

## Problem set: Constructing metamorphic phase diagrams using phase equilibria and the Clausius-Clapeyron equation

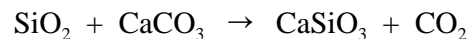
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Mineral assemblages preserved in metamorphic rocks record information about the temperatures and pressures of metamorphism, thereby providing clues to the geologic histories of the regions in which metamorphism occurred. But how do we know the temperatures and pressures at which a particular mineral assemblage is stable? One way to figure this out would be to conduct an enormous number of experiments at various temperatures and pressures, using rocks of a wide variety of chemical compositions, to determine the conditions at which particular mineral assemblages form. Such **phase equilibrium experiments** are difficult and time-consuming, however, so it would be better if we could conduct a smaller number of experiments and somehow extrapolate from them. In this problem set, you will use the thermodynamic expression known as the **Clausius-Clapeyron equation** to extrapolate the results from a small number of phase-equilibrium experiments to construct a pressure-temperature phase diagram for some petrologically useful metamorphic reactions.

### Metamorphic reactions and the Clausius-Clapeyron equation

Consider a metamorphic reaction such as:



(quartz + calcite  $\rightarrow$  wollastonite + fluid)

As the reaction proceeds from left to right, consuming quartz and calcite and producing wollastonite and carbon dioxide, the volume of the system will change because the combined volumes of the products (1 mole of wollastonite + 1 mole of CO<sub>2</sub>) will be different from the combined volumes of the reactants (1 mole of quartz + 1 mole of calcite). Likewise, the entropy of the system will change because the combined entropies of the products will be different from the combined entropies of the reactants. We can quantify these changes as follows:

$$\text{change in volume} = \Delta V = V(\text{products}) - V(\text{reactants})$$

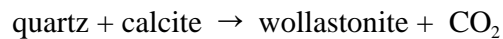
$$\text{change in entropy} = \Delta S = S(\text{products}) - S(\text{reactants})$$

If the volume of the products is *greater* than the volume of the reactants, then  $\Delta V$  will be *positive*; that is, the volume of the system will *increase* as the reaction proceeds. If the volume of the products is *less* than the volume of the reactants, then  $\Delta V$  will be *negative*; that is, the volume of the system will *decrease* as the reaction proceeds. The same principle applies to  $\Delta S$ . The quantities  $\Delta V$  and  $\Delta S$  are referred to as the **volume of reaction** and **entropy of reaction**, respectively.

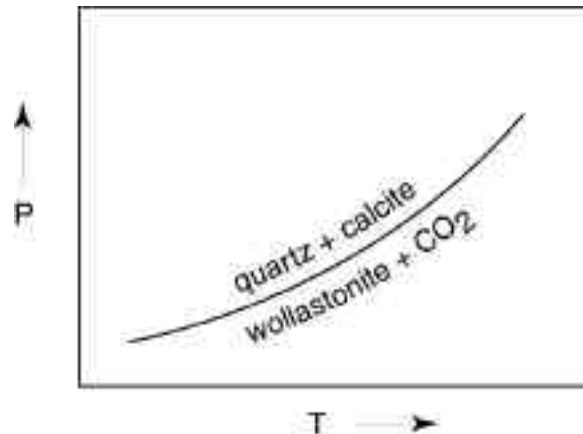
The Clausius-Clapeyron equation relates the changes in volume and entropy during a reaction to the variables pressure (P) and temperature (T) as follows:

$$\frac{dP}{dT} = \frac{S}{V}$$

in which dP and dT represent incremental changes in pressure and temperature along a univariant reaction curve. The quantity dP/dT thus represents the slope of the univariant reaction curve on a graph of P vs. T (recall that the slope of a line is simply the change in Y divided by the change in X). To help illustrate the relationship expressed by the Clausius-Clapeyron equation, consider the reaction mentioned earlier:



Because there is net production of fluid (carbon dioxide), the volume and entropy of the system are both likely to increase as the reaction proceeds: fluids have low densities and thus large volumes, and fluids are highly disordered and thus have high entropies. Because volume and entropy both increase as the reaction proceeds, the values of  $\Delta V$  and  $\Delta S$  are both positive and the value of  $\Delta S / \Delta V$  must also be positive. According to the Clausius-Clapeyron equation, the value of dP/dT must then be positive too. This means that on a graph of P vs. T the univariant reaction curve will have a positive slope:



For this particular reaction we can infer that the products should occupy the lower right-hand side of the diagram, because the assemblage that contains the fluid phase will typically be stable at higher temperature (which favors higher-entropy assemblages) and at lower pressure (which favors lower-density, higher-volume assemblages).

