(A)

1. $T_1 = 1420\ K$

$T_2 = 1670\ K$

$\frac{k_2}{k_1} = 3{,}76 \longrightarrow \frac{k_1}{k_2} = \frac{1}{3{,}76} = 0{,}266$

$\Delta_r H^{\ddagger}_1 = \Delta_r H^{\ddagger}_2$

$$\Delta_r S^{\ddagger}_1 \Big/ \frac{J}{mol\,K} = 8{,}079 \cdot 10^{-3} \cdot 1420 - 34{,}20 = -22{,}7$$

$$\Delta_r S_2^{\ddagger} \Big/ \frac{J}{mol\,K} = 8{,}079 \cdot 10^{-3} \cdot 1670 - 34{,}20 = -20{,}7$$

$$k = \frac{k_B T}{h} \cdot \exp\left(-\frac{\Delta_r H^{\ddagger}}{RT}\right) \exp\left(\frac{\Delta_r S^{\ddagger}}{R}\right)$$

$$\left.\begin{aligned} \ln k_1 &= \ln \frac{k_B T_1}{h} - \frac{\Delta_r H^{\ddagger}}{R T_1} + \frac{\Delta_r S_1^{\ddagger}}{R} \\ \ln k_2 &= \ln \frac{k_B T_2}{h} - \frac{\Delta_r H^{\ddagger}}{R T_2} + \frac{\Delta_r S_2^{\ddagger}}{R} \end{aligned}\right\} \ominus$$

$$\ln \frac{k_1}{k_2} = \frac{\Delta_r H^{\ddagger}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \frac{1}{R}\left(\Delta_r S_1^{\ddagger} - \Delta_r S_2^{\ddagger}\right) + \ln\frac{T_1}{T_2}$$

$$\Delta_r H^{\ddagger} = \left(\ln\left(\frac{k_1}{k_2}\frac{T_2}{T_1}\right) - \frac{1}{R}\cdot\left(\Delta_r S_1^{\ddagger} - \Delta_r S_2^{\ddagger}\right)\right) \cdot R \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1}$$

$$\Delta_r H^{\ddagger} = 46670\ J/mol = \underline{\underline{46{,}67\ kJ/mol}}$$

2. $$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

$$B \xrightarrow{k_2} C + D$$

$$C \xrightarrow{k_3} E + D$$

a) $$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B] - k_3[C]$$

$$\frac{d[D]}{dt} = k_2[B] + k_3[C]$$

$$\frac{d[E]}{dt} = k_3[C]$$

b) $[A]_0 = 0{,}0240 \ \frac{mol}{dm^3}$

$t = 60\ s$

$[A]_t = ?$

$$\frac{d[B]}{dt} \cong 0 = k_1[A] - k_{-1}[B] - k_2[B]$$

$$k_1[A] = k_{-1}[B] + k_2[B] = (k_{-1} + k_2)[B]$$

$$[B] = \frac{k_1}{k_{-1}+k_2}[A]$$

$$\frac{d[A]}{dt} = -k_{-1}[A] + k_{-1}[B] = -k_{-1}[A] + k_{-1} \cdot \frac{k_1}{k_{-1}+k_2}[A]$$

$$\frac{d[A]}{dt} = \Bigg(\underbrace{\frac{k_{-1}k_1}{k_{-1}+k_2} - k_{-1}}_{k'}\Bigg) \cdot [A] \quad \Bigg\} \text{ elsőrendű kinetika}$$

$$[A]_t = [A]_0 \cdot \exp(-k' \cdot t)$$

$$[A]_t = 0{,}0240\ \frac{mol}{dm^3} \cdot \exp(-k' \cdot 60\,s)$$

$$k' = \frac{k_{-1} \cdot k_1}{k_{-1} + k_2} - k_{-1} = 2{,}906 \cdot 10^{-2}\ s^{-1}$$

$$[A]_t = \underline{\underline{4{,}20 \cdot 10^{-3}\ \frac{mol}{dm^3}}}$$

3. Számítsuk ki k_1 és k_2 értékét 10^{-1} és 10^6 bar nyomáson is!

$\underline{10^{-1}\text{ bar}}$: $[M] = \frac{P}{RT} = \frac{10^{-1}\cdot 100}{8{,}314\cdot 1400}\ \frac{mol}{dm^3} = 8{,}59\cdot 10^{-4}\ \frac{mol}{dm^3}$

$\underline{\hookrightarrow k_1}$: $P_r = \frac{k_0[M]}{k_\infty} = \frac{7{,}15\cdot 10^{-2}\cdot 8{,}59\cdot 10^{-4}}{5{,}38\cdot 10^3} = 1{,}14\cdot 10^{-8}$

