Thermodynamics. Problems. Set 4

1) Determine the entropy of metallic Ag at 25°C, from the data on molar heat capacities given in the table. Consider that the heat capacity near 0 K approximately follows Debye's law.

T (K)	C_P (J/mol K)
15	0.67
30	4.77
50	11.65
70	16.33
90	19.13
110	20.96
130	22.13
150	22.97
170	23.61
190	24.09
210	24.42
230	24.73
250	24.73
270	25.31
290	25.44
300	25.50

2) Determine the molar entropy of CS_2 at 25°C from data on the molar heat capacities given in the table. The melting temperature is 161.11 K and the heat of melting is 1049.0 cal/mol. Near 0 K the system follows Debye's approximation.

T (K)	C_P (cal/mol K)
15.05	1.65
20.15	2.87
29.76	4.96
42.22	6.97
57.52	8.50
75.54	9.57
89.37	10.31
99.00	10.98
108.93	11.59
119.91	12.07
131.54	12.58
144.31	13.05
156.83	13.53
163.93	18.10
192.30	17.91
227.34	17.93
269.69	18.08
278.22	18.06
297.43	18.17

3) At a temperature of -3 °C the vapor pressure (the pressure of the vapor in equilibrium with its condensed phase) of ice is 3.566 mmHg, and the one of ~~subcooled~~ undercooled water is 3.669 mmHg. Compute the variation of the Gibbs free energy for the transformation of 1 mol of ~~subcooled~~ undercooled water at -3 °C to solid ice at the same temperature.

4) One person weighting 60 kg requires 1.8 kJ of work to vertically escalate 3.0 m. Compute the minimum quantity of glucose ($C_6H_{12}O_6$) required to do that work assuming that the transformation of the glucose into work is done at the body temperature of 37°C and at the atmospheric pressure. We know that the standard enthalpy of combustion at 298 K for the glucose is -2808 kJ/mol, while the standard entropy at the same temperature for the combustion is 182.4 J/K mol. Neglect the variation of the enthalpy with the temperature in this calculation.

5) Compute the variation of the Gibbs free energy for the formation of 1.00 mol of liquid water from its elements at 25°C y 1 atm of pressure. The standard heat of formation of water at 298 K is -285.84 kJ/mol. At the same temperature the absolute entropies of the involved species, in their most stable state, are $S^0(H_2) = 130.59$ J/mol K; $S^0(O_2) = 205.03$ J/mol K; $S^0(H_2O) = 69.94$ J/mol K. Is it a spontaneous reaction? Why?

6) The heat of melting of ice at 0 °C and 1 atm is 79.1 cal/g, while the heat of evaporation of water at the same pressure and 100 °C is 539 cal/g. The mean heat capacity of water from 0 °C y 100 °C is 4.184 J/ K g. Compute the increase of entropy when 1 g of ice at 0 °C turns into vapor at 100 °C.

7) Compute the variation of U, H, S and volume, as well as the final temperature in an adiabatic expansion of 1 dm^3 of O_2 at 5.00 atm and 25 °C to 1.00 atm of pressure. $C_P = 7.0$ cal/ K mol. Assume ideal gas behavior.

8) 1.0 kg of ice at -10 °C is introduced in a thermally isolated recipient already containing 5.0 kg of water at 30 °C. What is the variation of entropy in the process? The heat of melting of ice is 79.67 cal/g, the heat capacity of ice is 0.482 cal/g K and 1.000 cal/g K the one of liquid water.

9)   a) The temperature of an ideal gas with constant heat capacity varies from T_1 to T_2. Demonstrate that the variation of entropy of the gas is larger if this process takes place at constant pressure than at constant volume.
      b) The pressure of an ideal gas varies from P_1 to P_2 either through an isothermal transformation or through an isochoric transformation. Compute the variations of entropy in both cases and demonstrate that they have ~~opposed~~ opposite sign.

10) 2.00 mol of an ideal gas expand from an initial volume of 4.0 L to a final volume of 40.0 L at a constant temperature of 27 °C. Compute the variation of entropy of the system and the one of the environment (surroundings) in each of the following processes: a) Reversible expansion. b) Expansion against a constant pressure of 1 atm. c) Expansion against ~~the void~~ a vacuum.

11) Complete the following table knowing that the liberated heat during the combustion of glucose in standard conditions and a temperature of 298 K is 2805 KJ/mol.
$$C_6H_{12}O_6 + O_2 \longrightarrow H_2O \text{ (l)} + CO_2 \text{ (g)}$$
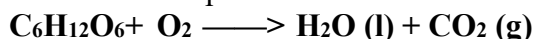
Compound	S^0 (J/mol K)	ΔS^0_f (J/mol K)	ΔH^0_f (KJ/mol)	ΔG^0_f (KJ/mol)
H_2O	69.9(l)		-285.83	
CO_2	213.6		-393.51	-394.41
$C_6H_{12}O_6$	209.19			-910.5
H_2	130.7			
O_2	205.2			
C	5.7			

Compute the associated ΔG to the reaction in standard conditions and at T=37°C and P= 1 atm.

Data:
C_p (CO_2)=0.844 KJ/kg K; C_p ($C_6H_{12}O_6$)=218.6 J/mol K; C_p (H_2O (l))= 4.18 J/g;
C_p (O_2)= 0.918 J/g;

12) Compute the maximum free work per mol that can be attained in a fuel cell in which the reaction of combustion of methane takes place at 298 K (use tables to obtain the required data).

13) What is more effective, eating glucose or saccharose? Compute the free work that can be produced in each case, the work of expansion and the total work done by the system from the combustion of 1.0 kg of glucose or saccharose in standard conditions at 25 °C when the products involve a) liquid water or b) water vapor.

14) A cylinder contains an internal piston at each side of which there are 1 mol of a monatomic ideal gas. The walls of the piston are rigid and diathermic and the system is submerged in a liquid bath of large capacity (a source of heat) at a 0 °C temperature. The initial volumes of the two gaseous subsystems are 10 liters and 1 liter, respectively. The piston is then displaced reversibly such that the final volumes are 6 liters and 5 liters, respectively. (i) Compute the work done <u>by</u> the system by means of the Helmholz free energy change (rather than direct computation of the reversible work). (ii) Compute the heat exchanged with the liquid bath. (iii) Did both subsystems absorb heat?

15) Two simple systems are within a cylinder, separated by a frictionless piston. Each subsystem is a mixture of ½ mol of N_2 and ½ mol of H_2 (which are considered to behave as ideal gases). Initially, the piston is at the center of the cylinder, having each subsystem a volume of 10 liters. The walls of the cylinder are diathermic. The system is in contact with a heat source at 0° C. The piston is permeable to H_2, but impermeable to N_2. Compute the work needed to displace the piston to a position where the subsystems' volumes are 5 and 15 liters.

16) Compute ΔG and ΔF for the vaporization of 1 mol of water at 1 atm and 100 °C. Density of water at those conditions is 0.958 g cm^{-3}.

17) Estimate $\left(\frac{\partial U}{\partial V}\right)_T$ for nitrogen gas at 25°C and 1 atm assuming that it satisfies the van der Waals equation. (The constants for nitrogen are a=1.346×10^6 cm^6 atm mol^{-2}, and b=38.52 cm^3 mol^{-1}). *Hint*: Consider the Gibbs equation for the internal energy, and then find the appropriate Maxwell relation to transform the partial derivative of S to a manageable derivative for this problem.