

## HW-Solution-set4

### 3.1, 3.6, 3.9, 3.10, 3.11, 3.20, 3.28, 3.31, 3.32, 3.36

**Problem 3.1.** In each case I'll use a centered-difference approximation, taking a difference of values just above and just below the point where I want the derivative. When  $q_A = 1$ ,

$$T_A = \frac{\Delta U_A}{\Delta S_A} = \frac{2\epsilon - 0\epsilon}{10.7k - 0k} = .19 \frac{\epsilon}{k} = 220 \text{ K},$$

where the last value is for  $\epsilon = .1 \text{ eV}$  (so that  $\epsilon/k = (.1 \text{ eV})/(8.62 \times 10^{-5} \text{ eV/K}) = 1160 \text{ K}$ ). Similarly,

$$T_B = \frac{\Delta U_B}{\Delta S_B} = \frac{100\epsilon - 98\epsilon}{187.5k - 185.3k} = .91 \frac{\epsilon}{k} = 1060 \text{ K}.$$

As expected, Solid B is much hotter when it has nearly all of the energy. However, at  $q_A = 60$ ,

$$T_A = \frac{61\epsilon - 59\epsilon}{160.9k - 157.4k} = .57 \frac{\epsilon}{k} = 660 \text{ K},$$

while

$$T_B = \frac{41\epsilon - 39\epsilon}{107.0k - 103.5k} = .57 \frac{\epsilon}{k} = 660 \text{ K}.$$

At this point the temperatures are essentially the same.

**Problem 3.6.** We're given that the multiplicity of the system has the form

$$\Omega = A \cdot U^{Nf/2},$$

where  $A$  is some constant that's independent of  $U$ . The entropy, therefore, is

$$S = k \ln \Omega = k \ln A + \frac{Nfk}{2} \ln U.$$

Differentiating with respect to  $U$  gives the temperature,

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{kNf}{2} \frac{1}{U},$$

and solving for  $U$  gives simply

$$U = \frac{NfkT}{2}.$$

This is the equipartition theorem: Each degree of freedom gets an average energy of  $kT/2$ , and the total energy is this times the number of degrees of freedom,  $Nf$ . The theorem is valid whenever our original formula for the multiplicity is valid, that is, when all the energy is in quadratic degrees of freedom and the number of energy units is much larger than the number of degrees of freedom (high-temperature limit). But the theorem cannot be valid for arbitrarily small values of  $U$ , because as  $U \rightarrow 0$ , its logarithm goes to  $-\infty$  and therefore the entropy becomes negative, which is impossible.

**Problem 3.9.** If each of the  $N$  CO molecules has two equally-likely orientations, then the multiplicity of the system would be  $2^N$ , and the associated entropy is simply

$$S = k \ln \Omega = k \ln(2^N) = Nk \ln 2.$$

For one mole  $N = 6 \times 10^{23}$ , this evaluates to  $4.2 \times 10^{23}$  units of entropy ( $S/k$ ), or a conventional entropy of 5.8 J/K.

**Problem 3.10.** (Melting an ice cube.)

(a) As the ice melts into water, its entropy increases by

$$\Delta S = \frac{Q}{T} = \frac{mL}{T} = \frac{(30 \text{ g})(333 \text{ J/g})}{273 \text{ K}} = 36.6 \text{ J/K}.$$

(b) As the water's temperature rises, its entropy increases by

$$\Delta S = \int_{T_i}^{T_f} \frac{C dT}{T} = C \ln \frac{T_f}{T_i} = (30 \text{ g})(4.186 \text{ J/g} \cdot \text{K}) \ln \frac{298 \text{ K}}{273 \text{ K}} = 11.0 \text{ J/K}.$$

(c) The heat lost by the kitchen is the same as the heat gained by the ice/water,  $mL + mc\Delta T$ . So the change in the kitchen's entropy is

$$\Delta S = \frac{Q}{T} = \frac{-(30 \text{ g})(333 \text{ J/g}) - (30 \text{ g})(4.186 \text{ J/g} \cdot \text{K})(25 \text{ K})}{298 \text{ K}} = -44.1 \text{ J/K}.$$

(d) The net change in the entropy of the universe due to these events is

$$\Delta S_{\text{total}} = 36.6 \text{ J/K} + 11.0 \text{ J/K} - 44.1 \text{ J/K} = 3.5 \text{ J/K}.$$

Since this is an irreversible process, the entropy of the universe has increased (but only slightly, since the temperatures of the ice and the kitchen differed by less than 10%).

