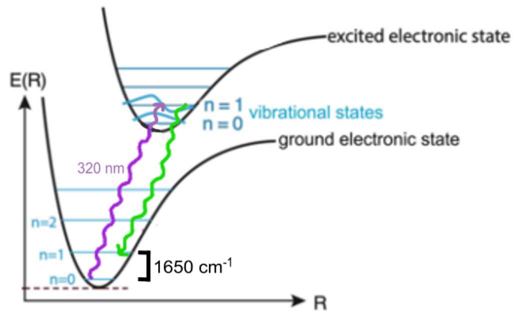
Hour Exam 2 - Solutions Spring 2022



1. (10 pts) In the above figure, a molecule absorbs light at wavelength $\lambda_1 = 320$ nm (purple arrow) and goes from the ground state to the excited electronic state and n=1 vibrational state. When the molecule emits light (green arrow), it goes back down to the ground electronic state in the n=1 vibrational state, which has a frequency of $\nu_{vib} = 1650$ cm^{-1} in "wavenumber" or "cm^{-1}" units.

a) (2) **What is** the frequency ν_1 of the 320 nm absorbed light in cm^{-1} units? [Hint: tip at end of exam.]

Solution: The relationship between the frequency (in cm^{-1} units) and the wavelength (in nm units) is given by $wavenumber\ (cm^{-1}) = \frac{10^7}{\lambda\ (nm)}$

So, $\nu_1 = \frac{10^7}{\lambda_1} = \frac{10^7}{320\ nm} = 31250\ cm^{-1}$

b) (4) **What is** the frequency ν_2 of the emitted light in terms of the absorbed frequency ν_1 and vibrational frequency ν_{vib}? **Write down** its value in cm^{-1} units. [Hint: energy is conserved]

Solution: According to the conservation law of the energy, the energy difference between the initial and the final state is equal to the energy difference between the absorbed light and the emitted light. That is,

$$\Delta E = E_1 - E_2 = h\nu_1 - h\nu_2 = h\nu_{vib}, \text{ or}$$

$$\nu_2 = \nu_1 - \nu_{vib}$$

where ν_1 is the frequency of the absorbed light, ν_2 is the frequency of the emitted light and ν_{vib} is the vibrational frequency. Thus, the frequency of the emitted light in units of cm^{-1} is

$$\nu_2 = \nu_1 - \nu_{vib} = 3.1250\ cm^{-1} - 1650\ cm^{-1} = 29600\ cm^{-1}$$

c) (2) **What is** the wavelength of the emitted light in nm?

Solution: Using the formula for converting cm-1 into nm again,

$$\lambda_2 = \frac{10^7}{\nu_2} = \frac{10^7}{29600\ cm^{-1}} = 338\ nm$$

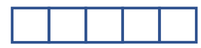
As expected from the drawing, the emitted energy is less and the emitted wavelength longer.

2. (10 pts) Let's think about arranging 4 particles.

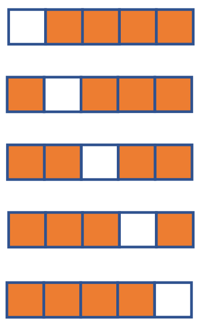
a. (4) How many ways are there of arranging N=4 <u>in</u>distinguishable particles in a box with M=5 compartments? **Write down** the formula and **calculate** the value.

Solution: The number of total arrangements is $\frac{M!}{N!(M-N)!}$

Thus, $\frac{5!}{4!1!} = 5$

b. (2) **Draw all** the different arrangements from (a) in boxes 

Solution:



c. (2) If all 4 particles were <u>distinguishable</u>, then **how many** arrangements are there?

Solution: The number of total arrangements is $\frac{5!}{1!} = 120$ (leave out 1/N! since particles are distinguishable).

d. (2) What is the difference in entropy between the two cases (c)-(a): give the **formula** and the **answer** in units of J/K.

