Four fundamental questions

why is the Earth hot?

how long does it take to cook a rock?

why are rocks made of minerals?

why are individual rocks made of so few minerals?

If you can answer these four questions then you will pass this course!

If you can understand the importance of these four questions then you will be a metamorphic geologist!

Preamble

Metamorphic geology is a *fantastic subject*!

This is not just because metamorphic rocks form the great proportion of all the rocks in the continents but, more importantly, because of the insight that metamorphic rocks provide into the history of ancient mountain systems in our planet earth. The life and death of mountains is, after all, what geology is about!

In order to understand what metamorphic rocks tell us about the history of mountain belts we need to understand:

- the basic petrological techniques for extracting information concerning the P-T evolution of metamorphic rocks, and

- the basic physical properties controlling the distribution of heat within the continental lithosphere and how this distribution is modified during deformation in orogenic zones.

We will!

The primary motivation for these notes is provided by the absence of a text that reflects my particular metamorphic prejudices[1]. Also, I strongly suspect that for most students note taking during lectures is something of a displacement activity tending to obscure the significant and fundamental meta-

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[1] An excellent general coverage of metamorphic geology is provided by Yardley, 1980, while Powell, 1978, is the best available text on theoretical phase petrology, and Chapter 4 in Turcotte and Schubert, 1982, provides an excellent introductory section on heat flow theory)

morphic transformation[2]. These notes, then, are designed to provide an alternative to lecture notes. In general the notes go beyond the scope of the lectures but, nevertheless, cover fundamental aspects of metamorphic geology[3]. The notes are by no means comprehensive, fundamental or final; they will evolve with my understanding and yours. Your comments on the errors, structure, usefulness, etc., of the notes are essential for the future.

Our aim is to understand the deep interior of mountain belts! We will follow the metamorphic rock along its pressure-temperature-time (P-T-t) journey through incorporation into, and excavation from, the mountain belt.

Good Luck!

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[2]Is there really an inverse correlation between note taking and understanding?

[3]Some sections of the notes, designated by asterisks, will not be covered in the lecture series but should provide a challenge to those of you who find the rest easy.

Chapter 1

The direction of metamorphic time

1.1   The concept of metamorphic time

Metamorphism proceeds as rocks are buried in, and excavated from, mountain belts. Metamorphic geologists view this burial - excavation cycle of a metamorphic rock as a pressure-temperature-time (P-T-t) path (Figure 1.1). The metamorphism is the transformation in the mineralogy and fabric in the rock in response to the changing physical and chemical environment encountered on the P-T-t path.
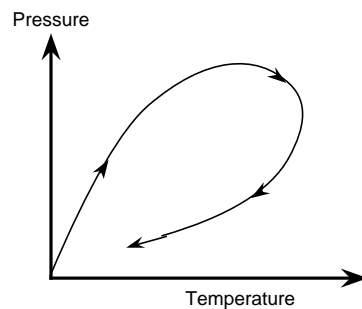

Figure 1.1:   The evolution of a metamorphic rock as it is buried and excavated from a mountain belt can be mapped as a path onto pressure-temperature (P-T) space. The time dimension of the P-T-t path, or the direction of metamorphic time, is indicated by the arrows.

In order to understand the precise behaviour of an individual rock as it travels through P-T-t space we need to understand the interaction between the forces that lead to change and those forces that oppose change:

The driving force for change. A change in the mineralogy of a metamorphic rock is always driven by the tendency to reduce the particluar form of chemical energy known as *Gibbs free energy*. Just as in a gravitational field all spontanaoues movement (reaction) is to reduce gravitational potential energy, all spontaneous reaction in a chemical system is driven by the potential to reduce the Gibbs free energy of the chemical system, which is a function of the physical environment (i.e., P and T) and the mineralogical and textural makeup of the rock. Much of metamorphic geology involves the application of principles of equilibrium thermodynamics, which are based on the assumption that metamorphic rocks preserve mineralogical associations that represent minimum Gibbs free energy configurations. At most, this assumption can be only partly true (since metamorphic rocks are manifestly not in equilibrium at the Earths surface). The assumption requires that at least for some part of their P-T-t history metamorphic rocks follow a sort of *chemical path of least resistance* in which there is little or no hinderance to chemical reaction.

The resistance to change. Like so many things of this world, change in chemical systems is resisted by a sort of *chemical inertia* or *sloth* associated with the high energies associated with transition from one state to another.

The interaction of these opposing forces leads to complex textural relationships between minerals in metamorphic rocks: textural relationships which encode in some fundamental way information about the P-T-t path. In other words, metamorphic textures provide the key indication of the direction of metamorphic time.

In order to unravel the P-T-t history of ancient metamorphic rocks we need, in addition to a sound textural interpre-

tation, an ability to understand two somewhat abstract, and not altogether unrelated, notions concering *reaction* and *projection*. The chemical and mineralogical systems that are the individual metamorphic rocks are complex. This raises the importnat question of /em how can one begin to know what transformations or reactions are possible for a given rock as it travels along its P-T-t path? Fortunately, very simple principles apply to the reaction possibilities between the discrete phases that make up rock systems, which may be formalised in linear algebra. What is less obvious is the way in which very small variations in composition may radically alter the potential reaction history along any given P-T-t path. In order to illustrate this subtle dependence of the reaction possibilities on composition, metamorphic geologists rely heavily upon the device called the *projection*.

1.2 Textures

In this course we will assume some familiarity with textural relationships in metamorphic rocks (remember 2nd year practicals), and therefore not discuss textures in any formal way. However, it is important to remember that understanding textures is fundamental since textures provide critical information concerning[1]:

- the relative timing of growth of, and nature of reactions that may have occurred between, the minerals that make up a metamorphic rock;

- whether textural (and hence chemical) equilibration has occurred between different mineral types; and

- the nature of the strain or deformation history during and subsequent to mineral growth.

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[1]For those interested, the papers by Vernon and also Bell and co-workers in recent issues of the *Journal of metamoprhic Geology* provide some idea of the types of insights (and controversies) obtainable from the interpretation of metamorphic textures (see also the book by Spry, Metamorphic Textures.

1.3   Metamorphism and rest of geology

As with all branches of the science, metamorphic geology cannot be viewed in isolation from the other Earth science sub-disciplines; especially, structural and igneous geology. Because metamorphism results from the passage of rocks through the crust, it is intimately associated with deformation processes, and consequently there is a great overlap between metamorphic geology and structural geology. Similarly, the reactions that lead to the formation of silicate melts within the deep interior of the Earth are fundamentally metamorphic transformations, and consequently metamorphic and igneous geology have much in commmon. In a similar vein, ore genesis and metamorphic geology share many common threads, while the fundamental equations expressing the conservation of energy, and which dictate the thermal evolution of metamorphic rocks, are at the heart of solid-Earth geophysics.

Despite this the techniques of metamorphic geologists (particularly metamorphic petrologists) have their own distinct flavour and it is this flavour that we wish to impart in this course!

Chapter 2

The heat of the matter

To understand what controls the P-T-t paths experienced by rocks as they travel through mountain belts we need to understand the factors that govern the baric (or pressure) and thermal (or temperature) evolution of material points within deforming orogenic belts.

Pressure changes experienced by metamorphic rocks can largely be related to changes in the depth of burial. The two prime factors that control the depth of burial of rocks in orogenic belts are *deformation* and *erosion*, and therefore the baric record of metamorphic rocks provides an insight into the relative rates of deformation and erosion in ancient mountain systems. Note that while erosion always results in exhumation and consequently decompression of metamorphic rocks, deformation can result in both burial and exhumation. In active mountain systems, deformation and erosion are intimately coupled, such that the structural geometry, as well as thermal regime, may be dictated by the erosional regime, which in turn is strongly influenced by the climatic regime. This coupling is so profound, that some geologists have suggested that the *weather-facing* of orogenic systems will be reflected in an asymmetry in structural and metamorphic features preserved in orogenic belts! During typical orogenic cycles rocks are routinely buried to, and subsequently exhumed from, depths of between 10 and 30 kilometres. In rare cases, rocks are exhumed from much deep levels, with some metamorphic terranes preserving

records of exhumation from depths of up to 120 kilometres (eg., Doria Maira in the western Italian Alps, and Dabie Shan in China).

At our level, the concepts needed to understand the thermal evolution of metamorphic rocks (ie., T-t paths) are more comlex than the associated baric changes (although, at a still deeper level, the factors controlling the mechanical evolution of orogenic belts remain one of the most complex of all issues in Earth science!) This chapter focuses on the basic principles needed to understand thermal regimes in orogenic belts.

The Earth is a heat engine, and as with all such devices it is doomed eventually to die! Indeed, it is this very heat loss that is responsible for lithospheric growth and ultimately provides the energy source driving the motions of the lithosphere. Heat loss from the Earth's interior is accompanied both by conduction and advection, which can be simply codified in terms of the requirement for the conservation of energy - and which therefore can serve to illustrate one of the great conservation principles of physics.

Conservation principles express the simple reality of *what goes in must come out!*

2.1   Conduction and advection

Thermal energy may be transported in two fundamentally different modes; namely by conduction and by advection. In the former heat diffuses through matter while in the latter it is carried by the physical transport of the matter.

Conduction

Everyday experience witnesses the fact that thermal energy is transferred from hot bodies to cool bodies, with the rate of thermal energy transfer, or heat flow, dependent on the nature of the material and the temperature difference across which the heat flows. Fourier postulated that the heat flow, q, is proportional to the negative of the temperature gradient, because heat flows down temperature gradients, with the constant of proportionality given by a material dependent parameter known as the conductivity, k, a postulate consistent with

most subsequent experimental investigation:

$$q = -k \operatorname{grad} T \qquad (2.1)$$

Written in this form grad T signifies the gradient of T (often written in the equivalent form ∇T) and as such is a vector operator. That is, grad defines the magnitude and direction of the gradient of a scalar quantity such as temperature.

Advection

The physical motion of material results in advective transport of heat. Using a *Eulerian description* it is easy to see that the rate of heat advected through a fixed point is dependent on the velocity of material transport and the temperature gradient. Thus, as either the temperature gradient or the velocity tends to zero, the rate of heat advection must also tend to zero.

2.2 The thermal energy balance*

In order to understand the thermal evolution of material subject to conductive heat transfer it is necessary to derive the thermal energy balance that expresses the fundamental physical constraint provided by the requirement of *conservation of energy*. Ignoring the advection of heat through the movement of the medium, then the thermal energy balance in a control volume can be expressed simply as:

rate of gain of thermal energy

=

rate of thermal energy flowing into the control volume

-

rate of thermal energy flowing out of control volume

+

rate of heat production in control volume

$$(2.2)$$

Since the thermal energy of a volume of unit dimensions is given by:

$$C_p \, \rho \, T$$

In a three-dimensional orthogonal coordinate system, x, y, z, grad T is:

$$\operatorname{grad} T = \nabla T$$

$$= \left(\frac{\partial T}{\partial z}, \frac{\partial T}{\partial y}, \frac{\partial T}{\partial z} \right)$$

That is, the gradient of T is perpendicular to the planes of constant temperature or isotherms.

