Week 3 Recitation

Chapter 3

Homework: pages 55-75 (reading) and 93-95 (equations)

Review: Significant Figures

1. All non-zero digits are significant.
2. Zeros between non-zero digits are significant.
3. Zeroes to the left of the first non-zero digit are NOT significant.
4. Zeros to the right of a decimal point ARE significant.

Ex.

123 = 3 sig figs

1203 = 4 sig figs

0.0123 = 3 sig figs

1.50000 = 6 sig figs

Review: Significant Figures in Math

Addition and Subtraction:

The number with the fewest decimal places determines the number of sig figs in the answer.

Ex.

3200 + 12.34 = 3212

Multiplication and Division:

The number with the fewest digits determines the number of sig figs in the answer.

Ex.

12.1 * 12 = 140

Finally, never round halfway through a calculation – always at the end!

Common HW1 Mistakes

2.1a

Heat to **evaporate** liquid water at 20 deg C = **2.44e3 kJ**

2.8d

Number of cells of 1 micrometer diameter (1e-6 m) to encircle the Earth at the equator (r_{eq} = 6378.1 km)

$2*pi*r_{eq}*1000/d$ = **4.0e13 cells**

2.9a

$w_T = p(V2 - V1) = p*nRT(1/P2 - 1/P1)$, Incorrect

$w_T = -nRTln(V2/V1) = -nRTln(P1/P2)$, Correct

Common HW1 Mistakes cont.

2.12c

Descriptions in this class are typically quantitative.

18 g ice melted in 180 g liquid water:

heat_temp + heat_melt + nCp(Tf – 0) = nCp(Tf – 20), isolate Tf.

print("c. The final state of the system is 198 g of liquid water at {0:.1f} degrees C.".format(Tf))

2.29c

The comparison of energy densities should be quantitative, take a ratio.

In this case, the answer was approx. **H_2 possesses 2.9-3 times more combustion energy per mass than n-octane.**

Questions we will work on today: Chapter 3 question 1, 2, 3, 4 and 5

1. One mole of an ideal monatomic gas is expanded from an initial state at 3 bar and 450 K to a final state at 2 bar and 250 K

a. Chose two different paths for this expansion, specify them carefully, and calculate w and q for each path.
- Both paths are reversible
- Specify the pressure and temperature of each step in the paths
- Characterize each step in the paths (e.g. isothermal, isobaric)
- Apply the correct calculation

b. Calculate dU and dS for each path

2. No example is known of an organism evolving a process or structure resembling a heat engine. Basing your answer on the properties of a Carnot cycle, propose reasons why a heat engine might never arise in natural evolution.

Review the Carnot cycle (textbook page 56) with your group first and discuss why that would not naturally occur in an organism

3. The temperature of the heat reservoirs for a Carnot-cycle (reversible) engine are T_{hot} =1200 K and T_{cold} = 300 K. The efficiency of the engine is calculated to be 0.75, from Eq. 3.5 (page 59)

a.   If w = -100 kJ, calculate q1 and q3 . Explain the meaning of the signs of w, q1 , and q3.

Refer to textbook page 58 and 59. Identify the meaning of q1 and q3.

b. The same engine can be operated in the reverse order. If w = +100 kJ, calculate q1 and q3 . Explain the meaning of the signs.

c. Suppose it were possible to have an engine with a higher efficiency, say, 0.80. If w = -100 kJ, calculate q'1 and q'3 . The superscript denotes quantities for this engine.

d. If we use all the work done by the engine in part (c) to drive the heat pump in part (b), calculate (q1 + q1) and (q3 + q3) the amount of heat transferred. Explain the signs. Note that the net effect of the combination of the two engines is to allow a "spontaneous" transfer of heat from a cooler reservoir to a hotter reservoir, which should not happen.

e. Show that if it were possible to have a reversible engine with a lower efficiency operating between the same two temperatures, heat could also be transferred spontaneously from the cooler reservoir to the hotter reservoir. (Hint: Operate the engine with lower efficiency as a heat pump.)
Assume an efficiency of reversible engine is lower than 0.75.

4. The Second Law of Thermodynamics states that entropy increases for spontaneous processes and that an increase in entropy is associated with transitions from ordered to disordered states. Living organisms, even the simplest bacteria growing in cultures, appear to violate the Second Law because they grow and proliferate spontaneously. They convert simple chemical substances into the highly organized structure of their descendants. Write a critical evaluation of the proposition that living organisms contradict the Second Law. Be sure to state your conclusion clearly and to present detailed, reasoned arguments to support it.

