Part I. Maxwell Relations.

a) As we did in class for G, derive the Maxwell relation for F.

$$dF = -SdT - PdV$$

$$dF = -\left(\frac{\partial F}{\partial T}\right)_V dT - \left(\frac{\partial F}{\partial V}\right)_T dV$$

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

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

b) How might this relation be useful if given appropriate physical constants? (Note: it is not as direct as for G; remember the cyclic rule.)

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left[\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T\right]^{-1}$$

$$= -\left(\frac{\partial V}{\partial T}\right)_P 1 \bigg/ \left(\frac{\partial V}{\partial P}\right)_T = \frac{-\alpha}{\kappa}$$

Part II. Using constraints to determine the equilibrium state of a system.

Consider a box at constant volume and in thermal equilibrium with its surroundings. Inside the box are two A-B liquid solutions of different composition, separated by an internal partition that is diathermal and impermeable to component B. The dividing wall has the property that its displacement (δV) and the flow of component A through it are coupled by the following relation: $\delta V = K \delta n_A$.

a) Draw a picture of this system, indicating constant parameters. What is the relevant equilibrium extremum principle to apply for such a system?

1	2
A, B $n_A^{\ 1}$	A, B $n_A^{\ 2}$
P_1	P_2

$T_1 = T_2 = T^{surr}$; $V_1 + V_2 = \text{const.}$
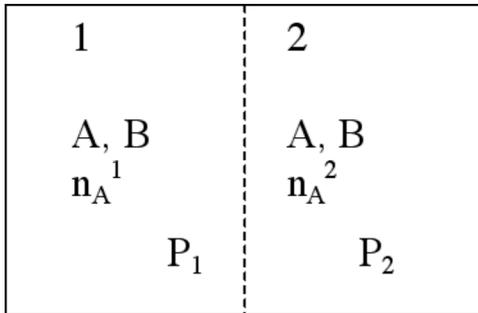
Since temperature and volume are both constant, the relevant equilibrium criterion is minimization of the Helmholtz free energy: $F(T, V, n)$.

b) What are the constraints on this system?

$$dn_A^{1} = -dn_A^{2}; dV_1 = dV_2$$

$$dV_x = Kdn_A^x; \quad (dn_B = 0)$$

c) Determine the equilibrium criterion for A in terms of its chemical potential and the pressure on each side of the box.

Consider the total Helmholtz energy, and the energy on either side of the box.

$$dF = -SdT - PdV + \sum_i^C \sum_j^P \mu_i^j dn_i^j$$

$$dF_1 = -SdT - P_1 dV_1 + \sum_i^C \mu_i^1 dn_i^1 = -P_1 dV_1 + \mu_A^1 dn_A^1$$

$$dF_2 = -SdT - P_2 dV_2 + \sum_i^C \mu_i^2 dn_i^2 = -P_2 dV_2 + \mu_A^2 dn_A^2$$

The above made use of the fact that the dn_B is equal to zero. Now we substitute in our first two constraints immediately, followed by the third one:

$$dF_{tot} = dF_1 + dF_2 = -P_1 dV_1 + P_2 dV_1 + \mu_A^1 dn_A^1 - \mu_A^2 dn_A^1$$
$$= -P_1 K dn_{dn_A^1 A}^1 + P_2 K dn_A^1 + \mu_A^1 dn_A^1 - \mu_A^2 dn_A^1$$
$$= dn_A^1 (K(P_2 - P_1) + \mu_A^1 - \mu_A^2)$$

For a minimum, dF must be equal to zero, and this must be true independent of minor fluctuations in the composition of the two liquid mixtures. Thus:

$$\mu_A^1 - KP_1 = \mu_A^2 dn_A^1 - KP_2$$

Note that if the partition did not have the magical quality of coupling volume and composition, the usual conditions for mechanical (equal pressures on either side) and chemical (equal chemical potentials on either side) equilibrium would hold.