Pledge and signature:

1. (5) Calculate the molar entropy \( S_m \) of carbon disulfide at 25\(^{\circ}\)C from the following heat capacity data (units J K\(^{-1}\) mol\(^{-1}\)) and the heat of fusion at the melting point (161.11 K): \( \Delta H_{m,fus} = 4389 \) J mol\(^{-1}\).

\[
\begin{array}{cccc}
T (K) & C_{P,m} & T (K) & C_{P,m} \\
15.05 & 6.90 & 75.54 & 40.04 \\
20.15 & 12.01 & 89.37 & 43.14 \\
29.76 & 20.75 & 99.00 & 45.94 \\
42.22 & 29.16 & 108.93 & 48.49 \\
57.52 & 35.56 & 119.91 & 50.50 \\
\end{array}
\]

2. (10) Consider the reaction, \( \text{CH}_4(g) + 2 \text{O}_2(g) \rightleftharpoons \text{CO}_2(g) + 2 \text{H}_2\text{O}(l) \).

(a) Use appendix data from Levine to calculate \( \Delta H^\circ, \Delta G^\circ, \Delta S^\circ, \Delta U^\circ, \) and \( \Delta A^\circ \) at 25\(^{\circ}\)C.

(b) Similarly, use appendix data to calculate \( \Delta H^\circ, \Delta G^\circ, \) and \( K^\circ \) at 1750 K for the similar reaction having the product \( \text{H}_2\text{O} \) in the gaseous state.

(c) In the original reaction (producing liquid \( \text{H}_2\text{O} \)), suppose the methane is just burned at 25\(^{\circ}\)C and \( P = P^\circ \). Calculate \( q \) and \( w \) for this process.

(d) Now suppose the reaction is carried out reversibly at 25\(^{\circ}\)C and \( P^\circ \) in a fuel cell. Calculate (1) the non-PV work done by the system on the surroundings; (2) the PV work done by the system on the surroundings; (3) the total work \( w \) done on the system; and (4) the heat \( q \) added to the system.

(e) What is the maximum total work obtainable from this reaction (\( w_{by} \)) in any constant-\( T \) process?

3. (3) Repeat the calculations of 2(b) using the tabulated free energy functions given below.

4. (4) Consider the gaseous dissociation reaction, \( \text{O}_2 \rightleftharpoons 2 \text{O} \). \( \Delta G^\circ_f \) for \( \text{O}(g) \) at 2900 K is 14.642 kcal/mol.

(a) Calculate \( K^\circ \) for this reaction at 2900 K.

(b) Calculate the equilibrium partial \( P \) of O at this \( T \) when the total \( P = 1.00 \) atm.

(c) What is the degree of dissociation \( \alpha \) in this case? [Hint: See Problem 3 on PS 8.]

(d) What is the total \( P \) at 2900 K if the equilibrium mixture is 90 mol % \( \text{O}_2 \)?

5. (4) A certain amount of NOBr(g) is sealed in a flask, which is then heated to 350K, where the NOBr partially dissociates to NO(g) and Br\(_2\)(g). At equilibrium the total pressure is 0.675 atm, and the vapor density is 2.219 g/L.

(a) Write a balanced chemical equation for this dissociation, with \( v = -1 \) for NOBr.

(b) Calculate the partial pressures of the three components at equilibrium, and the equilibrium constant \( K \).

Gaseous elements and compounds with values referenced to \( H_0^\circ \)

\[
\begin{array}{cccccc}
-\frac{(G_T-H_0^\circ)}{RT} & (H^\circ - H_0^\circ)/R & \Delta H^\circ_{f,0}/R \\
(298.15 \text{ K}) & (500 \text{ K}) & (1000 \text{ K}) & (1500 \text{ K}) & (2000 \text{ K}) & (10^3 \text{K}) \\
\hline
\text{H}_2 & 12.301 & 14.076 & 16.485 & 17.921 & 18.968 & 1018.5 & - \\
\text{CO} & 20.275 & 22.086 & 24.558 & 26.069 & 27.183 & 1042.9 & -13.69 \pm 0.02 \\
\text{CO}_2 & 21.934 & 24.001 & 27.246 & 29.445 & 31.138 & 1126.4 & -47.29 \pm 0.01 \\
\text{H}_2\text{O} & 18.716 & 20.802 & 23.674 & 25.493 & 26.881 & 1191.3 & -28.736 \pm 0.005 \\
\text{CH}_4 & 18.376 & 20.531 & 24.00 & 26.63 & 28.82 & 1204.7 & -7.999 \\
\end{array}
\]