5. Consider the process where n_A mol of gas A initially at 1 bar pressure mix with n_B mol of gas B also at 1 bar to form 1 mol of a uniform mixture of A and B at a final total pressure of 1 bar, and all at constant temperature T. Assume that all gases behave ideally.

a. Show that the entropy change, $\Delta_{mix}S_m$, for this process is given by $\Delta_{mix}S_m = \Delta S_A + \Delta S_B = -x_A R\ln x_A - x_B R\ln x_B$, where x_A and x_B are the mole fractions of A and B, respectively.

- Textbook page 71
- The partial pressures of A and B after mixing become $p_A = p[n_A/(n_A + n_B)] = x_A p$, and $p_B = p[n_B/(n_A + n_B)] = x_B p$
- Entropy changes are additive for components A and B; that is, $\Delta_{mix}S_m = \Delta S_m,A + \Delta S_m,B$.
- Pressure dependence of Entropy

b. What can you say about the value (especially the sign) of $\Delta_{mix}S_m$ and how does this correlate with the Second Law?

c. Derive an expression for $\Delta_{mix}G_m$ for the conditions of this problem and comment on values (and signs) of its terms.
- Textbook page 73

Breakout room group work: 25 mins

Solution and discussion

1. One mole of an ideal monatomic gas is expanded from an initial state at 3 bar and 450 K to a final state at 2 bar and 250 K

a. Chose two different paths for this expansion, specify them carefully, and calculate w and q for each path.

a) path 1 : (1 mole ideal gas, 3 bar, 450K) → (1 mol, 3 bar, 250 K) →(1 mol, 2 bar, 250 K)
   path 2 : (1 mole ideal gas, 3 bar, 450K) → (1 mol, 2 bar,450 K) →(1 mol, 2 bar, 250 K)

path 1: the first step is isobaric, the second is isothermal; both reversible
path 2: the first step is isothermal, the second is isobaric; both reversible

$$\text{work(path 1)} = -nR(250\text{-}450\text{K}) + nR(250\text{K})\ln(2\,\text{bar}/3\text{bar})$$
$$= -(1\text{mol}\times 8.314\,\text{Jmol}^{-1}\text{K}^{-1})(-200\text{K})$$
$$+ (1\text{mol}\times 8.314\,\text{Jmol}^{-1}\text{K}^{-1})(250\text{K})\ln(2\,\text{bar}/3\text{bar})$$
$$= 820.0408 \text{ J}$$
$$q(\text{path 1}) = nC_p(250-450\text{K}) - nR(250\text{K})\ln(2\,\text{bar}/3\text{bar})$$
$$= (1\text{mol}\times 2.5*8.314\,\text{Jmol}^{-1}\text{K}^{-1})(-200\text{K})$$
$$- (1\text{mol}\times 8.314\,\text{Jmol}^{-1}\text{K}^{-1})(250)\ln(2/3)$$
$$= -3314.2408 \text{ J}$$

$$\text{work(path 2)} = nR(450\text{K})\ln(2\,\text{bar}/3\text{bar}) - nR(250\text{-}450\text{K})$$
$$= (1\text{mol}\times 8.314\,\text{Jmol}^{-1}\text{K}^{-1})(450\text{K})\ln(2\,\text{bar}/3\text{bar})$$
$$- (1\text{mol}\times 8.314\,\text{Jmol}^{-1}\text{K}^{-1})(-200)$$
$$= 145.8334 \text{ J}$$
$$q(\text{path 2}) = -nR(450\text{K})\ln(2\,\text{bar}/3\text{bar}) + nC_p(250-450\text{K})$$
$$= -(1\text{mol}\times 8.314\,\text{Jmol}^{-1}\text{K}^{-1})(450\text{K})\ln(2\,\text{bar}/3\text{bar})$$
$$+ (1\text{mol}\times 2.5\times 8.314\,\text{Jmol}^{-1}\text{K}^{-1})(-200\text{K})$$
$$= -2640.0334 \text{ J}$$

