Problem Set #6, Chem 340, Fall 2013

– Due Friday, Oct 11, 2013

Please show all work for credit

To hand in:

Atkins

Chap 3 –Exercises: 3.3(b), 3.8(b), 3.13(b), 3.15(b)

Problems: 3.1, 3.12, 3.36, 3.43

Engel

Chap. 5: P5.14, P5.19, P5.20, P5.33

Extras :

Atkins

Chap 3 –Exercises: 3.4(b), 3.7 (b), 3.14(b)

Problems: 3.3, 3.7, 3.10, 3.11, 3.42, 3.45

To hand in :

Atkins

Exercises:

3.3(b) Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,\mathrm{m}} = 7/2\ R$, is changed from 25° C and 1.50 atm to 135° C and 7.00 atm. How do you rationalize the sign of ΔS?

3.8(b) Calculate the standard reaction entropy at 298 K of (*use tables in back of book*)

(a) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

(b) $C_{12}H_{22}O_{11}(s) + 12\ O_2(g) \rightarrow 12\ CO_2(g) + 11\ H_2O(l)$

3.13(b) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.50 bar increases from 1.20 dm^3 to 4.60 dm^3 in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{ex} = 0$, and (c) an adiabatic reversible expansion.

3.15(b) A certain heat engine operates between 1000 K and 500 K. (a) What is the maximum efficiency of the engine? (b) Calculate the maximum work that can be done by for each 1.0 kJ of heat supplied by the hot source. (c) How much heat is discharged into the cold sink in a reversible process for each 1.0 kJ supplied by the hot source?

Problems:

3.1 Calculate the difference in molar entropy (a) between liquid water and ice at −5° C, (b) between liquid water and its vapor at 95° C and 1.00 atm. The differences in heat capacities on melting and on vaporization are 37.3 J $K^{-1}mol^{-1}$ and −41.9 J K^{-1} mol^{-1}, respectively. Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

3.12 From standard enthalpies of formation, standard entropies, and standard heat capacities available from tables in the *Data section (back of book)*, calculate the standard enthalpies and entropies at 298 K and 398 K for the reaction $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$. Assume that the heat capacities are constant over the temperature range involved.

3.36 The protein lysozyme unfolds at a transition temperature of 75.5° C and the standard enthalpy of transition is 509 kJ mol^{-1}. Calculate the entropy of unfolding of lysozyme at 25.0° C, given that the difference in the constant-pressure heat capacities upon unfolding is 6.28 kJ K^{-1} mol^{-1} and can be assumed to be independent of temperature. *Hint*. Imagine that the transition at 25.0° C occurs in three steps: (i) heating of the folded protein from 25.0° C to the transition temperature, (ii) unfolding at the transition temperature, and (iii) cooling of the unfolded protein to 25.0° C. Because the entropy is a state function, the entropy change at 25.0° C is equal to the sum of the entropy changes of the steps.

3.43 The cycle involved in the operation of an internal combustion engine is called the *Otto cycle*. Air can be considered to be the working substance and can be assumed to be a perfect gas. The cycle consists of the following steps: (1) reversible adiabatic compression from A to B, (2) reversible constant-volume pressure increase from B to C due to the combustion of a small amount of fuel, (3) reversible adiabatic expansion from C to D, and (4) reversible and constant-volume pressure decrease back to state A. Determine the change in entropy (of the system and of the surroundings) for each step of the cycle and determine an expression for the efficiency of the cycle, assuming that the heat is supplied in Step 2. Evaluate the efficiency for a compression ratio of 10:1. Assume that in state A, $V = 4.00$ dm^3, $p = 1.00$ atm, and $T = 300$ K, that $V_A = 10V_B$, $p_C/p_B = 5$, and that $C_{p,m} = 7/2\,R$.

Engel

P5.14) The standard entropy of Pb(s) at 298.15 K is 64.80 J K^{-1} mol^{-1}. Assume that the heat capacity of Pb(s) is given by

$$\frac{C_{P,m}(\text{Pb},s)}{\text{J mol}^{-1}\,\text{K}^{-1}} = 22.13 + 0.01172\frac{T}{\text{K}} + 1.00\times 10^{-5}\frac{T^2}{\text{K}^2}$$

The melting point is 327.4°C and the heat of fusion under these conditions is 4770. J mol^{-1}. Assume that the heat capacity of Pb(l) is given by

$$\frac{C_{P,m}(\text{Pb},l)}{\text{J K}^{-1}\,\text{mol}^{-1}} = 32.51 - 0.00301\frac{T}{\text{K}}$$

a. Calculate the standard entropy of Pb(l) at 500°C.
b. Calculate ΔH for the transformation Pb(s,25°C) $\rightarrow$ Pb(l,500°C).

P5.19) Under anaerobic conditions, glucose is broken down in muscle tissue to form lactic acid according to the reaction $C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$. Thermodynamic data at T = 298 K for glucose and lactic acid are given here:

	ΔH_f° (kJ mol^{-1})	C_p° (J K^{-1} mol^{-1})	S°(J K^{-1}mol^{-1})
Glucose	–1273.1	219.2	209.2
Lactic acid	–673.6	127.6	192.1

Calculate the entropy of the system, the surroundings, and the universe at T = 310. K. Assume the heat capacities are constant between T = 298 K and T = 330. K.