**Problem 3.11.** The difference in temperature between the hot water and the cold water is  $45^\circ\text{C}$ , but there's twice as much hot water than cold, so the cold water will go up in temperature twice as much as the hot water comes down. This implies that the final temperature is  $15^\circ\text{C}$  less than the initial temperature of the hot water, that is, the final temperature is  $40^\circ\text{C}$ . Knowing this, we can calculate the change in entropy of the cold water,

$$\Delta S_{\text{cold}} = (25 \text{ kg})(4186 \text{ J/kg} \cdot \text{K}) \int_{283 \text{ K}}^{313 \text{ K}} \frac{dT}{T} = (104,650 \text{ J/K}) \ln \frac{313}{283} = 10,550 \text{ J/K},$$

and the change in entropy of the hot water,

$$\Delta S_{\text{hot}} = (50 \text{ kg})(4186 \text{ J/kg}\cdot\text{K}) \int_{328 \text{ K}}^{313 \text{ K}} \frac{dT}{T} = (209,300 \text{ J/K}) \ln \frac{313}{328} = -9800 \text{ J/K}.$$

The total change in the entropy of the system is, of course, positive:

$$\Delta S_{\text{total}} = 10,550 \text{ J/K} - 9800 \text{ J/K} = +750 \text{ J/K}.$$

**Problem 3.20.** For the numbers given, the quantity  $\mu B/kT$  is

$$x = \frac{\mu B}{kT} = \frac{(9.27 \times 10^{-24} \text{ J/T})(2.06 \text{ T})}{(1.38 \times 10^{-23} \text{ J/K})(2.2 \text{ K})} = 0.629.$$

The hyperbolic tangent of this number is 0.558, so

$$\frac{U}{N\mu B} = -\tanh x = -0.558; \quad \frac{M}{N\mu} = \tanh x = 0.558.$$

To find the entropy, you could use the formula derived in Problem 3.23 below. Alternatively, note from equation 3.25 that the total energy determines the fractions of up and down dipoles:

$$\frac{N_{\uparrow}}{N} = \frac{1}{2} \left( 1 - \frac{U}{N\mu B} \right) = 0.779; \quad \frac{N_{\downarrow}}{N} = 1 - \frac{N_{\uparrow}}{N} = 0.221.$$

From equation 3.28, the maximum possible entropy is  $Nk \ln 2$ , and the ratio of the actual entropy to the maximum is

$$\frac{S}{S_{\text{max}}} = \frac{1}{\ln 2} \left( \ln N - \frac{N_{\uparrow}}{N} \ln N_{\uparrow} - \frac{N_{\downarrow}}{N} \ln N_{\downarrow} \right) = -\frac{1}{\ln 2} \left( \frac{N_{\uparrow}}{N} \ln \frac{N_{\uparrow}}{N} + \frac{N_{\downarrow}}{N} \ln \frac{N_{\downarrow}}{N} \right).$$

Plugging our numbers into this formula gives 0.76, meaning that the entropy is about 3/4 what it would be if half the dipoles pointed up and half pointed down.

To achieve 99% of the maximum magnetization, we would need  $\tanh x = 0.99$  or  $x = 2.65$ , about 4.2 times greater than the value for our parameters. So we would need to increase the magnetic field to  $4.2 \times 2.06 \text{ T} = 8.65 \text{ T}$ , or decrease the temperature to  $2.2 \text{ K}/4.2 = 0.52 \text{ K}$ , or combine a somewhat smaller increase in the field strength with a somewhat smaller decrease in the temperature.

