

Thermodynamics Review Problems

Statistical Mechanics, PH 664

1) Compute $C_P - C_V$ for a van der Waals gas by first deriving an expression for $C_P - C_V$. What must this result reduce to in the limit as $P \rightarrow 0$?

2) Defining the adiabatic compressibility as, $K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$ and the isothermal compressibility as,

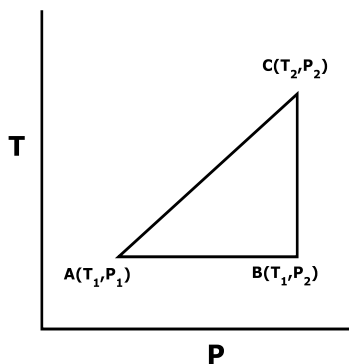
$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \text{ show that } K_T = \frac{C_P}{C_V} K_S.$$

3) The following identities are of great importance in thermodynamics because they permit the computation of the derivatives on the left hand sides of the expressions from the equation of state of the fluid. Derive these expressions and show they are zero for an ideal gas. There is an awkward in using b) for a van der Waals gas – what is the problem and how might you get around it, at least approximately?

$$\text{a) } \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

$$\text{b) } \left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P$$

4) One mole of an ideal gas is taken reversibly from the initial state $A(T_1, P_1)$ to the final state $C(T_2, P_2)$ via the two paths, ABC and AC. Calculate expressions for the work, W and the change in V , i.e., ΔV for each

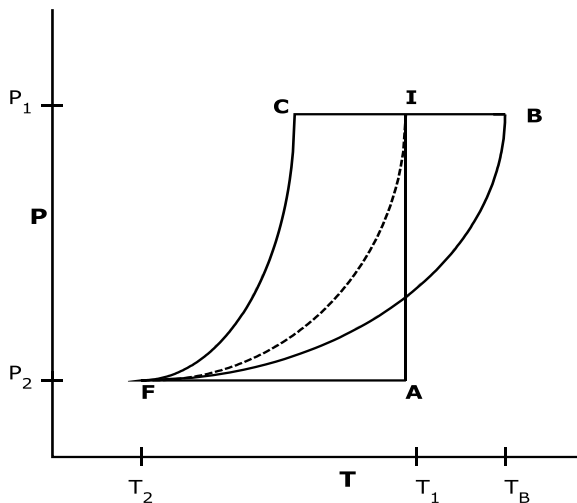


of the two paths and compare the results by filling in the following table.

	ABC	AC
ΔV		
W		

What can you conclude about path independency from your results (assuming of course that you have results and that they are correct!). Suppose you computed the cyclic integrals of dV and dW , i.e. $\oint dV$ and $\oint dW$. Are either or both zero? Which is exact and how would you prove it?

5) In the following diagram, F and I represent the Final and Initial states of a gas taken along a series of proposed paths, i.e., $\text{Gas}[P_1, V_1, T_1] \longrightarrow \text{Gas}[P_2, V_2, T_2]$ where $T_2 < T_1$ and $P_2 < P_1$.



The smooth curves CF and BF represent **reversible** adiabats and the dotted curve, IF represents the actual **irreversible** adiabat, i.e., the actual process which is carried out adiabatically.

Of the many possible reversible paths linking I and F, consider the following three possibilities:

- IAF: reversible isothermal expansion followed by reversible isobaric cooling
- IBF: isobaric heating followed by a reversible adiabatic expansion to F
- ICF: isobaric cooling followed by a reversible adiabatic expansion to F

Here are the questions:

- Begin by filling in the following table by computing expressions for each of the ΔS terms :

PATH	ΔS_{system}	$\Delta S_{\text{surroundings}}$	ΔS_{total}	Sign of ΔS_{system}
IAF				
IBF				
ICF				

- b) Are all three paths **physically** possible? If not, which path(s) are not?
- c) Is the point T_B unique or does there exist an arbitrary number of points on the line IB that would work just as well in order to drop a reversible adiabat to F? Prove your statement.
- d) Finally, why not just drop a reversible adiabat from I to F for your model of the actual process?
- e) State the Caratheodory Principle of the Second Law of Thermodynamics and discuss what relevance it has vis-à-vis this problem.
- 6) Calculate the absolute entropy, $S^\ominus(90\text{ K})$ at 90K using the following data:

T/K	11.75	15.12	15.57	16.94	18.32	20.26	21.84	22.24	25.02	30.63	37.59	42.21	46.00	52.00	60.00	70.00	90.00
C_p/R	0.483	0.805	0.901	1.13	1.36	1.76	2.11	2.19	2.73	3.49	4.57	5.40	5.55	5.56	6.40	6.43	6.53

You will also need the following phase transition data:

$$\Delta H/R(23.66\text{ K}) = 11.28\text{ K} \quad \text{first solid phase change}$$

$$\Delta H/R(43.75\text{ K}) = 89.4\text{ K} \quad \text{second solid phase change}$$

$$\Delta H/R(54.39\text{ K}) = 53.5\text{ K} \quad \text{fusion}$$

See attached for the procedure. Be sure to compare your results with the literature (citation below). Don't assume the gas phase is ideal. Here is the citation for the data given above:

<http://bc.barnard.columbia.edu/~schapman/bc3252/files/O2-Giuaque.pdf>