

A brief overview of the principles of thermobarometry

Cin-Ty Lee (2009)

Homogeneous system

For a one phase system (homogeneous system) characterized by a fixed composition, the state variable known as Gibbs Free energy G is defined as follows:

$$G \equiv H - TS \quad (1)$$

where H is enthalpy, T is temperature, and S is entropy are all state variables. Taking the total differential of eq. 1 and substituting in the fundamental equation for internal energy ($dU = TdS - PdV$), one can show that

$$dG = -SdT + VdP \quad (2)$$

where V is volume and P is pressure. This means that G is a function of the state variables T and P , the state variables of most interest to a geologist, hence

$$G(T, P) \quad (3)$$

G is essentially one way to express energy, just like internal energy U , enthalpy H , and Helmholtz Free energy A are different ways to express energy. For example, U is the energy in a system capable of doing pressure-volume work (PdV) or transferring heat. H is the amount of energy available for transferring heat at constant pressure. A is the amount of pressure-volume work available at a constant pressure. G is the amount of energy associated with changing temperature and pressure, which could potentially be used to drive other forms of work.

Except for T and P , all of the energy state variables (G , H , A , U) are extensive quantities, that is, the amount of G for a system depends on how big your system is. If, however, we allow our system to grow in size or change composition, then G will change. In other words, G is actually a function of T , P , **and** the number of n_i moles of various components in the system

$$G(T, P, n_i) \quad (4)$$

For example, if we were interested in the G of Mg_2SiO_4 , you would have to specify T , P and how many moles of Mg_2SiO_4 you have. We can take the total differential of Eq. 4 to give

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_i} dP + \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j \neq n_i} dn_i \quad (5)$$

comparison to Eq. 2 shows that

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P, n_i} \quad V = \left(\frac{\partial G}{\partial P} \right)_{T, n_i} \quad (6)$$

As for the third term in Eq. 5, we make the following definition

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j \neq n_i} \quad (7)$$

a quantity, which we call the **chemical potential** and Eq. 5 becomes

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad (8)$$

Eq. 8 shows that the change in G of a system depends on the change in T , P , and size (in mass) of the system. An important quality of G at any given T and P is that

$$G = \sum_i n_i \mu_i \quad (9)$$

Eq. 9 can be differentiated to yield

$$dG = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i \quad (10)$$

And substituting Eq. 10 into 8 yields

$$SdT - VdP + \sum_i n_i d\mu_i = 0 \quad (11)$$

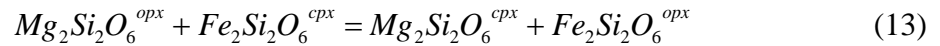
This equation is known as the *Gibbs-Duhem* equation and shows how changes in T, P and chemical potential are related. For a system composed of n components, there are $n+2$ intensive variables and $n+1$ variables can vary independently. From Eq. 9, we can also define the partial molar Gibbs Free energy \bar{G} of a given component

$$\mu_i = \bar{G} = \frac{G_i}{n_i} \quad (12)$$

Which is simply equal to the chemical potential of the pure-endmember component.

What does chemical potential mean? If you look at Eq. 7 carefully, you will see that the chemical potential is a measure of how much Gibbs Free energy would change in your system (for now, our system is a single phase) if you were to increase the mass of the system. For example, if you have 1 mole of Mg_2SiO_4 , the Gibbs free energy of your system would change by $2\mu_i$ if we added 2 more moles of Mg_2SiO_4 to the system.

Now, let's consider two phases, A and B, each containing two components, 1 and 2. This, for example, could be the exchange of $Mg_2Si_2O_6$ (1) and $Fe_2Si_2O_6$ (2) between clinopyroxene (A) and orthopyroxene (B),



Because we have two phases in our system now, the total change in Gibbs Free Energy of the system is the sum of the Gibbs Free energy changes of the two phases

$$dG_{sys} = dG^A + dG^B \quad (14)$$

$$dG_{sys} = (\mu_1^A dn_1^A + \mu_2^A dn_2^A) + (\mu_1^B dn_1^B + \mu_2^B dn_2^B) \quad (15)$$

