## Problem 1-11 Second-order reactions [V], half-life, temperature dependence

A second-order reaction between ideal gases, described by stoichiometry **$^5/_2$ A(g) → 2 R(g) + C(g)**, is realized in a closed reactor of constant volume at 434 K. If the reactor was filled by pure A to a pressure of 40 kPa, the half-life of 25 min was obtained.

(a) Calculate the rate constant of this reaction at the temperature of 434 K.

(b) What will be the partial pressure of A in the reaction mixture at this temperature after one hour and 12 minutes from the initiation of the reaction?

(c) Calculate the rate constant at the temperature of 390 K. Activation energy is $E^* = 68$ kJ mol$^{-1}$.

[(a) $k_{p1} = 4 \cdot 10^{-4}$ kPa$^{-1}$ min$^{-1}$; (b) $p_A =$ 10.309 kPa; (c) $k_{p2} = 4.772 \cdot 10^{-5}$ kPa$^{-1}$ min$^{-1}$]

Solution:

**$^5/_2$ A(g) → 2 R(g) + C(g)**

$a$ A → *products*

$$\frac{dp_A}{(-a)\,d\tau} = k_p \cdot p_A^2 \quad , \quad \frac{1}{p_A} - \frac{1}{p_{A0}} = a \cdot k_p \cdot \tau \quad ; \quad a = 2.5$$

(a) half-life: $p_A = p_{A0}/2$ , $\tau_{1/2} = 25$ min , $p_{A0} = 40$ kPa

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

$$\Rightarrow \quad \underline{k_{p1}} = \frac{1}{a \cdot p_{A0} \cdot \tau_{1/2}} = \frac{1}{2.5 \cdot 40 \cdot 25} = \underline{4 \cdot 10^{-4}\ \text{kPa}^{-1}\ \text{min}^{-1}}$$

(b) $\tau = 1$ h 12 min = 72 min , $p_A = ?$

$$\frac{1}{p_A} = \frac{1}{p_{A0}} + a \cdot k_p \cdot \tau = \frac{1}{40} + 2.5 \cdot 4 \cdot 10^{-4} \cdot 72 = 0.097$$

$\underline{p_A = 10.309_3\ \text{kPa}}$

(c) $$k_{p2} = k_{p1} \cdot \exp\left[\frac{E^*}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] = 4 \cdot 10^{-4} \cdot \exp\left[\frac{68000}{8.314} \cdot \left(\frac{1}{434} - \frac{1}{390}\right)\right]$$

$\underline{k_{p2} = 4.772 \cdot 10^{-5}\ \text{kPa}^{-1}\ \text{min}^{-1}}$