# Stat Mech (PHYS 370) Guide 7 Solutions

**Problems:**

(1) Sudden compression

    (a) The work done is

$$W = \int F \cdot dr = (2 \text{ kN})(0.001 \text{ m}) = 2 \text{ J}$$

    (b) Because it takes time to flow, no heat in transfered; $Q = 0$.

    (c) By conservation of energy $\Delta U = Q + W$ so $\Delta U = 2$ J.

    (d) From the thermodynamic identities

$$dS = \frac{dU}{T} + \frac{P}{V}dV = \frac{2}{300} - \frac{1}{300} = \frac{1}{300} \text{ J/K}$$

    so entropy was created in this irreversible process, even without heat flow.

(2) The chemical potential for an Einstein solid

    (a) From our earlier work in 3.25 the entropy is approximately

$$S \simeq k\left[(q + N)\ln(q + N) - N\ln N - q\ln q\right].$$

    To find the chemical potential we need the derivative

$$\frac{\partial S}{\partial N} = k\left[\ln(q + N) + 1 - \ln N - 1\right] = k\ln\left(1 + \frac{q}{N}\right).$$

    So the chemical potential

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

    which is what was given.

    (b) Now for the limits. For $q \ll N$ the fraction in the log is small so

$$\mu \simeq -kT\frac{q}{N}$$

    Adding a particle - assumed to be without energy - in this limit creates entropy,

$$\Delta S = -\mu\frac{dN}{T} \simeq kT\frac{qT}{N} = k\frac{q}{N}$$

    so $\Delta S/k$ is small - much less than 1. The first equality comes from the thermodynamic identity (and $dU = 0 = dV$). The quantity $dN$ is 1.

    For $N \ll q$ the fraction in the log is big so

$$\mu \simeq -kT\ln\left(\frac{q}{N}\right)$$

    When adding a particle - again assumed to be without energy - in this limit

$$\Delta S \simeq k\ln\left(\frac{q}{N}\right).$$

    Now $\Delta S/k$ is larger than before. All this makes sense because adding a particle to a system with a lot of energy means that more microstates are available. The system in the second limit 'wants' to gain particles more to allocate all that energy.

(3) Even though there is an initial cool draft, this is a terrible idea as the refrigerator dumps waste heat into the room. So rather, it is a way to heat the room!

(4) Earth energy flows
(a) The radiative forcing is the net heating of Earth from the Sun. So looking on the left of the diagram at the incoming (and reflected) solar radiation I find

$$RF_{\odot} = 341 - 79 - 23 = 239 \text{ W/m}^2 \simeq 240 \text{ W/m}^2.$$

Or, equivalently use the intensity on the Earth, 161, and on the atmosphere, 78.
(b) The incoming flows are 374 (from Earth), 17 (Thermals), 80 (Evaporation), and 78 (from Sun). Outgoing are 333 (to Earth), and 187+30 (to space). Summing up gives -1 W/m$^2$. So, no it would be cooling instead, although I admit to being cautious about reaching conclusions from this single digit! Could this be round off error? They should carry more sig figs.... It is interesting to see the role of convection and the evaporation of water in this flow.
(c) The incoming flows are 333 and 161 W/m$^2$. Outflows are 396, 17 and 80 W/m$^2$. The net is +1 W/m$^2$. So, yes the Earth is heating up. (This agrees with the statement at the bottom of the graphic.) However, the same comment applies to the last answer. I wouldn't be convinced without much more of an argument, such as we did in class.
(d) The greenhouse effect of the atmosphere is the reason for the 33 warmer surface. The radiative forcing of the atmosphere must be the reason for this. To see the difference let's start with the no atmosphere version. In class we balanced the radiative power flows in and out giving

$$T_{equi} = \sqrt[4]{\frac{0.7 I_{\odot}}{4\sigma}} \simeq \sqrt[4]{\frac{239.8}{\sigma}} \simeq 255 \text{ K},$$

which is too cold. With the atmosphere we looking for the correct radiative forcing. Instead of about 240 W/m$^2$ we have, from the graphic, 333+161 W/m$^2$ incoming radiative flows. We have to remove the non-radiative flows due to evaporation (80) and convection (17) so

$$T_{earth} = \sqrt[4]{\frac{333 + 161 - 17 - 80}{\sigma}} = \sqrt[4]{\frac{397}{\sigma}} \simeq 289.3 \text{ K}.$$

The difference is about 34 K, accounting for the difference, and the greenhouse effect. Without the atmosphere the radiative forcing is about 240 W/m$^2$ and with the atmosphere it is about 397 W/m$^2$.