And because $dn_1^A = -dn_1^B$ and $dn_2^A = -dn_2^B$, Eq. 15 simplifies to

$$dG_{sys} = (\mu_1^A - \mu_1^B)dn_1 + (\mu_2^A - \mu_2^B)dn_2 \quad (16)$$

At equilibrium, G is minimized and therefore $dG_{sys}=0$. In general, setting Eq. 16 to zero requires that

$$\mu_1^A = \mu_1^B \quad \mu_2^A = \mu_2^B \quad (17)$$

This means that at equilibrium, the chemical potential of a component is equal in all phases! When the system is not at equilibrium, $dG < 0$, that is the system seeks to decrease G until it reaches a minimum in G . If, for example, $\mu_1^A > \mu_1^B$, then component 1 will tend to "flow" out of phase A and into phase B until the chemical potentials of component 1 in phases A and B are equal.

Chemical potential is thus analogous to T and P. If T is the same in two phases, there will be no flow of heat. If one phase has a higher T than another adjacent phase, heat will flow from the hotter phase to the cooler phase until T is equal between the two phases (equilibrium).

Similarly, gases into compartments held at different pressure but allowed to flow freely between the two compartments will eventually equalize their pressures. Chemical potential is thus like a “chemical pressure” that drives chemical reactions.

Heterogeneous system

We now consider a heterogeneous system, that is, a system composed of more than one type of phase. For example, assume we have a system that can be described by the following phase components, A, B, C, and D. Let’s assume that these components can be related to each other stoichiometrically by the following reaction (this reaction is not unique):



We can define a progress variable, which is a measure of how many moles component

$$d\xi = \frac{dn_C}{c} = \frac{dn_D}{d} = -\frac{dn_A}{a} = -\frac{dn_B}{b} \quad (19)$$

Or more generally

$$d\xi = \frac{dn_i}{v_i} \quad (19a)$$

Where v_i represent the stoichiometric coefficients for each component in the reaction, e.g., a , b , c , and d with the property that it is positive if the component is on the right side of the reaction and negative if it is on the left side. Plugging Eq. 19a into Eq. 8, yields the general equation of dG for the **entire system** in the form of the progress variable

$$d\Delta G_{sys} = -S_{sys}dT + V_{sys}dP + \sum_i v_i \mu_i d\xi \quad (20)$$

$$d\Delta G_{sys} = -S_{sys}dT + V_{sys}dP + \Delta\mu_{rxn} d\xi \quad (21)$$

Which for the example at hand

$$dG_{sys} = -S_{sys}dT + V_{sys}dP + (c\mu_C + d\mu_D - a\mu_A - b\mu_B)d\xi \quad (22)$$

At constant T and P and assuming equilibrium ($dG_{sys}=0$)

$$0 = (c\mu_C + d\mu_D - a\mu_A - b\mu_B)d\xi \quad (23)$$

This implies that at equilibrium

$$0 = (c\mu_C + d\mu_D - a\mu_A - b\mu_B) \quad (24)$$

Or more generally, at equilibrium,

$$0 = \sum_i v_i \mu_i = \Delta\mu_{rxn} \quad (25)$$

which means that for any reaction, the sum of the chemical potentials of the reactants is equal to the chemical potentials of the products, hence there is no net “chemical pressure” driving the reaction forward or backward.

Equilibrium constant

In impure systems, for example, a phase consisting of a solid solution of two components - like olivine being a solid solution of forsterite and fayalite endmember components, e.g., $(Mg,Fe)_2SiO_4$ - the chemical potential of one component is decreased from its pure state by a factor related to the entropy of mixing. The chemical potential in general is given by

$$\mu_i = \mu_i^o + RT \ln(a_i) \quad (26)$$

Where the first term represents the chemical potential of the pure endmember component and the second term accounts for impurities in the form of dilution. The value a_i represents the activity of a component in a given phase. For an ideal solution, the activity is simply equal to the mole fraction of that component in the phase, that is, $a_i = X_i$. Activity is in some sense a measure of the concentration of the component in a phase. In the case of a gas species within a mixture of gases, activity is equal to the partial pressure of the gas species under ideal conditions. By ideal, we mean the case in which the molecules of interest (gas species of molecular components) do not interact with each other, e.g., no electrostatic interactions and no loss of energy during collisions (any collisions are perfectly elastic). In reality, when one mixes two components together, there are electrostatic interactions. Two immiscible liquids will repel each other, driving the effective “pressure” or “activity” of each liquid component down. In another case, the two components that mix actually attract each other electrostatically, increasing the effective activity. In these non-ideal scenarios, $a_i = \gamma_i X_i$, where $\gamma_i = 1$ under ideal conditions.

