Exercise week 39: FYS2160, Thermodynamics and statistical physics, Fall 2022

Problems from Schroeder: 5.1, 5.6, 5.10, 5.21, 5.22, 5.32, 5.43, 5.76

Solution:

Problem 5.1. The energy of a mole of argon is given by the equipartition theorem:

$$U = \frac{3}{2}NkT = \frac{3}{2}nRT = \frac{3}{2}(1)(8.31 \text{ J/K})(300 \text{ K}) = 3.74 \text{ kJ}.$$

The entropy is given by the Sackur-Tetrode equation:

$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right] = Nk\left[\ln\left(\frac{kT}{P}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right) + \frac{5}{2}\right],$$

where I've used the ideal gas law and equipartition in the last expression. Since an argon atom has a mass of about 40 times the proton mass, the argument of the logarithm is

$$\frac{[(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})]^{5/2}}{1.01 \times 10^5 \text{ N/m}^2}\left(\frac{(2\pi)(40)(1.67 \times 10^{-27} \text{ kg})}{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})^2}\right)^{3/2} = 1.02 \times 10^7.$$

Therefore

$$S = Nk\left[\ln(1.02 \times 10^7) + \frac{5}{2}\right] = Nk(18.6) = (18.6)R = 155 \text{ J/K}.$$

The enthalpy is

$$H = U + PV = U + nRT = \frac{5}{2}nRT = \frac{5}{2}(8.31 \text{ J/K})(300 \text{ K}) = 6.23 \text{ kJ}.$$

The Helmholtz free energy is

$$F = U - TS = (3.74 \text{ kJ}) - (300 \text{ K})(155 \text{ J/K}) = -42.6 \text{ kJ},$$

while the Gibbs free energy is

$$G = F + PV = F + RT = (-42.6 \text{ kJ}) + (8.31 \text{ J/K})(300 \text{ K}) = -40.1 \text{ kJ}.$$

Since the term TS is much larger in magnitude than U or PV, both of the free energies turn out to be negative. But the sign of F or G isn't any more significant than the sign of U: it's *differences* that matter, not actual values. (If we planned on tapping the rest energies, mc^2, of the argon atoms, then we would want to include this energy in U, and then U, H, F, and G would all be increased by an enormous amount.)

Problem 5.6. (Muscle as a fuel cell.)

(a) The data as tabulated on pages 404 and 405 are (for one mole of each substance under standard conditions):

	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)
Glucose	-1273	-910	212
O_2 (g)	0	0	205
CO_2 (g)	-393.5	-394.4	214
H_2O (l)	-285.8	-237.1	70

To obtain ΔH or ΔG for the reaction glucose $+ 6O_2 \rightarrow 6CO_2 + 6H_2O$, we subtract Δ_f of the reactants from Δ_f of the products. Therefore, in kilojoules,

$$\Delta H = 6 \cdot (-393.5) + 6 \cdot (-285.8) - (-1273) = -2803$$

(as computed in Problem 1.51), and

$$\Delta G = 6 \cdot (-394.4) + 6 \cdot (-237.1) - (-910) = -2879.$$

(b) The maximum "other" work performed is just the amount by which G decreases for the system: 2879 kJ for each mole of glucose consumed.

(c) Under ideal conditions, the amount of work output, 2879 kJ, is *more* than the amount by which the system's enthalpy decreases (2803 kJ). To make up for the net loss of enthalpy, 76 kJ of heat must flow *into* the system.

(d) The total entropy of the reactants is (in J/K)

$$212 + 6 \cdot 205 = 1442,$$

while the total entropy of the products is (in J/K)

$$6 \cdot 214 + 6 \cdot 70 = 1704.$$

Therefore the system *gains* 262 J/K of entropy during this reaction. Because the entropy increases, heat can flow into the system. In the ideal case, the amount of heat entering is the maximum allowed for this entropy increase, namely (262 J/K)(298 K) = 78 kJ. (This number agrees reasonably well with the result of part (c), 76 kJ; the small difference gives some indication of the uncertainties in the data.)

(e) Under nonideal operation, new entropy would be created in the system during the reaction, allowing less heat to enter (or even requiring that heat be expelled, if the entropy created exceeds 262 J/K). Therefore less energy would leave the system as "other" work. The values of ΔH and ΔG, however, are the same whether the operation is "ideal" or not.