(6) The absorption refrigerator, often powered by propane, works with an additional heat flow from a flame. The heat engine-style sketch is
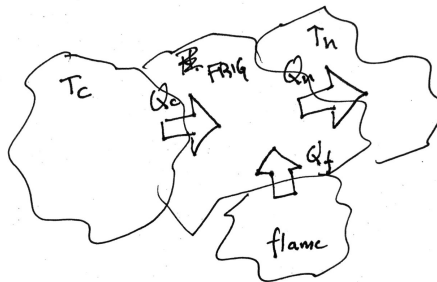
(a) The coefficient of performance (COP) is "benefit/cost". As a refrigerator the benefit is cooling so $Q_c$ and the cost is from operating the flame, $Q_f$. Hence, the coefficient is $COP = Q_c/Q_f$.

(b) From the diagram it is clear that $Q_h = Q_c + Q_f$. The heat $Q_h$ is the heat expelled into the kitchen or the room where the frig is installed. At this stage it may be tempting to re-express the COP as we did before but, resist!! The simple ratio works best.

(c) By the second law

$$\Delta S \geq 0 \implies \frac{Q_h}{T_h} - \frac{Q_f}{T_f} - \frac{Q_c}{T_c} \geq 0.$$

With the expression for energy conservation we can eliminate the heat flowing to the room, $Q_h$, from the expression. Gathering terms with $Q_c$ and $Q_f$ gives

$$\frac{Q_c}{T_h} + \frac{Q_c}{T_c} \geq \frac{Q_f}{T_f} - \frac{Q_f}{T_h}$$

Solving for the ratio of the heats,

$$\frac{Q_c}{Q_f} \geq \frac{\frac{1}{T_f} - \frac{1}{T_h}}{\frac{1}{T_h} - \frac{1}{T_c}}.$$

Multiplying by a -1, so the temperature differences are positive, and combining the temperatures gives the result

$$\text{COP} = \frac{Q_c}{Q_f} \leq \frac{T_c(1 - T_h/T_f)}{(T_h - T_c)}.$$

High COPs occur for small room-frig temperature differences and for high temperature flames, $T_f$, as expected.

(7) A natural gas fuel cell

(a) Subtracting the energies for the products from the reactants, for one mole

$$\Delta H = (2)(-285.8) - 393.5 + 74.8 \simeq -890.4 \text{ kJ}.$$

Similarly,

$$\Delta G = 2(-237.1) - 394.4 + 50.7 \simeq -817.9 kJ.$$

(b) Under ideal conditions the loss of Gibbs free energy is all 'other' work. Thus the electrical work is about - 818 kJ; the electrical work output is 818 kJ. (We can see this from equation 5.8, $W \geq \Delta G$, so $W \geq -818$ kJ.)

(c) The waste heat is required by the second law and given by the difference in the enthalpy and Gibbs energy - see pg 153 -

$$Q \geq \Delta H - \Delta G \text{ so } \simeq 72.5 \text{ kJ}$$

(d) As you recall from 295, $W = qV$ so the voltage is the work over the electrical charge. But how much charge is moved? This is shown in the reactions given in part (d); there are 8 electrons on the move. So for one mole of methane

$$V = \frac{800}{8 \cdot 1.6 \times 10^{-19} \cdot 6.02 \times 10^{23}} \simeq 1.06V.$$

(8) Starting with the thermodynamic identity

$$dU = TdS - PdV + \mu dN$$

we can say that for const $S$ and $N$ processes

$$\frac{\partial U}{\partial V} = -P.$$

Meanwhile for const $V$ and $N$ processes

$$\frac{\partial U}{\partial S} = T.$$

This whole problem involves constant particle number so I will only label the others quantities.

