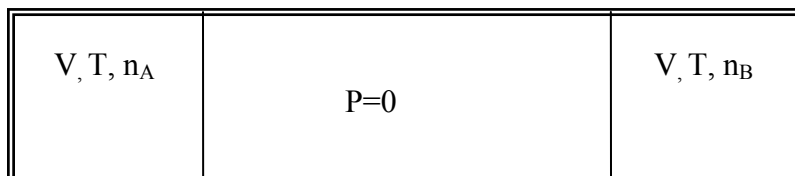


### P317 midterm 2 solutions (k07)

- 1) Consider the following. Two distinct ideal gases are each initially confined to  $\frac{1}{4}$  of the volume of an isolated container. The remaining  $\frac{1}{2}$  of the container is evacuated.
- a.** Calculate the change in entropy when both gases are allowed to fill the entire container. State clearly what strategy you are using to solve the problem.



Use change in Gibbs function to calculate change in entropy. In the initial state,  $G_i = n_A (RT \ln P_A + \phi_A(T)) + n_B (RT \ln P_B + \phi_B(T))$ , where  $P_A = n_A RT/V$  and  $P_B = n_B RT/V$ . In the final state, the temperature will be unchanged (no heat flow and no work on the surroundings, so internal energy is constant which, for ideal gas, means  $T$  constant) we use the partial pressures to find  $G_f = n_A (RT \ln p_A + \phi_A(T)) + n_B (RT \ln p_B + \phi_B(T))$ , where  $p_A = n_A RT/(4V)$  and  $p_B = n_B RT/(4V)$ . Then  $\Delta G = -(n_A + n_B) RT \ln 4$ . Then from  $S = -(\partial G/\partial T)_P$ ,  $\Delta S = (n_A + n_B) R \ln 4$ .

- b.** What would the entropy change be if the two gases were of the same substance? Then it's a pure free expansion with  $V_f/V_i=2$ :  $\Delta S = (n_A + n_B) R \ln 2$ .

- 2) The work done by a magnetic system in the presence of an external field  $H$  is  $W = -HdM$ , where  $M$  is the magnetic moment of the system. For such a system the first two TdS equations are
- $$TdS = c_M dT - T(\partial H/\partial T)_M dM \text{ and}$$
- $$TdS = c_H dT + T(\partial M/\partial T)_H dH$$
- Assume the equation of state  $M = C_C H / T$  with  $C_C$  a positive constant. Show that the specific heat at constant magnetic field is greater than the specific heat at constant magnetic moment.

$c_H - c_M = -T(\partial H/\partial T)_M(\partial M/\partial T)_H$ . From the eqn of state,  $(\partial H/\partial T)_M = M/C_C$  and  $(\partial M/\partial T)_H = -M/T$ , so  $c_H - c_M = M^2/C_C = HM/T = C_C H^2/T^2 > 0$ .

- 3) Under what conditions (i.e. isolated or non-isolated, quantity  $X$  held constant, etc.) is the enthalpy of a system a non-decreasing function of time? Be specific.

This question was not what I intended to ask; it doesn't have a unique answer. The question I should have asked is "What can we say about the enthalpy change in a spontaneous process at fixed entropy and pressure?"