On Being a Student of Thermodynamics: Trust Your Eyes; Use Your Imagination

Reid F. Cooper*

I am a student of thermodynamics. Yes, I have been teaching the subject to baccalaureate and graduate students in petrology and materials science for about 25 years. But in every course, almost every lecture, I perceive something new: some new (to me) subtlety in the ideas that facilitates deeper appreciation and understanding of some of the experimental data generated in my research group and that fosters a profound admiration for the many scholars who brought forth these ideas in the nineteenth century and refined them in the twentieth. In this process, I have identified and shared with my fellow learners two pieces of advice that are particularly valuable in applying thermodynamics to the analysis of textures in rocks, which is so very often the center of our interest in thermodynamics: trust your eyes; use your imagination. Let me explain, or at least try...

The textures of rocks—that is, the spatial distribution of minerals, the morphologies of the interfaces between grains (grain and heterophase boundaries), and the spatial differences of oxide composition (including compositional gradients)—are a result of a convolution of thermodynamics and kinetics. Beginning petrology students frequently struggle to understand that there is no textural information in an equilibrium phase diagram (indeed, there is no time in equilibrium thermodynamics). The amount of creative synthesis involved in the thought experiment of logically stepping through a time (t)–temperature (T)–pressure (P) protocol with an equilibrium phase diagram so as to predict a texture is profound. I might add that learning to teach this synthesis is simultaneously humbling and rewarding. For many students of petrology, this is the first example and practice of “trust your eyes” in doing predictive science: we (the community) construe that the texture observed is a result of a chemical system subjected to a time-varying set of thermodynamic potentials, and so we apply equilibrium thermodynamic arguments—like phase diagrams—step-wise in time to develop an interpretation that is extrapolative.

One can learn to trust one’s eyes at a finer scale, too, which is particularly important in studying mineral reactions. As a simple, practical, and provocative illustration, consider the oxidation of solid-solution, ferromagnesian olivine beyond its stability limit. For the fayalite end-member, the chemical reaction is straightforward:

\[ 3\text{Fe}_2\text{SiO}_4 + \text{O}_2 = 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2; \Delta G^\circ_{\text{FMQ}} \]

fayalite + oxygen gas = magnetite + \(\alpha\)-quartz

where \(\Delta G^\circ_{\text{FMQ}}\) is the standard Gibbs free energy of this reaction. If we were considering the oxidation breakdown of pure fayalite, this reaction would describe the FMQ (fayalite–magnetite–quartz) oxygen buffer. In the actual case of ferromagnesian olivine, though, the fayalite component is dissolved into forsterite; as a consequence, the reaction (at a given \(P\) and \(T\)) would occur only at an oxygen activity (fugacity) that is greater than FMQ. The reaction texture is illustrated schematically in Figure 1. When exposed to an oxygen activity exceeding the stability of the fayalite component (e.g., annealing at \(-900^\circ\text{C}\) and 1 atm in air), one discovers that the texture of the incomplete reaction includes (1) a specular, polycrystalline thin film of periclase (MgO) and magnesioferrite (MgFe\(_2\)O\(_4\)) covering the original surface (between \(\xi = 0\), the original surface, and \(\xi = \xi^\circ\)); (2) fine (nanometer-scale) precipitates of pure magnetite (Fe\(_3\)O\(_4\)) and amorphous silica precipitated on lattice dislocations in the olivine and existing in a “matrix” of pure forsterite between \(\xi = 0\) and an internal reaction interface \(\xi = \xi^\circ\); and (3) yet-to-be-reacted olivine solid solution at \(\xi > \xi^\circ\) (Wu and Kohlstedt 1988). This process is “dislocation decoration”; deformation-effected dislocations in olivine can be studied with standard petrographic techniques following such oxidation (Kohlstedt et al. 1976); see Figure 2.

A strange texture! The reaction has not produced an equilibrium assemblage within the olivine: forsterite and silica should react to form enstatite (MgSiO\(_3\)); the chemical potential of MgO in the forsterite is sufficiently high that magnesioferrite should form instead of magnetite. The assemblage is metastable: if the specimen is annealed at high temperature for a time very, very long compared to that required for the reaction front at \(\xi = \xi^\circ\) to march through, say, a millimeter-scale experimental specimen, enstatite and magnesioferrite will form. Not evident in the schematic, but important in the texture nevertheless, is the fact that microprobe analyses of the forsterite matrix between 0 and \(\xi^\circ\) and ion-backscattering spectrometry analyses of the (new) surface thin film reveal no concentration gradients whatsoever of the component ions.

