

Homework Set 1

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February 10, 2008

■ Problem 1 (6 points)

■ Part a (2 points)

First of all, the atomic mass of carbon is ~ 12 Daltons; thus, there are 12 g per mole (6.022×10^{23}) of carbon. This means that 1 kg of carbon is $1000\text{g}/12\text{g} = 83.3$ moles.

Since we get 1 carbon per carbon dioxide, this means we need 83.3 moles of carbon dioxide. Furthermore, since the percent composition are percent by volume, this means that we need $83.3/0.00046 = 1.81 \times 10^5$ moles of air!

For an ideal gas pressure, volume, temperature, and number of moles are related via

$$pV = nRT$$

$$\text{Thus, } V = \frac{nRT}{p} = (1.81 \times 10^5 \text{ mol}) (0.082 \frac{\text{L atm}}{\text{K mol}}) \frac{(273 + 25 \text{ K})}{1 \text{ atm}} = 4.4 \times 10^6 \text{ L}$$

■ Part b (2 points)

This requires some assumptions. First let's assume that the atmosphere only extends up to the troposphere (~ 10 km), which is reasonable since wikipedia tells me that 75% of the gas in the atmosphere is in the troposphere.

If we assume that the pressure and density of the atmosphere is constant throughout the troposphere (which it is not!) and that there is no atmosphere beyond the troposphere (again not true), then the amount of carbon in the earth's atmosphere can be calculated from the density found above ($1 \text{ kg}/4.4 \times 10^6 \text{ L}$) and the volume of the troposphere:

The volume between two spherical shells is related to the radius simply the difference in the volume of the two spheres; thus, the volume of the troposphere is

$$V = \frac{4}{3} \pi (r_2^3 - r_1^3) = \frac{4}{3} \pi ((6371 \text{ km} + 10 \text{ km})^3 - (6371 \text{ km})^3) = 5.1 \times 10^9 \text{ km}^3 = 5.1 \times 10^{21} \text{ L}$$

Thus, there are $(1 \text{ kg}/4.4 \times 10^6 \text{ L}) (5.1 \times 10^{21} \text{ L}) = 1.2 \times 10^{15} \text{ kg}$ of carbon in the atmosphere.

The surface area of the Earth is

$$S = 4 \pi (6371 \text{ km})^2 = 5.1 \times 10^8 \text{ km}^2 = 5.1 \times 10^{14} \text{ m}^2$$

Thus, the amount of carbon above each m^2 is $1.2 \times 10^{15} \text{ kg} / 5.1 \times 10^{14} \text{ m}^2 = 2.4 \text{ kg}$

■ **Part c (2 points)**

If 1 kg of carbon is fixed by each m^2 of forest each year, then the total time to fixation (assuming that the entire earth is covered in forest!) is only 2.4 years!

■ **Problem 2 (6 points)**

■ **Part a (2 points)**

In a vertical tube of incompressible liquid, the pressure increases linearly with increasing depth via $p = p_0 + \rho gh$. We will assume that the water is not significantly compressed; thus,

$$p = (1 \text{ atm}) + (1000 \text{ kg/m}^3)(9.8 \text{ m/s}^2)(2500 \text{ m}) = 1 \text{ atm} + (1.01 \times 10^5 \text{ Pa}) = 244 \text{ atm}$$

■ **Part b (2 points)**

Isothermal compressibility is defined as $\beta_T = -1/V \Delta V/\Delta p$. Recall that the density is related to the volume via, $\rho = m/V$. Thus, for small changes in density, $\Delta V/V = \Delta\rho/\rho$. Thus, the density change is

$$\Delta\rho = \beta_T \rho \Delta p = (49.5 \times 10^{-6} \text{ atm}^{-1})(1000 \text{ kg/m}^3)(243 \text{ atm}) = 12 \text{ kg/m}^3$$

Thus, the percent change in the density of water is $12/1000 = 1.2\%$.

■ **Part c (2 points)**

Recalling the ideal gas law, $pV = nRT$. The number of moles are constant in the balloon, so we can write

$$\frac{p_1 V_1}{p_2 V_2} = \frac{T_1}{T_2} \Rightarrow V_2 = \frac{p_1}{p_2} \frac{T_2}{T_1} V_1 = \frac{(1 \text{ atm})}{(244 \text{ atm})} \frac{(277 \text{ K})}{(293 \text{ K})} 10 \text{ L} = 0.039 \text{ L} = 39 \text{ mL}$$

■ **Problem 3 (8 points)**

■ **Part a (4 points)**

The ideal gas law tells us that at 100 C (373 K) and 1 atm, the volume of the water vapor is

$$V = nRT/p = (1 \text{ mol})(0.082 \text{ L atm/Kmol})(373 \text{ K})/(1 \text{ atm}) = 30.6 \text{ L}$$

Because the pressure was constant throughout this process, the work done is simply the product of the pressure and the change in volume, $w = p\Delta V = (1 \text{ atm})(30.6 \text{ L}) = 30.6 \text{ atm L}$. Since $1 \text{ atm L} = 0.1 \text{ kJ}$. The work done in this process is 3.1 kJ.