At equilibrium, reaction between various components i requires that

$$0 = \sum_i \nu_i \mu_i = \sum_i \nu_i \mu_i^o + RT \ln \prod (a_i^{\nu_i}) \quad (27)$$

And upon re-arranging,

$$\Delta \mu_{rxn}^o = -RT \ln \prod (a_i^{\nu_i}) \quad (28)$$

Where the equilibrium constant is given as

$$K = \prod_i (a_i^{\nu_i}) \quad (29)$$

and

$$\Delta \mu_{rxn}^o(P, T) = -RT \ln K \quad (30)$$

Note that the chemical potentials in the above equations refer to that of the pure endmembers (standard state) **at the T and P of interest**. Eq. 30 shows that the activities of various components in the phases associated with a given reaction must be related to each other according to the equilibrium constant. Because the left hand side of the equation depends on P and T, K should depend on P and T, that is, there is a unique K for any given P and T. This is the basis for thermobarometry. If we can measure K , then we can infer P and T.

Thermobarometry

In order to apply Eq. 30 as a thermobarometer, we need to calculate how $\Delta \mu_{rxn}^o$ varies as a function of T and P. This requires that we calculate the chemical potential of each component involved in the reaction at different T and P. To do so, we calculate the Gibbs Free Energy of each component, starting from STP conditions, 298 K and 1 bar. Note that chemical potential is simply the partial molar free energy; everything below refers to the partial molar free energy. The individual Gibbs Free energies of the pure endmember components are denoted by their Gibbs Free energy of formation from pure compounds. At STP conditions, we have

$$\Delta \bar{G}_{f,298K,1bar}^o = \Delta \bar{H}_{f,298K,1bar}^o - 298 \bar{S}_{298K,1bar}^o \quad (31)$$

To calculate the variation with T and P, we can integrate over any P-T path because G is a state variable and is hence path-independent. However, some integration paths are easier than others. We will first integrate up in temperature at constant pressure (1 bar), and then we will integrate up in P at the temperature of interest. Integrating first with temperature yields

$$\Delta \bar{G}_{f,T,1bar}^o = \left[\Delta \bar{H}_{f,298,1bar}^o + \int_{298}^T c_p dT \right] - T \left[\bar{S}_{298K,1bar}^o + \int_{298}^T \frac{c_p}{T} dT \right] \quad (32)$$

To integrate up in pressure, we make use of the following relationship.

$$\Delta \bar{G}_{f,T,P}^o = \Delta \bar{G}_{f,T,1bar}^o + \int_{1bar}^P \left(\frac{\partial \bar{G}}{\partial P} \right)_T dP = \Delta \bar{G}_{f,T,1bar}^o + \int_{1bar}^P \bar{V}_T dP \quad (33)$$

Note that V_T represents the molar volume at the temperature of interest, which means that in theory, we should have calculated V_T from $V_{298K,1bar}$. This is done by accounting for thermal expansion (not shown). We can combine the above equations to yield:

$$\Delta \bar{G}_{f,T,P}^o = \left[\Delta \bar{H}_{f,298,1bar}^o + \int_{298}^T c_p dT \right] - T \left[\bar{S}_{298K,1bar}^o + \int_{298}^T \frac{c_p}{T} dT \right] + \int_{1bar}^P \bar{V}_T dP \quad (34)$$

where the heat capacity is given by

$$c_p = a + bT + \frac{c}{T^2} + \frac{d}{T^{1/2}} \quad (35)$$

For a **reaction**, Eq. 34 can be modified accordingly.

