Physical Chemistry

PC 1 The bi-directional reaction

$$A_{(s)} \rightleftharpoons B_{(g)} + C_{(g)} + D_{(g)}$$

where the subscripts indicate the physical state of each substance, has a standard *Gibbs* free energy of -7 kJ at the reaction temperature of 400 K. The process takes place in a sealed, isothermal container, and the initial mixture contains 2 mol A, 0.2 mol B and 0.1 mol C and D each. Find the maximum volume of the container for whtich the equilibrium state is reachable.

(10 points)

PC 2 Let A and B be the two components of a binary system whose liquid–phase non–ideality is accurately enough described by the *Hildebrandt* model:

$$G^E = H^E = Kx_Ax_B$$
$$RT\ln\gamma_A = Kx_B^2 \qquad RT\ln\gamma_B = Kx_A^2$$

where K is a temperature–independent parameter, equal to $5820\,{}^{\text{J}}/_{\text{mole}}$, G^E is the molar excess *Gibbs* free energy and H^E is the molar enthalpy of mixing.

A quantity of 7 mol of B (at temperature T^0) is added, slowly, under continuous stirring, to 1 mol of A at the same temperature. The heat capacities of A and B are equal, $C_{P,A} = C_{P,B} = 30\,{}^{\text{J}}/_{\text{molK}}$. The experiment is carried out, at constant pressure, in such a way, that any heat exchange between the system and its sorroundings can be neglected.

a) Show that the solution to the liquid (')—liquid (") equilibrium equations:

$$x_i'\gamma_i' = x_i''\gamma_i'', \quad i = \overline{A,B}$$

always satifies $x_A' = 1 - x_A''$ and use this fact to prove that the phase diagram is symmetric and, further, to compute it as a function $T = T(x_A)$.

b) Find the equation of the titration curve in T—x_A coordinates. Show that it too is symmetric.

c) Compute the lowest possible value of T^0 for which no phase split occurs during the titration.

(20 points)