In many problems in fluid mechanics we can distinguish between a Eulerian and Lagrangian description. In the former, the description is in terms of a fixed spatial reference frame through which the fluid flows while in the latter the description is in terms of a moving reference frame attached to individual fluid particles.

where C_p is the heat capacity, the first term in Eqn 2.2, the *rate of gain of thermal energy*, can be expressed simply as

$$\frac{\partial (C_p \, \rho \, T)}{\partial t}$$

which for temperature independent ρ and C_p is equivalent to

$$C_p \, \rho \, \frac{\partial T}{\partial t}$$

The difference between the second and third terms in Eqn 2.2 gives the negative of the divergence of the heat flow across the boundary of the control volume:

$$-\operatorname{div} q$$

The divergence of a vector field such as q is a scalar quantity and can be expresses equivalently as

$$\operatorname{div} q = \nabla \cdot q = \frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z}$$

Note that the negative sign arises because divergence actually measures the rate of loss whereas in Eqn 2.2 we are really interested in the rate of gain (or convergence). Assuming that k is independent of T then the difference between the second and third terms in Eqn 2.2 can be expressed in terms of T by substituting the expression for q given in Eqn 2.1:

$$
\begin{aligned}
k \operatorname{div} (\operatorname{grad} T) \; &= k \, \nabla \cdot (\nabla T) \\
&= k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right)
\end{aligned}
$$

The final term in Eqn 2.2 is given by:

$$\rho \, H$$

where H is the heat production per unit mass.

Thus the thermal energy balance given by Eqn 2.2 can be expressed in the following mathematically equivalent ways:

$$
\begin{aligned}
\frac{\partial T}{\partial t} \; &= \kappa \left(\operatorname{div} (\operatorname{grad} T) \right) + \frac{H}{C_p} \\
&= \kappa \left(\nabla \cdot \nabla T \right) + \frac{H}{C_p} \\
&= \kappa \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + \frac{H}{C_p} \qquad (2.3)
\end{aligned}
$$

a : Temp (scalar field)   b : dT/dz (ºC m⁻¹)   c : d2T/dz2 (ºC m⁻²)

grad T gives:
slope of T field

div (grad T) gives
(1) slope of grad T, or
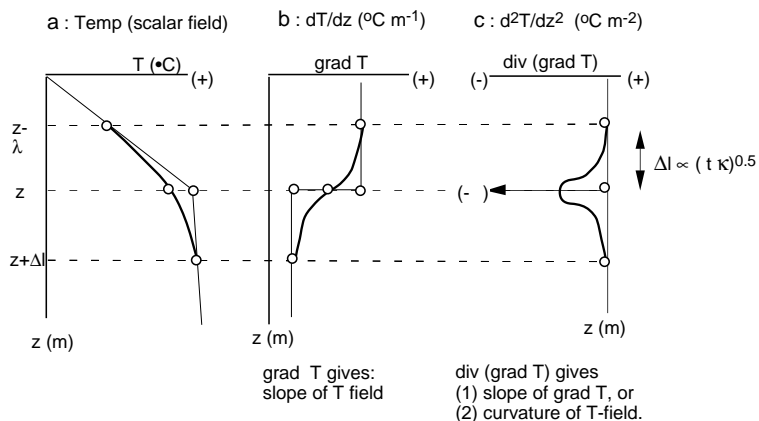(2) curvature of T-field.

Figure 2.1: Schematic relationship between a temperature field (a) and its first (b) and second (c) derivative.

where κ is the thermal diffusivity:

$$\kappa = \frac{k}{\rho\, C_p'}$$

The various forms of the thermal energy balance in Eqn 2.3 form the *diffusion equation* or, alternatively, the heat equation.

The *diffusion-advection equation* appropriate to whole rock advection, is obtained by adding an additional term to Eqn 2.3 which expresses the rate at which heat is advected through a point. This advective contribution is given by the product of the velocity and the temperature gradient, giving:

$$\frac{\partial T}{\partial t} = \kappa \nabla^2 T - v.\nabla\, T + \frac{H}{C_p} \qquad (2.4)$$

where the second term on the right is the *advective* term.

For many purposes, it is useful to recast Eqn 2.4 in a dimensionless form:

$$\frac{\partial T'}{\partial t'} = \nabla^2 T' - Pe_T\, \nabla\, T' \qquad (2.5)$$

where the dimensionless variable T' and t' are given by

$$T' = T/T_0$$

$$z' = z/l$$

$$t' = t\kappa/l^2$$

where l is the appropriate length-scale (for example, the thickness of the lithosphere), and T_0 is the characteristic temperature difference at the appropriate length-scale. In Eqn 2.5 Pe_T is the thermal Peclet number which is a dimensionless variable

$$Pe_T = \frac{v\,l}{\kappa}$$

The Peclet number expresses the ratio of the advective to diffusive terms. For $Pe_T > 10$ the advective term dominates the thermal evolution and diffusion can be largely ignored (ie., the first term on the right of Eqn 2.4 is small compared to the second term), while for $Pe_T < 1$ diffusion dominates and the advective term can be largely ignored. For $1 < Pe_T < 10$ both diffusion and advection contribute to the thermal evolution.

2.3   Thermal time constants

It is useful to define the characteristic diffusive response time to thermal perturbations when heat is transferred by conduction. For example consider a bunsen burner applied to the base of a conducting plate (geologically, this is analagous to the impingement of a mantle plume on the base of the lithosphere). We are interested in how long it takes for the top surface to feel the effect of the perturbed lower boundary condition. Clearly the response time depends on the length-scale (i.e. the thickness of the plate) and (inversely) on the thermal conductivity (or, equivalently, diffusivity). In this problem we can ignore the effects if internal heat production (which does not change the response time to a change in boundary conditions). From Eqn 2.3 the term on the left, $\frac{\partial T}{\partial t}$, gives the order the temperature divided by the timescale for thermal response, τ. Similarly the first term on the right of Eqn 2.3, $\kappa\,(\mathrm{div}\,(\mathrm{grad}\,T))$, is of order $\kappa T/l^2$, where l is the appropriate length scale. Equating the two quantities gives :

$$\tau \propto \frac{l^2}{\kappa}$$

The constant of proportionality normally used is $1/\pi^2$ giving:

$$\tau = \frac{l^2}{\pi^2 \, \kappa}$$

For the lithosphere typical parameter values are $l = 125$ km and $\kappa = 10^{-6}$ m ^{2} s^{-1} giving $\tau = 50$ Ma.

An important feature of the thermal time constant is its dependence on l^2. For the lithosphere this implies that short wavelength fluctuations are damped on timescales which are very short compared to lithospheric-scale perturbations (and, incidently, explains why a 3 m deep cellar is insensitive to seasonal atmospheric temperature fluctuations).

2.4   Continental geotherms

In the steady-state, that is when $\frac{\partial T}{\partial t} = 0$, and when heat flow is only in one direction, z, Eqn 2.3 reduces to the ordinary differential equation:

$$0 = k \frac{d^2 T}{d z^2} + \rho \, H \tag{2.6}$$

With knowledge of how H varies with depth, and appropriate boundary conditions, Eqn 2.6 can be integrated to yield a geotherm (ie., and expression for T in terms of z). For example, assuming a constant distribution of heat producing elements with depth, Eqn 2.6 can be integrated using the boundary conditions appropriate to the continental lithosphere: $q = -q_s$ at $z = 0$ (i.e., the heat flow at the surface of the lithosphere in the direction of increasing depth is the negative of the surface heat flow), and $T = T_s$ at $z = 0$ (i.e., the temperature at the top of the lithosphere is the surface temperature). The resulting integration yields the expression

$$T_z = T_s + \frac{q_s \, z}{k} - \frac{\rho \, H \, z^2}{2k} \tag{2.7}$$

relating the temperature at any depth, z, to the conductivity, surface temperature, T_s, surface heat flow, q_s, and heat production, H. The base of the lithosphere is defined by the temperature sensitive rheological properties of peridotite and can

therefore be treated as an isotherm, $T_l = 1280^{o}C$. The heat flow at the surface of the lithosphere, q_s, therefore reflects the thickness of the lithosphere as well as the distribution of heat sources within the lithosphere.

2.5 P-T-t paths

Chapter 3

Sloth

3.1 Kinetics, Nucleation and Reaction Rates

To understand why metamorphic rocks are able to persist in the atmospheric environment where they are obviously metastable we need to understand something of the driving forces for, and kinetics of, mineral reactions. The fundamental driving force for reactions is provided by the Gibbs energy difference between reactants and products (ΔG), with reactions proceeding towards the lowest energy configuration. Equilibrium coexistence of reactants and products will occur only under the environmental conditions at which $\Delta G = 0$; a relationship which we will make extensive use of in the application of thermodynamics. As we can see from Figure 3.1, and its mechanical analogue in Figure 3.2, in order to pass from a metastable to stable equilibrium we need to pass through an activated or transition state where the Gibbs energy exceeds that of the initial metastable state. The energy difference between the activated state and the initial metastable state provides an activation barrier to reaction. It is this energy of activation (E_a) that allows the possibility of the persistence of mineral assemblages beyond their own stability field.

