Junior honours Thermodynamics Assessed Problem 2: Superheated steam

Hand in solutions to the Physics teaching office by 12 noon Tuesday of Week 8 (7th Nov).

Background : *Part (a) looks at whether a given process is allowed or disallowed by the laws of thermodynamics aiming to improve understanding of the second law. The question then examines an approximate description of a real gas, superheated steam and the calculation of changes of entropy for different changes of state. Parts (g)-(i) look at the changes in entropy when this substance is taken around a simple cycle. Hints are provided at the end.*

(a) A device executing a cyclic process is shown in the figure. In each cycle 800 J of heat is extracted from a reservoir at 800 K and 600 J from a reservoir at 600K. 800 J is observed to be rejected to a reservoir at 400 K and 500 J of work is done pushing a piston Explain whether the cyclic process shown satisfies or violates
 (i) the first law of thermodynamics
  (ii) the second law of thermodynamics.
Assuming that all the given measurements are correct, what else might be going on?
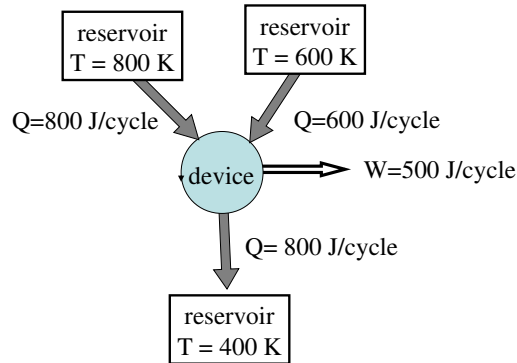
(b) The figure shows plots of PV versus P for superheated steam at two different constant temperatures T_1 and T_2. The product PV is plotted against pressure for 1 kg of steam at two different constant temperatures T_1 and T_2 (note that the right-hand axis is used for the T_1 data and the left hand axis for T_2.)
V is the specific volume [ie m^3/kg]. Estimate the temperatures T_1 and T_2 and explain your reasoning (you may assume the molar weight of steam is 18 g/mole and R=8.314 J/K/mol].
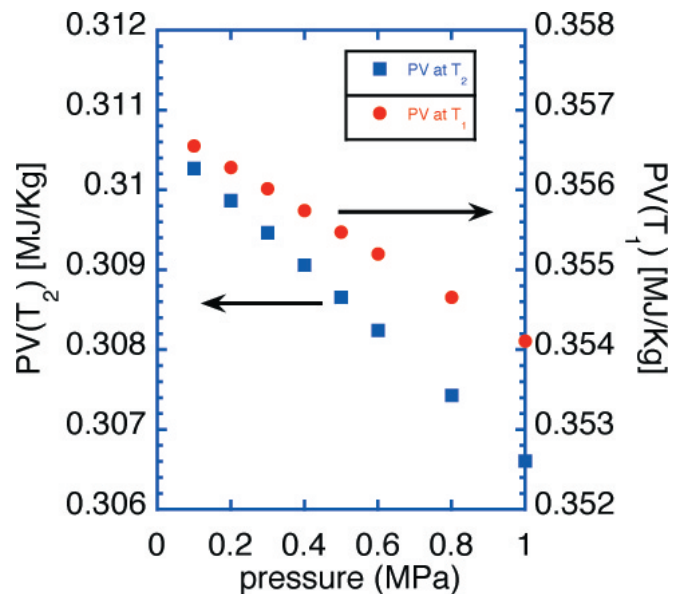
(c) Van der Waals equation can be written as follows,

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

where v is the molar volume. Explaining your steps carefully, show that the first terms of a Virial expansion in powers of $1/v$ for a Van der Waals gas are given by:

$$Pv = RT\left(1 + \left(b - \frac{a}{RT}\right)\frac{1}{v} + O(v^{-2})\right) \tag{1}$$

(d) Explain the physical significance of the coefficients a and b in the Van der Waals equation (one sentence for each is sufficient). In the light of your explanation and the expected signs of a and b comment on the observation that the slope of the line in part (b) at higher temperature is greater (less negative) than that at the lower temperature.