Solution: The entropy is related to the total accessible states by the Boltzmann formula, so in case (a) the entropy is

$$S_a = k_B \ln(5)$$

and in and case (c),

$$S_c = k_B \ln(120)$$

So the entropy difference is

$$\Delta S = S_c - S_a = k_B \ln(120) - k_B \ln(5)$$

$$= k_B \ln\left(\frac{120}{5}\right) = k_B \ln(24)$$

$$= +4.39 \cdot 10^{-23} \text{J/K}$$

The entropy is larger for the distinguishable particles because there are more ways of arranging them (a higher potential for disorder).

3. (10 pts) Let's see how much the entropy of water changes when it is heated by 1 degree Kelvin.

a. (2) Based on what you know about microstates, **does** the entropy of water increase or decrease when water is heated up?

Solution: Increases: when heated up, the number of accessible microstates increases.

b. (2+2) **Write down the formula** that relates entropy change dS to heat capacity C_p, temperature T and temperature change dT. When you integrate this formula from T_1=298 K to T_2=299 K, on the left side you get $\Delta S=S(299\text{ K})-S(298\text{ K})$. Assuming that the heat capacity is constant, **write down** the integral from T_1=298 to T_2=299 K on the right side as well.

Solution:

$$dS = \frac{C_P dT}{T}$$

Integrate left and right sides separately from T_1=298 K to T_2=299 K,

$$Left = \int_{S(T_1)}^{S(T_2)} dS' = Right = \int_{T_1}^{T_2} \frac{C_P(T')dT'}{T'}$$

Given, C_P is a constant $\Rightarrow C_P$ doesn't vary with temperature, so we can pull it out of the integral:

$$\Rightarrow \Delta S = S(T_2) - S(T_1) = C_P \int_{T_1}^{T_2} \frac{dT'}{T'}$$

c. (2) **Evaluate** the integral on the right side to obtain a formula for ΔS in terms of C_p, T_2 and T_1.

Solution:

$$\Rightarrow \Delta S = C_P\,[ln\,T_2 - ln\,T_1] = C_P\,ln\frac{T_2}{T_1}$$

d. (2) The heat capacity of water is about 4.18 J K^{-1} g^{-1}. So, for 1 g of water, **how much** does the entropy change, in J/K when 1 gram of water is heated by 1 degree from 298 to 299 K?

Solution:

$$\Delta S = 4.18\,(J\,K^{-1}g^{-1}) * 1\,(g) * ln\frac{299}{298}$$

$$\Rightarrow \Delta S = 4.18\,(J\,K^{-1}g^{-1}) * 1\,(g) * ln\frac{299}{298} = 0.014\,J\,K^{-1}$$

4. (10 pts) In a steam locomotive, compressed gas expands in a cylinder to drive wheels. Let's assume the expansion is slow enough so that the gas remains at the same temperature as the surrounding cylinder, T= 298 K. Assume the gas is 'ideal.'

a) (2) **Write down** the formula for mechanical work dw in terms of pressure P and volume change dV.

Solution: $dw = PdV$ is the work done by the surroundings on the system (i.e. If the gas expands and does work, dw is positive, so the work done by the system on the surroundings, -dw, is negative. The energy of the system would decrease if no heat is allowed to flow into the system while it does work.)

b) (2+2) Assuming the ideal gas law, **eliminate pressure** as a variable in (a), and **integrate** both sides to obtain w as the volume changes from V_1 to $V_2>V_1$.

Solution: $PV=nRT \Rightarrow dw = \frac{nRT}{V}dV$; $w=\int_{V_1}^{V_2}\frac{nRT}{V}dV = nRT\ln(\frac{V_2}{V_1})$. (By assuming T is constant, heat must be flowing into the gas when it does work on the surroundings; this increases the entropy of the gas.)

c) (2) If 20 moles of gas expand to twice the volume in the cylinder, what is the work done in Joules?

Solution: $w = 20 \cdot 8.31 \cdot 298 \cdot \ln(2) \approx 34000$ J. Note that if the piston moves every second, that's 34 kW, a respectable power output.

d) (2) **By how much** did the entropy of the gas increase while doing this work**?**

Solution: $\Delta S = w/T$ = 34000/298 = 115 Joules/K. A gas that expands without heat flowing in will experience a decrease in temperature while it does work, and its energy will decrease. But here we assume T ias constant, so heat must be flowing into the gas to keep T constant, increasing its entropy.