Now "mixed partial derivatives are equal" so for $U = U(S,V)$,

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}.$$

Implicitly in these partial derivatives we keep the "other" variable fixed so

$$\frac{\partial U}{\partial S} = \left(\frac{\partial U}{\partial S}\right)_V.$$

Hence substituting our results from the thermo identity

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

If you feel queasy about fixing $S$ and $V$ then think about it not as fixing them both simultaneously (nothing would happen!) but rather fixing first $S$ and then $V$.

The other relations with the thermodynamic potentials work the same way. For enthalpy

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P.$$

Using the Helmhotz free energy

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T.$$

Using the Gibbs free energy

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T.$$

(9) Making use of Maxwell relations to find a relation among heat capacities

   (a) Generally for any function $S = S(T,V)$

$$dS = \frac{\partial S}{\partial T}dT + \frac{\partial S}{\partial V}dV.$$

From problem 3.33 though

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

so the first term in the above relation for entropy is $C_V/T$.

(b) As before for $V = V(T, P)$ (like the ideal gas law)

$$dV = \frac{\partial V}{\partial T}dT + \frac{\partial V}{\partial P}dP.$$

So for constant $P$ processes we can use this $dV$ in the relation for $dS$ and obtain

$$(dS)_P = \left[\frac{C_V}{T} + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right]dT.$$

Or, the change in entropy with temperature is

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} = \frac{C_V}{T} + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P,$$

where the first equality is again from the solution to 3.33. Now the Helmholtz Maxwell relation of 5.12 gives another expression for the $\partial S/\partial V$ derivative and

$$\Delta C = C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P. \tag{1}$$

Hooray!

(c) Problem 1.46 gives us two useful quantities, the thermal expansion coefficient

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

"what is the fractional squish if you raise the temperature" and the isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

"what is the fractional squish if you raise the pressure". Now using the relation from 1.46,

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T},$$

we see that the derivative

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\beta V}{-\kappa_T V} = \frac{\beta}{\kappa_T}.$$

Also

$$\left(\frac{\partial V}{\partial T}\right)_P = \beta V$$

by definition. Then equation (1) becomes

$$C_P = C_V + \frac{TV}{\kappa_T}\beta^2. \tag{2}$$

(d) For an ideal gas, and from equation 1.48

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{kNf}{2}$$

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \frac{kNf}{2} + Nk = Nk\left(\frac{f+2}{2}\right) \tag{3}$$

Computing the derivatives for an ideal gas $\beta = 1/T$ and $\kappa_T = 1/P$ so equation (2) becomes

$$C_P = C_V + PV = Nk\left(\frac{f+2}{2}\right)$$

as above. They agree!

(e) The heat capacity of constant pressure is generally larger than the heat capacity at constant volume because at constant pressure the system usually expands and work is done - it just takes more energy to increase the temperature when work is also done. Mathematically, since $Nk$ is positive the heat capacity of constant pressure is generally larger than the heat capacity at constant volume. More generally $T, V, \beta^2$, and $\kappa_T$ are positive (the last because adding pressure decreases volume) so $C_P \geq C_V$.

(f) The data in problem 1.46 has what we need to compute $\Delta C$. You don't have to but I chose to work with 1 kg of $H_2O$, for which $C_V = 4180$ J/kg K and

$$\Delta C \simeq 43.5 \text{ J/K, and } \frac{\Delta C}{C_V} \simeq 1\%.$$

While for one mole of mercury,

$$\Delta C \simeq 3.58 \text{ J/K, and } \frac{\Delta C}{C_V} \simeq 13\%$$

(The molar heat capacity is on page 405.)

