Notes on a question about the Maxwell Construction from class on Thursday, 2/1.

Fig 2.9 from Chandler, which shows the Maxwell Construction method, is reproduced below.

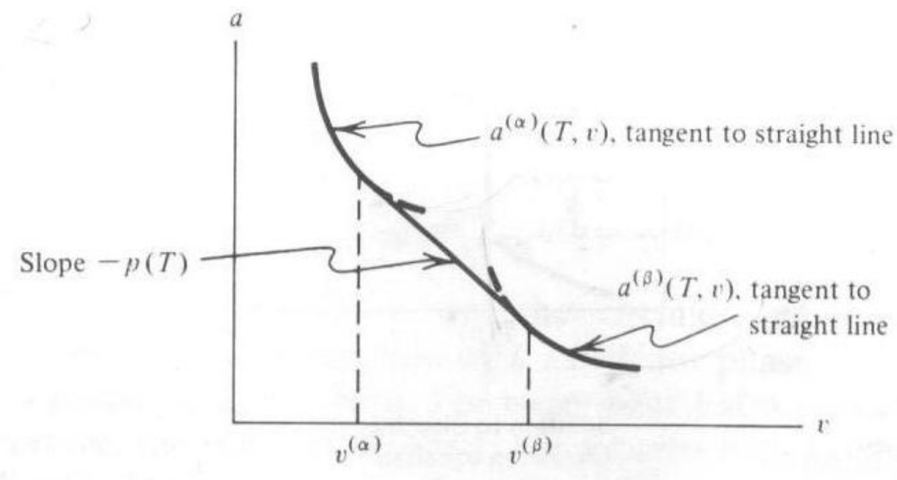

Fig. 2.9. The Helmholtz free energy per mole on an isotherm.

The Maxwell construction method arises from the relation

$$\left(\frac{\partial a}{\partial v}\right)_T = -p \qquad (1)$$

where $a=A/n$ and $v=V/n$. At equilibrium there will be one p in the system. If you have an equation of state (e.g., the VDW equation) you can solve for $a(v)$ and use the common tangent technique to solve for $v^{(\alpha)}$ and $v^{(\beta)}$ at equilibrium. But as several of you pointed out in class, there are several points on this plot where the slopes are the same. I've drawn a few (in red) on the diagram below.

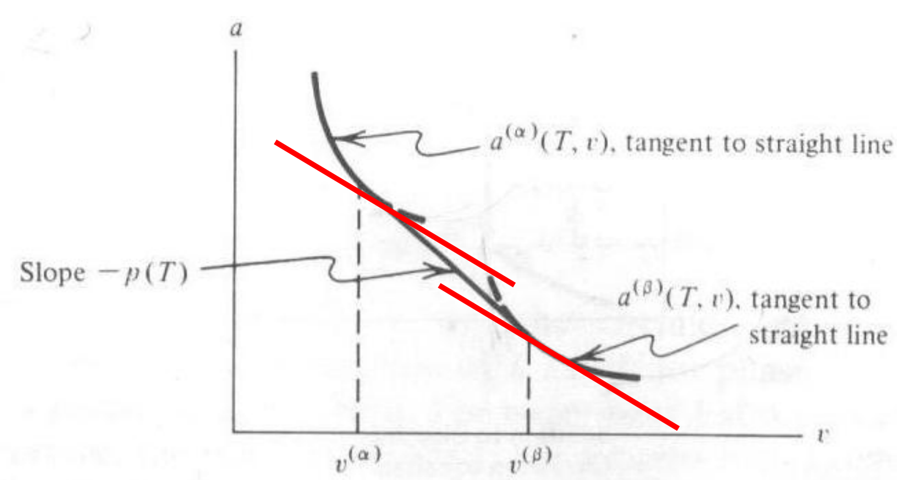

Fig. 2.9. The Helmholtz free energy per mole on an isotherm.

Thus, just because we have the same value of *p* (given by (1)) doesn't mean that we are at equilibrium. The lines must have the same slope and the same intercept. Of course, if you use a graphical common tangent approach the intercepts must be the same. But if we're just looking at the math we need to include another equilibrium criteria,

$$\mu^{(\alpha)} = \mu^{(\beta)} . \tag{2}$$

Note that from the definition of the Helmholtz energy

$$\mu = a + pv . \tag{3}$$

Thus the criteria that $\mu^{(\alpha)} = \mu^{(\beta)}$ implies that

$$(a + pv)^{(\alpha)} = (a + pv)^{(\beta)} . \tag{4}$$

Note that the equation for a line is given by y=mx+b. Thus, the intercept is given by b=y-mx; if we have a point and a slope then we can find the intercept. Using the notation in Fig. 2.9, one point is ($v^{(\alpha)}$, $a^{(\alpha)}$), and the other point is ($v^{(\beta)}$, $a^{(\beta)}$). The intercept for the first point/slope combination is $b^{(\alpha)}=a^{(\alpha)}+pv^{(\alpha)}$ and for the second point/slope combination $b^{(\beta)}=a^{(\beta)}+pv^{(\beta)}$. But from equation (4) above we see that the intercepts must be equal.

To summarize, equilibrium is assured (for a one-component system) when there is a single value of the temperature, pressure, and chemical potential in all the phases. Drawing a common tangent on a plot of *a* vs. *v* satisfies all three equilibrium criteria. If you are just looking at the equations, in addition to setting the pressures equal also set the chemical potential of each phase equal to ensure that the equilibrium criteria are met.