$$\Delta \bar{G}_{rxn,T,P}^o = \left[\Delta \bar{H}_{rxn,298,1bar}^o + \int_{298}^T \Delta c_p dT \right] - T \left[\Delta \bar{S}_{rxn,298K,1bar}^o + \int_{298}^T \frac{\Delta c_p}{T} dT \right] + \int_{1bar}^P \Delta \bar{V}_{rxn,T} dP = 0 \quad (35)$$

Eq. 35 describes the P-T curve for a reaction involving pure phases. If the phases are not pure, then one needs to account for modifications to the chemical potential and Eq. 35 becomes

$$\Delta \bar{G}_{rxn,T,P}^o = \left[\Delta \bar{H}_{rxn,298,1bar}^o + \int_{298}^T \Delta c_p dT \right] - T \left[\Delta \bar{S}_{rxn,298K,1bar}^o + \int_{298}^T \frac{\Delta c_p}{T} dT \right] + \int_{1bar}^P \Delta \bar{V}_{rxn,T}^o dP = -RT \ln K \quad (36)$$

Eq. 36 describes the P-T curve of a reaction for given equilibrium constants K .

Eq. 36 can be applied directly to a barometer by integrating upwards in T and P from 298 K and 1 bar. However, in practice, a simplified version of Eq. 36 is used:

$$\Delta \bar{G}_{rxn,T,P}^o = \Delta \bar{H}_{rxn,T,P}^o - T \Delta \bar{S}_{rxn,T,P}^o + (P - 1bar) \Delta \bar{V}_{rxn}^o = -RT \ln K \quad (37)$$

Here, one assumes that the enthalpy of reaction $\Delta \bar{H}_{rxn,T,P}^o$, entropy of reaction $\Delta \bar{S}_{rxn,T,P}^o$, and molar volume change of reaction $\Delta \bar{V}_{rxn}^o$ are roughly constant over the T and P range of interest. Note that this is of course an approximation and these values for enthalpy, entropy and molar volume are based on empirical calibrations in the T and P of interest using laboratory experiments. This means that this approximate equation (37) should never be applied outside of the T-P range over which the equation was experimentally calibrated.

Recognizing the approximations that went into Eq. 37, we can re-arrange 37 to give $\ln K$ as a function of P and T

$$\ln K = \frac{T\Delta S_{rxn} - \Delta H_{rxn} - (P - 1\text{bar})\Delta V_{rxn}}{RT} \quad (38)$$

or expressed as a thermometer

$$T = \frac{(P - 1\text{bar})\Delta V_{rxn} + \Delta H_{rxn}}{\Delta S_{rxn} - R \ln K} \quad (39)$$

or as barometer

$$P = \frac{T\Delta S_{rxn} - RT \ln K - \Delta H_{rxn}}{\Delta V_{rxn}} + 1 \quad (40)$$

Application of thermobarometers and what makes a good thermometer or barometer

Application of Eq. 38 as a thermobarometer requires empirical calibration of the entropy, enthalpy and volume of reaction constants. These constant can also be theoretically calculated by integrating up in T and P from the standard states of each phase participating in the reaction. Once the calibration constants are known, Eq. 37 is applied as follows. One first has to determine the activities of the components in each phase in order to calculate K . This is done by measuring the composition of each phase participating in the reaction and then calculating mole fractions of the components of interest accordingly. If the system is ideal, then the mole fractions are all that are needed. If the system is not ideal, activity coefficients must be estimated. Unfortunately, in many cases, the non-ideal terms are not known very well. For these reasons, many empirical thermobarometers do not treat non-ideal terms explicitly, but rather add on extra compositional terms in their thermobarometric equations (39, 40) in order to approximate non-ideal effects.

