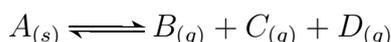




Physical Chemistry

PC 1 The bi-directional reaction



where the subscripts indicate the physical state of each substance, has a standard *Gibbs* free energy of -7 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 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 J/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, $C_{P,A} = C_{P,B} = 30\text{ J/molK}$. 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)