Ge 212 Problem Set 2

Due Friday October 18, 2019

1. In class, it was (or will be?) asserted that, for any stable or metastable material, the reversible adiabats are steeper in *P*-V space than the isothermals. Once we learn the second law we will see that this is equivalent to the statement (∂V/∂*P*)S ≥ (∂V/∂*P*)*T*. Use the table of Jacobians (<http://www.asimow.com/jacobiantable.jpg>) and the constraint (coming later) that *Cp* > 0 for any stable or metastable material to prove that this is always true, regardless of the sign of (∂V/∂*T*)*P*. It is possible for (∂*V*/∂*T*)*P* to be zero as well; what happens then?
2. Consider an electric circuit consisting of a capacitor with capacitance *C* (in farads, 1 farad = 1 coulomb/volt) in series with a resistor with resistance *R* (in ohms, 1 ohm = 1 volt/amp, and 1 amp = 1 coulomb/second). Let *V*0 be the voltage to the left of the capacitor, *V*1 the voltage between capacitor and resistor, and *V*2 the voltage to the right of the resistor. So the charge on the capacitor is C(*V*0 – *V*1) and the current across the resistor is (*V1 – V2)*/*R.* When the left and right sides are shorted so that *V*0 = *V*2, this circuit obeys the equation *C*(d(*V0 – V1)*/d*t*) – (*V1 – V0)*/*R* = 0 and its only equilibrium state is *V*1 = *V*0 = *V*2 with no charge on the capacitor. Say instead we connect the ends of this circuit to a variable voltage source so we can apply a difference V2 – V0 and we want to charge up the capacitor *reversibly…*
	1. What does it mean to change voltage reversibly in this case? What is a criterion for assessing whether the change in reversible?
	2. What is the value of the time constant  we should use to evaluate whether we are approaching reversible changes or not?
3. Say we have a sphere of matter with thermal conductivity *k* (in W/m/K), heat capacity *C*p (in J/K/kg), density  (in kg/m3), and radius *R* (in m). Say we want to heat this sphere *reversibly* by changing the surface temperature…
	1. What does it mean to change temperature reversibly in this case? What is a criterion for assessing whether the change in reversible?
	2. What is the characteristic time  that we have to think about to determine whether a temperature change will approach reversibility?
4. Let’s think about component transformations for a little while…Consider the component sets **n** = {CaO, Al2O3, SiO2} and **n’** = {CaSiO3, Al2SiO5, CaAl2Si2O8}. Write the matrix ****i’i that maps a composition in terms of component set **n’** to **n**. In class I asserted that the reverse transformation matrix ****ii’ = {****i’i}–1. Is this true here? If not, what is wrong with this example?
5. *Craziness with components, because why not?*

Consider first the three-component system C-H-O, with units being moles of atoms. Get or make some ternary plotting paper (e.g., <https://www.waterproofpaper.com/graph-paper/triangular-grid-graph-paper.pdf>) and define the space with H at the lower-left corner, O at lower-right, C at top … use the whole triangle. Now, plot the locations of the following compositional features:

 • carbon, C

• oxygen, O

• hydrogen, H

• methane, CH4

 • carbon dioxide, CO2

 • carbon monoxide, CO

 • The CH4-CO-CO2 triangle

 • Water, H2O

 • Formaldehyde, CH2O

 • Acetic acid, CH3-COOH

 • Sucrose, C6H12O6

• Ethanol, CH3-CH2-OH (notice anything at this point about metabolism, fermentation, photosynthesis, methanogenesis, methanotrophy, etc.? Feel free to explore more biochemistry here if you wish)

• THC, C21H30O2

• Place hatching marks along the outside edge of the physically accessible region that you can make with non-negative amount of all elements.

OK, now get a new sheet of ternary plotting paper. Use only the middle of it to draw a quarter-size equilateral triangle (i.e. the corners are at (0.5, 0.25, 0.25), (0.25, 0.5, 0.25), and (0.25, 0.25, 0.5)) representing the component space with CH4 at lower-left, CO2 at lower right, and CO at the top. The units now are *moles of carbon* coming from each component (So, for example, deoxyribose C5H10O4 can be expressed as 2.5 CH4 + 1.5 CO2 + 1 CO, so the mole fractions of the components for this composition in this space are $X\_{CH\_{4}}=\frac{2.5}{2.5+1.5+1}=0.5$, $X\_{CO\_{2}}=\frac{1.5}{2.5+1.5+1}=0.3$, and $X\_{CO}=\frac{1}{2.5+1.5+1}=0.2$. ).

• Now plot all fourteen of the features you drew in C-H-O moles-of-atoms space in this new CH4-CO2-CO moles-of-carbon component space (some things may not be plottable, in which case draw arrows that point towards where they would be if your paper were infinitely big).

Bonus section: try to draw a three-dimensional perspective diagram (or construct it digitally so it can be viewed from multiple perspectives) of the Cartesian space C-H-O with units of moles of atoms. Locate the C-H-O triangle and where the composition vectors we’ve been looking at pierce the plane of the triangle. Now locate the CH4-CO2-CO moles-of-carbon triangle and where the composition vectors pierce the plane of this triangle. In this view, can you rationalize how the positions of H, O, H2O, and the third side of the physically accessible triangle appeared in the previous part of this problem?

1. *Component transformation in real life*

In the MELTS model, pyroxenes are represented as a seven-component system using these components:

 En Enstatite Mg2Si2O6

 Di Diopside CaMgSi2O6

 Hd Hedenbergite CaFe2+Si2O6

 Jd Jadeite NaAlSi2O6

 Abf Alumino-buffonite\* CaTi0.5Mg0.5AlSiO6

 Bf Buffonite CaTi0.5Mg0.5Fe3+SiO6

 Es Essenite CaFe3+AlSiO6

(\* I am not making this up)

a. How many oxides are present in this model (counting FeO and Fe2O3 separately)?

b. Consider that you are given a composition in terms of moles of the 7 components, which you can write as a vector {En, Di, Hd, Jd, Abf, Bf, Es}. Give me the transformation matrix you would premultiply by this vector in order to obtain this composition in moles of oxides (make sure you specify the order of the oxides in the resulting vector, please!).

c. Now consider the reverse problem, which occurs in real life when you measure a pyroxene composition by electron probe and Mössbauer or by wet chemistry and then need to express it in pyroxene components: given the composition as a vector of moles of oxides, is there a matrix you can multiply by in order to obtain the composition in moles of the 7 components? If not (hint, hint), why not? – please explain this both mathematically and *conceptually*.

d. Assuming you answered ‘no’ to the first part of (c), propose a reasonable method to accomplish the task of converting from an oxide analysis to component moles. Is there a sense in which your method does this task as well as possible?