due Mon. Feb. 21

Chemistry 342

Problem Set 5

1. Find the molar increase in U, H, S, A, and G in expanding one liter of an ideal gas at 25°C to 100 liters at the same temperature.

2. (a) One mole of an ideal gas in 22.4 L is expanded isothermally and reversibly at 0°C to a volume of 224 L. Calculate W, q, ΔU, ΔH, ΔA, ΔG, and ΔS for the gas. Calculate ΔS for the gas plus its surroundings.

(b) One mole of an ideal gas at 0°C in 22.4 L is allowed to expand isothermally and irreversibly into an evacuated vessel such that the final volume is 224 L. Calculate W, q, ΔU, ΔH, ΔA, ΔG, and ΔS for the gas. Calculate ΔS for the gas plus its surroundings.

3. One mole of an ideal gas is expanded adiabatically, but completely irreversibly, from a volume V_1 to a volume V_2; no work is done. Does the temperature of the gas change? (a) What is the ΔS of the gas and the ΔS of its surroundings? (b) If the expansion were performed reversibly and isothermally, what would be the ΔS of the gas and of its surroundings?

4. One mole of an ideal gas in contact with a heat reservoir at 25°C expands isothermally from 100 atm to 1 atm pressure. Make a table showing the ΔS for the gas, for the heat reservoir, and for the two systems combined, if in the expansion: (a) 2730 cal of work is done; (b) 1000 cal of work is done; (c) no work is done.

5. Based on the following data calculate the third law entropy of CH_3NO_2 gas (in units of cal mol^{-1} K^{-1}) at 298.1 K and 1 atm pressure (assuming ideal gas behavior).
The following values for C_p (cal mol^{-1} K^{-1}) of nitromethane have been reported:

T	15 K	20 K	30 K	40 K	50 K	60 K	70 K	80 K	90 K	100 K
C_p	0.89	2.07	4.59	6.90	8.53	9.76	10.70	11.47	12.10	12.62

T	120 K	140 K	160 K	180 K	200 K	220 K	240 K	260 K	280 K	300 K
C_p	13.56	14.45	15.31	16.19	17.08	17.98	18.88	25.01	25.17	25.35

The normal melting point is 244.7 K, heat of fusion is 2319 cal mol^{-1}. The vapor pressure of the liquid at 298.1 K is 3.666 cm Hg. The heat of vaporization at 298.1 K is 9147 cal mol^{-1}.

6. At high temperature and pressure, a quite good equation of state for gases is $p(V-b) = RT$. Calculate the fugacity f of N_2 at 1000 atm and 1000°C according to this equation, if $b = 39.1 \times 10^{-3}$ L mol^{-1}.

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7. At 200 K, the compressibility factor $Z = pV/RT$ of oxygen varies with pressure as shown in the table below. Evaluate the *fugacity* of oxygen at this temperature and 100 atm.

p /(1 atm)	1.0000	4.00000	7.00000	10.0000	40.00	70.00	100.0
Z	0.9971	0.98796	0.97880	0.96956	0.8734	0.7764	0.6871

8. The molar Gibbs energy of a certain gas is given by
$\overline{G}$ = RT ln(p/1) + A′ + B′p + (1/2)C′p^2 + (1/3)D′p^3
where A′, B′, C′, and D′ are constants. Obtain the equation of state of the gas.

9. The entropy ($S_T - S^\circ_{298}$)of saturated water at 100 °C is 0.31 cal K^{-1} per gram, and that of saturated steam at at 100 °C is 1.76 cal K^{-1} per gram.
(a) Determine the heat of vaporization of water at 100 °C and 1 atm.
(b) The enthalpy ($H_T - H^\circ_{298}$) of saturated steam at 100 °C is 640 cal per gram. From (a) calculate the enthalpy ($H_T - H^\circ_{298}$) of saturated water at 100 °C.
(c) Calculate the Gibbs free energy ($G_T - G^\circ_{298}$) of saturated water and of saturated steam at 100 °C and verify that the two are equal.

10. At 25°C and 1 atm, the heat of combustion of diamond is 94.484 kcal mol^{-1} and that of graphite is 94.030. The molar entropies (third law entropies) are 0.5829 and 1.3609 cal K^{-1} mol^{-1} respectively. Find the ΔG for the transition
graphite $\rightarrow$ diamond at 298 K and 1 atm. The densities are 3.513 g cm^{-3} for diamond and 2.260 for graphite. Estimate the pressure at which the two forms would be in equilibrium at 25°C and 1000°C. You may assume the density to be independent of pressure. (Actually the assumption of constant densities will lead to a figure that is much too low an approximation)