Problem 5.10. From the relation $(\partial G/\partial T)_P = -S$, we can write the change in G as $\partial G = -S\,dT$. The table on page 405 lists the entropy of a mole of water under standard conditions as 69.91 J/K, so the change in G from 25°C to 30°C is

$$dG = -(69.91 \text{ J/K})(5 \text{ K}) = -349.6 \text{ J}.$$

In other words, the Gibbs free energy is about 350 J lower at 30°C than at 25°C. If we now imagine increasing the pressure at fixed temperature, the relation $(\partial G/\partial P)_T = V$ tells us that $dG = V\,dP$, where V is the volume of a mole of water, 18.07×10^{-6} m^3. Raising the pressure therefore increases G. To produce an increase of 349.6 J, we would need to increase the pressure by

$$dP = \frac{dG}{V} = \frac{349.6 \text{ J}}{18.07 \times 10^{-6} \text{ m}^3} = 1.93 \times 10^7 \text{ Pa} = 193 \text{ bars}.$$

The moral of the story is that temperature changes tend to have much larger effects on G than pressure changes, at least within the realm of conditions familiar to us in everyday life.

Problem 5.21. Heat capacity (C) is extensive, since the heat required to raise the temperature of an object by a given amount is directly proportional to the size of the object. For $C_V = (\partial U/\partial T)_V$, we can also see this from the fact that U is extensive and T is intensive: Dividing an extensive quantity by an intensive quantity results in an extensive quantity. Specific heat capacity, $c = C/m$, is intensive, because it is the ratio of two extensive quantities. It doesn't depend on how much of the stuff you have.

Problem 5.22. In Section 3.5 I showed that the chemical potential of a monatomic ideal gas is

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

In the last expression I've substituted $V/N = kT/P$, since equation 5.40 is written in terms of pressure rather than volume. To bring in the reference pressure $P°$, multiply and divide by it inside the logarithm:

$$\mu = -kT \ln\left[\frac{P°}{P}\frac{kT}{P°}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] = -kT \ln\left[\frac{kT}{P°}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + kT \ln(P/P°).$$

This expression is now in the form of equation 5.40, with the first term equal to $\mu°(T)$, a function of temperature but not pressure. (The reference pressure, $P°$, is just a constant, conventionally taken to be 1 bar.)

Problem 5.32. (The water-ice phase boundary.)

(a) As ice melts into water the change in entropy (or the latent heat) is positive, while the change in volume is negative (since ice is less dense), so the slope of the phase boundary, $\Delta S/\Delta V$, must be negative. In more fundamental terms, converting ice to water lets the entropy of the environment increase (by making more volume available), and this effect is more important at high pressure since $P = T(\partial S/\partial V)$. So high pressures tend to push the equilibrium in the direction of the phase that takes up less volume.

(b) Instead of considering a mole of ice/water, let's just consider one gram. Then the latent heat is 333 J, the volume of the ice is $(917,\!000)^{-1}$ m^3 = 1.091×10^{-6} m^3, and the volume of the water is 1.000×10^{-6} m^3. Therefore the slope of the phase boundary is

$$\frac{dP}{dT} = \frac{L}{T\,\Delta V} = \frac{333 \text{ J}}{(273 \text{ K})(-.091 \times 10^{-6} \text{ m}^3)} = -1.35 \times 10^7 \text{ Pa/K} = -135 \text{ bar/K}.$$

So if the temperature decreases by one degree (from 0 to $-1°$C), the pressure must increase by 135 bars to remain on the phase boundary. In other words, ice will melt at $-1°$C if the pressure is above 135 bars (or 133 atmospheres).

(c) Treating the glacier ice as a fluid, the increase in pressure at depth z is simply $\rho g z$, where ρ is the density. (To derive this formula, consider a column of ice extending down to depth z. The weight of the column per unit area is $\rho g z$, and this must be balanced by the pressure from below.) In our case, to reach a pressure of 135 bars,

$$z = \frac{P}{\rho g} = \frac{135 \times 10^5 \text{ N/m}^2}{(917 \text{ kg/m}^3)(9.8 \text{ N/kg})} = 1500 \text{ m}.$$

That's pretty deep, just to lower the melting temperature by one degree. Apparently the flow of glaciers is not caused primarily by lowering of the melting point under pressure.

