Geology 633
Metamorphism and Lithosphere Evolution

Thermodynamic calculation of mineral reactions I:
Reactions involving pure phases

The formulation for the free energy change of any reaction involving pure phases (which is why we use the ‘°’) at elevated P and T is calculated as follows:

\[ \Delta_r G^°_{P,T} = \Delta_r H^°_{P,T} - T \Delta_r S^°_{P,T} \]

where ‘\( \Delta_r \)’ is the change in \( G^°_{P,T}, H^°_{P,T} \) and \( S^°_{P,T} \) in the reaction.

At equilibrium:

\[ \Delta_r G^°_{P,T} = \Delta_r H^°_{P,T} - T \Delta_r S^°_{P,T} = 0 \]

thus

\[ \Delta_r G^°_{P,T} = 0 = [ \Delta_r H^°_{1,298} + 298\int_T^T (\partial \Delta_r H^°/\partial T)_P \, dT + \int_P^P (\partial \Delta_r H^°/\partial P)_T \, dP ] \]

\[ - T [ \Delta_r S^°_{1,298} + 298\int_T^T (\partial \Delta_r S^°/\partial T)_P \, dT + \int_P^P (\partial \Delta_r S^°/\partial P)_T \, dP ] \]

we will assume that the variation of S with pressure is negligible (ie, \( \int_P^P (\partial \Delta_r S^°/\partial P)_T \, dP = 0 \)), and substitute in expressions for the other variation terms:

\[ = [ \Delta_r H^°_{1,298} + 298\int_T^T \Delta_r C_P \, dT + \int_P^P \Delta_r V^° \, dP ] \]

\[ - T [ \Delta_r S^°_{1,298} + 298\int_T^T \Delta_r C_P / T \, dT ] \]

1. Solids-only reactions

If we are dealing with a solids-only reaction, we will assume that the molar volume of crystalline solids (minerals) does not change significantly with P and T (ie, \( \alpha \approx \beta \approx 0 \)), so that \( \int_P^P \Delta_r V \, dP = \Delta_r V^°_s (P - 1) \). (By adding the subscript ‘s’ to \( \Delta_r V^°_s \), we remind ourselves that this approximation only holds for solid phases, not fluids). Note that in this expression, pressure units are in bars.

\[ = [ \Delta_r H^°_{1,298} + 298\int_T^T \Delta_r C_P \, dT + \Delta_r V^°_s 1,298 (P - 1) ] \]

\[ - T [ \Delta_r S^°_{1,298} + 298\int_T^T \Delta_r C_P / T \, dT ] \]

To complete the formulation, we need to know the formula for \( \Delta_r C_P \), the heat capacity expression. Heat capacity in general is a complex function of T, such as:

\[ C_P = a + bT + cT^2 + dT^{-0.5} + eT^{-2} \]
or, for the reaction:

\[
\Delta C_p = \Delta a + \Delta bT + \Delta cT^2 + \Delta dT^{-0.5} + \Delta eT^{-2}
\]

This expression is substituted in the two places in the above formula for ‘\(\Delta C_p\)’. The expression must then be broken into its parts, integrated and solved between the limits of 298K and T, similar to what you did in Glgy 429. Note that we are concerned with \(\Delta C_p\), so that each term in the general expression below (a, b, c, etc.) has to be calculated for the reaction (ie, \(\Delta a, \Delta b, \Delta c\), etc.).

**Simplifications for first order analysis of a solids-only reaction involving pure phases**

For a solids-only reaction, it turns out that the change in the heat capacities between reactants and products going from \(1, 298\) to \(P,T\) is usually small. So, for first order analysis of a solids-only reaction, we can make the assumption that \(\Delta C_p = 0\). Note that this is NOT the same as saying that the enthalpy and entropy of an individual phase involved in the reaction does not change with T – they do! It is just that the changes between the reactant phases and product phases is often about the same, which algebraically is the same as setting \(\Delta C_p = 0\).

Thus, the above equation simplifies considerably to:

\[
\Delta G^{\circ}_{P,T} = \Delta H^{\circ}_{P,T} - T \Delta S^{\circ}_{P,T} = 0 \text{ at equilibrium}
\]

\[
= \Delta H^{\circ}_{1,298} + \Delta V^{\circ}_{s1,298} (P - 1) - T \Delta S^{\circ}_{1,298}
\]

Note that this simplified formula is used for first-order calculations only. With the widespread use of computers, it is not that complicated to code in the full expressions and these will provide more accurate results.

