Problem

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.

Solution

The equilibrium state is described by the well–known equation:

$$K_a = \prod_{i=1}^{C} a_i^{\nu_i} = \exp\left(-\frac{\Delta^r G_T^0}{RT}\right)$$

where a_i is the thermodynamic activity of component i, defined as the ratio of its fugacity in the mixture to its standard–state fugacity:

$$a_i = \frac{f_i}{f_i^0}$$

the superscript 0 referring to the standard state. For convenience, in cases such the one under discussion, we may take the standard state as the pure component at the system temperature and 1 bar of pressure. Since a change in pressure does not affect the fugacity of the solid reagent A, its activity is equal to 1, so the equilibrium constant becomes:

$$K = P_B P_C P_D = \exp\left(-\frac{\Delta^r G_T^0}{RT}\right) \tag{1}$$

with the partial pressures P_A, P_B and P_C *measured in bar*. Denoting by ξ the reaction extent, we have:

$$\exp\left(-\frac{\Delta^r G_T^0}{RT}\right) = \frac{(n_B^0 + \xi)(n_C^0 + \xi)(n_D^0 + \xi)}{(n_B^0 + n_C^0 + n_D^0 + 3\xi)^3} P^3$$

3 points

Expressing the pressure from the ideal gas law and solving for v, the total volume of the system, we obtain the following relation between v and the reaction extent ξ:

$$v = RT \sqrt[3]{\frac{(n_B^0 + \xi)(n_C^0 + \xi)(n_D^0 + \xi)}{\exp\left(-\frac{\Delta^r G_T^0}{RT}\right)}} \tag{2}$$

3 points

The maximum possible value for the reaction extent at equilibrium arises from the condition:

$$n_i > 0, i = \overline{1,4} \Longrightarrow \xi \in [-0.1, 2] \tag{3}$$

from which we are interested only in the upper bound for ξ since it it obvious that, when the volume increases, the reaction unfolds to the right.

3 points

The requested volume is, thus, given by the relation:

$$v = RT \sqrt[3]{\frac{\left(n_B^0 + \xi_{max}\right)\left(n_C^0 + \xi_{max}\right)\left(n_D^0 + \xi_{max}\right)}{\exp\left(-\frac{\Delta^r G_T^0}{RT}\right)}} \tag{4}$$

$$= 42.8\,\mathrm{L} \tag{5}$$

so the answer is:

$$\boxed{v = 42,8\,\mathrm{L}}$$

1 point
Total: 10 points