Activation barriers exist because of the high energy configuration of any component of the reacting system in the activated state, and because of the additional contribution of surface or, more strictly, interfacial energy terms to the total Gibbs energy
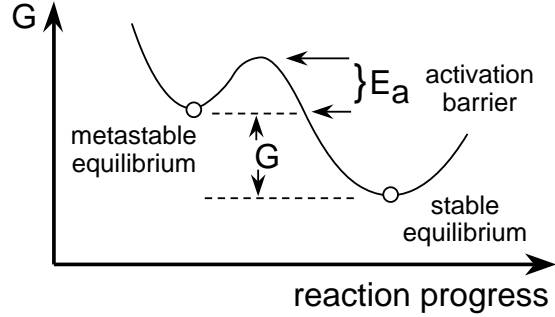
Figure 3.1: Schematic diagram showing Gibbs energy as a function of reaction progress between a metastable and stable configuration.
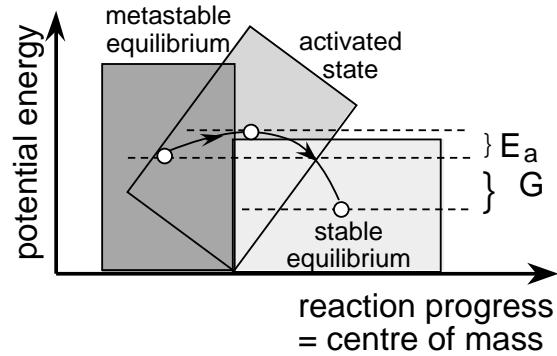

Figure 3.2: Mechanical analogue to metastability and activation.

for very small crystal nuclei or embryos. Consider the effect of nucleating a very small embryo of a new phase β in an old phase α. The Gibbs energy of formation of a new embryo is a function of its radius, r, and is given by the relation:

$$\Delta G_r = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

where ΔG_v is the difference in free energy of α and β per unit volume without consideration of interfacial energy terms, γ is the interfacial energy of the α - β interface. The second term, the interfacial energy term, is always positive. If the temperature is such that α is the stable phase ($T > T_c$ in Figure

3.3) then the first term, the volume energy term, is also positive and there is no energetic gain provided by the transformation to β. If β is the stable phase ($T < T_c$ in Figure 3.3) then the first term is negative, but for small r is less important than the second term. With increasing r the ΔG_r passes through a maximum which represents the critical radius, r_c. Growth of embryos with radius smaller than r_c leads to an increase in ΔG_r, the tendency is therefore for such embryos to shrink rather than grow. Embryos larger than r_c are stable because increased growth is accompanied by a decrease in ΔG_r (Figure 3.3).
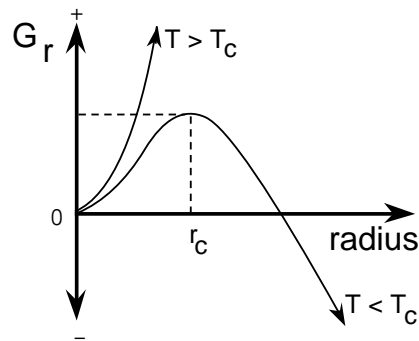
Figure 3.3:   The Gibbs energy of formation of spherical embryos as a function of radius for a temperature above ($T > T_c$) and below ($T < T_c$) the equilibrium temperature for reaction. At $T < T_c$ embryos with radius smaller than r_c are unstable, because increased growth increases ΔG_r.

The critcal radius, r_c, is defined as the radius where

$$\frac{\partial \left(\Delta G_r \right)}{\partial r} = 0$$

$$= 4 \pi r^2 \Delta G_v + 8 \pi r \gamma$$

therefore

$$r_c = \frac{-2\gamma}{\Delta G_v}$$

and the Gibbs energy of activation ΔG^* (i.e., ΔG_r at r_c) is therefore,

$$\Delta G^* = \frac{16 \pi}{3} \frac{\gamma^3}{\Delta G_v^2}$$

To understand the nature of reactions in the metamorphic environment, consider Figure 3.4, which shows schematically how the driving force for a reaction increases with increasing overstepping of the equilibrium conditions of reaction. In an environment where temperature is decreasing (ie., a retrograde metamorphic regime), the corresponding increase in ΔG or the driving force for reactions with increased undercooling is countered by the fact that reaction rates decrease significantly with decreasing temperatures. The relationship between reaction rate and temperature is given by the rate equation:

$$\text{Rate} = A\,exp^{\left(\frac{-E_a}{RT}\right)}$$

where A is a constant termed the frequency factor, E_a is the activation energy, and R is the gas constant.
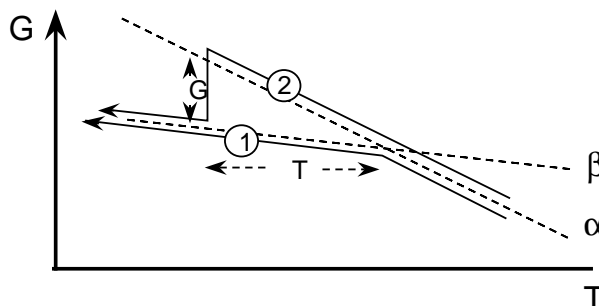
Figure 3.4:   Schematic $T - G$ diagram showing two possible reaction histories on a cooling path from α stable high temperature assemblage, α, to the stable low temperature assemblage, β. The equilibrium co-existence of the two phases occurs at the temperature where they have identical Gibbs energy (T_c). Path 1 shows the phase transition occurring at T_c and therefore is an equilibrium or reversible transition. Path 2 shows the metastable persistence of phase a beyond T_c, with transition occurring after undercooling by ΔT, and hence is a non-equilibrium or irreversible transition. Notice the greater the undercooling the greater the ΔG between reactants and products and hence the greater the driving force for the reaction.

The amount of overstepping before a given reaction will depend particularly on the rate of change of temperature through

the critical temperature. The common preservation of metastable metamorphic assemblages at the surface of the Earth indicates that cooling rates have been sufficiently fast that retrograde reaction has been prohibited. We can illustrate the influence of cooling rates and reaction conveniently on temperature-time-transformation $(T - T - T)$ diagrams (Figure 3.5).

In contrast with retrograde environments, in prograde environments (increasing temperature, see Figure 3.6) both the driving force for reaction and the rate of reaction increase with increasing overstepping of equilibrium transformation temperature. Thus we can see that any tendency for metastable persistence must be inherently more limited in the prograde metamorphic environment than in the retrograde environment.
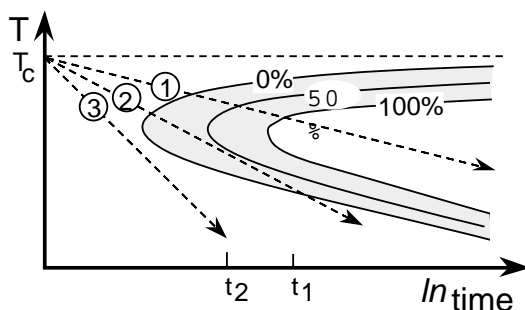
Figure 3.5: Schematic T-T-T diagram showing the characteristic C-shape of retrograde transformation curves in temperature-lntime space. Tc is the equilibrium temperature of the transformation. The stippled region shows the region of active transformation bounded by the 0%, 50% and 100% transformation progress curves. Three simple temperature-time paths are shown, with cooling rate slowest in path 1 and fastest in path 3. In path 1 reaction goes to completion at time t_1. In path 2 reaction progress is 50% at time t_2 but reaction does not go to completion. In path 3 there is no reaction.

The rate of a sluggish reaction can be increased by providing a catalyst or by adding energy to the metastable system, and thus reducing the Gibbs energy of activation. Deformation provides energy to mineral systems, largely accommodated by creation and movement of defects in the crystal lattice and thus we may expect that the tendency for metastability is greatly
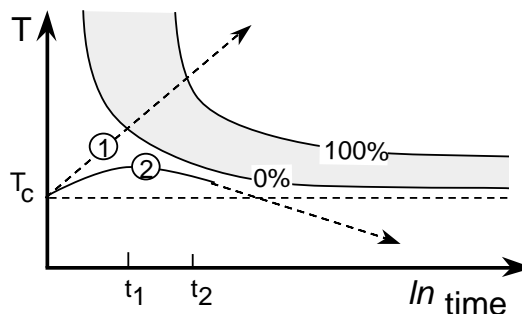
Figure 3.6: Schematic $T - T - T$ diagram showing the character-
istic shape of prograde transformation curves in temperature-lntime
space. T_c is the equilibrium temperature of the transformation. The
stipled region shows the region of active transformation bounded
by the 0% and 100% transformation progress curves. Two simple
temperature-time paths are shown. In path 1 reaction begins at t_1
and goes to completion at time t_2. In path 2 there is no reaction.

reduced during active deformation. Deformation and prograde
metamorphism are often related in time. This is not merely
fortuitous, but rather is due to a fundamental link between the
deformation and heating of the continental lithosphere. Be-
cause of this link, prograde assemblages tend to react quickly
as they pass beyond their own stability field. Contrawise, the
retrograde environment is not typically accompanied by defor-
mation, with reaction rates tending to be slow, and metastable
assemblages persisting well outside their appropriate stability
field. Retrograde shear zones in high grade gneissic terrains
provide ample testimony to this intimate relationship between
deformation and metamorphic reaction.

Further Reading

Burke, J., 1965, The kinetics of phase transformations in
       metals. Pergamon Press.
       - advanced if somewhat dated reading on the kinetics of phase
       transformations.

Putnis, A., and McConnell, J.D.C., 1980, Principles of Min-

eral Behaviour. Blackwell Scientific Publications.
- a good summary of Burke (1965), $G - X$ diagrams and TTT
diagrams.

Chapter 4

Projection and reaction

4.1 A choice of Components

Assemblages are, by definition, composed of one or more phases. Since the phases present in any given assemblage (usually) have different compositions, we need a formal way of describing this compositional variation. We describe the composition of phases in terms of components, such that each phase consists of one or more components. The way in which we choose components is critical to the subsequent analysis of the assemblages and systems. We must choose our components to minimize the number of chemical entities that are required to describe completely the compositions of all the phases in the system of interest. If this is done the components are said to be independently variable.

Worked Example

The way in which we describe the system consisting of aluminium, silicon and oxygen depends on the phases we are interested in. If the system includes quartz (SiO_2), sillimanite (Al_2SiO_5) and corundum (Al_2O_3), then the minimum number of independently variable components needed to describe the system is two (i.e., SiO_2 and Al_2O_3). Since sillimanite is a mixture of these two components, we do not need a third component to describe its compostion. On the other hand, if we are interested in a system with only the Al_2SiO_5 polymorphs, sillimanite, kyanite and andalusite then the minimum number of independently variable components needed to describe the

composition of the three phases is just one, namely Al_2SiO_5.

It is obvious from Figure 4.1 that sillimanite lies in a compositional space between corundum and quartz, and therefore it is possible to write a reaction between the three phases:
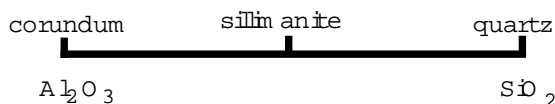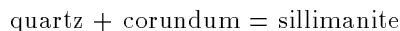
quartz + corundum = sillimanite

Figure 4.1:   Graphical representation of the binary system Al_2O_3-SiO_2 with the phases quartz, sillimanite and corundum.

One of the most important consequences of choosing components correctly is that it is always possible to write a balanced reaction between $(n + 1)$ phases, where n is the number of independently variable components. The important lesson is that if we *choose the components correctly the reactions fall out!*

While there is necessarily a minimum number of independently variable components to describe any system of specified phases, the choice of the components is not necessarily unique. For instance, the pelite system containing the phases quartz, andalusite, chlorite, biotite, muscovite, rutile and staurolite can equally well be described by each of the following seven component systems :

K_2O-Al_2O_3-FeO-MgO-SiO_2-TiO_2-H_2O
or
$KAlO_2$-Al_2O_3-FeO-MgO-SiO_2-TiO_2-H_2O

Each set is an equally valid set of independently variable components, and the choice between them is largely irrelevant to the subsequent analysis.

