

**Answer 5 of the following 6 questions**

**Physical Constants**

$$\sigma = 5.6705 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$$

$$R = 8.3145 \text{ J}/(\text{K} \cdot \text{mol})$$

$$N_A = 6.0221 \times 10^{23}$$

$$k_B = 1.3807 \times 10^{-23} \text{ J}/\text{K}$$

$$1 \text{ eV} = 1.6022 \times 10^{-19} \text{ J}$$

$$1 \text{ atm} = 1.0133 \times 10^5 \text{ Pa}$$

**Properties of H<sub>2</sub>O**

$$L_V = 2256 \text{ J}/\text{g}$$

$$c_w = 4.19 \text{ J}/(\text{g} \cdot \text{K})$$

$$L_f = 333 \text{ J}/\text{g}$$

$$c_i = 2.22 \text{ J}/(\text{g} \cdot \text{K})$$

$$\rho_w = 1000 \text{ kg}/\text{m}^3$$

1. A 250 g copper container is at a temperature of 22°C. Water (250 g at 95°C) and ice (50 g at -10°C) are placed in the container. What will be the equilibrium temperature of this system? (specific heat of copper:  $c_{\text{Cu}} = 0.385 \text{ J}/(\text{g} \cdot \text{K})$ )
2. The entropy of 1 g of liquid water (at  $T = 25^\circ\text{C}$  and  $p = 100 \text{ kPa}$ ) is 3.883 J/K.
  - (a) How many microstates are consistent with the above macro variables?
  - (b) A small amount of heat  $dQ$  is added to the water and the number of microstates increases to a billion ( $10^9$ ) times the previous number. Find the change in entropy,  $dS$ ; find the amount of heat added,  $dQ$ .
  - (c) With that added heat, the temperature of the water will change. Find the change in temperature,  $dT$ .

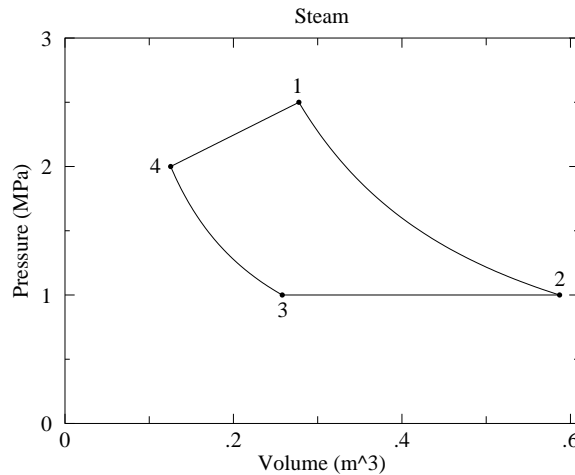
Rhetorical question: do you think these changes are measurable?

3. A selection of rows from a run of StatMech with  $N_A = 100$  (atoms),  $N_B = 100$ , and total energy  $U = 2000\varepsilon$  can be found as the final page of this exam. This Einstein solid has  $\varepsilon = .005 \text{ eV}$ .
  - (a) What is the dimensionless entropy of system  $A$  (i.e.,  $S_A/k_B$ ) for  $U_A = 0\varepsilon$ ?  $U_A = 10\varepsilon$ ?  $U_A = 100\varepsilon$ ?  $U_A = 1000\varepsilon$ ?
  - (b) Approximate  $\frac{\partial S}{\partial U}$  as a (small) finite difference  $\frac{\Delta S}{\Delta U}$ . Use this result to find an equation for the temperature of this Einstein solid. Simplify your result using the properties of logarithms. Calculate  $T_A$  (the temperature of system  $A$ ) using  $\Delta U = 1\varepsilon$  for  $U_A = 100\varepsilon$ ,  $U_A = 200\varepsilon$ ,  $U_A = 1900\varepsilon$ , and  $U_A = 2000\varepsilon$ .
  - (c) Compare the change in temperature that results when  $100\varepsilon$  of heat is added in the process:  $U_A : 100\varepsilon \rightarrow 200\varepsilon$  to the change in temperature that results in the process:  $U_A : 1900\varepsilon \rightarrow 2000\varepsilon$ . Does the specific heat seem approximately constant? Which case has the smaller specific heat?