Finally, to obtain two extremely useful relations in determining the general slope of a reaction, recall the Gibbs-Helmholtz relation:

\[
dG = -SdT + VdP
\]

which when compared to the total differential of \(G\):

\[
dG = (\partial G/\partial T)_P \, dT + (\partial G/\partial P)_T \, dP
\]

gives the following two key relations:

\[
(\partial G/\partial T)_P = -S \quad \text{(or, for a reaction: } (\partial \Delta G^{\circ}_{P,T} / \partial T)_P = -\Delta S^{\circ}_{P,T})
\]

\[
(\partial G/\partial P)_T = V \quad \text{(or, for a reaction: } (\partial \Delta G^{\circ}_{P,T} / \partial P)_T = \Delta V^{\circ}_{P,T})
\]
In using these expressions for solids-only reactions, it is usually sufficient to assume that:

\[ \Delta_r V^\circ_{P,T} = \Delta_r V^\circ_{1,298} \quad \text{and} \quad \Delta_r S^\circ_{P,T} = \Delta_r S^\circ_{1,298} \]

finally, to calculate the slope of a reaction (meaning, at equilibrium where \( dG = 0 \)):

\[ \left( \frac{\partial P}{\partial T} \right)_{P,T} = \frac{\Delta_r S^\circ_{P,T}}{\Delta_r V^\circ_{P,T}} \]

but for our assumptions about \( S \) and \( V \) in solids, this end up being:

\[ \left( \frac{\partial P}{\partial T} \right)_{P,T} \sim \left( \frac{\partial P}{\partial T} \right)_{1,298} = \frac{\Delta_r S^\circ_{1,298}}{\Delta_r V^\circ_{1,298}} \]

Data

Below are thermochemical data for each of the minerals from Robie et al. (1978). In Robie’s tabulation, variation of heat capacity with temperature may be expressed by the equation:

\[ C_p = a + bT + cT^2 + dT^{-0.5} + eT^{-2} \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Anorthite</th>
<th>Quartz</th>
<th>Grossular</th>
<th>Wollastonite</th>
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<td>41.46</td>
<td>255.5</td>
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<td>1529.3</td>
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<td>-0.69900</td>
<td>1.4373 x 10(^{-2})</td>
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<tr>
<td>c</td>
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<td>2.53 x 10(^{-4}) 0</td>
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<td></td>
</tr>
<tr>
<td>d</td>
<td>-4.5885 x 10(^{3}) 0</td>
<td>-1.8943 x 10(^{4}) 16.936</td>
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<td>e</td>
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Exercise

1. Balance a reaction between the pure, solid phases grossular (Grs - Ca\(_3\)Al\(_2\)Si\(_3\)O\(_{12}\)), wollastonite (Wo - CaSiO\(_3\)), quartz (Qtz - SiO\(_2\)) and anorthite (An - CaAl\(_2\)Si\(_2\)O\(_8\)). (You must do this right, or the rest of the exercise will fail!)

2. Let’s do some first order analysis using the heat capacity simplifications to get a feel for the approximate slope and position of the reaction. Answer the following questions:

(a) Which assemblage is more stable at 1 bar, 298K?

(b) Which assemblage is favoured by increasing pressure?
(c) Which assemblage is favoured by increasing temperature?

(d) What is the slope of the reaction?

(e) At P = 1 bar, what is the equilibrium temperature of the reaction?

(f) Based on all of the above, plot on some graph paper the position of the reaction, correctly labelled (i.e., reactant and product phases placed on the correct side of the reaction). (Don’t make your plot go above 10 kbar)

3. Now let’s be more rigorous. Using the full expression for $\Delta_r G_{P,T}^o$, calculate and plot the P-T position of the reaction using Excel (again, don’t go above 10 kbar). For temperature, don’t extrapolate beyond the limits of applicability of the heat capacity equations, which is 300 – 1800 K.

4. By plotting the equilibrium curves on one chart/graph, how do the two curves compare? In this case, is the heat capacity simplification justified?

5. You will now use above results (recognizing that what you have calculated is a thermodynamic model of the real reaction) to make some interesting geological inferences.