4.2   Projections

In binary systems it is obvious that we can write reactions between three phases, as is easily shown graphically in one dimension. However, there are very few natural rocks with phase

compositions that can be described by only two independently variable components. More frequently we have to deal with upwards of six or more independently variable components, and it is therefore not easy to visualize exactly what reaction relationships might exist between the phases in a given rock or sequence of rocks. For instance, many pelitic rocks have phase compositions that can, to a first approximation, be described by the components K_2O (or $KAlO_2$), FeO, MgO, Al_2O_3, SiO_2, TiO_2 and H_2O (which we abbreviate to KFMASTH). In order to graphically portray the compositional variance of this 7-component system we would need to be able to visualise a 6-dimensional space. This is clearly not easy, and potentially provides a severe limitation to the graphical representation of the phase relationships amongst pelitic (and other) rocks.

The problem of having to deal with multidimensional compositional space in portraying metamorphic phase relations, including all the potential reaction relationships between phases, is alleviated in rocks in which certain minerals are invariably present, independent of the other phases in the assemblage. For instance, at low and medium metamorphic grades, pelitic rocks invariably contain quartz, muscovite, and an Fe-Ti oxide (ilmenite and/or rutile). Such phases are termed saturating phases. Moreover, during metamorphism pelitic schists almost certainly contained a metamorphic fluid phase dominated by H_2O. Because these saturating phases are always present during the low-medium grade metamorphism of pelitic rocks, there is no need to illustrate the compositional control on their appearance. The significance of the saturating phase in pelitic rocks can be seen with respect to the reaction below:

$$chl + st + mu + qtz + ilm = and + Ti\text{-}bt + v \quad (1)$$
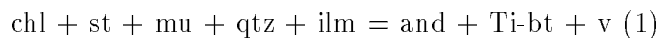
This prograde reaction would continue after heating beyond the critical temperature of reaction until one of the reactant phases is exhausted. For normal pelitic compositions, the saturating phases muscovite, quartz, vapour and rutile are sufficiently abundant never to be exhausted by this or indeed any other reaction, thus either chlorite or staurolite would disappear and the final assemblage at the completion of reaction would be either:

mu - qtz - ilm - Ti-bt - and - v - chl

or

mu - qtz - ilm - Ti-bt - and - v - st

The important point is that the saturating phases (or those phases in excess) do not limit the extent of reaction, or the phase assemblage, at the completion of reaction. Ignoring the saturating phases the reaction above can equally well be written:

chl + st = and + Ti-bt (+ qtz, mu, ilm, v)

The univariant reaction written this way (i.e., without explicitly including the saturating phases) includes only four phases. According to the phase rule (see later), the composition of four phases in reaction relationship can be described in terms of only three components. In writing the reaction in this way we have effectively used each one of our saturating phases to remove one of the seven independently variable components in our KFMASTH pelite system. Specifically, we have used quartz to remove SiO_2, ilmenite to remove TiO_2, vapour to remove H_2O, and muscovite to remove either K_2O, Al_2O_3 or $KAlO_2$ depending on our choice of system components. If we use muscovite to remove the $KAlO_2$ (or K_2O) then the remaining three components are Al_2O_3-FeO-MgO or AFM which can easily be portrayed graphically in two dimensions on a ternary compatibility diagram. Two different AFM compatibility diagrams are shown in Figures 4.2 & 4.3 indicating the phase relations prior to and following reaction (1).

To illustrate how we have effectively removed the component KAlO2 by treating muscovite as a saturating phase consider the reduced four component system KAFM in the Figure 4.4, which shows the projection of biotite, from muscovite onto the AFM plane. Using projections from saturating phases, as in the above example pelitic system, it is possible to reduce the number of controlling compositional dimensions of many systems sufficiently that the important phase relationships including all potential reaction relationships between non-saturating phases can be easily portrayed graphically. Once we have developed the mathematical basis for projections it will also possible to use the projective compatibility diagrams to illustrate,

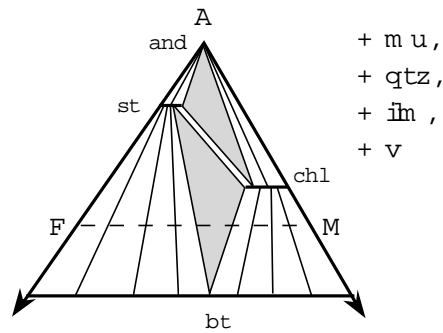quantitatively, the compositional variation of minerals in metamorphic assemblages.

Figure 4.2: AFM compatibility diagram showing the compositions of possible coexisting phases prior to reaction (1). Note that both biotite and andalusite can exist at temperatures below the critical temperature for reaction (1), but they cannot coexist.

4.3 Reactions in Metamorphic Rocks

Compatibility diagrams such as the AFM diagram provide a useful tool for understanding two fundamentally different types of reactions that occur in metamorphic rocks. Figure 5.5 illustrates one of these reaction types, the discontinuous reaction. In a discontinuous reaction a tieline connecting one pair of minerals (e.g., chlorite and staurolite) becomes unstable with respect to another tieline (e.g., biotite and andalusite). Consequently, discontinuous reactions are manifest as a *radical reorganization of the compatibility relationships amongst coexisting phases*, and mark the appearance of a new phase and/or the disappearance of a phase fin a given rock. At any given pressure a discontinuous reaction occurs at a specific temperature, and vice versa. Discontinuous reactions involve one more phase than the number of independently variable components needed to describe the compositional variation of the phases in the reaction (for an elaboration of this relationship see the section on
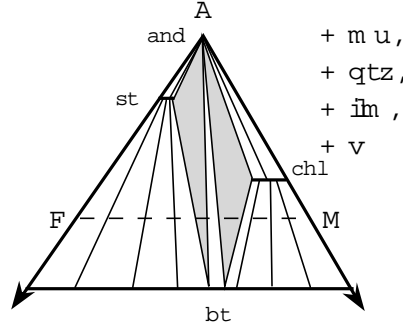
Figure 4.3:   AFM compatibility diagram showing the compositions of possible coexisting phases following reaction (1).

the Phase Rule). Therefore. on a ternary diagram, such as the AFM diagram, discontinuous reactions involve four phases.

The second reaction type, the continuous reaction, is the reaction that is produced as a consequence of the gradual changing composition of individual minerals with changing pressure and/or temperature (Figure 4.6). Thus, as illustrated in Figure 4.6, with increasing temperature we find that the composition of coexisting staurolite and chlorite in andalusite bearing assemblages (+ quartz, rutile and muscovite) becomes more magnesian. For a specific bulk composition, the proportion of these phases must change as a consequence of the changing compositions of the Fe-Mg phases. The continuous reaction written for increasing temperature can be written:

$$\text{chl}_1 = \text{st} + \text{chl}_2 \ (+ \text{ and, qtz, mu, ilm})$$
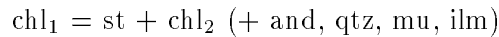
where chl_2 is more magnesian than chl_1.

Both the continuous and discontinuous reactions illustrated in Figures 4.5 and 4.6 can be mapped onto a T-X (or P-X) diagram by projecting the staurolite, biotite and chlorite compositions from coexisting andalusite onto the Fe-Mg binary at the appropriate temperature (Figure 4.7). An important aspect of Figure 4.7 is that it shows schematically that the composition of coexisting minerals is a continuous function of pressure and temperature.
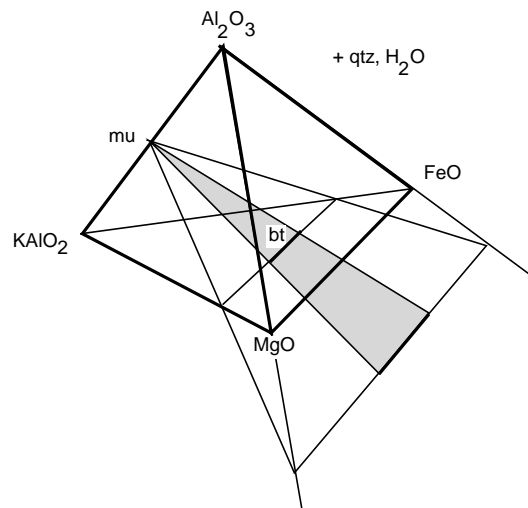
Figure 4.4: AFM projection from the quaternary pseudosystem $KAlO_2$-Al_2O_3-FeO-MgO, showing the projection of biotite from muscovite onto the AFM plane. Note that biotite projects below the FM line, indicating that for biotite the projective co-ordinate of A is negative.

4.4 Balancing Reactions

Using projection schemes as outlined above it is possible to easily determine the reaction relationships that must exist even in very complex systems consisting of many components. Indeed, this is the main purpose served by projections. However, projections do not provide quantitative information about the relative proportions of the phases involved in the reaction. In simple cases balancing reactions, or determining the reaction coefficients of the individual phases can be done by inspection. However, in most reactions we will deal with, balancing by inspection is not possible. To balance reactions we need a more formal approach, involving the setting up and solution of a set of simultaneous equations. To demonstrate this we will use an example:

Worked Example

The problem is to write a balanced reaction between the phases dolomite ($CaMg(CO_3)_2$), tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$), diopside
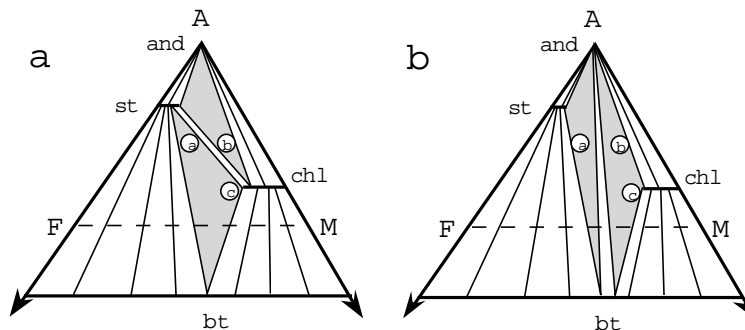
Figure 4.5: AFM diagrams showing the effect of the discontinuous reaction st + chl= bt + and on three distinct bulk compositions, a, b and c. Initial and final assemblages in a are st-chl-bt and st-bt-and, in b are st-and-chl and bt-and-chl and in c are st-chl-bt and bt-and-chl, respectively.

