Use of *Thermodynamics and Its Applications*, 3rd ed. and 10.40 class notes and handouts and a hand calculator are permitted. No other aids or documents are permitted. Please answer each question in a <u>separate</u> exam book. Be careful about managing your time and be aware of the maximum points allotted to each part of the 3 problems.

1. (40 points) This is a 6 part problem worth a total of 40 points

   (a) (6 points) If for a given system, closed, with one component, we had a function $A=A(U,T)$, could this function contain the equivalent amount of information as the fundamental equation for intensive properties? Briefly explain your answer.

   (b) (6 points) Express the following derivative in terms of measurable properties for a single component: $\left(\dfrac{\partial G}{\partial A}\right)_T$.

   (c) (6 points) Express $y^{(k)} = f(P, \underline{S}, N_A, \mu_B, N_C, ...)$ in terms of a Legendre transform of $\underline{H} = y^{(0)}$ for an n component system. Also express the total differential, $dy^{(k)}$, in terms of derived and primitive thermodynamic properties.

   (d) (10 points) Are there restrictions on the signs of C_p and α_p for any real, single component system? Explain your answer.

   (e) (6 points) For a system containing 5 components, considering only intensive properties, how many dimensions does the Gibbs surface have, not including the U dimension? Explain the significance of a plane tangent to the Gibbs surface at two points.

   (f) (6 points) Express $\underline{G}_{PT}$ in terms of derivatives of $\underline{H}$ for an n component system.

2. (30 points) *Technology Review* (December 1975) describes a new invention for producing power – the Nitinol Engine. "Nitinol is a unique nickel-titanium alloy whose mechanical and electrical properties change drastically during a crystalline phase change [occurring at] modest temperatures [about 40°C]. The result is a memory for shape: if deformed while cool, nitinol will return to its undeformed shape when warmed. Alternately heating and cooling it causes motion – a conversion of heat to mechanical energy." The article also contained the illustration shown below and a quote by A.D. Johnson who claims that 30 W of shaft output were generated with a hot water stream flowing at 10 grams/s at 50°C.

MITY Industries needs your help to decide whether it should apply for a patent based on Johnson's invention. Develop an appropriate analysis to evaluate whether the claim is thermodynamically viable. If your analysis shows that the Nitinol engine is thermodynamically viable, is the claimed output possible from a practical point of view? You can assume favorable conditions where a very large flow of cold water is available at 20°C.

Image removed due to copyright considerations. Please see "*Technology Review* 78, no. 2 (December 1975): 19."

3. (30 points) A French Physicist, Emile Amagat (1841-1915) developed a diagram of *PV versus P* to represent important volumetric behavior for a single component system. Amagat claims that his diagram, illustrated below in reduced coordinates for a general pure substance, provides the same information content as the *P versus V* diagram we have discussed frequently in class, but that it allows for improved visualization of behavior at low and high pressures or densities. On the Amagat diagram three parabolic curves (C, M, and J) are shown along with a number of isotherms at multiple values of T_c. The outer curve J is the locus of Joule-Thompson coefficient inversion temperatures where the partial derivative of T as a function of P at constant H changes sign.

   (a) (10 points) The intermediate curve M is the locus of *PV* product minima as a function of *P*. Show that the intercept of this locus with the reduced *PV* axis at $P_r = 0$ corresponds to the reduced Boyle temperature of the fluid.

(b) (10 points) At high pressures the isotherms become nearly parallel. Develop an analysis based on the VdW EOS that shows this to be reasonable and estimate the limiting value of PV/P as $P \rightarrow \infty$.

(c) (10 points) The inner curve C is the locus of points representing liquid and vapor phase co-existence or the binodal curves meeting at the critical point with a vertical tangent. Is this behavior consistent with the stability criteria described in chapter 7 of the text? Specifically show that the criteria given by Equations (7-16 and 7-39) are satisfied at the critical point. Explain your answer.
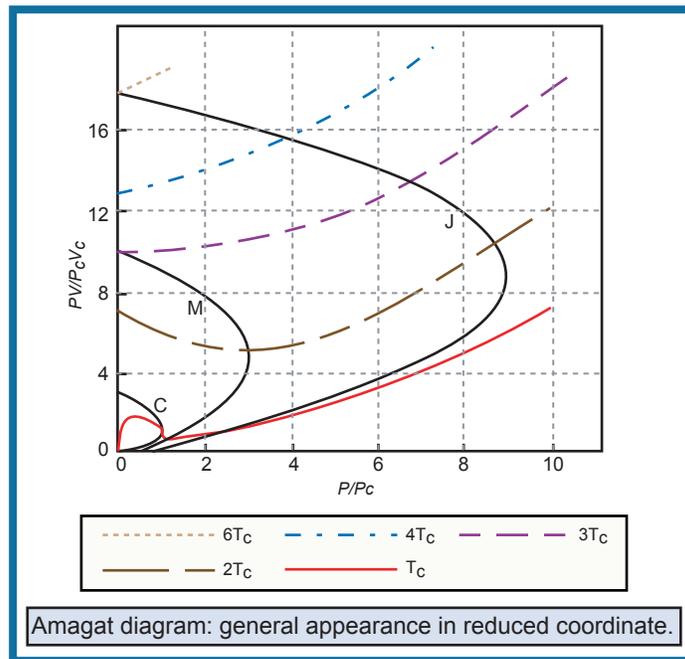

Amagat diagram: general appearance in reduced coordinate.

Image by MIT OCW.