HW-Solution-set6

5.1, 5.2, 5.5, 5.10, 5.11, 5.22, 5.24, 5.28, 5.32, 5.35

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 5.2. Because the reactants N_2 and H_2 are elements in their most stable states, the ΔH and ΔG values for this reaction are just the values for the "formation" of ammonia listed on page 405, times 2 because we're forming two moles of ammonia. To check the relation $\Delta G = \Delta H - T\,\Delta S$, we also need to know ΔS, the entropy of two moles of ammonia minus the entropies of a mole of N_2 and three moles of H_2:

$$\Delta S = 2(192.45\ \text{J/K}) - 191.61\ \text{J/K} - 3(130.68\ \text{J/K}) = -198.75\ \text{J/K}.$$

Therefore we should have

$$\begin{aligned}\Delta G = \Delta H - T\,\Delta S &= 2(-46.11\ \text{kJ}) - (298\ \text{K})(-198.75\ \text{J/K}) \\ &= -92.22\ \text{kJ} + 59.23\ \text{kJ} = -32.99\ \text{kJ}.\end{aligned}$$

And indeed, the tabulated ΔG value is -16.45 kJ per mole of ammonia, or -32.90 kJ for two moles, in very good agreement.

Problem 5.5. (Methane fuel cell.)

(a) Subtracting Δ_f of the reactants from Δ_f of the products, we have

$$\begin{aligned}\Delta H &= 2(-285.83\ \text{kJ}) + (-393.51\ \text{kJ}) - (-74.81\ \text{kJ}) = -890.36\ \text{kJ}; \\ \Delta G &= 2(-237.13\ \text{kJ}) + (-394.36\ \text{kJ}) - (-50.72\ \text{kJ}) = -817.90\ \text{kJ}.\end{aligned}$$

(b) Under ideal conditions, all of the decrease in G comes out as electrical work, so the electrical work output is 818 kJ.

(c) The decrease in enthalpy of 890 kJ is the sum of the electrical work output plus the heat given off. Under ideal conditions the work output is 818 kJ, so the heat is the difference, 72 kJ.

(d) For each methane molecule that reacts, eight electrons are pushed around the circuit. Therefore the voltage is

$$\text{voltage} = \frac{\text{electrical work done}}{\text{total charge}} = \frac{818\ \text{kJ}}{(8)(6.02\times 10^{23})(1.6\times 10^{-19}\ \text{C})} = 1.06\ \text{V}.$$

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, $18.07 \times 10^{-6}\ \text{m}^3$. 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 5.11. (Hydrogen fuel cell at 75°C.)

(a) Under an "infinitesimal" temperature change dT, the Gibbs free energy changes by $dG = -SdT$. Taking $dT = 50$ K and looking up the room-temperature entropies, we obtain (for a mole of each substance)

$$\begin{aligned} H_2&: \quad G = 0 - (131\ \text{J/K})(50\ \text{K}) = -6550\ \text{J}; \\ O_2&: \quad G = 0 - (205\ \text{J/K})(50\ \text{K}) = -10250\ \text{J}; \\ H_2O&: \quad G = -237000\ \text{J} - (70\ \text{J/K})(50\ \text{K}) = -240500\ \text{J}. \end{aligned}$$

(Of course, the entropies are not constant over this temperature interval, so it would be better to first estimate the entropy of each substance in the middle of the interval, at 323 K, and use that value instead of the room-temperature value. For H_2, the increase in entropy between 298 K and 323 K is approximately $C_P \ln(T_f/T_i) = (29\ \text{J/K}) \ln(323/298) = 2.3$ J/K. The entropies of the O_2 and H_2O are likewise only slightly greater at 323 K.)