(g) Figure 1.14 shows $C_P$. Both volume and compressibility are not strongly temperature-dependent in solids. So $\Delta C$ scales as $\beta^2 T$. If the plot of $\beta$ is similar then the heat capacity difference $\Delta C$ goes to zero at low temperatures. We see this in the figure. If $\beta$ is roughly constant at high temperatures then the difference $\Delta C$ should grow linearly with temperature. That is roughly what we see in Fig 1.14 as the data ($C_P$) diverges from the theoretical value ($C_V$). Cool! (or should I say 'Hot'!)

(10) The Helmholtz free energy for the first excited state of H. With the given information

$$F = U - TS = 10.2 - kT \ln 4.$$

This is negative for $T$ larger than $10.2/k \ln 4 \simeq 8.5 \times 10^4$ K, and positive for $T$ less than this temperature. This is a very hot. The Sun is cool is comparison.

(11) The grand potential $\Phi = U - TS - \mu N$

(a) The potential $\Phi$ can change as

$$d\Phi = dU - TdS - SdT - d\mu N - \mu dN$$

but $dU = TdS - PdV + \mu dN$ by the thermodynamic identity. (This is a statement that results from (1) entropy is a function of $U, V$, and $N$ and (2) the definitions of temperature, pressure, and particle number.) So

$$d\Phi = -SdT - PdV - d\mu N.$$

Thus, keeping pairs of system quantities fixed

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}, \quad P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}, \text{ and } N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{V,T}.$$

(b) From the general relation for $d\Phi$ above, for constant$-T$ and $-\mu$ processes,

$$d\Phi = dU - TdS - \mu dN.$$

Meanwhile for a system in contact with a reservoir

$$dS_{tot} = dS + dS_R.$$

If the reservoir is at fixed volume then $dS_R = dU_R/T - \mu dN_R/T$. But any change in the reservoir energy and particle number is balanced by a change in the system's energy and particle number, i.e. $dU_R = -dU$ and $dN_R = -dN$ so

$$dS_{tot} = dS - \frac{dU}{T} + \mu\frac{dN}{T} = -\frac{1}{T}\left(dU - TdS - \mu dN\right) = -\frac{1}{T}d\Phi$$

Ho-ho! The increase of entropy overwhelmingly recommended by the second law means that the grand potential tends to decrease for a system in thermal and diffusive equilibrium (and constant volume reservoir); $d\Phi \le 0$.

(c) Let's run this one through the Gibbs free energy. Adding a convenient form of 0 to the grand potential

$$\Phi = U - TS - \mu N = U - TS + PV - PV - \mu N = G - PV - \mu N = -PV$$

where the last two equalities comes from the definition of the $G$ and $G = \mu N$.

(d) Free protons in the sun? Let's find out using the grand potential. For the H atoms (Schroeder calls these 'occupied')

$$\Phi_H = U - TS - \mu N = -13.6 \text{ eV } - 0 - \mu(1)$$

for the one electron that is now bound. As for the chemical potential we can following the hint and compute it from the Sackur-Tretrode relation (see equation 3.63)

$$\mu = -kT \ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] \simeq -8.9 \text{ eV}$$

at 5800 K. The log works out to about 17.8. Hence,

$$\Phi_H \simeq -4.7 \text{ eV}.$$

The free protons have potential

$$\Phi_p = U - TS - \mu N = 0$$

since we are comparing the energy to the bound state energy of the electron; we're neglecting degeneracy so the entropy vanishes; and there are no electrons. Hence, hydrogen is thermodynamically more stable than free protons in this atmosphere.

The temperature $T_*$ at which there are roughly equal numbers of hydrogen and free protons is when $\Phi_H = 0$. The log doesn't grow too much with temperature so as a first try at the answer we can just find the temperature through the chemical potential, i.e.

$$0 = \Phi_H = -13.6 - \mu(T_*) \implies T_* \simeq \frac{13.6}{k(17.8)} \text{ or } T_* \simeq 8800 \text{ K}.$$

Using the mathematica command "FindRoot" with the full expression I found $T_* \simeq 8600$ K so the approximation isn't too bad. (I'm a bit surprised at this number but that will have to wait.)