

1. (20pts) The initial state of a quantity of monatomic ideal gas is  $P = 1 \text{ atm}$ ,  $V = 1 \text{ liter}$  and  $T = 373 \text{ K}$ . The gas is isothermally expanded to a volume of 2 liters and is then cooled at constant pressure to the volume  $V$ . This volume is such that a reversible adiabatic compression to a pressure of 1 atm returns the system to its initial state. All of the changes of state are conducted reversibly. Calculate the value of  $V$  and the total work done or by the gas. (gas constant,  $R = 0.08206 \text{ liter} \cdot \text{atm} / \text{mole} \cdot \text{K} = 8.3144 \text{ J} / \text{mole} \cdot \text{K}$ )

2. (20pts) Answer the following equations.

(a) (5pts) Combining the First and Second Laws of Thermodynamics, derive the fundamental relationship of  $dU(S, V)$  for a closed system undergoing a reversible process and only  $PdV$  work.

(b) (5pts) On the basis of the above relationship, derive the fundamental equations for the auxiliary functions of  $H$ ,  $A$ , and  $G$ .

(c) (5pts) Derive the following Gibbs-Helmholtz equation applicable to a closed system of fixed composition undergoing processes at constant pressure. Briefly discuss the usefulness of this equation.

$$\frac{d(G/T)}{dT} = -\frac{H}{T^2}$$

(d) (5pts) From the fundamental equations ( $dU$ ,  $dH$ ,  $dA$ , and  $dG$ ) for a closed system (assumed a reversible process and only  $PdV$  work), derive the fundamental equations for a closed system undergoing a process involving a reversible change in composition (e.g., a reversible chemical reaction).

3. (15pts) Answer the following questions.

(a) (5pts) A rigid container is divided into two compartments of equal volume by a partition. One compartment contains 1 mole of ideal gas  $A$  at 1 atm, and the other contains 1 mole of ideal gas  $B$  at 1 atm. Calculate the increase in entropy which occurs when the partition between the two compartments is removed.

(b) (10pts) Assuming that a silver-gold alloy is a random mixture of gold and silver atoms, calculate the increase in entropy when 10 g of gold are mixed with 20 g of silver to form an ideal homogeneous alloy. The gram atomic weights of Au and Ag are, respectively, 198 and 107.9.

4. (20pts) The adiabatic thermoelastic effect describes the change in temperature with pressure for a brittle solid when it is loaded rapidly (i.e., the rate of loading is much more rapid than the rate of heat transfer). This effect has been used to measure the stresses that develop around defects in composite materials using cyclic loading and a high speed thermal imaging camera. Using Maxwell's relations, derive an expression for the adiabatic thermoelastic effect. Estimate the change in temperature for a piece of alumina that is loaded 500 MPa. (1MPa =  $10^6$  N/m<sup>2</sup>)

Data: Initial temperature 298 K,  $\alpha = 2.2 \times 10^{-5}/\text{K}$ ,  $c_p = 80$  J/mole·K

molar volume of alumina ( $\text{Al}_2\text{O}_3$ ) =  $2.56 \times 10^{-5}$  m<sup>3</sup>/mole

(Hint: This problem requires the calculation of the variation in temperature with pressure at constant entropy.)

5. (25pts) Answer the following questions.

(a) (10pts) For a closed system of fixed composition undergoing changes in both  $P$  and  $T$ , prove that

$$\Delta H = H(P_2, T_2) - H(P_1, T_1) = \int_{T_1}^{T_2} c_p dT + \int_{P_1}^{P_2} V(1 - \alpha T) dP$$

(b) (10pts) and also prove that

$$\Delta S = S(P_2, T_2) - S(P_1, T_1) = \int_{T_1}^{T_2} \frac{c_p}{T} dT - \int_{P_1}^{P_2} \alpha V dP$$

(c) (5pts) Calculate the entropy change of an ideal gas experiencing an isothermal expansion from  $V_1$  to  $2V_1$ . Is this process spontaneous or not?