(a) For a temperature of 950 K (a temperature typically found for this assemblage), estimate the depth in the earth at which the full assemblage involved in the reaction would be found (i.e., where the equilibrium occurs). Use the curve obtained in (3) to get your pressure. Assume an average rock density of 2.6 g cm$^{-3}$. (Recall that P = $\rho$gh).

(b) What would be the average geothermal gradient, in K (or °C) km$^{-1}$? How does this compare to the earth’s average geothermal gradient? What sort of geological setting might provide the temperature conditions necessary for the formation of this assemblage at this depth?

2. Thermodynamic calculations of reactions with fluids

Recall from above that, at equilibrium:

$$\Delta_r G_{P,T}^o = [ \Delta_r H_{1,298}^o + 298 \int_T T (\partial \Delta_r H^o / \partial T)_P dT + \int_P T (\partial \Delta_r H^o / \partial P)_T dP ]$$

$$- T [ \Delta_r S_{1,298}^o + 298 \int_T \Delta_r S^o / \partial T)_P dT + \int_P (\partial \Delta_r S^o / \partial P)_T dP ]$$

$$= [ \Delta_r H_{1,298}^o + 298 \int_T \Delta_r C_p dT + \int_P (\partial \Delta_r H^o / \partial P)_T dP ]$$

$$- T [ \Delta_r S_{1,298}^o + 298 \int_T \Delta_r C_p / T dT ]$$

Whereas we assumed, for solids-only reactions, that:
we cannot do this for fluids because they are so compressible.

Instead, for fluids, we must use the expression:
\[ \int P \Delta r V_s^\circ \, dP = \Delta r V_s^{\circ \, 1, 298} (P - 1) \]
in which \( f \) stands for fugacity of a gas, and \( f^\circ \) stands for fugacity of a pure gas.

Because the properties of gases at a pressure of 1 bar (any \( T \)) are close to those of an ideal gas, the fugacity of a gas at a pressure of 1 bar (any \( T \)) is assumed to equal 1 bar (i.e., the fugacity coefficient is 1). Thus:

\[
\begin{align*}
RT \ln f^\circ P \bigg|_1 &= RT \ln f^\circ P - RT \ln f^\circ 1 \text{ bar} = RT \ln \left( f^\circ P / f^\circ 1 \text{ bar} \right) = RT \ln \left( f^\circ / 1 \right) \\
&= RT \ln f^\circ \\
\end{align*}
\]

Because the degree of non-ideality, and thus the fugacity, of gases depends on \( P \) as well as \( T \), the general expression becomes:

\[ RT \ln f^\circ_{P,T} \]

where \( f^\circ_{P,T} \) stands for the fugacity of a pure fluid at any \( P \) and \( T \). If you do a units check for the above term, you might conclude that the units are J-bar, rather than J as we want! The reason is that in evaluating the integral between \( P \) and 1 bar, units of \( P \) (\( f^\circ_{P,T} \)) are divided by units of \( P \) (\( f^\circ_{1 \text{ bar}, T} \)) (look inside the natural log term), such that the \( P \) units cancel. Thus, you must be aware that the term \( RT \ln f^\circ_{P,T} \) as written implies division by a \( P \) term whose value is 1 bar, such that the units do ultimately work out to be in J.

Values of \( f^\circ_{P,T} \) are obtained directly from tables, or can be calculated from:

\[ f^\circ_{P,T} = \Gamma_{P,T} \, P \]

where \( \Gamma_{P,T} \) is the fugacity coefficient. You can think of the fugacity coefficient as a term that accounts for the non-ideal-gas behaviour of a real gas. Values of \( \Gamma \) can be calculated or obtained from tables. In this lab, values of \( \Gamma_{P,T} \) are provided for you.

** Note that for an ideal gas, \( f^\circ_{P,T} = P \). **

Calculation of an equilibrium involving fluids at elevated \( P \) and \( T \)

For a reaction involving solids and fluids, in order to calculate:

\[ \int P \left( \delta \Delta H^\circ / \delta P \right)_T \, dP = \int P \Delta r V^\circ \, dP \]
we separate the solids from the fluids as follows:

\[ \int_1^P \Delta_r V^\circ dP = \Delta_r V^\circ_{1,298} (P - 1) + or - \int_1^P V^\circ dP \]

The ‘+ or –’ refers to the fact that if the fluid is a reactant in the reaction, one subtrahs the fluid term, whereas if the fluid is a product, one adds the term.