What, then, can be said? Trust your eyes! The magnetite (Mt) and silica (Sil) precipitated on the dislocations are pure; the activity of each is unity, to first order (the Gibbs free energy of \(\alpha\)-quartz and vitreous silica being quite similar). Thermodynamically, then, the reaction is easily analyzed. Using the mass-action equation,

\[ K_{eq} = \frac{a_{\text{Mt}}a_{\text{Sil}}}{a_{\alpha\text{Q}}} = \exp\left(\frac{-\Delta G^\circ_{\text{FMQ}}}{RT}\right), \]

where \(K_{eq}\) is the equilibrium constant and \(a_i\) is the activity of species \(i\), one can substitute unity for \(a_{\text{Mt}}\) and \(a_{\text{Sil}}\) and so discern the trade-off between the activity of fayalite (\(a_{\text{Fa}}\)) in the olivine solid solution and the oxygen activity (\(a_{\alpha\text{Q}}\)) at which the fayalite component is no longer stable.

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* Reid F. Cooper is Professor of Geological Sciences at Brown University, Providence, RI, USA. His research emphases are experimental chemical and mechanical kinetics in upper-mantle minerals and rocks and reaction dynamics in silicate melts and glasses.

Department of Geological Sciences
Brown University, 324 Brook Street
Providence, RI 02612, USA
E-mail: reid_cooper@brown.edu

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FIGURE 1 Schematic diagram of the (incomplete) oxidation of ferromagnesian olivine beyond its limit of stability. The original surface is at location 0. The reaction sees both external and internal reaction fronts, \(\xi^\circ\) and \(\xi^\prime\), respectively. Reaction products include phase-pure magnetite and vitreous silica in a matrix of pure forsterite (Wu and Kohlstedt 1988).
[As an exercise, students can take experimental data of the breakdown oxygen activity for various olivine compositions and so calculate a solution model—determined as a function of \( X_{\text{Fe}} \)—for olivine (cf. Nitzan 1974).]

The texture and context reveal more. In this example, the oxygen activity at the free surface, \( \xi \), is that of air (i.e. \( a^{\text{O}_2} = 0.21 \)). The oxygen activity at \( \xi'' \) is that at which the olivine solid solution is no longer stable (as discerned from \( K_{\text{eq}} \)). So, clearly, there is a gradient in the chemical potential of oxygen (\( \mu_{\text{O}_2} \)) within the reacting specimen, i.e. 
\[
\frac{d\mu_{\text{O}_2}}{d\xi} = \frac{RT}{\xi} \ln \left( \frac{a^{\text{O}_2}}{a^{\text{O}_2}_{\xi''}} \right)
\]
And yet, as already noted, one cannot identify concentration gradients of ion species between \( \xi \) and \( \xi'' \). The thin film at the surface is a mixture of magnesium and ferric-iron oxides: there is no SiO\(_2\) component in this two-phase film. The silica-free, surface thin film is critical in interpreting the dynamics of the reaction.

And so the second exhortation: use your imagination. Interpreting the texture to comprehend the dynamics in this case involves identifying the physical manifestation of the oxygen activity in olivine. Now, the thermodynamics we teach in petrology classes is typically that of Clausius, Joule, and Gibbs, which is based on state variables, that is, enthalpy, entropy, Gibbs free energy, and activity. These are ensemble or average values representative of the bonding and the vibrational/translational “chaos” of ions and molecules making up a system: “black-box” variables masking an atomic reality. The activity of a component in a mineral has as its physical manifestation a collection of point defects on the lattice. Point defects in minerals are atomic vacancies, substitutionals, and interstitials; they are equilibrium defects: there is sufficient entropy associated with their deployment on the lattice to “overcome” the enthalpy of their formation. The concentration of these defects rarely reaches 0.1 atomic percent, making their quantitative characterization beyond the capabilities of, for example, X-ray spectrometry on a microprobe. One employs imagination in the sense of contemplating the variations of concentrations of defects at different locations within a reaction microstructure: if there are activity gradients, there must be, physically, gradients in the concentrations of point defects.

The physical manifestation of the oxygen activity in olivine is a charge-compensating pair of point defects—vacancies on the divalent-cation (\( \text{Me}^{2+} \rightarrow \text{Mg}^{2+} \) and \( \text{Fe}^{2+} \)) sublattice (octahedral sites in the \( \text{O}^{2-} \) array) and ferric-iron ions (\( \text{Fe}^{3+} \)) on the octahedral sites. It ends up that point defects in minerals have actual charges, that is, their presence in the lattice locally distorts the electronic structure of the mineral. Vacancies on the divalent cation sites in olivine have a 2− charge. \( \text{Fe}^{3+} \) occupying a site where an \( \text{Fe}^{2+} \) is “normally” present has an additional 1+ charge. Creating this latter defect requires only the removal of an electron from the \( \text{Fe}^{2+} \) present originally; the “lost” electron—called an electron “hole”—is highly mobile and easily “hops” from one iron ion to another nearby in the crystal.