(NOTE: From our analysis so far, it is clear that the curve should have a positive slope, but it is not obvious that it should also be concave upward — although we could predict this by assuming that fluids are compressed much more easily than are minerals. How would differing compressibilities affect the value of  $\Delta V$  as pressure increases?)

## Entropies and volumes of minerals

In order to *quantify* the relationships we have discussed — that is, to determine the actual pressures and temperatures for a particular univariant reaction curve — the entropies and volumes of the product and reactant phases must be determined. Fortunately for us, many years of industrious work have produced impressive arrays of thermodynamic data that we can use for our calculations. Because fluids are highly compressible, and therefore have volumes that are strongly dependent on pressure, we'll keep things relatively simple by considering mineral phases only.

Entropies of minerals are typically calculated from laboratory measurements of **heat capacity**, the amount of heat energy required to raise the temperature of a material by a specified amount. As a material absorbs heat ( $q$ ) under equilibrium conditions, its entropy increases proportionally ( $dS = dq/T$ ). Measurements of heat capacity can therefore be used to determine the entropies of minerals at various temperatures. For minerals with variable compositions or multiple structural states, the entropies can be adjusted by making theoretical or empirical corrections that take such variations into account (for example, by allowing for the disorder — and resulting entropy — produced by the mixing of Mg and Fe ions among octahedrally coordinated sites in olivine).

Molar volumes of minerals are commonly calculated from unit cell volumes determined by X-ray diffraction at low temperatures (although volumes could also, in principle, be determined from very accurate measurements of specific gravity). Because minerals expand slightly when heated and compress slightly when squeezed, the volumes of minerals are not exactly constant.

## Phase-equilibrium experiments

To create an accurate phase diagram it is generally necessary to perform at least *some* phase equilibrium experiments involving the minerals of interest, in order to determine at least one set of P-T conditions at which the products and reactants coexist in equilibrium (i.e., to locate at least one point on the univariant curve). Note that the Clausius-Clapeyron equation gives us only the *slope* of the curve — it does NOT give us the position of any particular P-T point through which the curve must pass! Therefore, in order to "anchor" the curve on a P-T graph, we must locate at least one point on the curve by experimental equilibration of the appropriate phases. Once such a point has been located, a line of the appropriate slope can be drawn through it. If the values of  $S$  and  $V$  are constant (or nearly so), then the line will be straight (or nearly so). If the values of  $S$  and  $V$  vary substantially with temperature and pressure, then the line will generally be curved.

## QUESTIONS:

Consider the stabilities of the three polymorphs of  $\text{Al}_2\text{SiO}_5$ : andalusite, sillimanite, and kyanite. From the phase rule, we predict that in this one-component system, a three-phase assemblage should be invariant — i.e. the three minerals will all coexist in equilibrium at only a single point on a P-T diagram (an invariant point). We further predict that a two-phase assemblage will be univariant, so that any two polymorphs should coexist only along a univariant line on a P-T diagram. Finally, a single-phase assemblage will be divariant, so that it occupies an area (a stability field) on a P-T diagram. The phase diagram for the  $\text{Al}_2\text{SiO}_5$  polymorphs should thus consist of three distinct stability fields separated by lines and meeting at a single point. Because these polymorphs are quite common in metapelites, their stabilities under various P-T conditions are of great interest to petrologists. We will use thermodynamic data and the Clausius-Clapeyron equation, together with the results of phase equilibrium experiments, to construct a P-T diagram that shows the stability fields of these important minerals.

