

Problem 1-09 Second-order reactions[V], temperature dependence

The steel autoclave was filled by equimolar mixture of gaseous A and B. The initial pressure was 92 kPa. In the course of the second-order reaction, schematically written as $\mathbf{A + B \rightarrow products}$, which takes place in the gaseous mixture at constant temperature of 313 K, one half of each of reactants was consumed during 108.7 minutes. Calculate

- (a) the value of the rate constant at the temperature of 313 K,
(b) the half-life of this reaction at the temperature of 323 K, if the initial mixture is the same as in the preceding case and the activation energy has the value $E^* = 63 \text{ kJ mol}^{-1}$.

$$[(a) k_{p1} = 2 \cdot 10^{-4} \text{ kPa}^{-1} \text{ min}^{-1}; (b) (\tau_{1/2})_2 = 51.37 \text{ min} (k_{p2} = 4.2318 \cdot 10^{-4} \text{ kPa}^{-1} \text{ min}^{-1})]$$

Solution:

$$\frac{dp_A}{(-1)d\tau} = \frac{dp_B}{(-1)d\tau} = k_p \cdot p_A \cdot p_B$$

$$p_{A0} = p_{B0} \Rightarrow p_A = p_B \Rightarrow -\frac{dp_A}{d\tau} = -\frac{dp_B}{d\tau} = k_p \cdot p_A^2 = k_p \cdot p_B^2$$

$$\frac{1}{p_A} - \frac{1}{p_{A0}} = k_p \cdot \tau$$

$$(a) \frac{1}{p_{A0}/2} - \frac{1}{p_{A0}} = k_p \cdot \tau_{1/2}$$

$$p = 92 \text{ kPa} = p_{A0} + p_{B0} \quad , \quad \Rightarrow \quad p_{A0} = p_{B0} = 92/2 = 46 \text{ kPa} \quad , \quad (\tau_{1/2})_1 = 108.7 \text{ min}$$

$$k_{p1} = \frac{1}{p_{A0} \cdot (\tau_{1/2})_1} = \frac{1}{46 \cdot 108.7} = 2 \cdot 10^{-4} \text{ kPa}^{-1} \text{ min}^{-1}$$

$$(b) \ln \frac{k_{p2}}{k_{p1}} = \frac{E^*}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$k_{p2} = k_{p1} \cdot \exp \left[\frac{E^*}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] = 2 \cdot 10^{-4} \cdot \exp \left[\frac{63000}{8.314} \cdot \left(\frac{1}{313} - \frac{1}{323} \right) \right]$$

$$k_{p2} = 2 \cdot 10^{-4} \cdot 2.11598 = 4.2318 \cdot 10^{-4} \text{ kPa}^{-1} \text{ min}^{-1}$$

$$(\tau_{1/2})_2 = \frac{1}{p_{A0} \cdot k_{p2}} = \frac{1}{46 \cdot 4.2318 \cdot 10^{-4}} = 51.37 \text{ min}$$