$(CaMgSi_2O_6)$, calcite $(CaCO_3)$, CO_2 and H_2O. Since this system contains five independently variable components, namely CaO, MgO, SiO_2, CO_2 and H_2O, the phase rule and the principles of graphical projection indicate that we must be able to write, and therefore balance, a reaction between these phases. For each component we can write a relation between the amount of that component in each phase; of course since we want to balance the reaction the sum of the amount of the components multiplied by the unknown reaction coefficient for that phase, must equal zero. For instance we can write for CaO:

2 trem + 1 di + 1 dol + 1 cc = 0

where the prefixes refer to the amount of CaO in each phase, and the abbreviations stand for the unknown reaction coefficients. Similarly for MgO we can write:

5 trem + 1 di + 1 dol = 0
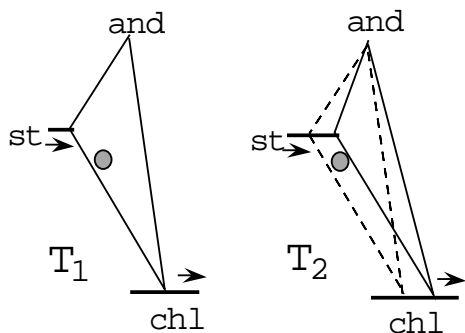
and for SiO_2:

8 trem + 2 di = 0

for CO_2:

Figure 4.6: Sections of AFM diagrams showing schematically how the changing composition of coexisting staurolite and chlorite (indicated by arrows) with increasing temperature ($T_2 > T_1$) effects a continuous reaction, manifested in the changing proportions of the phases in any given bulk composition.

$$2 \text{ dol} + 1 \text{ cc} + 1 \text{ CO}_2 = 0$$

and finally for H_2O

$$1 \text{ trem} + 1 \text{ H}_2\text{O} = 0$$

We have now constructed five equations in six unknowns. We can reduce the number of unknowns by one, by assuming the reaction coefficient for one of the phases. For example, by letting trem = 1, we reduce the system to five equations in five unknowns, which represents a tractable problem:

1 dol + 1 di + 1 cc = -2
1 dol + 1 di = -5
2 di = -8
1 cc + 2 dol + 1 CO2 = 0
1 H20 = -1

Solution of this example is trivial, the answer being:

di = -4, dol = -1, cc = 3, CO_2 = -1, H_2O = -1

In the language of linear algebra we have set up a matrix equation of the type:

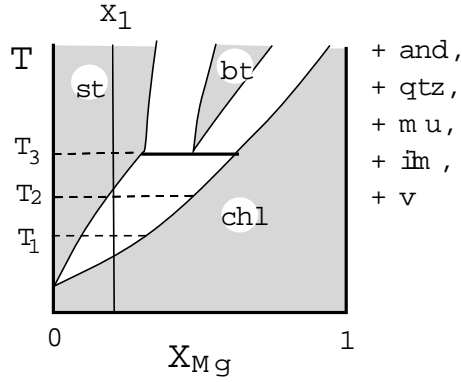$$\mathbf{A}.\mathbf{x} = \mathbf{0}$$

Figure 4.7: T-X diagram illustrating the continuous and discontinuous reactions illustrated in Figures 5.5 and 5.6. Note the different proportions and compositions of staurolite and chlorite at the temperatures t_1 and t_2 in the rock of composition X_i.

where

$$\begin{pmatrix} 2 & 1 & 1 & 1 & 0 & 0 \\ 5 & 1 & 1 & 0 & 0 & 0 \\ 8 & 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} \text{trem} \\ \text{di} \\ \text{dol} \\ \text{cc} \\ H_2O \\ CO_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

Which after the letting trem = 1, reduces to:

$$\begin{pmatrix} 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & 2 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} \text{di} \\ \text{dol} \\ \text{cc} \\ H_2O \\ CO_2 \end{pmatrix} = \begin{pmatrix} -2 \\ -5 \\ -8 \\ 0 \\ 1 \end{pmatrix}$$

In the language of linear algebra matrix equations of the type

$$\mathbf{A}.\mathbf{x} = \mathbf{0}$$

have solutions for x which are the nullspace of $\mathbf{A}$:

$$\mathbf{x} = \mathcal{N}(\mathbf{A})$$

Complex sets of simultaneous equations involving as many unknowns as equations are generally solvable (unless one of the

equations represents a linear combination of the others), using solution procedures such as Gaussian elimination, which can be found in any standard text on linear algebra.

4.5 Quantifying Projective Space

In order to determine the co-ordinates of a phase in a projection we simply need to write a balanced equation involving the phase to be projected, the phases being projected from, and the components defining the projection plane. The plotting co-ordinates are then given by the normalised reaction coefficients of the projection components.

Worked Example

The projective co-ordinates for biotite projected from muscovite, quartz and H_2O onto the AFM plane (e.g. Figure 4.4) can be determined for specific compositions, for example $K_2Fe_{3.5}Mg_{2.5}Al_2Si_6O_2(OH)_4$, by writing the following reaction:

$K_2Fe_{3.5}Mg_{2.5}Al_2Si_6O_{20}(OH)_4$ = 1 $K_2Al_6Si_6O_{20}(OH)_4$
(mu) + 3.5 FeO + 2.5 MgO - 2Al$_2$O$_3$
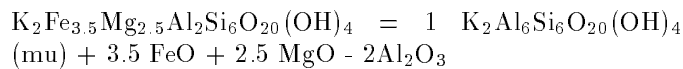
In terms of AFM co-ordinates, the projection point is:

A = $Al_2O_3/(Al_2O_3 + FeO + MgO)$ = -2/4 = -0.5
F = 3.5/4 = 0.875
M = 2.5/4 = 0.625

Where A has the co-ordinate 1, 0, 0; F = 0, 1, 0; and M = 0, 0, 1.

It should be immediately obvious that projection points can lie both inside the region of the projection plane bounded by positive values of the projection plane components, i.e., within the AFM triangle, or outside this region, in which case one of the projection co-ordinates must be negative.

4.6 The phase rule

One of the important principles we have demonstrated by graphical techniques is that we can only write a balanced reaction between minerals when we have one more phase than the number of independantly variable components needed to describe

the compositions of the phases. For instance in a ternary system, we need four phases to write a balanced reaction. The formal statement of this principal is known as the phase rule:

$$V = (n + 2) - p$$

where V is the variance of the system, n is the number of components in the system and p is the number of the phases in the system. Variance is a new concept which needs some explanation. In pressure-temperature (P-T) space, a balanced reaction traces out a line. The equilibrium coexistence of all the phases involved in the reaction can only occur at P-T co-ordinates along this line: if we fix the pressure, the temperature is also uniquely specified. If we move away from the reaction line in P-T space, then one or more of the phases will be consumed by reaction. The system is said to have one degree of variance, or more simply, it is univariant. Note that in a ternary system consisting of four phases, according to the phase rule, $V = 1$. Similarly, a ternary system consisting of five phases ($V = 0$) is said to be invariant, while a ternary system consisting of only three phases ($V = 2$) is said to be divariant. Thus discontinuous reactions are univariant, while the continuous reactions are divariant. The special feature of invariant assemblage is that they can only exist in equilibrium at one P-T co-ordinate. In divariant systems, both pressure and temperature can be varied independantly of each other without necessarily changing the phase assemblage.

Consider a system containing $(n+2)$ phases, for example, a ternary system consisting of five phases. Since we can write a balanced univariant reaction between any four of these phases, we must be able to write five univariant reactions in total by leaving out one or each of the five phases in turn. A convenient way of labelling the reactions, and one which is adopted by convention, is by marking the reaction by the absent phase enclosed in round brackets ( ). We have already pointed out that our invariant systems have the unique property that the equilibrium $(n + 2)$ invariant assemblage can only exist at a unique pressure and temperature. The five univariant reactions must pass through, and intersect at this unique point, since the

equilibrium coexistence of any four of the five phase lies on a univariant curve.

One of the most important, and simplifying, principles enabling the construction of petrological phase diagrams concerns the topological laws governing the distribution of univariant reactions around invariant points first elucidated by Schreinemakers. Schreinemakers showed that the arrangement of univariant curves around an invariant point is governed by relatively simple topological laws, the most important of which is: the metastable extension of the univariant reaction (X), i.e, the reaction that neither produces nor consumes X, must lie between two X-producing reactions.

Worked Example

Consider the $(n+2)$ system consisting of andalusite, staurolite, garnet, biotite, cordierite in a rock where muscovite, quartz and H_2O are saturating phases (or, are in excess). In reality this is a six component system with eight phases, but as we have already shown by the use of projective geometry (e.g. Figure 4.8), this system can be considered as a pseudoternary system with five phases and therefore can be graphically portrayed on an AFM diagram. The following reactions can be written between the five phases:

st = gt + and + cd (bt)
st = gt + and + bt (cd)
st + cd = and + bt (gt)
gt + cd = and + bt (st)
gt + cd = st + bt (and)
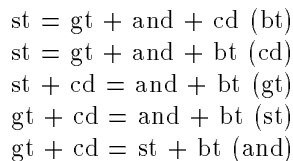
According to Schreinemakers principles the correct topology of these univariant curves about the invariant point where all five phases can coexist is shown in Figure 4.9.

It is critical to note that while the topology of the reactions is correct in the above diagram, that is, they occur in the correct sequence according to Schreinemakers principles, the slopes of the reactions, and the location of their intersection in P-T space is not specified by Schreinemakers principles. To constrain the slopes of the reactions and the P-T co-ordinates of the invariant point, we have to apply quantitative thermodynamic principles.
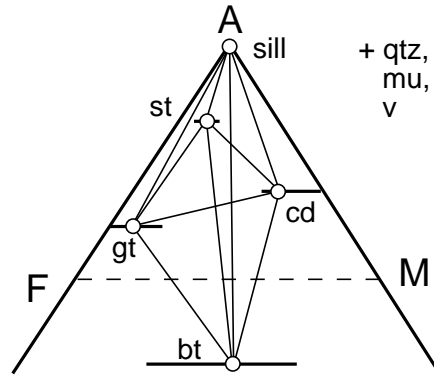
Figure 4.8: AFM projection showing the compositional range of garnet, biotite, staurolite and cordierite in typical pelitic rocks.
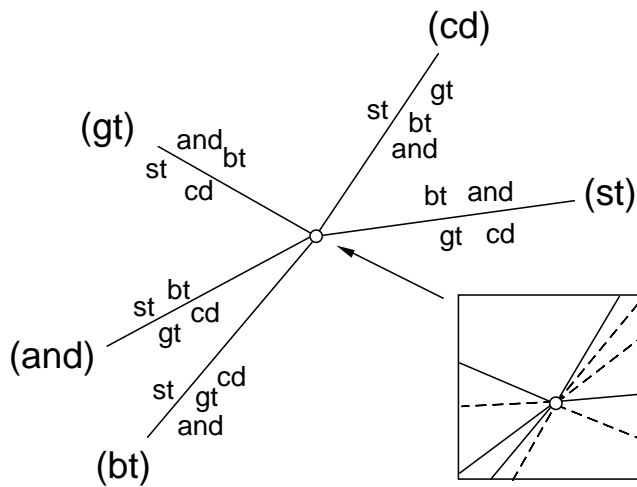

Figure 4.9:   P-T diagram showing a geometrically correct distribution of reactions about the invariant point in the Worked Example. The inset shows in detail the distribution of univariant curves around the invariant point. In the inset, stable parts of univariant curves are shown in bold, while metastable portions are shown by thin dashed lines.