Solution and discussion

b. Calculate dU and dS for each path

b) $\Delta U(\text{path 1})=q_{\text{path 1}}+w_{\text{path 1}}=820.0408-3314.2408=-2494.2 \text{ J}$ (first law)

$\Delta U(\text{path 2})=q_{\text{path 2}}+w_{\text{path 2}}=145.8334-2640.0334=-2494.2 \text{ J}$

$\Delta S(\text{path 1})=nC_p\ln(250\text{K}/450\text{K})-nR\ln(2 \text{ bar}/3 \text{ bar})$

$=(1\,\text{mol}\times2.5\times8.314\,\text{J mol}^{-1}\text{K}^{-1})*\ln(250/450)$

$-(1\,\text{mol}\times8.314\,\text{J mol}^{-1}\text{K}^{-1})*\ln(2\,\text{bar}/3\,\text{bar})$

$=\underline{-8.85 \text{ J K}^{-1}}$

$\Delta S(\text{path 2})=-nR\ln(2\,\text{bar}/3\text{bar})+nC_p\ln(250\text{K}/450\text{K})$

$=-(1\,\text{mol}\times8.314\,\text{J mol}^{-1}\text{K}^{-1})*\ln(2\,\text{bar}/3\text{bar})$

$+(1\,\text{mol}\times2.5\times8.314\,\text{J mol}^{-1}\text{K}^{-1})*\ln(250\,\text{K}/450\,\text{K})$

$=\underline{-8.85 \text{ J K}^{-1}}$

2. No example is known of an organism evolving a process or structure resembling a heat engine. Basing your answer on the properties of a Carnot cycle, propose reasons why a heat engine might never arise in natural evolution.

For a heat engine to have a good efficiency there must be a significant difference in the hot and cold baths that it utilizes. Temperatures are very uniform on the surface of the earth so that organisms have not been exposed to simultaneous temperature differences in their environment thus there can be no evolutionary pressure for a heat engine to come about. Of course, extremely high temperatures would be needed for the hot bath in order to achieve a good efficiency and it is unlikely that any stable molecules of life could evolve or be stable at such high temperatures.

3. The temperature of the heat reservoirs for a Carnot-cycle (reversible) engine are $T_{hot} = 1200$ K and $T_{cold} = 300$ K. The efficiency of the engine is calculated to be 0.75, from Eq. 3.5 (page 59)

a. If w = -100 kJ, calculate q1 and q3 . Explain the meaning of the signs of w, q1 , and q3.

a) $\text{Eff} = -w/q_1 = 0.75; q_1 = (100\,\text{kJ})/(0.75) = \underline{133.3\,\text{kJ}}$ (Eq. 3.3)

$q_1 + q_3 = -w; q_3 = -w - q_1 = (100\,\text{kJ}) - (133.3\,\text{kJ}) = \underline{-33.3\,\text{kJ}}$

q_1 (positive) is heat absorbed by the system at the hot temperature. q_3 (negative) is heat discharged by the system at the low temperature. w (negative) is the work done by the system.

b. The same engine can be operated in the reverse order. If w = +100 kJ, calculate q1 and q3 . Explain the meaning of the signs.

b) $w = +100\,\text{kJ} = -q_1 - q_3 = -q_1 + 0.25q_1$

Thus $q_1 = \underline{-133.3\,\text{kJ}}$ and $q_3 = \underline{+33.3\,\text{kJ}}$

Heat q_3 (positive) is absorbed by the system from a cold reservoir and heat q_1 (negative) is discharged to the hot reservoir when work w (positive) is done on the system. The engine is acting as a refrigerator.

3. The temperature of the heat reservoirs for a Carnot-cycle (reversible) engine are T_{hot} =1200 K and T_{cold} = 300 K. The efficiency of the engine is calculated to be 0.75, from Eq. 3.5 (page 59)

c. Suppose it were possible to have an engine with a higher efficiency, say, 0.80. If w = -100 kJ, calculate q'1 and q'3 . The superscript denotes quantities for this engine.

c) $$q'_1 = -w'/\text{Eff} = (100\,\text{kJ})/(0.80) = \underline{125\,\text{kJ}}$$
$$q'_3 = -w' - q'_1 = 100 - 125 = \underline{-25\,\text{kJ}}$$

d. If we use all the work done by the engine in part (c) to drive the heat pump in part (b), calculate (q1 + q1) and (q3 + q3) the amount of heat transferred. Explain the signs. Note that the net effect of the combination of the two engines is to allow a "spontaneous" transfer of heat from a cooler reservoir to a hotter reservoir, which should not happen.

