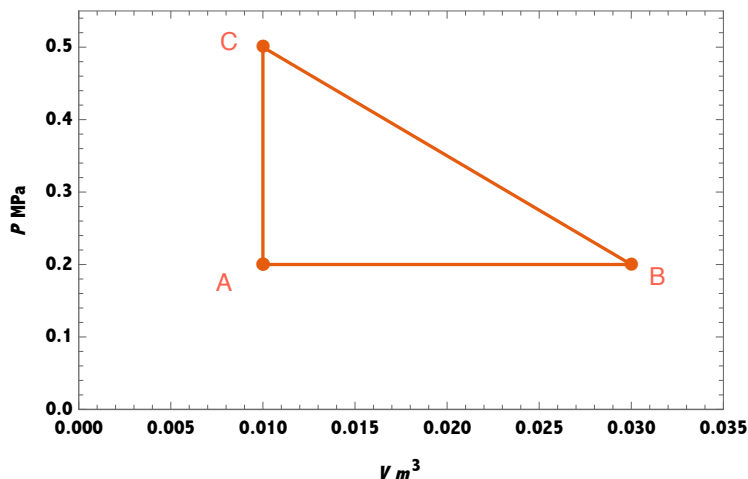


Solve each problem on separate sheets of paper, and clearly indicate the problem number and your name on each. Carefully and neatly document your answers. You may use a mathematical solver like Jupyter/iPython. Use plotting software for all plots.

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 ($A \rightarrow B$, $B \rightarrow C$, $C \rightarrow A$). 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 $a = 0.1 \text{ MPa}$, $b = 1 \times 10^3 \text{ MPa m}^{-6}$, 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 $\dot{d}q_{\text{qs}} = 0$, then $dU = \dot{d}w_{\text{qs}} = -PdV$. What else does dU equal?)

2 Is it fundamental enough?

The following ten equations are purported to be fundamental equations for various thermodynamic systems. Six, however, are inconsistent with the basic postulates of a fundamental equation and are thus unphysical. For each, plot the relationship between S and U and identify the six 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.

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

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

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

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

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

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 $9 \times 10^{-6} \text{ m}^3$ and 3 mol, respectively, and of system B are $4 \times 10^{-6} \text{ m}^3$ and 2 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 $U_A + U_B = 80 \text{ J}$. 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:

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

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

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

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

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