$k_1 = k_\infty\left(\frac{P_r}{P_r+1}\right) \approx k_\infty\cdot P_r = \underline{6{,}13\cdot 10^{-5}\ s^{-1}}$

$\underline{\hookrightarrow k_2}$: $P_r = \frac{k_0[M]}{k_\infty} = \frac{1{,}90\cdot 10^2\cdot 8{,}59\cdot 10^{-4}}{8{,}37\cdot 10^{-1}} = 0{,}195$

$k_2 = k_\infty\left(\frac{P_r}{P_r+1}\right) = k_\infty\cdot\frac{0{,}195}{1{,}195} = \underline{0{,}137\ s^{-1}}$

$\underline{10^6\text{ bar}}$: $[M] = \frac{P}{RT} = \frac{10^6\cdot 100}{8{,}314\cdot 1400}\ \frac{mol}{dm^3} = 8{,}59\cdot 10^3\ \frac{mol}{dm^3}$

$\underline{\hookrightarrow k_1}$: $P_r = \frac{k_0[M]}{k_\infty} = \frac{7{,}15\cdot 10^{-2}\cdot 8{,}59\cdot 10^3}{5{,}38\cdot 10^3} = 0{,}114$

$k_1 = k_\infty\left(\frac{P_r}{P_r+1}\right) = k_\infty\cdot\frac{0{,}114}{1{,}114} = \underline{551\ s^{-1}}$

$\underline{\hookrightarrow k_2}$: $P_r = \frac{k_0[M]}{k_\infty} = \frac{1{,}90\cdot 10^2\cdot 8{,}59\cdot 10^3}{8{,}37\cdot 10^{-1}} = 1{,}95\cdot 10^6$

$k_2 = k_\infty\left(\frac{P_r}{P_r+1}\right) \approx k_\infty = \underline{8{,}37\cdot 10^{-1}\ s^{-1}}$

A CHF_2OOH sorozatos reakcióban bomlik, így a sebességi együtthatókat megvizsgálva 10^{-1} bar nyomáson $k_2 \gg k_1$ és 10^6 bar nyomáson $k_1 \gg k_2$, ezért kis nyomáson a második, míg nagy nyomáson az első a sebességmeghatározó lépés.

Tehát:

10^{-1} bar:

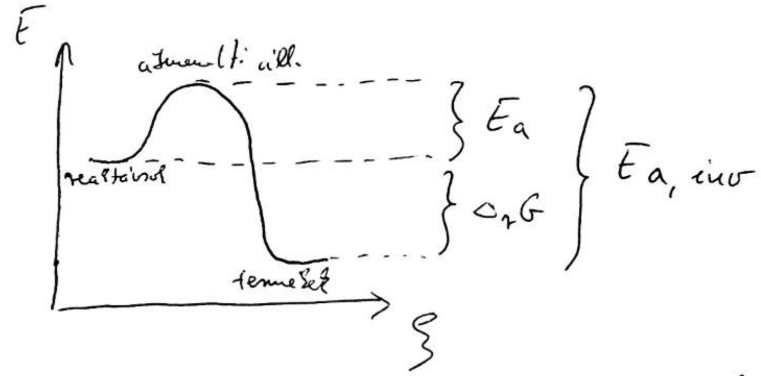
$$\frac{d[F_2]}{dt} = k_2\,[COF_2] \quad , \text{ahol} \quad k_2 = 0{,}137 \ s^{-1}$$

10^{6} bar

$$\frac{d[F_2]}{dt} = k_1\,[CHF_2OOH] \quad , \text{ahol} \quad k_1 = 551 \ s^{-1}$$

4. „Egyszerű" megoldás:

Tekintsük az alábbi energia-diagramot:



$E_{a,inv}$: a fordított (inverz) reakció aktiválási energiája

$$E_{a,inv} = E_a - \Delta_r G = 15{,}96 \text{ kJ/mol} + 53{,}93 \text{ kJ/mol}$$

$$E_{a,inv} = \underline{69{,}89 \text{ kJ/mol}}$$

Mivel $A = k \cdot \exp\left(\frac{E_\mathrm{a}}{RT}\right)$ és $k = \frac{k_\mathrm{B}T}{h}\frac{k_\mathrm{B}T}{p^\ominus}\exp\left(-\frac{\Delta_\mathrm{r}G^\ddagger}{RT}\right)$, és
$E_\mathrm{a,inv} = E_\mathrm{a} - \Delta_\mathrm{r}G$ és $\Delta_\mathrm{r}G^\ddagger_\mathrm{inv} = \Delta_\mathrm{r}G^\ddagger - \Delta_\mathrm{r}G$, így felírva:

