

Reaction Types & Curves Handout

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Reactions among solid and fluid phases can be categorized in several different ways, based on what the reaction does, how the reaction progresses, or based on the nature of phases involved.

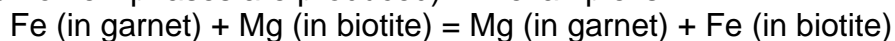
Categorization based on reaction effect

■ **Net-transfer reactions** involve chemical components being "transferred" from one phase or set of phases to others (new phases are produced as old ones disappear). An example is:



Net-transfer reactions may be *terminal reactions* or *tie-line flip reactions* (discussed below).

■ **Exchange reactions** involve chemical components being exchanged between phases, so compositions change, but modes remain the same (no phases disappear and no new phases are produced). An example is:



Categorization based on reaction progress

■ **Discontinuous reactions** are those that occur at a particular temperature (for a particular pressure). For these, a curve (or line) can be drawn on a pressure-temperature (P-T) diagram. (See the reactions on Figure 1.) On either side of the curve, a different phase, or set of phases, is stable. In a discontinuous reaction, products and reactants can only co-exist stably precisely at the equilibrium reaction conditions (on the reaction line in P-T space). Discontinuous reactions are always *net-transfer reactions*.

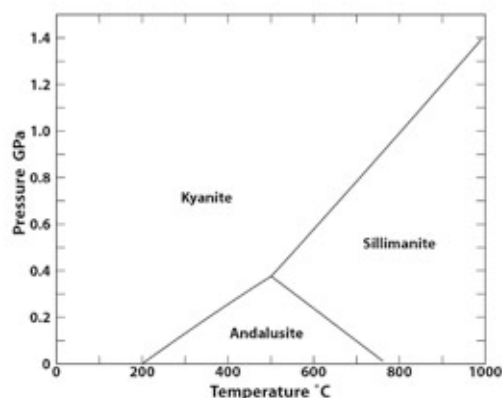


Figure 1. Phase diagram for the Al₂SiO₅ polymorphs.

For all discontinuous reactions, the phase (or combination of phases) with the lowest volume is stable on the high pressure side of the reaction curve. The phase (or combination of phases) with the greatest entropy is stable on the high temperature side of the curve. Because volume and entropy are roughly proportional for most minerals, this means that most discontinuous reactions have positive slopes. There are,

however, exceptions, especially for reactions that involve a fluid phase (H₂O or CO₂).

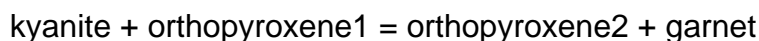
■ **Continuous reactions** (sometimes called **sliding reactions**) involve phases that may vary in composition. Such reactions are more common than discontinuous reactions because compositional variation, of either fluid or solid phases, is typical for geological materials. Continuous reactions occur over a range of conditions, so the products and reactants coexist stably over a range of conditions (but the composition of the phases changes systematically as conditions change). Continuous reactions may be *net-transfer reactions* or *exchange reactions*. Continuous reactions are difficult to plot on a P-T diagram without making assumptions or simplifications.

Categorization based on phases involved

■ **Solid-solid net transfer reactions** (often just called **solid-solid reactions**) occur among solid phases of differing composition (two or more minerals, if we are talking about geology). These phases may include elements found in fluids (H, C), but those elements are conserved in the solid phases so that no fluid phases (H₂O, CO₂) are involved as reactants or products. Solid-solid net transfer reactions can be continuous or discontinuous, and they may be *terminal*, or *tie-line flip* reactions (discussed below).

■ **Polymorphic reactions** are a special type of solid-solid reaction that involve phases of identical composition. Classic examples are the reactions among the aluminum silicates: kyanite-sillimanite-andalusite. See the photomicrograph (Figure 2) and phase diagram (Figure 1). The conversion of graphite to diamond at high pressure, and calcium carbonate (calcite-aragonite) equilibria, are other examples.

Many solid-solid reactions are continuous because they involve phases whose compositions are changing as their modes (the amount present) change. This occurs because the phases contain appreciable solid solution. Specific reactions are difficult to express, but schematically, one would be:



(the numbers 1 and 2 mean the two orthopyroxenes are not the same composition.)

