Thermodynamics

Answer all problems.

(40 pts.) 1. A rigid thermally-insulated cylinder, closed at both ends, is fitted with a frictionless non-porous heat-conducting piston that divides the cylinder into two parts. (Assume the thermal conductivity is infinite.) Initially the piston is clamped in the center with 1 liter of air at 300K and 2 atm pressure on one side and 1 liter of air at 300 K and 1 atm on the other. The piston is released and eventually reaches equilibrium (i.e., a negligible amount of friction brings it ultimately to rest.) Assume the air to be an ideal gas.

(a) Compute the final pressure and temperature of the air.

(b) Compute the entropy change of the universe.

(30 pts.) 2. Consider entropy S of a closed system as a function of pressure P and volume V; S = S(P,V).

(a) Starting from $dS = \left(\frac{\partial S}{\partial V}\right)_P dV + \left(\frac{\partial S}{\partial P}\right)_V dP$, derive the third form of the TdS equation:

$$TdS = C_P\left(\frac{\partial T}{\partial V}\right)_P dV + C_V\left(\frac{\partial P}{\partial T}\right)_V dP .$$

(b) Show that $\frac{K_T}{K_S} = \frac{C_P}{C_V}$

where $K_{T\text{ or }S} \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T\text{ or }S}$

are the isothermal and isoentropic compressibilities, and C_P and C_V are the specific heat at constant pressure and constant volume, respectively.

HINT: $\left(\frac{\partial T}{\partial P}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T$

(30 pts.) 3. (a) Demonstrate that in a first order phase transition between states 1 and 2 of a pure substance with a fixed number of moles, n_o, the phase coexistence curve in the pressure-temperature (P,T) plane is given by $g_1(P,T) = g_2(P,T)$ where g_1 and g_2 are the Molar Gibbs functions.

HINT: Write the Gibbs free energy $G = n_1 g_1 + n_2 g_2$, and recall that a first order phase transition is an isobaric, isothermal process.

(b) Show that $\frac{dP}{dT} = \frac{\Delta s}{\Delta v}$ on the coexistence curve where $\Delta s = s_2 - s_1$ and $\Delta v = v_2 - v_1$ are the changes in molar entropy and volume, respectively, between states 1 and 2.

HINT: $\left(\frac{\partial P}{\partial T}\right)_{\Delta g} = -\frac{(\partial \Delta g/\partial T)_P}{(\partial \Delta g/\partial P_T}$.