In $(n + 3)$ systems, and larger systems, we can of course define numerous bundles of reactions and associated intersections. Only some of the reactions and intersections will be stable, with many being metastable. The principal problem in Schreinemakers analysis in these large systems is deciding which of the many possible topologies is correct. The task is greatly simplified if we have some prior knowledge of the which assemblages actually occur in nature.

4.7   Additive and Exchange Components*

So far we have considered components in a relatively simple way, using only molecules combining positive proportions of elements. For instance from what we have learned so far, an obvious choice of independently variable components to describe a system consisting only of plagioclase feldspars would be $NaAlSi_3O_8$ (albite) and $CaAl_2Si_2O_8$ (anorthite). An alternative way of describing the compositional variation of mineral solid solutions such as the plagioclase series is to specify one additive component, usually one of the end members of the phase, and one or more exchange components which relate the composition of all physically realizable regions (and beyond) of the phase space to the additive component. Thus all plagioclase compositions can be described by the additive component $NaAlSi_3O_8$ and the exchange component $CaAlNa_{-1}Si_{-1}$. In this scheme, the composition of anorthite is specified by:

$$NaAlSi_3O_8 + CaAlNa_{-1}Si_{-1}$$

All natural plagioclase feldspars have compositions intermediate in composition between albite and anorthite and thus can be specified by between 0 and 1 units of the exchange component. In terms of compositional space additive components can be viewed as fixed points and exchange components as vectors.

While the description of systems in terms additive and exchange components may appear somewhat obscure, it has considerable merit in the analysis of the reaction relationships that exist between phases in complex systems. So far we have only described reactions which involve the formation of new phases at the expense of older phases. Such reactions require the physical transfer of matter and its rearrangement in a different structural state in new phases. Such reactions are termed net-transfer reactions. A different type of reaction termed an exchange reaction does not involve the growth or consumption of phases but rather the exchange of components between existing phases. Exchange reactions occur between minerals which share a common exchange component. For instance, biotites and garnets form Fe-Mg solid solutions, i.e., their composition can be described by the exchange vector $FeMg_{-1}$ in addition

to the Mg-end member additive components $Mg_3Al_2Si_3O_12$ and $K_2Mg_6Al_2Si_6O_20(OH)_4$ (natural biotites usually involve a number of other exchange components in addition to $FeMg_{-1}$). The exchange of Fe and Mg between coexisting garnet and biotite is an exchange reaction because it does not involve the formation of a new phase. In terms of exchange components the reaction is: $FeMg_{-1}$[garnet] $= FeMg_{-1}$[biotite]
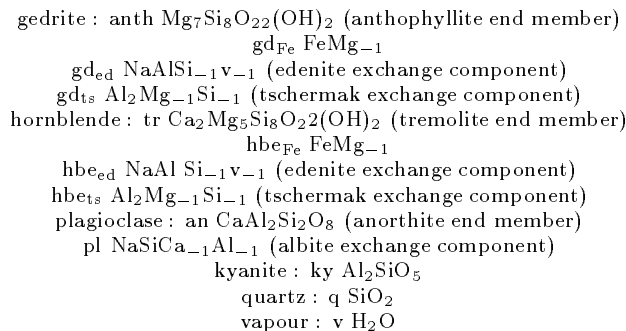
In terms of conventional mineral end members this reaction would be written:

$$Fe_3Al_2Si_3O_{12} + K_2Mg{-6}Al_2Si_6O_20(OH)_4 = Mg_3Al_2Si_3O_{12} +$$
$$K_2Fe_6Al_2Si_6O_20(OH)_4$$
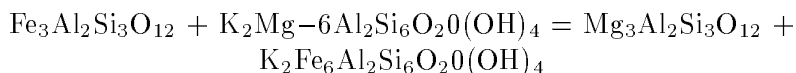
The advantage in dealing with exchange components should be obvious in this example, however, the real benefit of dealing with exchange components is in the analysis of reaction relationships in complex systems.

Worked Example

Consider the system consisting of gedrite, hornblende, plagioclase, kyanite, quartz and an aqueous vapour. In terms of additive and exchange components the compositional variation of these phases can be described in the following way :

$$\text{gedrite : anth } Mg_7Si_8O_{22}(OH)_2 \text{ (anthophyllite end member)}$$
$$gd_{Fe}\ FeMg_{-1}$$
$$gd_{ed}\ NaAlSi_{-1}v_{-1} \text{ (edenite exchange component)}$$
$$gd_{ts}\ Al_2Mg_{-1}Si_{-1} \text{ (tschermak exchange component)}$$
$$\text{hornblende : tr } Ca_2Mg_5Si_8O_22(OH)_2 \text{ (tremolite end member)}$$
$$hbe_{Fe}\ FeMg_{-1}$$
$$hbe_{ed}\ NaAl\ Si_{-1}v_{-1} \text{ (edenite exchange component)}$$
$$hbe_{ts}\ Al_2Mg_{-1}Si_{-1} \text{ (tschermak exchange component)}$$
$$\text{plagioclase : an } CaAl_2Si_2O_8 \text{ (anorthite end member)}$$
$$pl\ NaSiCa_{-1}Al_{-1} \text{ (albite exchange component)}$$
$$\text{kyanite : ky } Al_2SiO_5$$
$$\text{quartz : q } SiO_2$$
$$\text{vapour : v } H_2O$$

The sum (c_p) of the independent components needed to describe the compositional variation of each one of the phases is thirteen, i.e., four each for gedrite and hornblende, two for plagioclase, and one each for kyanite, quartz and the vapour. However, the number of independently variable system components (c_s) is seven; a suitable choice would be Na2O, CaO, FeO, MgO, Al_2O_3, SiO_2 and H_2O. The number of independent reactions (n_r), both net-transfer and exchange, that it is possible to write between an arbitrary number of phases is :

$$n_r = c_p - c_s$$

In our system the total number of independent reactions is six. The exchange reactions are easy to determine:

(1) $gd_{Fe} = hbe_{Fe}$
(2) $gd_{ed} = hbe_{ed}$
(3) $gd_{ts} = hbe_{ts}$

The general rule is the number of exchange reactions (n_{ex}) per exchange component is one less than the number of phases whose compositional description includes that exchange component. The number of net transfer reactions (n_{tr}) must equal the difference between the total number of reactions and the number of exchange reactions:

$$n_{tr} = n_r - n_{ex}$$

A full set of independent reactions including both the exchange and net-transfer reactions is given by solution of the matrix equation:

$$\mathbf{A} \quad .\mathbf{x} = 0$$

where A is the coefficient matrix:

$$
\begin{pmatrix}
0 & 0 & 0 & 7 & 0 & 8 & 2 \\
0 & 0 & 1 & -1 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 1 & -1 & 0 \\
0 & 0 & 0 & -1 & 2 & 1 & 0 \\
0 & 2 & 0 & 5 & 0 & 8 & 2 \\
0 & 0 & 1 & -1 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 1 & -1 & 0 \\
0 & 0 & 0 & -1 & 2 & 1 & 0 \\
0 & 1 & 0 & 0 & 2 & 2 & 0 \\
1 & -1 & 0 & 0 & -1 & 1 & 0 \\
0 & 0 & 0 & 0 & 2 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 2
\end{pmatrix}
$$

given by the compositions of the c_p phases in terms of the c_s system components.
    The solution is given by 2 :

$$x = N(AT)$$

yielding the following net-transfer reactions:

(4) 6 anth + 37 an + 9 pl_{alb} + 8 v = 9 gd_{ed} + 28 gd_{ts} + 14 tr
(5) 1 hbe_{ed} + 4 q = 1 pl_{alb} + 1 an
(6) 2 tr + 8 ky + 1 pl_{alb} = 3 an + 4 gd_{ts} + 1 gd_{ed} + 1 anth

Note that this is not a unique choice of independent reactions. However, while many more reactions can be written betwen these components, for instance:

(7) 1 gd_{ed} + 4 q = 1 pl_{alb} + 1 an

all additional reactions will be a linear combination of the six independent reactions. Reaction 7 is equivalent to a combination of reactions 5 and 2. The six reactions listed above are one combination of a reaction set which is linearly independent.

    The ability to evaluate the number and type of reaction relationships that exist between coexisting phases highlights the real benefit of using additive and exchange components.

Further Reading

Powell, R., 1978, Equilibrium thermodynamics in Petrology. Harper & Row.

- good worked examples on projections.

Thompson, J.B., 1983, Chapters 1 & 2 of Characterization of metamorphism through mineral equilibria. Reviews of Mineralogy, 10. Mineralogical Society of America.

- pretty difficult going on additive and exchange components by the person who invented the AFM projection.

Chapter 5

Equilibrium thermodynamics

5.1   Some basic thermodynamic concepts

Thermodynamics concerns itself with the energetics of chemical systems and particularly with changes or reactions in chemical systems. As with so many natural phenomona, chemical reactions can only proceed spontaneously if there is a reduction in energy. The particular form of energy that is reduced in spontaneous chemical reaction is termed the Gibbs free energy, G, and the criterion for spontaneous reaction is:

$$\Delta G < 0$$

Note that at equilibrium any slight reaction leading to the production of a new phase or a change in the composition of one of the phases present must lead to an increase in the free energy of the system (Figure 5.1). Since at equilibrium the energy is a minimum with respect to any reaction coordinate, the derivative of the free energy with respect to any reaction cordinate must be zero:

$$dG = 0$$

Note that, by itself, this condition is not enough to distinguish a stable equilibrium point from a metastable or even an

unstable point (Figure 5.1). Stable and metastable equilibria may be further distinguished from unstable equilibria with the additional constraint that $d^2G > 0$ (Figure 5.1b).
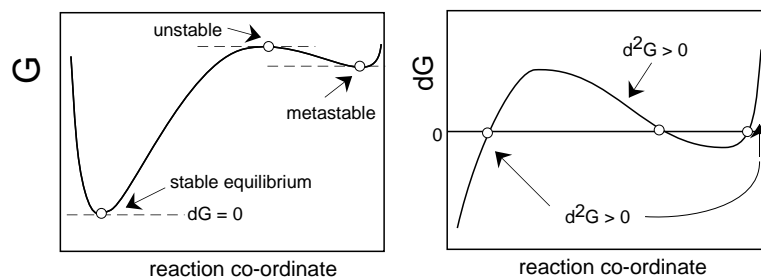

Figure 5.1: (a) schematic illustration of variation of G with reaction coordinate, illustrating the difference between stable, metastable and unstable equilibria. (b) stable and metastable equilbrium occur at the points where $dG = 0$ and $d^2G > 0$, while unstable equilibrium points are characterised by $dG = 0$ and $d^2G < 0$

To understand why it is the *free energy* change that directs reactions, and what contributes to the *unfree* energy in chemical systems, we need to introduce some thermodynamic state variables such as internal energy, U, enthalpy, H, volume, V, and entropy, S.

Internal energy

It is useful to think of a chemical system as posessing an internal energy, U, which is the sum of the kinetic and potential energies contributed by such things as the vibrational and electronic energies of individual atoms. While the absolute value of U for a chemical system is not readily measurable, the difference in the internal energy, ΔU, between two distinct states can be measured.

