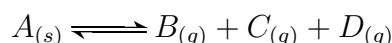




## Physical Chemistry

### PC 1 The bi-directional reaction



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

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

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

A quantity of  $7\text{ mol}$  of B (at temperature  $T^0$ ) is added, slowly, under continuous stirring, to  $1\text{ mol}$  of A at the same temperature. The heat capacities of A and B are equal,  $C_{P,A} = C_{P,B} = 30\text{ J/molK}$ . The experiment is carried out, at constant pressure, in such a way, that any heat exchange between the system and its surroundings 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 satisfies  $x'_A = 1 - x''_A$  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)