The heat of vaporization of water is 40.7 kJ/mol. Thus, it takes 40.7 kJ to vaporize the water, so $q = 40.7\text{kJ}$.

From the first law of thermodynamics, $\Delta E = q + w$, where q and w are defined as work done on the system and heat added into the system. To vaporize the water we added heat, but the water vapor then had to do work, so the final energy should be the difference between these two values. Thus, $\Delta E = 40.7\text{ kJ} - 3.1\text{ kJ} = 37.6\text{ kJ}$.

Finally, for a system at constant pressure $\Delta H = q$, so $\Delta H = 40.7\text{ kJ}$.

■ Part b (4 points)

ΔE and ΔH are state variables. In words, their values do not depend on the way in which the system gets to its final condition. Since the final volume and pressure are the same in this case, $\Delta E = 37.6\text{ kJ}$ and $\Delta H = 40.7\text{ kJ}$.

The work done by the system is zero in this case because there is no volume change.

From the first law, $\Delta E = q + w$, we can now calculate $q = \Delta E - w = 37.6\text{ kJ} - 0 = 37.6\text{ kJ}$.

Note that $q \neq \Delta H$ in this case because as the water vapor is increased the pressure inside the piston changes. It is only under constant pressure that these two quantities are equal.

Finally, the fact that the heat is less in this part as opposed to part a makes sense because the heat added does not have to go into the work necessary to move the piston!

■ Problem 4 (7 points)

■ Part a (3 points)

In the case of the negative entropy change: It is clear that the entropy of the polymer is increasing when it goes from the ordered helix to the disordered coil; thus, this process must be accompanied by a larger decrease in the entropy of the solvent. Most likely this is due to an ordering of the solvent around groups exposed by the polymer as it unfolds.

In the case of the negative enthalpy change: This implies that heat is released in the transition from an ordered helix to a disordered coil. This is surprising since it involves the breaking of favorable interactions in the helix (which typically requires adding heat!). Since heat is released, this must mean that more favorable interactions are now possible between the solvent and the exposed polymer.

Finally, because $\partial\Delta G/\partial T = -\Delta S$, and $\Delta S < 0$, increasing the temperature will increase ΔG and will oppose the helix-coil transition, i.e. at higher temperatures the equilibrium will be shifted towards the ordered helix!

■ Part b (2 points)

To calculate if the reaction is spontaneous, recall that

$$\Delta G = \Delta H - T \Delta S = (-4,000\text{ J/mol}) - (273 + 39\text{ K}) (-12\text{ J/Kmol}) = -256\text{ J/mol} < 0$$

Thus, the reaction is spontaneous!

The reaction will be reversible when $\Delta G = 0$, i.e. when $\Delta H = T \Delta S$. Thus, the melting temperature is $T_M = \Delta H / \Delta S$

In this case, $T_M = \Delta H / \Delta S = (-4000 \text{ J/mol}) / (-12 \text{ J/mol K}) = 333 \text{ K}$ or 60 C

■ Part c (2 points)

The second law of thermodynamics states that the entropy of the entire universe (system plus surroundings) can never decrease. Thus, an isolated system without surroundings cannot undergo a reaction that decreases its entropy.

Aside: the second law is a statistical law. It is only true on average. Thus, for very small systems, like perhaps the inside of cells, it is possible to have an event that violates the second law. It turns out it is just less probable to occur than an event that does not violate the second law. Has life evolved to capture these second law violating fluctuations?

■ Problem 5 (11 points)

■ Part a (4 points)

This reaction can be written in the simple form $A \leftrightarrow B$, where A represents the free oligonucleotide and B represents the basepaired oligonucleotide. Thus, the equilibrium constant is

$$K_1 = \frac{[B]}{[A]}$$

If we start with 1 mM of A, and no B, then the final concentration of A will be $[A] = [A]_{\text{int}} - x$, and the final concentration of B will be $[B] = x$, where x is the equilibrium concentration of the basepaired species. (For every oligonucleotide that basepairs, we lose one of A and gain one of B)

Thus, the equilibrium equation requires that

$$K_1 = \frac{x}{[A]_{\text{int}} - x} \Rightarrow K_1 [A]_{\text{int}} = x + K_1 x \Rightarrow x = \frac{K_1 [A]_{\text{int}}}{K_1 + 1} = \frac{0.001 \text{ M} \cdot 0.86}{0.86 + 1} = 462 \mu\text{M}$$

This implies that $[A] = 1000 \mu\text{M} - 462 \mu\text{M} = 538 \mu\text{M}$. Quickly checking the final equilibrium concentrations: $462 / 538 = 0.86!$

Since $[B] = [A] K_1$, the fraction of hairpin loop is $f_B = \frac{[B]}{[A] + [B]} = \frac{[B]}{[B] / K_1 + [B]} = \frac{K_1}{K_1 + 1}$. Since this is independent of the concentration of B (and A), increasing the amount of polynucleotide will not change the fraction that exists in hairpin loop!

