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20 points total/2 points per problem

1. (a) Calculate entropy changes associated with the each step of the themodynamic cycles analyzed in points 4a and 4b in Problem Set I. Indicate which of the processes is spontateous and which is not. Finally, calculate ΔS of the full cycle.

   (b) Since you are already looking at problem set I - Using data from point 10 in Problem Set I, plot a moloar entropy of sodium as a function of temperature.

2. (a) Calculate ΔS of 1/16 lbs of liquid water when heated from 35.0^oF to 125.0^oF under constant pressure and $C_{P,m}$=75.3 [J/mol·K].

   (b) The melting point of water at pressure of interest is 0.00^oC and the enthalpy of fusion is 6.010 [kJ/mol]. The boling point is 100^oC and the enthalpy of vaporization is 40.65 [kJ/mol]. Calculate ΔS for the transformation from ice to vapor: $H_2O(s, 0^oC) \rightarrow H_2O(g, 100^oC)$

3. (a) Explain a difference between Otto and Diesel cycles (I did not cover that during the lectures).

   (b) A refrigator is operated by 500W motor. If the interior is to be maintained at -15^oC, and the room temperature is 25^oC, what is maximum heat leak that could be tolerated, assuming 66% efficiency of the engine.

4. The shells of marine organisms contain calcium carbonate, $CaCO_3$, in a crystalline form of calcite., The second crystalline form of $CaCO_3$ is an aragonite. Their physical and thermodynamic properties at T=298K and P= 1 bar are listed below:

 | Property | Calcite | Aragonite |
   |---|---|---|
   | $\Delta H_f^o [kJ \cdot mol^{-1}]$ | -1206.9 | -1207.0 |
   | $\Delta G_f^o [kJ \cdot mol^{-1}]$ | -1128.8 | -1127.7 |
   | $C_{P,m}^o [J \cdot K^{-1} \cdot mol^{-1}]$ | 81.9 | 81.3 |
   | $S^o [J \cdot K^{-1} \cdot mol^{-1}]$ | 92.9 | 88.7 |
   | $\rho [gmL^{-1}]$ | 2.710 | 2.930 |

   (a) Would an isolated sample of calcite convert to aragonite at T=298 K and P=1 bar? Explain.

   (b) Can you induce this convertion by varying applied pressure (T=298K)? Explain. What would it be the conversion pressure?

   (c) Can you induce this convertion by varying temperature (P=1bar)? Explain. What would it be the conversion temperature?

5. The table below shows formation enthalpies, free energies and heat capacity of the following reaction:

   $$2CuO_{(s)} \rightleftarrows 2Cu_{(s)} + O_{2(g)} \tag{1}$$

Compound	$CuO_{(s)}$	$Cu_{(s)}$	$O_{2(g)}$
$\Delta H_f^o [kJ \cdot mol^{-1}]$	-157		
$\Delta G_f^o [kJ \cdot mol^{-1}]$	-130		
$C_{P,m} [J \cdot K^{-1} \cdot mol^{-1}]$	42.3	24.4	29.4

   (a) Calculate the ΔH_R^o of the reaction at 298 and 1298K. Assume that the heat capacities are temperature independent over the integration range.

   (b) Calculate the equilibrium constant at T_o=298K and at T_f=1298K. While calculating equilibiurm constant at 1298K, consider two cases: (1) the ΔH_R is temperature-independent ($\Delta H_R(1298K) = \Delta H_R^o$) and (2) the ΔH_R is temperature dependent ($\Delta H_R(1298K) = \Delta H_R^o + C_p$-related corrections). Does temperature-dependence of the enthalpy of the reaction affect the K_P significantly?

6. At what temperature the following reaction has $K_p = 5.50 \cdot 10^3$, if at 298 K the K_p equals to $3.32 \cdot 10^3$? Calculate the partial pressures of each gaseous component of the reaction.

$$H_2O_{(l)} + CO_{(g)} \rightleftarrows H_{2(g)} + CO_{2(g)}$$
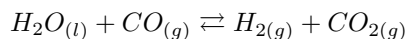
7. A 1.0 mole sample of Argon undergoes an isothermal reversible expansion from an initial volume of 1.00 L to a final volume of 50.0 L at 400 K. Calculate the heat transfer and the work done in this process using (1) ideal gas and (2) van der Waals equations of state. What fraction of work in the van der Waals case is due to the attractive term in the potential? $A_A r$=1.355 [bar· L^2 · mol −2], b$_A r$=0.032 [L · mol −1],

8. Show that:

(a) $P\kappa = 1 - P \left(\frac{\partial \ln z}{\partial P}\right)_T$, where κ is the isothermal compressibility.

(b) $T\beta = 1 + T \left(\frac{\partial \ln z}{\partial T}\right)_P$, where β is the thermal expansion.

(c) T_c, P_c and $V_{m.c}$ in a system described by a van der Waals equation of state depend only on a and b parameters.

9. (a) Vapor pressure of methanol in a temperature range between 275 and 338 K can be described by the following equation:

$$\ln \frac{P(T)}{[Pa]} = A(1) - \frac{A(2)}{T/[K] + A(3)} \tag{2}$$

where $A(1)$, $A(2)$ and $A(3)$ are equal to 23.593, 3.6971·10^3 and -31.317 respectively. Calculate the standard boiling temperature of methanol.

(b) Vapor pressure of methanol at room temperature is equal 13.02 kPa. Calculate the standard vaporization enthalpy and entropy of mehanol. What would be boiling temperature of methanol at pressure of 20 atm? We assume that ΔH_{vap} is temperature independent.

10. (a) Explain all features of the following phase diagrams that are not observed in real substances. Besides physical reasoning, present relevant equations that prohibit such features.
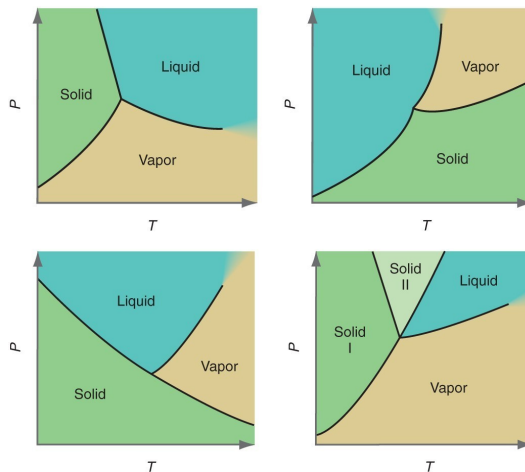
(b) Analyze the 'bunny-ear' and 'beheaded bunny' diagrams below and list all phases present (including an estimate for the composition) and phase transitions that occur (including estimated temperature) when increasing temperature along lines 1, 2 and 3.