- 1) The unit cell volumes for the  $\text{Al}_2\text{SiO}_5$  polymorphs have been determined by X-ray diffraction at a temperature of  $25^\circ\text{C}$ , as follows (with uncertainties  $\pm 0.32 \times 10^{-24} \text{ cm}^3$ )

<u>mineral</u>	<u>unit cell volume (<math>\text{cm}^3</math>)</u>	<u>formula units per unit cell (= Z)</u>
andalusite	$342.25 \times 10^{-24}$	4
sillimanite	$330.97 \times 10^{-24}$	4
kyanite	$293.41 \times 10^{-24}$	4

Determine the molar volumes of the three minerals at  $25^\circ\text{C}$  (the volume of one mole of the compound  $\text{Al}_2\text{SiO}_5$ ), ignoring uncertainties for now. **Show your calculations.** HINTS: You must take into account the fact that the unit cell contains four formula units, and your values should all end up somewhere between 40 and  $60 \text{ cm}^3$ .

- 2) The molar entropies of the three polymorphs at  $25^\circ\text{C}$  have been determined as reported in the table below. Note that according to the Clausius-Clapeyron equation, the value of  $S/V$  must be in units of P/T, that is,  $\text{bars}/^\circ\text{C}$ . Therefore, to use molar volumes in the Clausius-Clapeyron equation, you must convert units from  $\text{cm}^3$  to the (somewhat zany) units of joules/bar, using the conversion  $1 \text{ cm}^3 = 0.1 \text{ joules/bar}$ . Do the conversion and enter your results in the following table.

<u>mineral</u>	<u>molar entropy (<math>\text{joules}/^\circ\text{C}</math>)</u>	<u>molar volume (<math>\text{joules/bar}</math>)</u>
andalusite	91.39 ( $\pm 0.14$ )	_____
sillimanite	95.79 ( $\pm 0.14$ )	_____
kyanite	82.30 ( $\pm 0.13$ )	_____

- 3) In a set of phase equilibrium experiments, the equilibrium polymorphs at various temperatures and pressures were determined as follows:

Pressure (bars)	Temperature (°C)	stable phase
1800	605	andalusite
1800	655	sillimanite
2400	377	kyanite
2400	409	andalusite
3600	452	kyanite
3600	491	andalusite
3600	494	andalusite
3600	527	sillimanite

Using the data from these experiments and the molar entropy and molar volume data tabulated in question 2, determine the slopes of the univariant reaction lines and produce a P-T phase diagram for the system  $\text{Al}_2\text{SiO}_5$  over a temperature range from 200 to 800°C and a pressure range from 0 to 8000 bars. **Show your calculations.** As a first approximation, let's ignore the small uncertainties in  $S$  and  $V$ , and let's assume that  $S$  and  $V$  are constant (i.e. that they are not dependent on temperature or pressure). On your phase diagram, plot the results of the phase equilibrium experiments, the positions of the univariant lines that separate the divariant fields, and the position of the invariant point (the "triple point"). Label all of the important features clearly. (FOOD FOR THOUGHT: Given that the entropies of minerals are strongly dependent on temperature, how can we possibly justify making the approximation that  $S$  is *not* strongly dependent on temperature?).

- 4) Describe and comment on the ambiguities involved in determining the positions of the univariant lines and the triple point.
- 5) Now consider the uncertainties in the reported values of  $S$  and  $V$ , and comment briefly on the extent to which these uncertainties might affect your phase diagram.
- 6) The aluminosilicate polymorphs, like all minerals, expand slightly when heated. Kyanite, for example, undergoes a 2% increase in volume when heated from room temperature to 800°C. The proportional increase in volume is expressed as a quantity known as the **thermal expansivity**. Measurements of the molar volumes of aluminosilicate polymorphs at high temperatures show that andalusite and sillimanite have appreciably different thermal expansivities. Based on your phase diagram, which mineral do you think has the greater thermal expansivity, andalusite or sillimanite? Explain your reasoning. (HINT: How would different thermal expansivities affect the value of  $V$  for the andalusite-sillimanite reaction?)