For *exothermic* reactions $\Delta U < 0$, that is, they give off heat to the surroudings, while for *endothermic* reactions $\Delta U > 0$.

Enthalpy

For reactions carried out at constant pressure, there is the possibility of a change in volume, V, of the system. For example,

an increase in volume causes work to be done against the external environment, with a concomitant transfer of energy. The work done in expanding a system at constant pressure, P, is given by $P \Delta V$ with the consequence that the value of ΔU does not provide a true measure of the change in energy of the reaction. To account for this possibility of work being done to change the volume of the system we introduce the *enthalpy change*, ΔH, of a reaction (or heat of reaction) :

$$\Delta H = \Delta U + P\Delta V$$

Entropy

Spontaneous changes in chemical and mechanical systems are driven by tendencies to reduce potential energy, with the important side effect that work can be derived from this spontaneous reduction in energy (similarly, spontaneous changes can be reversed, and potential energies increased, if work is done on the system). Since the enthalpy change of a reaction is a measure of the change in internal energy of a reacting system (and includes both the potential and kinetic energies of the constituent particles), one might expect that spontaneous reaction should always be accompanied by a reduction in enthalpy. However, this clearly inconsistent with the observation that both exothermic and endothermic reactions occur spontaneously, which implies that reaction energetics cannot be completely understood in terms of enthalpy changes alone.

The missing factor in our analysis of reaction energetics concerns the *entropy changes*, ΔS, accompanying reaction. Entropy provides a measure of the disorder of the system. The disorder associated with entropy changes is most easily appreciated in cases of changes of state : gases are clearly more disordered (and have a higher entropy) than liquids (of the same composition) which, in turn, are clearly more disordered than solids (generalising, we may expect that disorder and entropy somehow increase with temperature). Similarly, disorder also occurs during mixing of compounds, such as mineral end-members of solid solutions. The chemical system is somehow more ordered when separated into the pure chemical

Consider a young child's room, firstly in a fully ordered state and then in a disordered state. In this system, spontaneous reaction due to the agency of the young child always occurs in the direction of increasing entropy and much work need to be put into the system to reverse the process.

end-members than when mixed together, with this mixing always producing an increase in entropy $\Delta S_{mix} > 0$ (see later section). The role of entropy in reaction energetics is postulated in the second "law" of thermodynamics which states that *the total entropy of a system and its surroundings must increase in all spontaneous processes.*

Gibbs free energy

A key part of the second law is the inclusion of the term *surroundings*. This allows spontaneous reactions that decrease the entropy of the system providing there is sufficent heat transferred from the system to its surroundings (i.e., an exothermic reaction) to cause an even greater increase in the entropy of the surroundings. Of course, it would be convenient to provide a criterion for reaction which is somehow independent of the entropy changes in the surrounding; that is, a criterion which is system-specific which we might expect would involve an enthalpy and an entropy term. Since the transfer of energy form the system to the surroundings is already incorporated in the enthalpy terms it is possible to define such a system-specific criterion in terms of the change in *Gibbs free energy* ΔG;

$$\Delta G = \Delta H - T\Delta S$$

Note that the *free energy* change represents that component of the enthalpy change (or internal energy change) that is not bound up with the entropy, or the disorder. Therefore, the disorder associated with the entropy change somehow must contribute to the *unfree chemical energy* in the system. The criterion for spontaneous reaction is that $\Delta G < 0$.

The Gibbs free energy of a system clearly depends on how large the system is; that is, on the amount of material in the system, and therefore it is an *extensive* property of the system. It is often more useful to express the Gibss energy in way that is independent of the amount of the material, as though it were an *intensive* property. The molar Gibbs free energy, or Gibbs free energy per unit mole of system components, $\overline{G}$, provides such a measure.

5.2 Energetics of solid-solutions

In petrology we are often concerned with minerals which show extensive solid-solution. Because thermodynamic data are usually only known for the end-members of these solid solutions we need to have some knowledge of the energetics of mixing in solid solutions. The free energy of mixing, ΔG_{mix}, is contributed to by both and enthalpy, ΔH_{mix}, and and entropy, ΔS_{mix}, of mixing.

Enthalpy of mixing

The enthalpy of mixing arises because of the fact that a change in the site ocupancy of a solid solution, for example by substituting Fe for Mg on an M_1 site in a pyroxene, must cause some distortion in the crystal lattice and thus is associated with a change in the internal energy of the crystal. The excess enthalpy of mixing is measured relative to the energy of purely mechanical mixing of the end-members of the solid-solution (Figure 2).
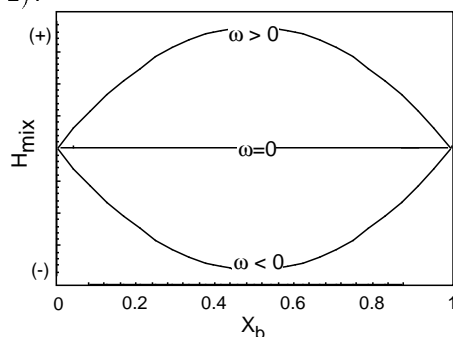

Figure 5.2: Schematic illustration of the excess enthalphy of mixing ΔH_{mix} in a two component system. The parameter ω represents the relative interaction enregies associated with mising $\omega = (2\omega_{AB} - \omega_{AA} - \omega_{BB})$ - see text

In the simplest model of mixing we can assume that the energy of interaction on substitutional sites is simply related to nearest neighbour interactions. We consider a two component solid solution between A and B end members with only one mixing site in the lattice. Each site is surrounded by z-nearest

neighbour sites, consequently the number of nearest neigbour pairs is $Nz/2$ where N is number of sites. The energy of interaction is given by three terms, ω_{AA} due to the interaction between nearest neighbour $A - A$ pairs, ω_{AB} due to the interaction between nearest neighbour $A - B$ pairs, and ω_{BB} due to the interaction between nearest neighbour $B - B$ pairs. For the case when the A and B are completely randomly mixed in relative proportions X_A and X_B:

$$\Delta H_{mix} = \frac{1}{2} N z X_A X_B (2\omega_{AB} - \omega_{AA} - \omega_{BB})$$

The sign of ΔH_{mix} depends on the sign of the bracketed term $(2\omega_{AB} - \omega_{AA} - \omega_{BB})$, given by the relative interaction energiesassociated with mixing ω. When $\omega = 0$ there is no excess enthalpy of mixing relative to the mechanical mixture. When $\omega > 0$ the excess enthalpy of mixing $\Delta H_{mix} > 0$, while for $\omega < 0$ $\Delta H_{mix} < 0$ (Figure 5.2).

Entropy of mixing

The entropy of mixing occurs because the mixed solid solution is clearly more disordered than an equivalent amount of material separated into the end-member compositions. For the $A - B$ solid solution discussed above the entropy of mixing is given by

$$\Delta S_{Mix} = -R(X_A \ln X_A + X_B \ln X_B)$$

Ideal solutions

Ideal solid solutions show no excess interaction energies (i.e., $\omega = 0$). Consequently, the free energy of mixing is given by the entopy term alone:

$$\Delta G_{mix}(\text{ideal}) = -T\Delta S_{mix}$$
$$= RT(X_A \ln X_A + X_B \ln X_B)$$

Because there is always an excess entropy of mixing which is symmetrical about the mid-point of the solid-solution series, $G - X$ curves for ideal solutions are characteristically downward facing loops, which become deeper (more sharply-curved) with increasing temperature.

Regular solutions

Regular solutions allow interaction energies on nearest neighbour sites as described above. Consequently the free energy of mixing is given by

$$\Delta G_{mix}(\text{regular}) = \Delta H_{mix} - T\Delta S_{mix}$$

$$= \frac{1}{2}NzX_AX_B(2\omega_{AB} - \omega_{AA} - \omega_{BB}) + TR(X_A\ln X_A + X_B\ln X_B)$$

For $\omega < 0$, regular solutions produce downward facing $G - X$ loops similar in form to ideal solutions. However, for $\omega > 0$ rather more complex $G - X$ loops are developed (Figure 5.3). At high temperatures the entropy term dominates, and the $G - X$ curves form simple downward facing loops. However, as temperatures are lowered the enthalpy term assumes greater significance eventually resulting in characteristic w-formed $G - X$ curves (Figures 5.3 and 5.4). These
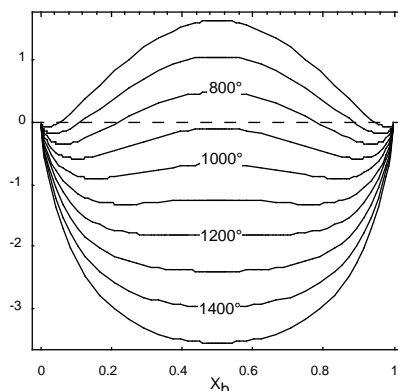

Figure 5.3: ΔG_{mix} for a regular solution. Note that at high temperatures the entropy of mixing dominates the $G-X$ relations giving rise to simple downward facing $G - X$ loops. At lower temperatures the ethalpy term becomes increasing significant producing the more complex ω-shaped curves associated with the devlopment of a solvus.

complex $G - X$ curves signify the onset of immisicibility in solid-solutions due to the excess interaction energies of mixing (Figure 5.4). Within the immiscible region (below 1200°C in Figures 5.4 and 5.5) bulk compositions within the immiscible
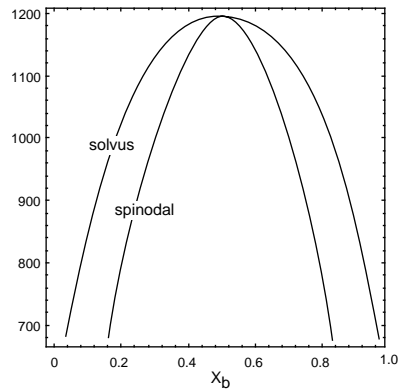
Figure 5.4: Solvus and spinodal in $T - x$ space

realm minimise the free energy of the system by unmixing into two discrete phases withthe *solvus* compositions. Because of the increase of the relative significance of the enthalpy term with decreasing temperature, the solvus (which marks the locus of stable compositions on a $T - X$ curve) must widen as temperature decreases (Figure 5.5).