■ **Devolatilization reactions** are net-transfer reactions that involve the liberation of a

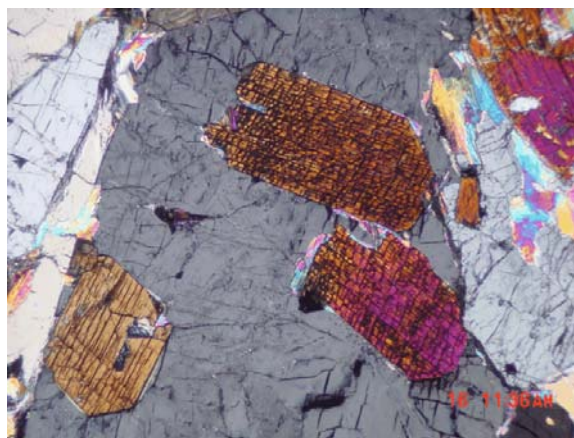
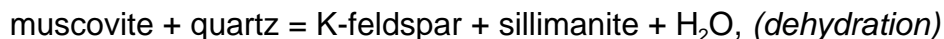


Figure 2. Kyanite grains inside andalusite
Kyanite inclusions (three tabular grains showing good cleavage and brown-pink interference colors) in andalusite (dark gray interference color, poorly developed cleavage) in a kyanite-andalusite-sillimanite (+ staurolite) quartz vein. This rock was "caught in the act" as kyanite reacted to form andalusite. The photo is from Donna Whitney. This sample is from Hamadan, Iran, and is discussed by Sepahi et al. (2004, J. Metam. Geology 22, 119-134).

volatile phase (H_2O for *dehydration reactions* or CO_2 for *decarbonation reactions*). Several examples are shown in Figure 3 (next page).

Other examples of a dehydration and a decarbonation reaction are:



Except under extremely unusual circumstance, the fluid is always on the high temperature side of such reactions. In essence, the fluid "boils" or "sublimates" away as temperature increases. If the fluid composition is fixed (stays constant), then devolatilization reactions are *discontinuous*, but if the fluid composition can vary as a result of the liberation of H_2O or CO_2 , then the reactions will be *continuous*.

Curvature: The curves for dehydration or decarbonation reactions on a P-T diagram will have shallow slopes at low pressure because the volume of a fluid phase is much larger than that of solid phases. However, the compressibility of a fluid leads to a rapid decrease in volume as pressure rises, so the slopes steepen with rising pressure, leading to substantial curvature. Some (rare) reactions curve around and gain a negative slope at high pressure.

■ **Terminal reactions** involve the creation of a new phase from two or three (or more) other phases, or (in the other direction) the decomposition of one phase into two or three others. They may be *solid-solid reactions* or they may involve a fluid phase. Figure 3 shows three dehydration reactions. The highest temperature one is an example of a terminal reaction:



At lower temperature, below the reaction curve, serpentine is stable. Above the

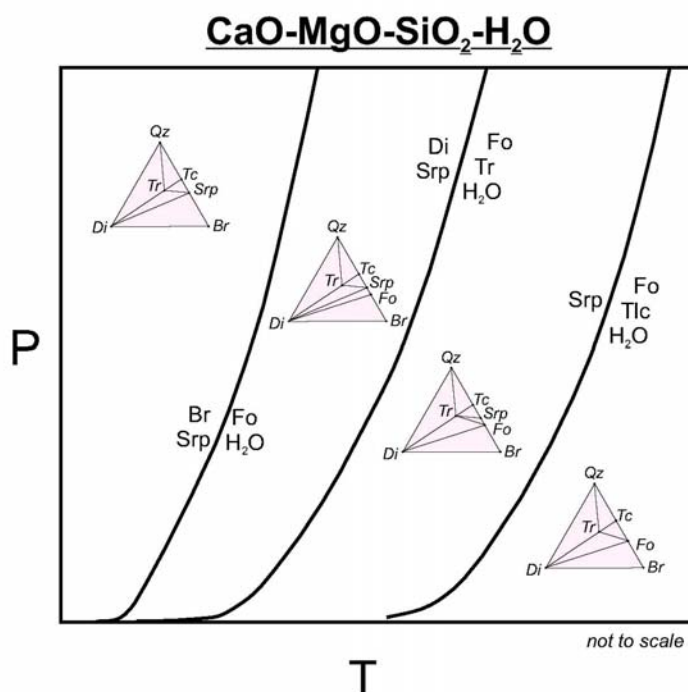


Figure 3. Dehydration reactions involving phases in the $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ system. These are all net-transfer reactions and they all involve H_2O on the high temperature side of the reaction.

reaction curve it is not. Forsterite, talc or H₂O may also be present at temperatures below the curve, *but not all three of them together*. All four minerals are stable together only on the reaction curve. At higher temperatures, any combination of forsterite + talc + H₂O is stable.

