due Wed. Feb. 2

Chemistry 342

Problem Set 3

1. Suppose that the energy per mole of a fluid has the form $\boldsymbol{U} = f(T) - a/\overline{V}$ for the gas as well as the liquid. At a given temperature T, at 1 atm, find the difference between the energy of one mole of gas and the energy of one mole of liquid, assuming that $\overline{V}_{gas}$ = 24 liters/mole and $\overline{V}_{liq}$ = 18 cm^3/mole. Given that a = 5.72 $liter^2$ atm $mole^{-2}$. Convert this energy difference to calories. Compare with the known $\Delta_{vap}H$ = 9820 cal mol^{-1} at that temperature.

2. One tenth of a mole of an ideal monatomic gas is heated from T_1 to T_2 along a path governed by the equation $V = a\exp(bT)$, in which a and b are constants.
(a) Derive expressions for the reversible heat and work attending this process.
(b) If $T_1 = 300$ K, $T_2 = 400$ K, and $b = 0.01\ K^{-1}$, calculate q, W, and ΔU in kJ.

3. One mole of an ideal monatomic gas is subjected to the following sequence of steps:
(A) The gas is heated reversibly at a constant pressure of 1 atm from 25°C to 100 °C. (In a reversible heating process direct heat flow must occur between vanishingly small temperature differences, just as reversible expansion and compression must involve infinitesimal differences in pressure between the opposing pressure and the pressure of the gas.)
(B) The gas is expanded reversibly and isothermally to double its volume.
(C) Finally the gas is cooled reversibly and adiabatically to 35°C.
Calculate ΔU, ΔH, q, and W, in kJ, for the overall process A+B+C.

4. One mole of an ideal gas (not necessarily monatomic) is subjected to the following sequence of steps:
(A) The gas is heated at constant volume from 25°C to 100 °C.
(B) The gas is expanded freely into a vacuum (Joule type experiment) to double its volume.
(C) Finally the gas is cooled reversibly at constant pressure to 25°C.
Calculate ΔU, ΔH, q, and W, in kJ, for the overall process A+B+C. Note that it is not necessary to know the heat capacity of the gas. Explain why.

5. Two containers are joined together as in the Joule experiment. One contains 0.5 mole of helium [$C_V = (3/2)R$] at 100°C, and the other contains 1 mole of oxygen (for which you may assume that $C_V = (5/2)R$ at 0°C. The gases are allowed to

diffuse into each other adiabatically. What is the final temperature, assuming the gases to be ideal?

6. An evacuated tank of 10-liter capacity is surrounded by a thermostat at 100°C. Inside the tank is a capsule containing exactly 1 mole of liquid water at 100°C. The capsule is now broken, and the water is allowed to flash into vapor until the pressure is 1 atm. Neglecting the volume of the capsule and the volume of any remaining liquid water, and assuming the vapor to be an ideal gas, calculate ΔU, ΔH, q, and W, in kJ, for the actual process. At 100°C and 1 atm, $\Delta_{vap}H = 9720$ cal mol^{-1}.

7. (a) Ten grams of ice at -10°C are dropped into 25 g of water at 15°C, and the system is allowed to reach equilibrium adiabatically. What is the final state of affairs ? Assume the specific heat capacities of water and ice to be 1.0 and 0.5 cal K^{-1}, and the $\Delta_{fus}H = 80$ cal g^{-1}.

(b) Suppose that 10 g of ice at -10°C were dropped into 100 g of water at 15°C and the system is allowed to reach equilibrium adiabatically. What would be the final state of affairs?

8. In the manufacture of "water gas", steam is passed through hot coke, and the following reactions occur:

$C + H_2O \rightarrow CO + H_2$ (principally)

$CO + H_2O \rightarrow CO_2 + H_2$ (to a small extent)

The water gas so obtained, when cooled to room temperature, can be considered a mixture of CO, H_2, and a little CO_2 if we neglect the water vapor.

(a) If only the first reaction occurred during manufacture, what would be the $\Delta_{comb}H$ at 25°C and 1 atm per liter of water gas if all the products of combustion were in the form of vapor?

(b) If 95% of the carbon should appear in CO and 5% in CO_2, what would be the $\Delta_{comb}H$ per liter of water gas? (Note the additional H_2 that accompanies the formation of CO_2.)

9. In the manufacture of "producer gas", dry air is passed over hot coke, and the following reactions occur:

$C + \frac{1}{2}O_2 \rightarrow CO$

$CO + \frac{1}{2}O_2 \rightarrow CO_2$

What is the heating value in calories per liter of producer gas at 25°C if 95% of the oxygen of the air ends up in CO and 5% in CO_2? Assume air to consist of 20 mole% oxygen and 80 mole% nitrogen.

10. Natural gas, which you may assume to be pure methane, is burned in a furnace employed for space-heating purposes.

(a) If twice the minimum amount of air is used for the combustion, and if the methane and air are initially at 20°C and the stack gases, including all of the water as vapor, are at 100°C, how much heat is liberated per mole of methane burned? Assume air to consist of 20 mole% oxygen and 80 mole% nitrogen. $\Delta_{comb}H$ of methane at 20°C is -212.91 kcal, and $\Delta_{vap}H = 10.57$ kcal mol^{-1}. For this problem you may assume C_p to have the following constant values: O_2(g) 7.02 cal K^{-1}, N_2(g) 6.96 cal K^{-1}, H_2O(g) 8.03 cal K^{-1}, CO_2(g) 8.87 cal K^{-1}.

(b) How much heat is liberated if the stack gases are cooled just to the point where they become saturated with water vapor, but without condensation? (You will need to see a handbook for vapor pressures of water.)