4. The following problem is based on “steam tables”—tables of  $V, T, E_{int}, S$  etc. which substitute for the nice equations like  $pV = nRT$ ,  $\Delta S = nC_p \ln(T_f/T_i)$  etc. that apply only to the mythical ideal gas. Again steam is a non-ideal gas; you must use the tabulated  $V, T, E_{int}, S$  etc. not formulas based on  $pV = nRT$ . Starting at a pressure of 2.5 MPa, volume  $0.2777 \text{ m}^3$ , and temperature  $1232^\circ\text{C}$ , 1 kg of water vapor goes through the following cycle:

- The steam expands adiabatically to pressure of 1 MPa.
- In an isobaric process, the steam is cooled until the volume is  $0.2579 \text{ m}^3$ .
- In an isothermal process (at  $300^\circ\text{C}$ ) the steam is compressed until a pressure of 2 MPa is achieved.
- A straightline process returns to the initial state.

The following graph displays this cycle and table reports state variables at the labelled points.

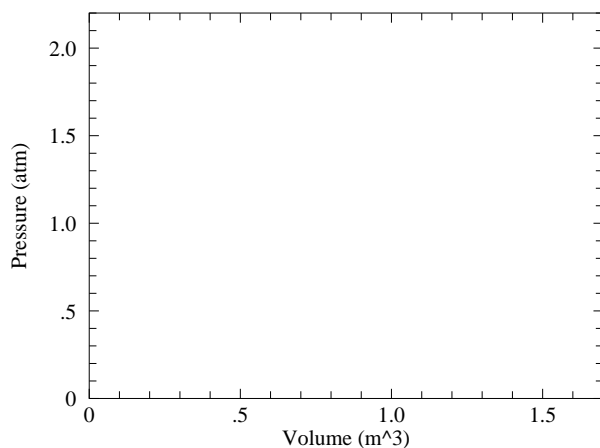


point	Volume (m <sup>3</sup> )	Pressure (MPa)	Temperature (°C)	$E_{int}$ (kJ)	Entropy (kJ/K)
1	0.2777	2.5	1232	4531	8.912
2	0.5871	1.0	1000	4051	8.912
3	0.2579	1.0	300	2793	7.123
4	0.1255	2.0	300	2773	6.766

- Estimate the value of the ratio of specific heats  $\gamma$  based on the adiabatic expansion  $1 \rightarrow 2$ . (In fact this ratio is not constant in this non-ideal gas, so it is of no use in the following parts.)
- Use the first law of thermodynamics to find the heat removed in the isobaric compression  $2 \rightarrow 3$ .
- Use  $\Delta S$  to find the heat removed in the isothermal compression  $3 \rightarrow 4$
- How much heat was added in the straightline expansion  $4 \rightarrow 1$ ?
- Use all your heats to find the *net work* performed by this cycle.

5. Consider the following cycle starting with  $0.5 \text{ m}^3$  of a monoatomic ideal gas at a pressure of 2 atm and a temperature of 500 K
- In a constant-temperature (a.k.a., isothermal) process, the volume is expanded to  $1 \text{ m}^3$ .
  - In an adiabatic process the volume is expanded until a pressure of 0.5 atm is obtained.
  - In a constant-pressure (a.k.a., isobaric) process, the volume is returned to  $0.5 \text{ m}^3$ .
  - A constant-volume (a.k.a., isochoric) process returns the temperature to 500 K.

On the below graph, plot each leg of this cycle. This will require calculating various  $pVT$  values at the end of each cycle. Fill in the below table giving the sign (+, -, 0) of the change in internal energy and entropy for each leg of the cycle. Report the amount of 'working fluid' (i.e., the gas) in moles.



path	$\Delta E_{int}$	$\Delta S$
a		
b		
c		
d		

6. Carbon dioxide ( $\text{CO}_2$ , that's  $^{12}\text{C}$  and  $^{16}\text{O}$ ) is a linear molecule. Report (source and value) the contributions you expect to the number of degrees of freedom  $f$  at room temperature. Report the per-mole and per-gram constant-pressure specific heats ( $c_p$ ) you expect for this  $f$ .  $\text{CO}_2$ 's lowest vibrationally excited states are at 0.083 eV and  $2 \times 0.083 \text{ eV}$ . Approximate the sum over all states by just these two excited states and the ground state. Find the partition function and the probability  $\text{CO}_2$  is in the 0.083 eV state at 300 K.