

Problems: See Below, they are not in the text

HW5B

Due Tuesday (02/12/08)

Q1) We know from the text that:

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

But lets suppose we start with the other related Maxwell relation:

$$B \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

Show that you can obtain the top relation (A), starting with relation B using the chain rule, followed by the cyclic rule.

Q2) Given a process (a change in a gas in the box) in which V is held constant but P changes, determine the entropy change. Assume you know the initial and final pressure but you don't want to bother computing the temperature (might be tricky to compute for the particular E.o.S. you are using).

- a) Write the entropy change for this process as a single integral and identify the single partial derivative you would need to do the integral. Beginning with:

$$\Delta S = \int dS$$

b) This partial derivative (developed from part a) is not one of our four favorite derivatives for the entropy. So use one of the rules of calculus that we have to recast this partial derivative in terms of derivatives that you know (and are in the text).

c) Evaluate the integral of part a) for the Ideal Gas E.o.S. assuming the gas is a monatomic gas, if the pressure changes (roughly) 2.72 fold. Why did I choose this pressure ratio?

[As practice and review, redo the three steps above for the change in the Energy (U); don't turn in unless you want to. These optional calculations will not be graded.]

Q3) We showed earlier that the difference between the constant pressure and constant volume heat capacities is related to two thermodynamic partial derivatives:

$$A \quad C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P$$

Now we know the heat capacities are closely related to the partial derivatives of the entropy with respect to temperature:

$$B \quad C_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad C_v = T \left(\frac{\partial S}{\partial T} \right)_v$$

Begin with the differential of the entropy as a function of T and V

$$dS = \left(\frac{\partial S}{\partial T} \right)_v dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

and derive relation A using the definitions in relations B, and the Maxwell relations for the entropy (stated in the first problem):

Q) In example problem 5.8 of the text, the total entropy is found for an irreversible, one step compression (or expansion). Consider the same problem more generally. Let us assume that the **one step** process happens because the system (consisting of n moles of a gas in a box with a movable piston on top) is initially in equilibrium with the mass on the piston and has the initial volume V_I . The mass is changed to a new one and so the external pressure is now different from the internal pressure and the piston moves to a final volume V_F . At the end of the process the internal pressure of the system and the external pressure are the same. There is a large heat reservoir that keeps the temperature fixed at T , so the process is isothermal **and irreversible**.

a) Find the entropy change for the system assuming an Ideal Gas, in terms of the

temperature and the compression ratio $r = \frac{V_F}{V_I}$.

b) Now assume that the actual heat that comes out (or goes into) the system causes an

entropy change in the environment: $\Delta S_{env} = \frac{-q}{T}$. Express this entropy in terms of the temperature and the compression ratio. [Hint: Because this is an Ideal Gas the energy change is zero: $\Delta U = 0$.]

c) Write the Total entropy change $\Delta S_{Tot} = \Delta S_{env} + \Delta S$ in terms of the temperature and the compression ratio.

d) Let us consider the function

$$f(x) = \ln(x) + \left(\frac{1}{x} - 1 \right)$$

Show that this function is closely associated with ΔS_{Tot} in the previous problem.

e) Show that this function (part d) is positive for all possible values of the compression ratio. [Hint: One way is to find the value of x where the function is at a minimum and evaluate the function at that point. Note that you'll need to demonstrate the point is a minimum and not a maximum—you might want to review your calculus textbook if you don't remember how to do this.]

f) Summarize in words what you learned and the implications for values of ΔS_{Tot} .