(d) The blade of an ice skate measures a few millimeters across by perhaps 25 cm long, so the total area is perhaps 10 cm^2. Even if you're leaning on the "corner" of the blade, the total area in contact with the ice is probably more than 1 cm^2 = 10^{-4} m^2. If your mass is 50 kg, then your weight is about 500 N so the pressure on the blade is roughly $(500 \text{ N})/(10^{-4} \text{ m}^2) = 5 \times 10^6$ Pa = 50 bars. Under this pressure the melting temperature drops by only $50/135 \approx .4°$C. This mechanism of friction reduction would work *only* if the ice temperature is already within less than half a degree of melting, and even then, only when you're minimizing the area of the blade in contact with the ice. In practice, the ability to glide doesn't depend so critically on the ice temperature or on how the blade touches the ice, so I don't think this mechanism can be very important.

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Problem 5.43. On the diagram below (the same one plotted in the previous problem), I've plotted the composition of the exhaled air (35°C, 90% relative humidity) and also one possible composition of the outdoor air (10°C) as dots. Consider, now, the mixing of parcels of air with these two initial temperatures and initial H_2O partial pressures. If the
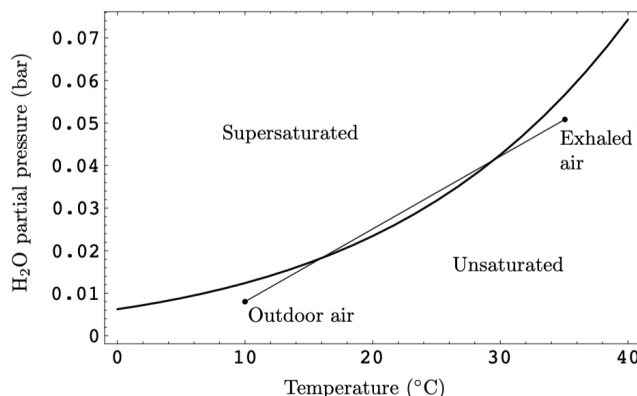
parcels have equal mass, then the mixture will end up at a temperature halfway between them (since the heat capacity of air is independent of its temperature), and also at an H_2O partial pressure that is halfway between the partial pressures of the initial parcels. More generally, for any value of the ratio of the initial masses, the mixture will have a temperature and H_2O partial pressure that lie somewhere on a straight line on the diagram, connecting the dots representing the two initial states. (As the exhaled air mixes with larger and larger amounts of environmental air, the state of the mixture will move downward along this straight line.) To get cloud droplets, the state of the mixture must lie above the curve representing the equilibrium vapor pressure; since this curve is concave-upward, this is possible even when both initial states lie below the curve. By moving the dot representing the outdoor air state vertically, we see that if it goes too low, the line will no longer cross the vapor pressure curve. The minimum H_2O partial pressure of the outdoor air in this case is about 0.0032 bar, corresponding to a relative humidity of about 25%. If we do get cloud droplets, therefore, we can conclude that the relative humidity is at least 25%.

Therefore, by van't Hoff's formula, the osmotic pressure is

$$P_2 - P_1 = \frac{n_B RT}{V} = \frac{(1.12 \text{ mol})(8.315 \text{ J/mol·K})(300 \text{ K})}{10^{-3} \text{ m}^3} = 3.0 \times 10^6 \text{ Pa} \approx 30 \text{ atm}.$$

(b) If you apply an excess pressure just barely greater than the osmotic pressure to the seawater, and force 1 liter of it through an osmotic membrane, the work performed is

$$P \Delta V = (3.0 \times 10^6 \text{ Pa})(10^{-3} \text{ m}^3) = 3000 \text{ J}.$$

This isn't much work—less than 1/1000 of a kilowatt-hour. As usual, though, this number represents the absolute minimum, and in practice the work required will be greater. First, to get the water to go through the membrane at an acceptable rate, you'll need to apply more than the minimum pressure. Second, the membrane probably won't be perfect, so some salt will get through and you'll need to repeat the process several times to reduce the salinity to an acceptable level.

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