Because \[ \int_1^P V^\circ dP = RT \ln f^{\circ}_{P,T} \] (see above), this results in:

\[ \int_1^P \Delta_r V^\circ dP = \Delta_r V^\circ_{1,298} (P - 1) + or - RT \ln f^{\circ}_{P,T} \]

Substituting into the full free energy equation:

\[ \Delta_r \Delta G^\circ_{P,T} = \Delta_r H^\circ_{1,298} + 298 \int T \Delta_r C_p dT + \Delta_r V^\circ_{s1,298} (P - 1) + or - RT \ln f^{\circ}_{P,T} \]

Note: despite having made a big deal about how fluids are special when it comes to their variation with pressure, fluid phases are treated like any other phase when calculating the change in the reaction (\( \Delta_r \)) of heat capacity, entropy, and enthalpy in the above equations.

If we assume that the change in the heat capacities between reactants and products going from 1, 298 to P,T is negligible, the above equation simplifies considerably to:

\[ \Delta_r \Delta G^\circ_{P,T} = \Delta_r H^\circ_{1,298} - T \Delta_r S^\circ_{1,298} + \Delta_r V^\circ_{s1,298} (P - 1) + or - RT \ln f^{\circ}_{P,T} = 0 \]

**Exercise**

1. Using the ideal gas law for one mole, PV = RT, calculate the volume of pure H2O at:

   - 200 °C, 1 bar
   - 200 °C, 1 kbar
   - 400 °C, 1 kbar

The specific volumes of water measured experimentally in cc/g are:

   - 200 °C, 1 bar  2171
   - 200 °C, 1 kbar  1.0811
   - 400 °C, 1 kbar  1.442
Comment on how the values based on the ideal gas law compare with those measured experimentally.

2. You will recall from Gilty 311 that a crucial reaction in metapelites is where muscovite and quartz are no longer stable together, reacting to form Al₂SiO₅ + K-feldspar + hydrous fluid (you may wish to refer to your petrogenetic grid from Gilty 311). This is a type of devolatilization reaction (it involves release of a fluid phase). Because the fluid is water, it is more specifically a dehydration reaction.

Devolatilization reactions are the most common sort of metamorphic reaction. Thus, the results you obtain for the Ms+Qtz reaction will be useful in illustrating a number of features that are common to all devolatilization reactions.

Note that what you will be calculating is a thermodynamic model of the reaction in a simplified chemical system, rather than an actual reaction such as one might infer from the change in mineralogy and texture going across an isograd in the field. It turns out that for this reaction, the thermodynamic model is likely a very good approximation to the reaction that occur in rocks.

a. Assuming that sillimanite is the stable form of Al₂SiO₅, write a balanced chemical reaction between these phases (first find the chemical formulae for the phases!).

b. Using the thermodynamic data from Philpotts (appended to the back of this lab), assuming that \( \Delta C_p = 0 \) and \( \Delta r V_s^\circ (P, T) = \Delta r V_s^\circ 1,298 \), and assuming that the water behaves as an ideal gas (ie, \( f_{H_2O}^{P,T} = P \)), calculate the equilibrium pressures for 300, 350, 400, 450, 500, 550, 600, 650 and 700 °C. Plot the values on a graph (either by hand or using Excel).

Note: the calculation of P in parts b. and d. have to be done by a trial and error method. This will be speeded up if you have the formulae in the spreadsheet, thereby allowing for rapid calculations for each new P you try.

c. Can you rationalize the shape of the slope of the reaction? (Hint: what two thermodynamic parameters are divided to obtain the slope of a reaction? How does each vary with P and T? – note that one of the reaction products is a gas!)

d. Repeat part b. for the same set of temperatures, only treat the water as the real gas that it is (ie, use fugacity of water rather than pressure of an ideal gas). To save time, here are the values for the fugacity coefficients that you should use (these are the values for the final P conditions of the equilibrium for each temperature):

\[
\begin{array}{|c|c|}
\hline
T \, ^\circ C & \Gamma_{P,T} \\
\hline
300 & 1 \\
350 & 0.95 \\
400 & 0.95 \\
\hline
\end{array}
\]
<p>| | |</p>
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<th></th>
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e. Plot the results of b. and d. on the same graph, and comment on the difference between the results.