$$A_\mathrm{inv} = \frac{k_\mathrm{B}T}{h}\frac{k_\mathrm{B}T}{p^\ominus}\exp\left(-\frac{\Delta_\mathrm{r}G^\ddagger_\mathrm{inv}}{RT}\right)\cdot\exp\left(\frac{E_\mathrm{a,inv}}{RT}\right) = \frac{k_\mathrm{B}T}{h}\frac{k_\mathrm{B}T}{p^\ominus}\exp\left(-\frac{\Delta_\mathrm{r}G^\ddagger - \Delta_\mathrm{r}G}{RT}\right)\cdot\exp\left(\frac{E_\mathrm{a} - \Delta_\mathrm{r}G}{RT}\right)$$

$$A_\mathrm{inv} = \frac{k_\mathrm{B}T}{h}\frac{k_\mathrm{B}T}{p^\ominus}\exp\left(\frac{E_\mathrm{a} - \Delta_\mathrm{r}G^\ddagger}{RT}\right) = \frac{k_\mathrm{B}T}{h}\frac{k_\mathrm{B}T}{p^\ominus}\exp\left(-\frac{\Delta_\mathrm{r}G^\ddagger}{RT}\right)\cdot\exp\left(\frac{E_\mathrm{a}}{RT}\right) = A = 1{,}40\cdot 10^{-17}\,\frac{\mathrm{m}^3}{\text{molekula s}}$$

Bonyolult megoldás:

Az $k = A\cdot\exp\left(-\frac{E_a}{RT}\right)$ és $k_{bi} = \frac{k_B T}{h}\cdot\frac{k_B T}{p^\ominus}\cdot\exp\left(-\frac{\Delta_r G^\ddagger}{RT}\right)$

Képleteket felhasználva: (valamint $\Delta_r G^\ddagger_{inv} = \Delta_r G^\ddagger - \Delta_r G$)

$$\left.\begin{array}{l} T_1 \longrightarrow k_1 \longrightarrow \Delta_r G_1^\ddagger \longrightarrow \Delta_r G^\ddagger_{1,inv} \longrightarrow k_{1,inv} \\ T_2 \longrightarrow k_2 \longrightarrow \Delta_r G_2^\ddagger \longrightarrow \Delta_r G^\ddagger_{2,inv} \longrightarrow k_{2,inv} \end{array}\right\} A_{inv}, E_{a,inv}$$

Ugyan arra az eredményre vezet.
(Kiszámoltam, tényleg!)

(B) Minden levezetés megegyezik az (A) ~~csoport-tal~~ csoportéval, így ide csak végeredményeket közlök.

1. $\Delta_r S_1^{\ddagger} = -12{,}8$ J/mol

$\Delta_r S_2^{\ddagger} = -8{,}02$ J/mol

$\Delta_r H^{\ddagger} = 6453$ J/mol $= \underline{64{,}53 \text{ kJ/mol}}$

2. b) $k' = 1{,}41 \cdot 10^{-3}$ s^{-1}

$[A]_t = \underline{0{,}154 \ \frac{mol}{dm^3}}$

3. $\underline{10^{-1} \text{ bar}}$:

$\hookrightarrow \underline{k_1}$: $k_1 = 7{,}60 \cdot 10^{-5}$ s^{-1}

$\hookrightarrow \underline{k_2}$: $k_2 = 1{,}92 \cdot 10^{-1}$ s^{-1}

$\underline{10^{6} \text{ bar}}$:

$\hookrightarrow \underline{k_1}$: $k_1 = 6{,}54 \cdot 10^{2}$ s^{-1}

$\hookrightarrow \underline{k_2}$: $k_2 = 7{,}82 \cdot 10^{-1}$ s^{-1}

Tehát:

$\underline{10^{-1} \text{ bar}}$:

$\frac{d[Cl_2]}{dt} = k_2 [COCl_2]$, ahol $k_2 = 1{,}92 \cdot 10^{-1}$ s^{-1}

$\underline{10^{6} \text{ bar}}$:

$\frac{d[Cl_2]}{dt} = k_1 [CCl_3OOH]$, ahol $k_1 = 6{,}54 \cdot 10^{2}$ s^{-1}

4. $E_{a,\,inv} = 119870$ J/mol $= \underline{119{,}9 \text{ kJ/mol}}$

$A_{inv} = A = \underline{6{,}10 \cdot 10^{-18} \ m^3 \ molekula^{-1} \ s^{-1}}$