P5.20) Consider the formation of glucose from carbon dioxide and water, that is, the reaction of the following photosynthetic process: $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$. The following table of information will be useful in working this problem:

***T* = 298 K**	**CO_2 (*g*)**	**H_2O (*l*)**	**$C_6H_{12}O_6$(*s*)**	**O_2(*g*)**
ΔH_f° kJ mol^{-1}	–393.5	–285.8	–1273.1	0.0
S° J mol^{-1} K^{-1}	213.8	70.0	209.2	205.2
$C_{P,m}^\circ$ J mol^{-1} K^{-1}	37.1	75.3	219.2	29.4

Calculate the entropy and enthalpy changes for this chemical system at T = 298 K and T = 330. K. Calculate also the entropy of the surrounding and the universe at both temperatures.

P5.33) An electrical motor is used to operate a Carnot refrigerator with an interior temperature of 0.00°C. Liquid water at 0.00°C is placed into the refrigerator and transformed to ice at 0.00°C. If the room temperature is 20.°C, what mass of ice can be produced in 1 min by a 0.25-hp motor that is running continuously? Assume that the refrigerator is perfectly insulated and operates at the maximum theoretical efficiency. (1 hp = 746 Watt)

Extras :

Atkins

Exercises:

3.4(b) A sample consisting of 2.00 mol of diatomic perfect gas molecules at 250 K is compressed reversibly and adiabatically until its temperature reaches 300 K. Given that $C_{V,\mathrm{m}}$ = 27.5 J K^{-1} mol^{-1}, calculate q, w, ΔU, ΔH, and ΔS.

3.7(b) The enthalpy of vaporization of methanol is 35.27 kJ mol^{-1} at its normal boiling point of 64.1° C. Calculate (a) the entropy of vaporization of methanol at this temperature and (b) the entropy change of the surroundings.

3.14(b) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of propane at 298 K.

Problems:

3.3 A block of copper of mass 2.00 kg ($C_{p,\mathrm{m}}$ = 24.44 J K^{-1} mol^{-1}) and temperature 0° C is introduced into an insulated container in which there is 1.00 mol H_2O(g) at 100° C and 1.00 atm. (a) Assuming all the steam is condensed to water, what will be the final temperature of the system, the heat transferred from water to copper, and the entropy change of the water, copper, and the total system? (b) In fact, some water vapor is present at equilibrium. From the vapor pressure of water at the temperature calculated in (a), and assuming that the heat capacities of both gaseous and liquid water are constant and given by their values at that temperature, obtain an improved value of the final temperature, the heat transferred, and the various entropies.
(*Hint*. You will need to make plausible approximations.)

3.7 The standard molar entropy of NH_3(g) is 192.45 J K^{-1} mol^{-1} at 298 K, and its heat capacity is given by eqn 2.25 with the coefficients given in Table 2.2. Calculate the standard molar entropy at (a) 100° C and (b) 500° C.

equation 2.25 and Table 2.2 (*This is in Chap 2, and a bigger one, also 2.2, is at end of text*):

Table 2.2* Temperature variation of molar heat capacities, $C_{p,\mathrm{m}}/(\mathrm{J\,K^{-1}\,mol^{-1}}) = a + bT + c/T^2$

	a	$b/(10^{-3}\,\mathrm{K})$	$c/(10^{5}\,\mathrm{K}^2)$
C(s, graphite)	16.86	4.77	−8.54
CO_2(g)	44.22	8.79	−8.62
H_2O(l)	75.29	0	0
N_2(g)	28.58	3.77	−0.50

* More values are given in the *Data section*.

3.10 A gaseous sample consisting of 1.00 mol molecules is described by the equation of state $pV_\mathrm{m} = RT(1 + Bp)$. Initially at 373 K, it undergoes Joule–Thomson expansion from 100 atm to 1.00 atm. Given that $C_{p,\mathrm{m}} = 5/2\,R$, μ = 0.21 K atm^{-1}, B = −0.525(K/T) atm^{-1}, and that these are constant over the temperature range involved, calculate ΔT and ΔS for the gas.

3.11 The molar heat capacity of lead varies with temperature as follows:

T/K	10	15	20	25	30	50
Cp,m /(J K−1 mol−1)	2.8	7.0	10.8	14.1	16.5	21.4
T/K	70	100	150	200	250	298
Cp,m /(J K−1 mol−1)	23.3	24.5	25.3	25.8	26.2	26.6

Calculate the standard Third-Law entropy of lead at (a) 0° C and (b) 25° C.

3.42 Suppose that an internal combustion engine runs on octane, for which the enthalpy of combustion is −5512 kJ mol^{-1} and take the mass of 1 gallon of fuel as 3 kg. What is the maximum height, neglecting all forms of friction, to which a car of mass 1000 kg can be driven on 1.00 gallon of fuel given that the engine cylinder temperature is 2000° C and the exit temperature is 800° C?

3.45 The expressions that apply to the treatment of refrigerators also describe the behavior of heat pumps, where warmth is obtained from the back of a refrigerator while its front is being used to cool the outside world. Heat pumps are popular home heating devices because they are very efficient. Compare heating of a room at 295 K by each of two methods: (a) direct conversion of 1.00 kJ of electrical energy in an electrical heater, and (b) use of 1.00 kJ of electrical energy to run a reversible heat pump with the outside at 260 K. Discuss the origin of the difference in the energy delivered to the interior of the house by the two methods.