The name *terminal reaction* refers to the fact that a reaction terminates (eliminates) a single phase. The phase is stable to the right or left of the curve, but not both.

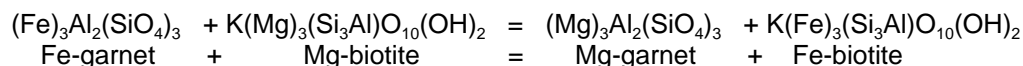
■ Tie line flip reactions

involve two (or more) phases becoming stable together that were previously unstable together, and vice versa. As with *terminal reactions*, they may be *solid-solid reactions* or may involve a fluid phase. In Figure 3, both of the two lower temperature reactions are tie-line flip reactions.

The name *tie-line flip reaction* describes what happens to the triangular compatibility diagrams (in a 3-component system). (Triangular diagrams are often more difficult to use/plot if there are more than three components.)

Look at Figure 4. Some of the reactions shown are *terminal reactions* (they are labeled with a single phases on one side of the reaction curve), some are *tie-line flip* reactions (more than one phase on each side of the curve). Look and see what happens to the lines on the triangular diagrams as a reaction curve is crossed.

■ **Ion-exchange reactions** (generally just called "**exchange reactions**") involve two phases that both share a solid solution exchange such Fe⁺² being replaced by Mg. For example consider garnet, (Fe,Mg)₃Al₂(SiO₄)₃ and biotite, K(Fe,Mg)₃(Si₃Al)O₁₀(OH)₂ (both formulas are simplified). We can write an exchange reactions as follows:



Reactions of this type are all continuous, and differ from the others kinds of reactions

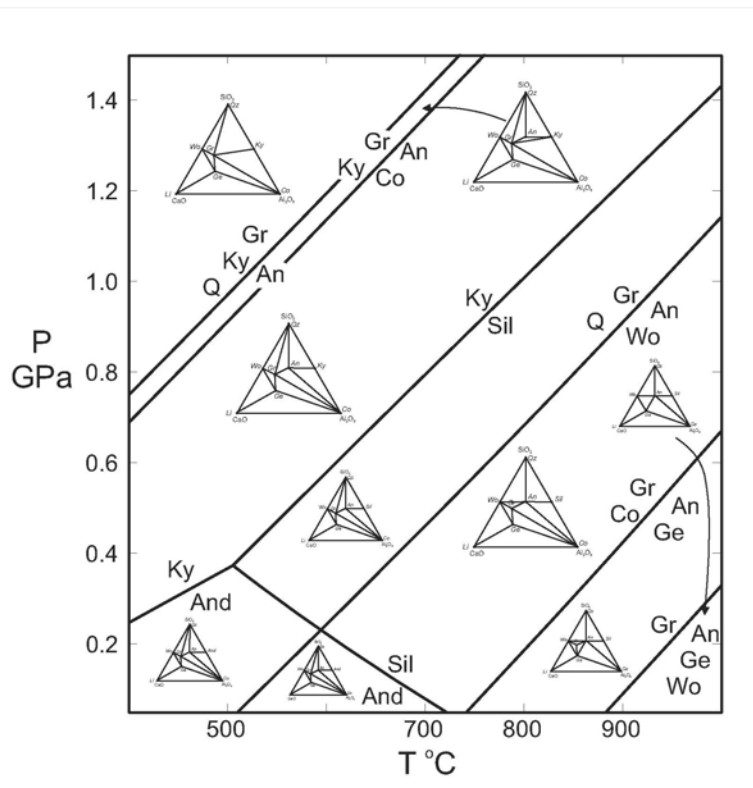


Figure 4. Some reactions in the CaO-Al₂O₃-SiO₂ system. These reactions are all solid-solid reactions. Some are terminal reactions, some are tie-line flip reactions.

discussed above in that there is no real product or a reactant. Instead, across the complete range of conditions over which the two minerals are stable, both are changing in composition.

The general thermodynamics of all exchange reactions are the same: at low temperature, the elements being exchanged separate as much as possible – each element being strongly partitioned into one of the minerals. At high temperature, mixing is complete, so the elements are equally partitioned between the two minerals. However, the temperature dependence varies depending on the elements and minerals being considered.