Equilibrium thermodynamics is enforced for point defects: one can articulate defect-formation reactions, but these have requirements not only of conservation of matter but also of conservation of charge and, in minerals, conservation of lattice sites (that is, conservation of the mineral structure proper). So, relating oxygen activity to defect concentration in olivine can be written as:

\[
3\text{Fe}^{3+}\text{Me}^{2+} + \frac{1}{2}\text{O}_2 = 2\text{Fe}^{2+}\text{Me}^{2+} + \text{V}_{\text{Me}} + \text{FeO} = 2h^* + \text{V}_{\text{Me}} + \text{FeO} \quad \xi'' G^0
\]

In this (Kröger-Vink) notation, the subscripts refer to lattice sites and the superscripts refer to charge on that site relative to whatever species occupies the site in the perfect crystal (e.g. Schmalzried 1981, p. 39). Thus, \( \text{Fe}^{3+}\text{Me}^{2+} \) is an \( \text{Fe}^{2+} \) octahedral site; it is electrically neutral (“\( x \)”) as a divalent cation normally occupies the site. A “dot” superscript denotes relative positive charge; a “prime” superscript denotes relative negative charge. Thus, \( \text{Fe}^{3+}\text{Me}^{2+} \) is a charge-compensating pair of point defects (because of the high mobility of charge transfer, it is identified alternatively as an electron hole, \( h^* \)), and \( \text{V}_{\text{Me}} \) is a divalent-site vacancy with a 2− charge. Note the balances: beyond mass conservation, charge neutrality is maintained on both sides of the equation, as is site conservation (three octahedral sites accounted for on each side). Mass-action applies:

\[
K_{\text{eq}} = \frac{a^{\text{Fe}^{2+}\text{Me}^{2+}} a^{\text{V}_{\text{Me}}} a^{\text{FeO}}}{a^{\text{Fe}^{2+}} a^{\text{V}_{\text{Me}}} a^{\text{O}_2} \xi'' G^0} = \exp \left( \frac{-\Delta G_{\text{eq}}}{RT} \right)
\]

In the equation, the activities of \( \text{Fe}^{2+}\text{Me}^{2+} \) and \( \text{FeO} \) are essentially fixed (constant), set by the situation, that is, by the fayalite composition of the olivine and by the fact that olivine (in its natural context) is also in equilibrium with orthopyroxene. Thus, one sees in the equation that an increase in oxygen activity results in an increase in the activities—and so the concentrations—of the defect species \( h^* \) and \( \text{V}_{\text{Me}} \).

One realizes, then (trust your eyes!), that in the olivine the equilibrium concentrations of vacancies and holes are much higher at \( \xi = 0 \) than at \( \xi = \xi'' \): flux of the defects “inward” (\( j_{\text{Me}^{2+}} \) and \( j_{\text{V}_{\text{Me}}} \) and attendant arrows in Figure 1) and the physically required counterflux of \( \text{Me}^{2+} \) “outward” (\( j_{\text{Fe}^{3+}} \)) is how the external oxygen activity is transferred into the reacting crystal. The loss of the cations from the olivine to the free surface—where they react with environmental oxygen to produce the silica-free, oxide thin film (plus \( h^* \))—means that the divalent cation/oxygen anion ratio within the olivine is decreasing. The olivine oxidizes internally not by adding oxygen but rather by losing cations; too, one sees that oxidation occurs not by diffusion of an oxygen species but rather by the diffusive motion of the divalent cations in response to a gradient in \( \mu_{\text{O}_2} \) (and proceeds at the rate of the cation flux). The high mobility of the electron holes “decouples” the fluxes of anions and cations, which is critical in facilitating the dynamics and so the texture. All minerals containing even low concentrations of transition-metal cations can anticipate similar decoupling.

This is a rather simple example of a thermodynamic approach to apprehending the development of a complex texture. As a fellow student, what I recommend is identifying points in a reaction texture where one can identify unequivocally (eyes) values of certain chemical potentials (activities) and ask how those points “communicate” via defects (imagination!). Dealing similarly with more complex textures, for example, the development of a metamorphic symplectite, involves additional thought and information regarding, for instance, interface stability. Nevertheless, the eyes/imagination approach still applies, and is quite powerful.

REFERENCES

FIGURE 1 Dislocations in experimentally deformed San Carlos (A2) peridot (transmitted, plane-polarized light). The ubiquitous dark dots are dislocation lines viewed end-on. The dislocations are visible because the crystal has been oxidized subsequent to deformation. This is the structure imaged between 0 and \( \xi'' \) in Figure 1.

Equation, as is site conservation (three octahedral sites accounted for on each side). Mass-action applies: