

**Solutions:**

(1) Clearly heat flows from the kitchen at 25°C to the ice.

(a) Melting into water at 0°C requires  $Q = m\ell$  of heat. So

$$\Delta S_{melt} = \frac{Q}{T_c} = \frac{m\ell}{T_c} = \frac{30 \cdot 333}{273} \simeq 36.6 \text{ J/K}$$

(b) As the melted ice warms,

$$\Delta S_{warm} = \int_{273}^{298} \frac{CdT}{T} = mc \ln(298/273) \simeq 11.0 \text{ J/K}$$

(c) In both processes, the kitchen loses heat at 298 so

$$\Delta S_{kitchen} = -\frac{m\ell}{T_K} - \frac{mc\Delta T}{T_K} \simeq -44.1 \text{ J/K}$$

(d)

$$\Delta S = \Delta S_{melt} + \Delta S_{warm} + \Delta S_{kitchen} \simeq 3.5 \text{ J/K} > 0$$

as expected by the second law for an irreversible process.

(2) Sunlight and life

(a) The heat is transferred via radiation from the Sun to the Earth. The amount of heat is

$$Q_{sun} = 10^3 \text{ W/m}^2 \cdot 1 \text{ m}^2 \cdot t_{sunlight} \simeq 1.05 \times 10^{10} \text{ J}$$

where the time is the amount of direct sunlight over the year. The assumption used here is 8 hours per day (it cannot be 24 hours!). So the entropy loss by the sun is

$$\Delta S_{sun} = \frac{-Q_{sun}}{T_{sun}} \simeq -1.75 \times 10^6 \text{ J/K}$$

while the entropy gained by the Earth is

$$\Delta S_{earth} = \frac{Q_{sun}}{T_{earth}} \simeq 3.5 \times 10^7 \text{ J/K}$$

So for this 1 m<sup>2</sup> patch of grass the change of entropy is

$$\Delta S \simeq 3.3 \times 10^7 \text{ J/K}$$

(b) Now in this patch of grass, organized things grow! To estimate the change in entropy let's assume that in one year a few kilograms of grass, weeds and other organisms grow. We have carbon-based life here on Earth so this 5 kg of stuff represents about 400 moles of mostly-carbon stuff. (The molar mass of carbon is  $m_C = 12g$ .) The entropy of assembly - a reduction in entropy due to the structured nature of organisms - then is roughly

$$\Delta S_{life} \sim -Nk = -nR \simeq -3500 \text{ J/K}$$

which is about 10<sup>4</sup> lower than the gain in entropy from the sunlight. So including life would reduce the gain in entropy, but at a level too small to affect the above estimate. Because of the number of orders of magnitude involved, variations in the estimate in this part of the problem don't affect the result - the gain in entropy from sunlight swamps the local loss in entropy due to life.

Some folks have observed that this may be *the* characteristic of life - taking in steady stream of energy flux to locally reduce entropy. I don't know enough chemistry to know whether obviously-non-living reactions can do the same.

- (3) Metallic  $C_V$ 's: For a molar heat capacity of

$$C_V \simeq aT + bT^3$$

the molar entropy is

$$S = \frac{Q}{T} = \int_0^{T_f} \frac{C_V}{T} dT = aT_f + \frac{b}{3}T_f^3$$

Using the given numbers for  $a$  and  $b$ ,

$$S \simeq 0.0014 \text{ J/K or } 9.8 \times 10^{19} \text{ in dimless units at 1 K}$$

and

$$S \simeq 0.022 \text{ J/K or } 1.6 \times 10^{21} \text{ in dimless units at 10 K.}$$

At the lower 1 K temperature the result is essentially all due to the linear term. The cubic term kicks in at 10 K. The dimensionless results are way lower than  $N_A \sim 10^{23}$  so at these low temperatures most degrees of freedom much be frozen out. (More on this story in Chapter 7!)

- (4) The thermo of erasure

- (a) Each bit has two states so the multiplicity of one bit is 2. A byte contains 8 bits. It then has  $2^8$  possible states. One gigabyte is  $2^{30}$  bytes and  $2^{33}$  bits. Thus, before it was erased, the memory could have in any one of the

$$\Omega = 2^{2^{33}} \text{ possible microstates.}$$

After erasing the memory is in only one of these states, for example a random configuration of on average 1/2 1's and 1/2 0's. This random state of  $N$  bits would have multiplicity

$$\Omega = \binom{N}{\frac{N}{2}} \simeq \frac{N^N e^{-N}}{\left[ e^{-N/2} \left(\frac{N}{2}\right)^{N/2} \right]^2} = \dots = 2^N$$

where the dots represent some very nice cancelation.  $N = 2^{33}$ . The entropy associated to the total multiplicity of the possible microstates is

$$S = k \ln \Omega = k 2^{33} \ln 2 \simeq 8.2 \times 10^{-14} \text{ J/K.}$$

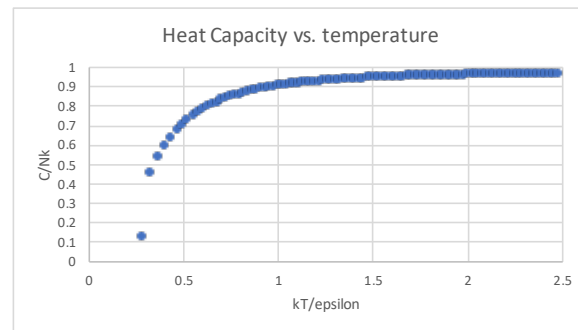
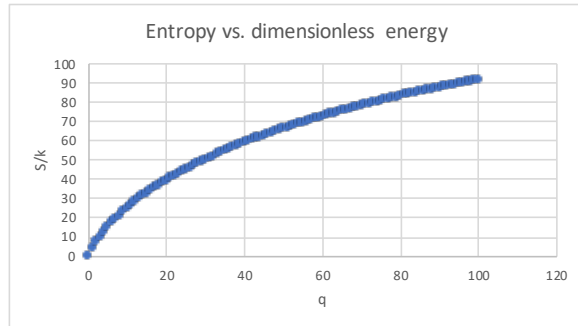
- (b) To dump this entropy into a room temperature environment, say 298 K, would mean transferring at least

$$Q = T \Delta S \simeq (298 \text{ K}) (k 2^{33} \ln 2) \simeq 2.4 \times 10^{-11} \text{ J}$$

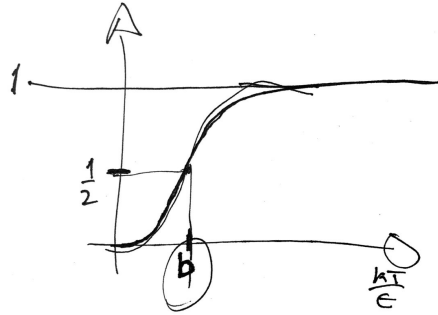
which is tiny (but still way above the energy scale of atomic physics). There is much more than 24 pJ of waste heat getting dumped by the memory (and computing) in modern machines due to resistance in the circuitry. Also, short cuts of "erasing" are often used so every bit of the memory may not have been reset.

- (5) Spreadsheets an Einstein solid: Here's the spreadsheet for  $N = 50$  (The  $N = 5000$  plots are similar for  $S$  and only show a short, steep section of the  $C_V$  plot.)

Einstein Solid	N	50		
q	Omega	S/k	kT/e	C/Nk
0	1	0	0	0
1	50	3.912	0.27969	0.12183
2	1275	7.1507	0.32834	0.45361
3	22100	10.003	0.36788	0.53618
4	292825	12.587	0.40294	0.59374
5	3162510	14.967	0.43524	0.63777
6	28989675	17.182	0.46566	0.67304
7	2.32E+08	19.262	0.49468	0.70212
8	1.65E+09	21.226	0.52263	0.7266
9	1.06E+10	23.089	0.54973	0.74752
10	6.28E+10	24.864	0.57614	0.76563
11	3.43E+11	26.56	0.60197	0.78146
12	1.74E+12	28.186	0.62732	0.79541
13	8.31E+12	29.748	0.65226	0.80781
14	3.74E+13	31.252	0.67684	0.81888
15	1.6E+14	32.703	0.70111	0.82883
16	6.48E+14	34.105	0.7251	0.83782
17	2.52E+15	35.461	0.74885	0.84597
18	9.36E+15	36.776	0.77238	0.8534
19	3.35E+16	38.051	0.79572	0.86018
20	1.16E+17	39.289	0.81888	0.86641
21	3.85E+17	40.493	0.84189	0.87213
22	1.24E+18	41.665	0.86475	0.87741
23	3.89E+18	42.806	0.88748	0.88229
24	1.18E+19	43.918	0.91009	0.88681
25	3.51E+19	45.004	0.93258	0.89101
26	1.01E+20	46.063	0.95498	0.89493
27	2.85E+20	47.098	0.97728	0.89858
28	7.83E+20	48.109	0.99949	0.90199
29	2.11E+21	49.099	1.02163	0.90518
30	5.54E+21	50.067	1.04368	0.90817



I used these  $N = 50$  results to compare to the plots in Fig 1.14. Now these results are for  $C_V$  not  $C_P$  shown in the figure. However the leveling off at the value expected from the equipartition theorem is clear for lead and aluminum. The increase in the heat capacities at constant pressure are due to the differences between  $C_V$  and  $C_P$ , as we're told in the caption. So I'll assume that the heat capacities level off  $C_V$  at  $C_V = Nk$  and compare them to dimensionless maximum value,  $C_V/Nk = 1$ , in the plots. Since the curves are all of the same functional form and there is only one scale,  $\epsilon$ , the values for  $\epsilon$  can be obtained by matching a point like this:



The spreadsheet plot reaches  $1/2$  its maximum of 1 at  $b = kT_{1/2}/\epsilon \simeq 0.34$ . The data of Al reaches this point in Fig 1.14 at about  $T_{1/2} = 100$  K. Thus,

$$\epsilon \simeq \frac{k100}{0.34} \simeq 0.025 \text{ eV.}$$

For lead the same procedure gives  $\epsilon = 0.0063$  eV. Since the  $N = 5000$  curve is better at low temperatures, I used the  $N = 5000$  curve for diamond. Matching the  $1/5$  (of maximum) point at  $kT/\epsilon = 0.211$  to the  $1/5$ (maximum) at  $T = 280$  K on the data plot for diamond gives  $\epsilon \simeq 0.11$  eV. (You can also get a similar result using extrapolation.) These results make physical sense because  $\epsilon$  is the basic unit of energy for an oscillator - think bond strength, or  $\omega = \sqrt{k/m}$ . Lead is relatively “floppy” (has a relatively small spring constant) compared to diamond and so its  $\epsilon$  is much smaller than diamond. Stiffer materials vibrate at higher temperatures.

Your results will differ but probably not by more than a factor of 2 or 3.

- (6) For this one I worked from the earlier house model spreadsheet and added the entropy calculations. Keep in mind that the total change in entropy is the net change of the entropy change due to the heat flow out of the house at the interior temperature and the entropy change from the heat flow to the outside at the outside temperature. The entropy lost from the heat leaving the interior is

$$\Delta S_{IN} = \frac{-Q}{T_{IN}} \simeq \frac{-1 \times 10^9}{291} \simeq -3.42 \times 10^6 \text{ J/K.}$$

Make sure you have the correct temperature! While the entropy created as the heat arrives in the exterior is

$$\Delta S_{OUT} = \frac{Q}{T_{OUT}} = \frac{1 \times 10^9}{263} \simeq 3.78 \times 10^6 \text{ J/K}$$

So

$$\Delta S = \Delta S_{IN} + \Delta S_{OUT} \simeq 3.61 \times 10^5 \text{ J/K} > 0$$

This is greater than 0 as it must be. After the examples we have done, it is about a moose’s entropy a day (!) which seems large to me.

- (7) (2 pts.) The large  $N$  and  $q$  Einstein solid. The multiplicity is approximately

$$\Omega \simeq \left( \frac{q+N}{q} \right)^q \left( \frac{q+N}{N} \right)^N$$

- (a) The entropy is

$$S = k \ln \Omega \simeq kq \ln \left( \frac{q+N}{q} \right) + kN \ln \left( \frac{q+N}{N} \right)$$

We can safely leave out the terms from the extra square roots from the Stirling's approximation since the log of these factors are small relative to the terms proportional to  $q$  and  $N$  above.

- (b) The inverse temperature is

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial q}{\partial U} \frac{\partial S}{\partial q} = \frac{1}{\epsilon} \frac{\partial S}{\partial q}$$

Prior to differentiating it may be helpful to write the  $q$  dependent terms in the entropy

$$S/k = q \ln(q + N) - q \ln q + N \ln(q + N) + \text{Junk}$$

Differentiating and a bit of algebra yields

$$\frac{1}{T} = \frac{k}{\epsilon} \ln \left( 1 + \frac{N}{q} \right) = \frac{k}{\epsilon} \ln \left( 1 + \frac{N\epsilon}{U} \right)$$

- (c) Exponentiating, gathering terms in  $U$ , and solving finally gives

$$U = \frac{N\epsilon}{e^{\epsilon/kT} - 1}$$

so now we can differentiate again to find

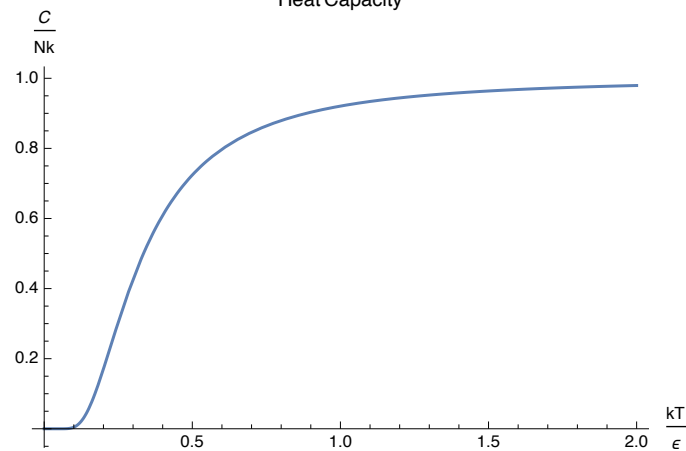
$$C_V = \frac{\partial U}{\partial T} = \frac{N\epsilon^2}{kT^2} \frac{e^{\epsilon/kT}}{(e^{\epsilon/kT} - 1)^2}$$

- (d) At high temperatures we can expand the exponents to find

$$C_V \simeq \frac{N\epsilon^2}{kT^2} \frac{1 + \frac{\epsilon}{kT}}{\left[ \frac{\epsilon}{kT} + \frac{1}{2} \left( \frac{\epsilon}{kT} \right)^2 \right]^2} \simeq Nk$$

after the dust clears. For the final approximation we only needed the leading order terms from the expansions of the exponents. This is just what we expect for a system with  $f = 2$  (from the equipartition theorem). Hooray! The high temperature limit makes sense!

- (e) The curve is complicated enough so I plotted it



By comparing this to the previous problem and its heat capacity, we see that the two plots for  $C_V$  differ at low temperatures. The new heat capacity has a much flatter approach to  $T \rightarrow 0$ . While no surprise ( $N = 50$  and  $q = 100$  are hardly “large”) we might worry that the estimates for the  $\epsilon$ 's would also change. But since I chose a “1/2” max value point for matching the differences are small and the results (and methods) are essentially the same

as in the last problem; it is easy to see from this plot that the 1/2 max condition is met at about 0.3, as before.

- (f) To save some writing I am going to define a dimensionless inverse temperature

$$\beta = \frac{\epsilon}{kT}$$

Then,

$$\frac{C_V}{Nk} = \frac{\beta^2 e^\beta}{(e^\beta - 1)^2}.$$

To derive *how*  $C_V$  approaches  $NK$  at high temperatures we need to expand and pick out the leading order term in  $1/T$  or  $\beta$ . Expanding then

$$\begin{aligned} \frac{C_V}{Nk} &\simeq \frac{\beta^2 (1 + \beta + \frac{1}{2}\beta^2)}{(\beta + \frac{1}{2}\beta^2 + \frac{1}{6}\beta^3)^2} \simeq \frac{(1 + \beta + \frac{1}{2}\beta^2)}{(1 + \frac{1}{2}\beta + \frac{1}{6}\beta^2)^2} \\ &\simeq \left(1 + \beta + \frac{1}{2}\beta^2\right) \left(1 - \beta + \frac{5}{12}\beta^2\right) \\ &\simeq 1 - \frac{1}{12}\beta^2 \\ &\implies C_V \simeq Nk \left[1 - \frac{1}{12} \left(\frac{\epsilon}{kT}\right)^2\right] \end{aligned}$$

where the 5/12 in the second line comes from the first and second order terms in the handy relation  $(1+x)^n \simeq 1 + nx + n(n-1)/2 x^2$  where  $x$  is both  $\beta$  terms in the denominator. This is what we wanted to show - the approach to the asymptotic value is as  $1/T^2$ . The expansion can also be done easily in Mathematica with the `Series` command.

- (8) Thermodynamics of a simple rubber band model

- (a) If we assume that the band can go only right (R) or left (L) then it is the analog of a random walk (or another two-state system). The multiplicity is

$$\Omega = \binom{N}{N_R} = \frac{N!}{N_R!(N - N_R)!}$$

where  $N_R$  is the number of rightward directed links. The entropy is

$$\frac{S}{k} = \ln \Omega \simeq N \ln N - N_R \ln N_R - N_L \ln N_L$$

where  $N_L$  is the number of leftward directed links. The total is  $N = N_R + N_L$ . Stirling's approximation was used in the second step.

- (b) Each rightward link of length  $\ell$  increases the length while each leftward directed link reduces the length by  $-\ell N_L$ . Thus,

$$L = \ell(N_R - N_L) = \ell(2N_R - N) \implies N_R = \frac{1}{2} \left( \frac{L}{\ell} + N \right)$$

- (c) We are taking the force to be positive if the force pulls in (just the opposite convention for springs). Working (ack the pun!) by analogy the work done

$$dW = FdL \text{ while in thermo } dW = -PdV$$

Hence it looks like the  $-PdV$  term in the thermodynamic identity goes to  $FdL$  in this system,

$$dU = TdS + FdL.$$

- (d) So for a const.- $U$  process

$$0 = TdS + FdL \implies F = -T \left( \frac{\partial S}{\partial L} \right)_U$$

Now evaluating the partial derivative, chain rule is helpful

$$\frac{\partial S}{\partial L} = \frac{\partial N_R}{\partial L} \frac{\partial S}{\partial N_R} = \frac{1}{2\ell} \frac{\partial S}{\partial N_R}$$

Carrying through with the partial derivative of  $S$  using the result from part (a),

$$F = -\frac{kT}{2\ell} \ln \left( \frac{N - N_R}{N_R} \right)$$

after some algebra. Expressing this in terms of  $L$  gives

$$F = \frac{kT}{2\ell} \ln \left( \frac{1 + L/\ell N}{1 - L/\ell N} \right)$$

- (e) For a bunched up band,  $L$  is small relative to  $N$  and we can expand the log.

$$F \simeq \frac{kT}{2\ell} \ln [(1 + L/\ell N)(1 + L/\ell N)] \simeq \frac{kT}{2\ell} \ln \left[ 1 + \frac{2L}{\ell N} \right] \simeq \frac{kT}{\ell^2 N} L$$

which is a Hooke's law expression with  $L$  for 'x' and 'spring constant'  $kT/\ell^2 N$ . (Recall the sign convention of positive for inward pulling.)

- (f) At high temperatures and fixed tension, the spring constant increases causing the band to contract. This makes sense in that at high temperatures the bands' links will be randomly oriented and thus the length will be shorter.
- (g) For adiabatic processes,  $\Delta S = 0$ . So as we stretch the bands the configuration entropy - the one we have been working on in this solution - decreases. This reduction in configuration entropy must be compensated by an increase in vibrational entropy and the temperature must increase. You can observe this by rapidly stretching a rubber band and feeling the temperature increase.

- (9) Adding potential energy

- (a) The energy  $U$  is the same as it was before plus the potential  $mgz$  for each particle or  $U_g = Nm gz$  for the collection. Thus when calculating

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{S,V}$$

we obtain the same result as before for an ideal gas [see equation (3.63)] *plus*  $mgz$ , as expected.

- (b) When the two gasses are in diffusive equilibrium then

$$\frac{\partial S}{\partial N} \text{ is constant or } \mu(z) = \mu(0)$$

when  $T$  is constant as we assumed in problem 1.16. Then we can pull out a bunch of factors in the log - 'Junk' - and

$$\ln N(z) + Junk + \frac{mgz}{kT} = \ln N(0) + Junk.$$

Canceling the 'Junk' terms and exponentiating the equation gives the result

$$N(z) = N(0)e^{-mgz/kT}$$

which is the same behavior that  $P(z)$  had in problem 1.16.

(10) A big power plant

(a) Maximum efficiency is determined by the temperatures of the reservoirs,

$$e = 1 - \frac{T_c}{T_h} = 1 - \frac{293}{773} \simeq 62\%$$

This is high due to the large temperature difference.

(b) At the higher temperature

$$e = 1 - \frac{T_c}{T_h} = 1 - \frac{293}{873} \simeq 66\%.$$

The increase in production is  $(66/62 - 1)$  of 1 GW or 0.069 GW. Running the unit conversion ( $3.6 \times 10^6 \text{ J} = 1 \text{ kWh}$ ) on this output over one year gives about \$30 million.