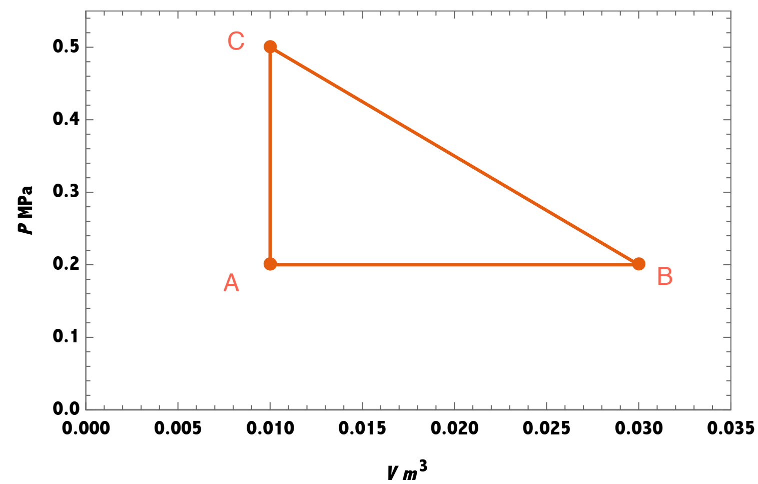
Advanced Chemical Engineering Thermodynamics (CBE 60553)

Homework 1 **Due September 1, 2017**

Solve each problem on separate sheets of paper, and clearly indicate the problem number and your name on each. Carefully and neatly document your answers. You may use a mathematical solver like Jupyter/iPython. Use plotting software for all plots.

1 Choose your path wisely

A particular system has the equation of state $U = \frac{5}{2}PV + C$, where C is an undetermined constant.



1. The system starts at state A, in which $P = 0.2\,\text{MPa}$ and $V = 0.01\,\text{m}^3$. It is taken quasistatically along the path shown in the figure ($A \to B$, $B \to C$, $C \to A$). Calculate the heat transferred from the surroundings, q, and the work done on the system, w, for each step along the path.

2. Calculate q and w for a quasistatic process starting at A and ending at B along the path $P = a + b(V - c)^2$, where $a = 0.1\,\text{MPa}$, $b = 1 \times 10^3\,\text{MPa}\,\text{m}^{-6}$, and $c = 0.02\,\text{m}^3$.

3. The system exchanges both heat and work with its surroundings along the paths above. An *adiabat* is a particular quasistatic path along which work is done but no heat is transferred. Find the form of the adiabats $P = P(V)$ for the system described by $U = \frac{5}{2}PV + C$. (*Hint:* If $đq_{\text{qs}} = 0$, then $dU = đw_{\text{qs}} = -PdV$. What else does dU equal?)

2 Is it fundamental enough?

The following ten equations are purported to be fundamental equations for various thermodynamic systems. Five, however, are inconsisent with the basic postulates of a fundamental equation and are thus unphysical. For each, plot the relationship between S and U and identify the five that are unacceptable. v_0, θ, and R are all positive constants and, in the case of fractional exponents, the real positive root is to be implied.

$$S = \left(\frac{R^2}{v_0\theta}\right)^{1/3} (NVU)^{1/3} \qquad S = \left(\frac{R}{\theta^2}\right)^{1/3} \left(\frac{NU}{V}\right)^{2/3}$$

$$S = \left(\frac{R}{\theta}\right)^{1/2} \left(NU + \frac{R\theta V^2}{v_0^2}\right)^{1/2} \qquad S = \left(\frac{R^2\theta}{v_0^3}\right) \frac{V^3}{NU}$$

$$S = \left(\frac{R^3}{v_0\theta^2}\right)^{1/5}\left(N^2U^2V\right)^{1/5} \qquad S = NR\ln\left(\frac{UV}{N^2R\theta v_0}\right)$$

$$S = \left(\frac{NRU}{\theta}\right)^{1/2}\exp\left(-\frac{V^2}{2N^2v_0^2}\right) \qquad S = \left(\frac{NRU}{\theta}\right)^{1/2}\exp\left(-\frac{UV}{NR\theta v_0}\right)$$

$$U = \left(\frac{NR\theta V}{v_0}\right)\left(1+\frac{S}{NR}\right)\exp\left(-S/NR\right) \qquad U = \left(\frac{v_0\theta}{R}\right)\frac{S^2}{V}\exp\left(S/NR\right)$$

3 Find your equilibrium

The fundamental equations of both systems A and B are

$$S = \left(\frac{R^2}{v_0\theta}\right)^{1/3}(NVU)^{1/3}$$

The volume and mole number of system A are $9\times10^{-6}\,\mathrm{m}^3$ and $3\,\mathrm{mol}$, respectively, and of system B are $4\times10^{-6}\,\mathrm{m}^3$ and $2\,\mathrm{mol}$, respectively. First suppose A and B are completely isolated from one another. Plot the total entropy S_A+S_B as function of $U_A/(U_A+U_B)$, where $U_A+U_B = 80$ J. If A and B were connected by a diathermal wall and the pair allowed to come to equilibrium, what would U_A and U_B be?

4 Exactly right

The Helmholtz energy A is a thermodynamic state function. Show that

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \text{ and } \left(\frac{\partial A}{\partial T}\right)_V = -S \text{ implies } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

5 A difference of degree

Determine whether the following five expressions are homogeneous and, if so, what their degree of homogeneity is:

$$u = x^2y + xy^2 + 3xyz$$

$$u = \sqrt{x+y}$$

$$u = \frac{x^3+x^2y+y^3}{x^2+xy+y^2}$$

$$u = e^{-y/x}$$

$$u = \frac{x^2+3xy+2y^3}{y^2}$$

