due Mon Feb 14

Chemistry 342

Problem Set 4

1. (a) What is the maximum possible efficiency of a heat engine which has a hot reservoir of water boiling under pressure at 125°C and a cold reservoir at 25°C? Under what conditions may this maximum efficiency be achieved?

(b) Liquid helium boils at about 4 K and liquid hydrogen boils at about 20 K. What is the efficiency of a reversible engine operating between heat reservoirs at these temperatures?

(c) If we wanted the same efficiency as in (b) for an engine with a cold reservoir at ordinary temperature (300 K), what must the temperature of the hot reservoir be?

2. A refrigerator is operated by a 1/4 hp motor (1 hp = 10.688 kcal/min). If the interior of the box is to be maintained at -20°C against a maximum exterior temperature of 35°C, what is the maximum heat leak into the box (cal/min) which can be tolerated if the motor runs continuously. Assume that the coefficient of performance is 75% of the value for a reversible engine.

3. Consider the following cycle using 1 mole of an ideal gas, initially at 25°C and 1 atm pressure.

Step 1. Isothermal expansion against zero pressure to double the volume (Joule expansion).

Step 2. Isothermal, reversible compression from 1/2 atm to 1 atm.

(a) Calculate the value of $\oint dq/T$. Note that the sign conforms with Clausius inequality.

(b) Calculate ΔS for Step 2.

(c) Realizing that for the cycle $\Delta S_{cycle} = 0$, find ΔS for Step 1.

(d) Show that ΔS for Step 1 is NOT equal to the q for Step 1 divided by T.

4. What is the entropy change if the temperature of one mole of an ideal gas is increased from 10 K to 300 K, $C_V = (3/2)R$,

(a) if the volume is constant?

(b) if the pressure is constant?

(c) What would the change in entropy be if three moles were used instead of one mole?

5. (a) What is the entropy change if one mole of water is warmed from 0°C to 100°C under constant pressure; $C_p = 18.0$ cal deg^{-1} mol^{-1}.

(b) The melting point is 0°C and the heat of fusion is 1.4363 kcal mol^{-1}. The boiling point is 100°C and the heat of vaporization is 9.7171 kcal mol^{-1} . Calculate ΔS for the transformation

ice (0°C, 1 atm) $\rightarrow$ steam (100°C, 1 atm).

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6. (a) At the transition temperature 95.4°C, the heat of transition from rhombic to monoclinic sulfur is 0.09 kcal mol^{-1} . Calculate the entropy of transition.

(b) At the melting point, 119°C, the heat of fusion of monoclinic sulfur is 0.293 kcal mol^{-1} . Calculate the entropy of fusion.

(c) The values given in (a) and (b) are for one mole of S, that is for 32 grams. However, in crystalline and liquid sulfur the molecule is S_8. Convert the values in parts (a) and (b) to ones appropriate to S_8. These converted values are more representative of the usual magnitudes of entropies of fusion and transition. How well does Trouton's rule predict your answer?

7. One mole of an ideal gas, initially at 25°C, is expanded

(a) isothermally and reversibly from 20 to 40 liters mol^{-1} , and

(b) isothermally and irreversibly against zero opposing pressure (Joule expansion) from 20 to 40 liters mol^{-1} .

Calculate $\Delta \boldsymbol{U}$, $\Delta \boldsymbol{S}$, q, and W for both (a) and (b). Note the relation between $\Delta \boldsymbol{S}$ and q, in (a) and (b).

8. (a) One mole of an ideal gas, $C_V = (3/2)R$, is expanded adiabatically and reversibly: Initial state is 300 K and 1 atm. Final state is 0.5 atm. Calculate q, W, $\Delta \boldsymbol{U}$, $\Delta \boldsymbol{S}$.

(b) The same gas, initially at 300 K and 1 atm, is expanded adiabatically against a constant opposing pressure equal to the final pressure, 0.5 atm. Calculate q, W, $\Delta \boldsymbol{U}$, $\Delta \boldsymbol{S}$.

9. In a Dewar flask (an adiabatic enclosure) 20 g of ice at -5°C are added to 30 g of water at +25°C. If the heat capacities are C_p(liquid) = 1.0 cal deg^{-1} g^{-1} and C_p(ice) = 0.5 cal deg^{-1} g^{-1} , what is the final state of the system? (The pressure is constant.) $\Delta_{fusion}\boldsymbol{H} = 80$ cal g^{-1}. Calculate $\Delta \boldsymbol{S}$ and $\Delta \boldsymbol{H}$ for the transformation.

10. How many grams of water at 25°C are required in the Dewar flask in problem 9 to satisfy the following conditions? Compute the entropy change in each case.

(a) The final temperature is -2°C, all the water freezes.

(b) The final temperature is 0°C, half the water freezes.

(c) The final temperature is 0°C, half the ice melts.

(d) The final temperature is 10°C, all the ice melts.

Predict the sign of $\Delta \boldsymbol{S}$ in each case before doing the calculation.