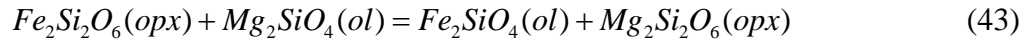
Once K is known, the equation can be solved to generate a univariant line in P-T space. There are unfortunately two unknowns, P and T. This means that one needs at least two equations as constraints, or essentially two reactions. The best bet is to get two reactions with different sensitivities to T and P, that is, different dP/dT so that the two equations can be solved simultaneously for T and P with minimal error. The common solution essentially represents the intersection of the two univariant lines in P-T space. A thermobarometer that is sensitive to temperature requires that the T term in Eq. 38 be large, and hence a large $\Delta \bar{S}_{rxn,T,P}^o$ is preferred. A thermobarometer that is more sensitive to pressure is one that requires the P term to be large, hence a large $\Delta \bar{V}_{rxn}^o$ is preferred. The T-P dependency of a univariant line describing a reaction between pure phases is given by the Clapeyron slope

$$\left(\frac{dP}{dT} \right)_{rxn} = \frac{\Delta \bar{S}_{rxn}^o}{\Delta \bar{V}_{rxn}^o} \quad (41)$$

If the phases are not pure, there is still a Clapeyron slope for a given equilibrium constant K .

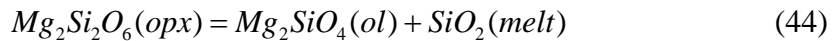
$$\left(\frac{dP}{dT}\right)_{rxn} = \frac{\Delta S_{rxn}^{\circ} - R \ln K}{\Delta V_{rxn}^{\circ}} \quad (42)$$

There are basically two types of reactions that are worth examining in detail. The first is called an **exchange** reaction, wherein a certain cation is exchanged between two different phases. For example, we have the exchange of Fe and Mg between olivine and orthopyroxene:



The volume change of this reaction is likely to be very small because no new phases are generated in this reaction. Instead, the entropy change of reaction is likely to be more important. As a consequence, exchange reactions are typically temperature sensitive and pressure-insensitive.

Net transfer reactions are more likely to be pressure-dependent because the phases on either side of the reaction are not the same. An example is as follows:



Which represents the reaction of SiO₂ component in a melt with the forsterite component in olivine to generate enstatite component in pyroxene. Because olivine and melt have very different densities (inverse of molar volume) than orthopyroxene, the volume change of reaction is likely to be non-negligible. Such a reaction will thus have a pressure-sensitivity.

Problem Set

1. You are given a suite of peridotites, ultramafic rocks consisting of garnet, clinopyroxene, orthopyroxene, and olivine as the dominant phases. Each of these phases can be described by a set of phase components.

Olivine

Mg ₂ SiO ₄	Forsterite
Fe ₂ SiO ₄	Fayalite
Ca ₂ SiO ₄	Monticellite

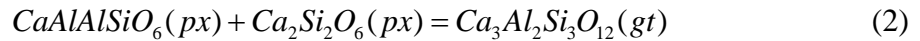
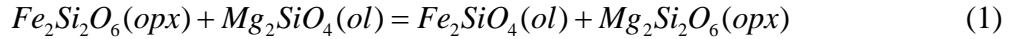
Pyroxene

CaMgSi ₂ O ₆	Diopside
Fe ₂ Si ₂ O ₆	Ferrosilite
Ca ₂ Si ₂ O ₆	Wollastonite
Mg ₂ Si ₂ O ₆	Enstatite
CaAlAlSiO ₆	Ca-Tschermakite
MgAlAlSiO ₆	Mg-Tschermakite

Garnet

Mg ₃ Al ₂ Si ₃ O ₁₂	Pyrope
Fe ₃ Al ₂ Si ₃ O ₁₂	Almandine
Ca ₃ Al ₂ Si ₃ O ₁₂	Grossular

Write out at least five reactions that involve these different components. We will give you two examples to start with:



Using Table 5 in Holland and Powell (1998), calculate $\Delta\bar{S}_{rxn,T,P}^o$ and $\Delta\bar{V}_{rxn}^o$ (at 298 K, 1 bar). Use these values to estimate the Clapeyron slope. Note which reactions are pressure-sensitive and temperature-sensitive.

