} \ln\left(y_{\mathrm{H_2O}}\right) + y_{\mathrm{CO_2}} \ln\left(y_{\mathrm{CO_2}}\right) + y_{\mathrm{CH_4}} \ln\left(y_{\mathrm{CH_4}}\right)\right] \qquad 12.32$$

and, for the sake of simplicity, neglecting non-ideality

$$\Omega^{\mathrm{sol}} = \Omega^{\mathrm{mech}} - TS^{\mathrm{conf}}$$

which after substituting the expressions for $y_{\mathrm{CO_2}}$ and $y_{\mathrm{CH_4}}$ as functions of X_{O} and y_{H2O} from 12.29 and 12.28 can be differentiated with respect to y_{H2O} and equated to zero to solve for y_{H2O} as a function of X_{O}, pressure and temperature. This expression is too ugly to produce here, but it is easily generated and solved in maple (Problem 9.1).

PROBLEM

11.1 Using the graphite-saturated COH fluid speciation model as formulated in the preceding example to calculate the speciation at 1000 K and 1 kbar for $X_{\mathrm{O}} = 0.1$, 1/3 and 0.8. At these conditions $\Delta\Omega$ for reaction 12.30 is -80000 J/mol H_2.