In the following consider the superheated steam to obey the Virial equation neglecting powers of $\frac{1}{v}^2$ and higher. It can be shown that to this approximation the molar internal energy, u, is given by

$$u = 3RT - \frac{aP}{RT} + O((1/v)^2) \tag{2}$$

(e) Assuming superheated steam is well described by EQNs 1 & 2 (and ignoring P^2 and higher order corrections), derive an algebraic expression for the change in entropy when 1 mole of this substance undergoes an isobaric change of temperature from T_i to T_f at pressure P.

(f) Derive an algebraic expression for the change in entropy when 1 mole of the same substance undergoes an isothermal change of pressure from P_i to P_f at temperature T

(g) Consider a closed cycle with superheated steam as the working substance. The working substance moves along isotherms at T_1 and T_2 and undergoes isobaric processes between T_1 and T_2 From the results derived in the last two parts show explicitly that the total change of entropy of superheated steam going around the cycle $\{T_2, P_1\} \rightarrow \{T_1, P_1\} \rightarrow \{T_1, P_2\} \rightarrow \{T_2, P_2\} \rightarrow \{T_2, P_1\}$ shown in the figure is zero. Explain in one sentence why the change in entropy of any working substance taken around any closed cycle that may also include irreversible processes must always be zero.
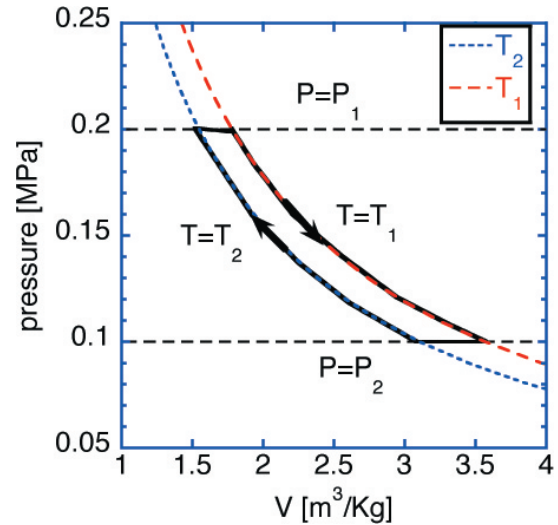
(h) Assuming that:

- all the heat transferred to the superheated steam is transferred by direct thermal contact with a reservoir at T_1 (both for the constant pressure process at $P = P_1$ and the constant temperature process at $T = T_1$).

- all the heat removed from the superheated steam is transferred by direct thermal contact with a reservoir at T_2 (for both the constant pressure process at $P = P_2$ and the constant temperature process at $T = T_2$).

Derive an algebraic expression for the following sum round the cycle shown above.

$$\sum_i \frac{q_i}{T_{Res(i)}} \tag{3}$$

where q_i is the heat transferred to the working substance in each process and $T_{Res(i)}$ is the temperature of the reservoir with which the heat is exchanged. Show that this sum is less than zero.

(i) Write down an expression for the increase in entropy of the universe (system + surroundings) when 1 mole of superheated steam is taken round the cycle described above.

Hints

(b) All gases are expected to behave as ideal gases in the limit of low pressure. (c) The equation of state can be expanded in P or $1/V$ using Taylor's theorem. For y=Pv, the derivative $y'(0, T)$ can be found most easily by implicit differentiation of the equation of state.

(d) The approximation of only keeping the lowest term in the Virial expansion clearly has a limited range of validity since as $T \rightarrow 0$ this would imply that the heat capacity becomes negative. This instability is connected with the transformation of the steam to water. In the present problem the temperature is sufficiently high that we can ignore these shortcomings.

(e,f) Several methods are possible. One is to calculate q using the First Law. Another is to obtain $S(T, P)$ strting with the central equation. You can get change of entropy can be calculated by integrating $đq/T$ along an equivalent reversible path.