2. **Thermometry.** Read Ellis and Green 1979. Answer the following questions.
 - a. What reaction is this thermometer based on? What mineral phases are required for this thermometer to work?
 - b. Explain how they got the generalized thermobarometer equation (Eq. 3) and the meaning of each term; what assumptions have gone into making this equation.
 - c. Derive Eq. 4
 - d. Explain the meaning of Eq. 5
 - e. Table 2. Show that you can reproduce their values of K_D from their clinopyroxene and garnet compositions.
 - f. Show that the form of Eq. 9 is the same as Eq. 3 except for the extra compositional term to account for Ca. Explain the motivation for this extra empirical term – why Ca?

3. **Barometry.** Read Harley and Green (1982). Answer the following questions.
 - a. What reaction is the barometer based on? What mineral phases are required for this barometer to work?
 - b. Eq 2 is the generalized simple form of a thermobarometer equation. Explain how this differs (or not) from that used in Ellis and Green 1979.
 - c. The authors have started off in a simple system MAS (Mg-Al-Si). On page 698, they show that $a_{En}^{opx} a_{MgTs}^{op} = X_{Al}^{M1} (1 - X_{Al}^{M1}) \gamma_{Mg}^{M1} \gamma_{Al}^{M1}$. Explain how this was derived from activity solution models.
 - d. In moving from the MAS system to more realistic natural systems, which have other components, such as Ca, the authors have been forced to deal with non-ideal effects. Explain qualitatively how they accounted for these non-ideal effects. What non-ideal effects were they mostly worried about?

4. **Application of thermobarometers.** Continents are underlain by thick thermal boundary layers, typically thicker than what is seen beneath ocean basins. These thick thermal boundary layers have a number of geodynamic implications for heat flow through the continents as well as the long-term stability of continents. Thus, it is important for us to know how thick continents truly are. If we could map out the thermal state of the continents with depth, we would gain valuable insight into the structure of continents. One way to do this is to investigate mantle xenoliths carried up as fragments in magmas

of deep origin, such as kimberlites, the same magmas that bring up diamonds. These xenoliths are thought to have been transported to the surface very rapidly and are thought to have quenched, “freezing” in whatever geochemical signatures they at the time they were residing in the mantle just prior to entrainment in the host kimberlite. The assumption is that the distribution of elements between mineral phases in these xenoliths reflects equilibrium conditions and that these mineral chemistries are frozen in at eruption. Kopylova et al. (1999) present electron microprobe data on minerals from mantle xenoliths from the Canadian craton. These xenoliths contain garnet, clinopyroxene, orthopyroxene, and olivine. They thus have the appropriate mineral assemblage for estimating P and T of equilibration using the thermobarometers just discussed. To do this, you will have to set up a spreadsheet where you convert major element oxides in wt. % for each mineral into cation percents. Convert into cations for the appropriate number of oxygens per formula unit:

Olivine = 4 oxygens

Pyroxene = 6 oxygens

Garnet = 12 oxygens

For a few samples in Kopylova et al. (1999), calculate the activities of various components in garnet and pyroxenes, which are appropriate for the Ellis and Green (1979) and Harley and Green (1982) thermobarometers.

Ellis and Green (1979) gt-cpx Mg-Fe exchange thermometer

$$T(^{\circ}K) = \frac{3104X_{Ca}^{gt} + 3030 + 10.86P(kbar)}{\ln K_D + 1.9034}$$

And the Harley and Green (1982) barometer is

$$P(kbar) = \frac{1}{\Delta V_r} \left[(R \ln K - 2.93)T + 5650 + 5157(1 - X_{Al}^{M1})(1 - 2X_{Al}^{M1})X_{Fe}^{opx} - 6300(X_{Ca}^{gt}X_{Fe}^{gt} + (X_{Ca}^{gt})^2) \right]$$

where T is in Kelvin

$$K = \frac{X_{Al}^{M1}(1 - X_{Al}^{M1})}{(1 - X_{Ca}^{gt})^3}$$

$$\Delta V_{rxn} = -[183.3 + 178.98(X_{Al}^{M1}(1 - X_{Al}^{M1}))] \quad (\text{cal/kbar})$$

5. **Thermobarometry recap.** Discuss the results of your calculations in the context of the thermal state of the Earth or continental lithosphere. What assumptions have gone into your calculations.