The *spinodal* is given by the locus of points in $T - X$ space in which $d(\Delta H_{mix})^2 = 0$ and separates an internal region where any small fluctation in the composition is unstable because $d(\Delta H_{mix})^2 < 0$ (and therefore any small fluctuation in composition decreses the resulting G of the system) from an external region where $d(\Delta H_{mix})^2 > 0$ and small fluctations in composition are damped.
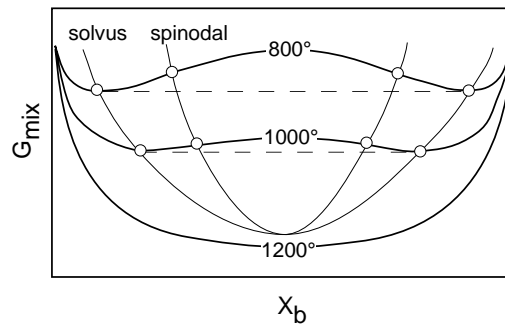
Figure 5.5: Solvus and spinodal n $G - x$ space

5.3 The concept of chemical potential

Another useful intensive property is the chemical potential μ, which is defined as the partial molar Gibbs energy of a component in a phase. We have already defined the stable equilibrium assemblage at any given pressure and temperature as the assemblage that minimizes the Gibbs energy. This relation provides the fundamental basis of equilibrium thermodynamic calculations. In this section the consequences of this fundamental equilibrium relationship are investigated. In order to derive the quantitative equilibrium relationship between coexisting phases we need to develop the concept of chemical potential, commonly represented as μ. Consider a binary system consisting of two components, 1 and 2, and one phase, α, as shown in Figure 5.6. In this one phase, two component sys-
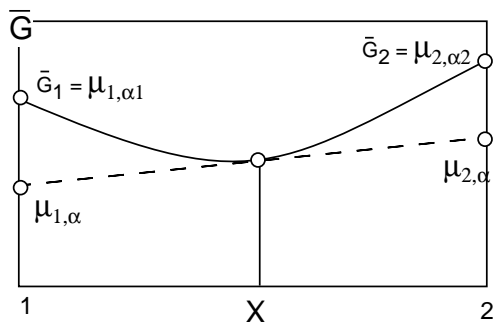

Figure 5.6: G-X diagram where G is the Gibbs energy of one mole of the phase. See text for discussion.

tem the equilibrium composition of α is controlled by the bulk composition, X, of the system. For any arbitary composition of α the chemical potential of components 1 and 2 in α, i.e. $\mu_{1,\alpha}$ and $\mu_{2,\alpha}$ are defined as the intercepts of the tangent to the $G - X$ curve with the end member component axes 1 and 2, respectively. Thus the molar Gibbs energy of α must equal the sum of the chemical potentials of the two end member components multiplied by the molar proportion of the end member components in α:

$$G_\alpha = \mu_1\ n_1 + \mu_2\ n_2$$

Where n_1 is the mole proportion of 1 in α. Obviously, when a phase consists of only one component then the chemical potential of that component is equal to the molar Gibbs energy of the phase. Figure 5.7 shows schematically that as the equilibrium composition of the phase is changed the tangent must swing around the $G - X$ curve, and so the intercepts of the tangent with the component axes, and therefore the chemical potentials of these components in the phase must also change. Specifically, the chemical potential $(\mu_{i,\alpha})$ of any component i in a phase must increase as the mole proportion of i in the phase is increased. In fact, the chemical potential of any component,
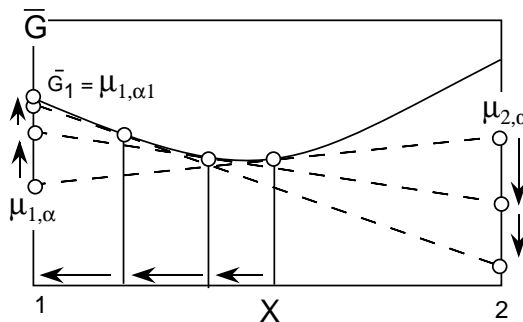

Figure 5.7: Schematic $G - X$ diagram illustrating that the chemical potential of any component, 1, in a phase, α, must increase as the molar proportion of component 1 in a is increased.

i, in a phase, α, is defined quantitatively as the partial derivative of molar Gibbs energy of α with respect to an infintesimal change in the molar proportion of component i, keeping the the thermodynamic state functions and the molar proportions of all other components constant:

$$\mu_{i,\alpha} = \left(\frac{\partial G_\alpha}{\partial n_i} \right)_{T,P,n_j}$$

where n_i is the mole proportion of component i in the phase and n_j refers to the mole proportion of any other component. Summarizing then, the chemical potential of a component, i, in a phase, α, is the partial molar Gibbs energy of i in α. Now we consider the binary system in Figure 5.6, but now with two phases, α and β, coexisting at equilibrium (Figure 5.8). For
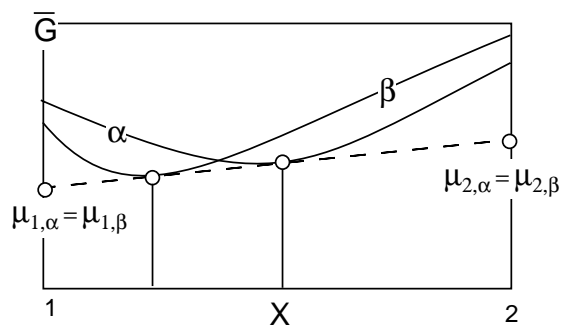
Figure 5.8: Schematic G-X diagram showing that at equilibrium in a system containing two phases, α and β, and two components, 1 and 2, $\mu_{1,\alpha} = \mu_{1,\beta}$, and $\mu_{2,\alpha} = \mu_{2,\beta}$. Note that while the Gibbs energies of system change with changing bulk composition, the compositions of the phases, and chemical potentials of the end member components in the phases, is fixed in the two phase field.

bulk compositions in this binary system which allow the coexistence of α and β, (i.e., bulk compositions between X_α and X_β) both the composition of α and β and the chemical potential of the end member components in α and b are fixed, even though the Gibbs energy of the system as whole changes with the bulk composition (in this example the bulk composition, X_α, has a lower Gibbs energy than the bulk composition X_β). Since at equilibrium the compositions of phases α and β are given by the intercepts of the respective $G - X$ curve with the common tangent, the following equilibrium relations must also hold true:

$$\mu_{1,\alpha} = \mu_{1,\beta}$$

$$\mu_{2,\alpha} = \mu_{1,\beta}$$

These statements are a necessary corollary of the way in which we have defined chemical potential and provide the critical equilibrium relationship. For what follows, it is essential to understand why these statements must be true.

For the system illustrated in the above diagram it is possible to write balanced chemical reactions between the end-member components of the type:

Component 1 in α = Component 1 in β
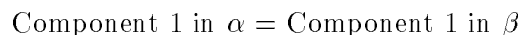
Component 2 in α = Component 2 in β

For these reactions the equilibrium condition, which must apply when phases α and β form part of equilibrium assemblage, indicates that:

$$\partial \mu = 0$$

This relationship holds true for any chemical reaction we can write at equilibrium between end-member components of phases or pure phases.

5.4 Quantitative Calculations

Calculation of equilibrium thermodynamic equations requires an expression for m of pure phases and of end-member components in phases consisting of more than one end-member component. For a pure phase, i.e., a phase consisting of only one component, $\mu = G$. As shown in the following sections, the Gibbs energy of a phase is a function of pressure and temperature and is of the form:

$$G = E + PV - ST = H - ST$$

where H is the molar enthalpy (kJ/mole), S is the molar entropy (kJ/K/ mole), T is the temperature (K), P is the pressure (kbar) and V is the molar volume (kJ/kbar/mole).

For a phase consisting of more than one component, the chemical potential of any of the end members in the phase is defined as the partial molar Gibbs energy of that component in the phase, and therefore is dependent on the molar Gibbs energy of the pure end member and a composition dependent term which expresses the proportion of the end member in the phase. The appropriate expression is

$$\mu_{1,\alpha} = \overline{G} + R\,T\,ln\,(a_{1,\alpha})$$

where $\overline{G}$ is the molar Gibbs energy of the end member component 1 at the temperature and pressure of interest and $a_{1,\alpha}$ is the activity, or effective concentration of component 1 in phase

α, which is related to composition, $X_{1,a}$, by a dimensionless parameter termed the activity coefficient γ:

$$a_{1,\alpha} = \gamma \, X_{1,\alpha}$$

In the ideal case where there are no excess energy terms introduced by mixing end-members in a particular phase (ideal mixing) $\gamma = 1$ and $a_{1,\alpha} = X_\alpha$. Note that for a pure phase $a_{1,\alpha} = 1$, therefore:

$$ln\,(a_{1,\alpha}) = 0$$

consistent with the requirement for a pure phase $\mu_{1,\alpha} = \overline{G}$

For a system in equilibrium we can write, for any balanced reaction between the phases in that system, or between end member components of the phases in that system the equilibrium relation:

$$\Delta\mu = 0 = \Delta(\overline{G} + RT\ln(a))$$

$$= \Delta\overline{G} + RT\ln K$$

where K is the equilibrium constant for the reaction. For a reaction involving m products phases and n reactants each with a reaction coefficient r_c, K is given by the

$$K = \frac{\prod_{i=m}\left(a_i^{r_c}\right)}{\prod_{j=n}\left(a_j^{r_c}\right)}$$

that is products of the activities of each of the product phases divided by the product of the activites of each reactant phase.

Worked Example

In an equilibrium assemblage consisting of clinopyroxene, plagioclase and quartz we can write a balanced chemical reaction between the end memer component $NaAlSi_2O_6$ (jadeite) in clinopyroxene, $NaAlSi_3O_8$ (albite) in plagioclase and SiO_2 (quartz):

$$NaAlSi_2O_6 \text{ (cpx)} + SiO_2 \text{ (qtz)} = NaAlSi_3O_8 \text{ (plag)}$$
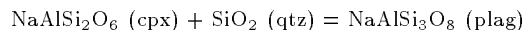
It is important to realise that this reaction represents a valid equilibrium relationship between coexisting clinopyroxene, plagioclase and quartz independently of how much jadeite there is in the clinopyroxene, or how much albite there is in the plagioclase. The equilibrium constant for this reaction is:

$$K = \frac{a_{NaAl_2Si3O_8,pl}}{a_{NaAl_2Si2O_6,cpx}\,a_{SiO_2,qtz}}$$

the equilibrium relation for this reaction is:

$$\Delta\mu = \Delta\overline{G} + RT\ln K = 0$$

$$0 = \mu_{NaAlSi_3O_8,pl} - \mu_{NaAlSi_2O_6,cpx} - \mu SiO_2, qtz$$

from tabulated thermodynamic data we calculate:

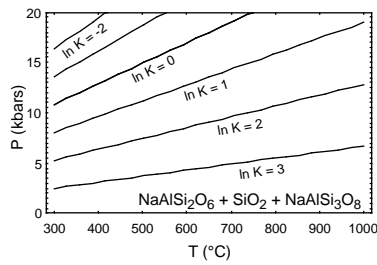$$\Delta\overline{G} = 1.55 - 0.0352T + 1.72P$$

as illustrated in Figure 5.9.

Figure 5.9: P-T equilibria for the reaction $NaAlSi_2O_6$ (cpx) + SiO_2 (qtz) = $NaAlSi_3O_8$ (plag)