d) Net heat absorbed at $T_{cold} = q_3 + q'_3 = 33.3 - 25 = \underline{8.3\,\text{kJ}}$

Net heat discharged at $T_{hot} = q_1 + q'_1 = -133.3 + 125 = \underline{-8.3\,\text{kJ}}$

No net work done. In this hypothetical reversible cycle heat has been transferred from a cold reservoir to a hot reservoir with no input of work. This cannot happen.

e. Show that if it were possible to have a reversible engine with a lower efficiency operating between the same two temperatures, heat could also be transferred spontaneously from the cooler reservoir to the hotter reservoir. (Hint: Operate the engine with lower efficiency as a heat pump.)
Assume an efficiency of reversible engine is lower than 0.75.

e) Assume an efficiency of 0.6. Then $-w''/q_1'' = 0.6$

For $w'' = +100\,kJ$, $q_1'' = -(100\,kJ)/(0.60) = -167\,kJ$; $q_3'' = +67\,kJ$

Engine (a) could then be used to drive this one in reverse, as a refrigerator. As a result

$q_3 + q_3'' = -33 + 67 = 34\,kJ$, heat absorbed at T_{cold}

$q_1 + q_1'' = 133 - 167 = -34\,kJ$, heat discharged at T_{hot}

No net work done. Again, an impossible result occurs.

4. The Second Law of Thermodynamics states that entropy increases for spontaneous processes and that an increase in entropy is associated with transitions from ordered to disordered states. Living organisms, even the simplest bacteria growing in cultures, appear to violate the Second Law because they grow and proliferate spontaneously. They convert simple chemical substances into the highly organized structure of their descendants. Write a critical evaluation of the proposition that living organisms contradict the Second Law. Be sure to state your conclusion clearly and to present detailed, reasoned arguments to support it.

The organisms in the culture grow by using chemical energy from the nutrient medium. The gain in entropy from breakdown of complex foodstuffs into much simpler, higher entropy molecules, more than compensates for the loss in entropy associated with the "growth" of the organism. Metabolic processes also release heat into the surroundings, further raising the entropy of the surroundings.

5. Consider the process where n_A mol of gas A initially at 1 bar pressure mix with n_B mol of gas B also at 1 bar to form 1 mol of a uniform mixture of A and B at a final total pressure of 1 bar, and all at constant temperature T. Assume that all gases behave ideally.

a. Show that the entropy change, $\Delta_{mix}S_m$, for this process is given by $\Delta_{mix}S_m = -x_AR\ln x_A - x_BR\ln x_B$, where x_A and x_B are the mole fractions of A and B, respectively.

a) $\Delta S_{mix} = \Delta S_A + \Delta S_B = -n_A R\ln(p_A/1\text{bar}) - n_B R\ln(p_B/1\text{bar})$ from Eq. (3.21)

Now $n_A + n_B = 1$; therefore $X_A = n_A/(n_A + n_B) = P_A/(1\text{bar})$ and $X_B = n_B/(n_A + n_B) = p_B/(1\text{bar})$

$$\Delta S_{m,mix} = \Delta S_{mix}/(n_A + n_B) = -X_A R\ln X_A - X_B R\ln X_B$$

b. What can you say about the value (especially the sign) of $\Delta_{mix}S_m$ and how does this correlate with the Second Law?

b) $\Delta S_{m,mix} > 0$, because $X_A < 1$ and $\ln X_A < 0$, etc

A positive value for $\Delta S_{m,\ mix}$ means that the process should occur spontaneously in an isolated system, which is what we expect for the mixing process.

c. Derive an expression for $\Delta_{mix}G_m$ for the conditions of this problem and comment on values (and signs) of its terms.

c)   At constant temperature, $\Delta G_{m,mix} = \Delta H_{m,mix} - T\Delta S_{m,mix}$ (Eq. 3.32)

$\Delta H_{m, mix}$ can be positive, negative or zero. For ideal gases or for the formation of an ideal liquid solution, $\Delta H_{m, mix} = 0$. In this case $\Delta G_{m, mix} = -T\Delta S_{m, mix} < 0$, which is what we expect for the spontaneous mixing process.