**Problem 3.28.** For a diatomic gas such as air,  $C_P = \frac{7}{2}nR$ ; in this case,  $nR = PV/T = (10^5 \text{ N/m}^2)(10^{-3} \text{ m}^3)/(300 \text{ K}) = 1/3 \text{ J/K}$ . Since the volume of the gas doubles but the pressure doesn't change, the ideal gas law tells us that the temperature also doubles. Therefore,

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT = \frac{7}{2}nR \cdot \ln \frac{T_f}{T_i} = \frac{7}{2} \left( \frac{1}{3} \text{ J/K} \right) \ln 2 = 0.81 \text{ J/K}.$$

**Problem 3.31.** To find the change in entropy, just divide  $C_P$  by  $T$  and integrate:

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT = \int_{T_i}^{T_f} \frac{a + bT - cT^{-2}}{T} dT = a \ln \frac{T_f}{T_i} + b(T_f - T_i) + \frac{c}{2} \left( \frac{1}{T_f^2} - \frac{1}{T_i^2} \right).$$

Plugging in our numbers gives

$$\begin{aligned} \Delta S &= (16.86 \text{ J/K}) \ln \frac{500}{298} + (.00477 \text{ J/K}^2)(202 \text{ K}) + \frac{8.54 \times 10^5 \text{ J}\cdot\text{K}}{2} \left( \frac{1}{(500 \text{ K})^2} - \frac{1}{(298 \text{ K})^2} \right) \\ &= (8.725 \text{ J/K}) + (0.964 \text{ J/K}) + (-3.100 \text{ J/K}) = 6.59 \text{ J/K}. \end{aligned}$$

The entropy at 298 K is given on page 404 as 5.74 J/K, so the entropy at 500 K should be approximately 12.33 J/K.

**Problem 3.32.** (A non-quasistatic compression.)

(a) The work I do is the force I exert times the displacement:

$$W = (2000 \text{ N})(.001 \text{ m}) = 2 \text{ J}.$$

(b) Absolutely no heat has been added. There was no spontaneous flow of energy from a hot object to a cold one.

(c) By the first law,  $\Delta U = Q + W = 0 + 2 \text{ J} = 2 \text{ J}$ .

(d) The change in volume is  $\Delta V = -(0.01 \text{ m}^2)(.001 \text{ m}) = -10^{-5} \text{ m}^3$ , so

$$\Delta S = \frac{1}{T} \Delta U + \frac{P}{T} \Delta V = \frac{2 \text{ J} + (10^5 \text{ N/m}^2)(-10^{-5} \text{ m}^3)}{300 \text{ K}} = \frac{2 \text{ J} - 1 \text{ J}}{300 \text{ K}} = \frac{1}{300} \text{ J/K}.$$

I've created entropy, because this is an irreversible, non-quasistatic compression; the force exerted on the piston from outside was twice as great as the force exerted by the gas from inside.

**Problem 3.36.** (Chemical potential of a large Einstein solid.)

(a) We computed the entropy in Problem 3.25(a):

$$S = kq \ln\left(1 + \frac{N}{q}\right) + kN \ln\left(1 + \frac{q}{N}\right).$$

To compute the chemical potential, we need the derivative

$$\begin{aligned} \frac{\partial S}{\partial N} &= kq \left( \frac{1}{1 + N/q} \right) \frac{1}{q} + k \ln\left(1 + \frac{q}{N}\right) + kN \left( \frac{1}{1 + q/N} \right) \left( -\frac{q}{N^2} \right) \\ &= k \left( \frac{q}{q + N} \right) + k \ln\left(1 + \frac{q}{N}\right) - k \left( \frac{q}{N + q} \right) \\ &= k \ln\left(1 + \frac{q}{N}\right). \end{aligned}$$

The chemical potential is therefore

$$\mu = -T \frac{\partial S}{\partial N} = -kT \ln\left(1 + \frac{q}{N}\right).$$

- (b) In the limit  $N \gg q$ , the logarithm is approximately  $q/N$ , so  $\mu \approx -kTq/N$ . This says that when we add a “particle” to the system but no energy, the entropy in fundamental units increases by  $q/N$ , a number much less than 1. In the other limit,  $N \ll q$ , the logarithm is approximately  $\ln(q/N)$ , so  $\mu \approx -kT \ln(q/N)$  and therefore, when we add a “particle” to the system but no energy, the entropy in fundamental units increases by  $\ln(q/N)$ —a number somewhat larger than 1. This is a significantly larger increase than in the first case. In other words, when there’s already a large excess of particles over energy, adding yet another particle doesn’t increase the entropy by much. But when there’s an excess of energy units over particles, adding another particle gives a significant increase in entropy. Basically, the system “wants” to gain particles more in the second case than in the first.