■ Part b (3 points)

First of all, with the equilibrium constant at this new temperature (37 C), we can immediately calculate the ΔG . Recall that

$$\Delta G = -RT \ln K = -(8.31 \text{ J/molK}) (273 + 37 \text{ K}) \ln(0.51) = 1.7 \text{ kJ/mol}$$

Now to calculate the other parameters, recall that for all temperatures $\Delta G = \Delta H - T \Delta S$. Thus, we have two sets of equations (assuming that ΔH and ΔS are independent of temperature)

$$\Delta G_1 = \Delta H - T_1 \Delta S \text{ and } \Delta G_2 = \Delta H - T_2 \Delta S$$

Thus, if we calculate the ΔG for the first temperature (from the equilibrium constant from part a), which is 0.37 kJ/mol, we will have a system of two equations with two unknowns.

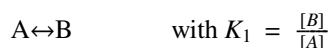
The solutions are

$$\Delta H = \frac{\Delta G_2 T_1 - \Delta G_1 T_2}{T_1 - T_2} = \frac{(-1.7 \text{ kJ/mol})(273+25) - (0.37 \text{ kJ/mol})(273+37)}{(273+25) - (273+37)} = -33 \text{ kJ/mol}$$

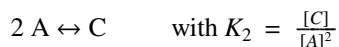
$$\Delta S = \frac{\Delta G_2 - \Delta G_1}{T_1 - T_2} = \frac{(-1.7 \text{ kJ/mol}) - (0.37 \text{ kJ/mol})}{(273+25) - (273+37)} = -0.11 \text{ kJ/mol K}$$

■ Part c (4 points)

If we write out the first reaction as



and the second reaction as



Let's calculate the final concentrations given a starting concentration of $[A]_{\text{Int}} = 0.1 M$ with all other concentrations zero. We start by assuming that b molecules of A will form the hairpin loop (species B) while $c/2$ molecules of A will come together to form a dimer (species c). Thus the final concentrations of everything will be $[A] = [A]_{\text{Int}} - b - c/2$, $[B] = b$, and $[C] = c$. For simplicity, let the final concentration of $[A] = a$.

We have two equilibrium equations that must be satisfied at these final concentrations, so we can write

$$K_1 = \frac{b}{a} \text{ and } K_2 = \frac{c}{a^2}$$

With the added constraint that $[A]_{\text{Int}} = a + b + 2c$

Note that we can solve the equilibrium expressions for b and c above, and then substitute them into this constraint. This yields

$$[A]_{\text{Int}} = a + a K_1 + 2 K_2 a^2$$

We can now find a from the quadratic formula

$$a = \frac{-(1+K_1) + \sqrt{(1+K_1)^2 + 8 K_2 [A]_{\text{Int}}}}{4 K_2}$$

Plugging in all the numbers this gives us a final concentration of $[A] = a$ of 53.7 mM.

Now, returning to the equilibrium equations above, this implies that the final concentration of $[B] = b$ is

$$b = a K_1 = (53.7 \text{ mM})(0.86) = 46.2 \text{ mM}$$

and of $[C] = c$

$$c = K_2 a^2 = (1 \times 10^{-2} \text{ M}^{-1})(0.0537 \text{ M})^2 = 28.9 \mu\text{M}$$

Remembering all of the labels this implies that

$$ss = 53.7 \text{ mM}, ds = 28.9 \mu\text{M}, \text{ and } h = 46.2 \text{ mM}$$

■ Problem 6 (3 points)

Consider the reaction $2 \text{ S} \leftrightarrow \text{ D}$, with $K = \frac{[D]}{[S]^2}$.

If the initial concentration of S is c , then we have $c = s + 2d$, where s and d are the concentrations of S and D at equilibrium. Because we are interested in the number of *single strands* in the duplex at equilibrium is

$$f = \frac{2[D]}{[S]+2[D]} = \frac{2d}{s+2d} = \frac{2d}{c}. \text{ This implies that } d = cf/2, \text{ a quantity that will be useful below.}$$

Writing out the equilibrium constant, we have

$$K = \frac{d}{s^2} = \frac{d}{(c-2d)^2} = \frac{cf/2}{(c-cf)^2} = \frac{1}{2c} \frac{f}{(1-f)^2}$$