(b) At 75°C, ΔG for the reaction is

$$G_{H_2O} - G_{H_2} - \tfrac{1}{2}G_{O_2} = -240500\ \text{J} + 6550\ \text{J} + 5125\ \text{J} = -229\ \text{kJ}.$$

Thus, the maximum electrical work done by the cell is only 229 kJ (per mole of hydrogen consumed), about 3.5% less than the room-temperature value of 237 kJ. Why the difference? The reacting gases have a lot of entropy, which must be gotten rid of by dumping waste heat into the environment. At the higher temperature, we need to dump *more* waste heat to get rid of this entropy, so less of the energy is left to perform electrical work.

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:

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

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

Problem 5.24. We're free to choose an arbitrary reference point for measuring G values, so for convenience let's take $G = 0$ for graphite at 1 bar. Then for diamond, $G = 2.9\ kJ$ at 1 bar. The equations of the lines drawn in Figure 5.15 are

$$G_g = V_g P \qquad \text{and} \qquad G_d = V_d P + (2.9 \text{ kJ}),$$

where the subscripts are g for graphite and d for diamond, and technically, P is measured relative to 1 bar, though we'll soon see that the difference between 0 bar and 1 bar is negligible. To find the intersection of the lines, set these expressions equal and solve for P:

$$V_g P = V_d P + (2.9 \text{ kJ}) \qquad \Rightarrow \qquad P = \frac{(2.9 \text{ kJ})}{V_g - V_d} = \frac{2900 \text{ J}}{1.89 \times 10^{-6} \text{ m}^3} = 1.53 \times 10^9 \text{ Pa}.$$

So the intersection is at 1.53 GPa, which is 15.3 kbar.

Problem 5.28. (Calcite and aragonite.)

(a) The table on page 404 gives the molar Gibbs free energies of formation of both calcite and aragonite, with the value for calcite being lower by 1.0 kJ. This means that the Gibbs free energy of a mole of calcite is less than that of a mole of aragonite by this amount, under standard conditions. Calcite is therefore the more stable phase, at room temperature and atmospheric pressure.

(b) In analogy with the diamond-graphite system, we can imagine plotting G vs. P (at fixed T) for both calcite and aragonite. The slopes of the two graphs are $V_c = 3.693$ kJ/kbar and $V_a = 3.415$ kJ/kbar, according to the data in the table and the conversion factor derived in Problem 5.25. Since the volume of aragonite is less, it should become stable at high pressure, that is, the two lines should intersect at some $P > 0$. For convenience, I'll set $G_c = 0$ at $P = 0$; then $G_a = 1.0$ kJ at $P = 0$. The equations of the two lines are then

$$G_c = V_c P \qquad \text{and} \qquad G_a = V_a P + (1.0 \text{ kJ}).$$

Equating these two expressions and solving for P gives the transition pressure,

$$P = \frac{1.0 \text{ kJ}}{\mathrm{V_c} - \mathrm{V_a}} = \frac{1.0 \text{ kJ}}{0.278 \text{ kJ/kbar}} = 3.6 \text{ kbar}.$$

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 $= 1.091 \times 10^{-6}$ 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 $\text{cm}^2 = 10^{-4}\ \text{m}^2$. If your mass is 50 kg, then your weight is about 500 N so the pressure on the blade is roughly $(500\ \text{N})/(10^{-4}\ \text{m}^2) = 5 \times 10^6\ \text{Pa} = 50$ bars. Under this pressure the melting temperature drops by only $50/135 \approx .4°\text{C}$. 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.

Problem 5.35. (Vapor pressure equation.) Neglecting the volume of the condensed phase and using the ideal gas law for the volume of the gas, the difference in volume between the two phases is approximately

$$\Delta V \approx V_g \approx \frac{RT}{P},$$

assuming one mole. Therefore the Clausius-Clapeyron equation becomes

$$\frac{dP}{dT} = \frac{LP}{RT^2}, \qquad \text{or} \qquad \frac{dP}{P} = \frac{L}{R}\frac{dT}{T^2}.$$

Integrating both sides then gives

$$\ln P = -\frac{L}{RT} + (\text{const}), \qquad \text{or} \qquad P = (\text{const})e^{-L/RT}.$$