DST 2023

(1)

A-1)

	A	$\longrightarrow$	$2B$	$+$	C	
t_0	n_0		0		0	
t	$n_A = n_0(1) - \xi$		2ξ		ξ	$n_T = n_0 + 2\xi$

φ gaz.

1

A-2) $P_A = n_A \frac{RT}{V} = (n_0 - \xi)\frac{RT}{V}$

$P_T = n_T \frac{RT}{V} = (n_0 + 2\xi)\frac{RT}{V} = n_0\frac{RT}{V} + 2\xi\frac{RT}{V} = P_0 + 2\xi\frac{RT}{V}$

$\Rightarrow P_A = n_0\frac{RT}{V} - \xi\frac{RT}{V}$

$= P_0 - \left(\frac{P_T - P_0}{2}\right)$

1 $\boxed{P_A = \frac{1}{2}(3P_0 - P_T)}$ CQFD

1 A-3)

	0	20	40	80	120
P_A (bar)	0,2393	0,2011	0,1690	0,1193	0,0843

1 A-4) Décomposition ⇒ processus unimoléculaire ⇒ ordre 1

A-5) $\boxed{-\frac{dn_A}{n_A} = k\,dt}$ 1 $\Rightarrow -\ln n_A = kt + C^{te}$

à $t = 0$, $n_A = n_0 \Rightarrow n_A = n_0 e^{-kt}$

$\Rightarrow \boxed{P_A = P_0 e^{-kt}}$ 1

A-6) $k = \frac{1}{t}\ln\left(\frac{P_0}{P_A}\right)$

	0	20	40	80	120
k (min^{-1})	X	0,0087	0,0087	0,0087	0,0087

1 $\Rightarrow \boxed{k = C^{te} = 0{,}0087 \text{ min}^{-1}}$ ⇒ ordre 1 vérifié 1

$\boxed{\tau = \frac{\ln 2}{k} = 79{,}7 \text{ min}}$ 1 $\simeq 80$ min $\begin{cases} t = 0 \text{ et } t = 80 \Rightarrow P_A/2 \\ t = 40 \text{ et } t = 120 \Rightarrow P_A/2 \end{cases}$ ordre 1 ok

A-7) $k_T = A e^{-E_A/RT} \Rightarrow \frac{k_{420}}{k_{433}} = \frac{A e^{-E_A/R420}}{A e^{-E_A/R433}} = \frac{k_{420}}{2k_{420}}$

$\Rightarrow E_A = \left(\frac{R}{\frac{1}{433} - \frac{1}{420}}\right)\ln\frac{1}{2} \Rightarrow \boxed{E_A = 80\,617 \text{ J/mol} \simeq 80{,}6 \text{ kJ/mol}}$ 2

2

B-1) $\Delta_r H^\circ = \Delta_f H^\circ_{PCl_3} + \Delta_f H^\circ_{Cl_2} - \Delta_f H^\circ_{PCl_5}$ (g)

$= \boxed{87 \text{ kJ/mol.}}$ 1

B-2) $\Delta_r S^\circ = S^\circ_{PCl_3} + S^\circ_{Cl_2} - S^\circ_{PCl_5}$

$= \boxed{170{,}3 \text{ J/mol.}}$ 1

B-3) $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ avec $T = 298K$

$= \boxed{36{,}25 \text{ kJ/mol.}}$ 1

B-4) $K_{298K} = e^{-\frac{\Delta_r G^\circ}{RT}} \Rightarrow \boxed{K_{298K} = 4{,}42\,10^{-7}.}$ 1

B-5) $PCl_5 \longrightarrow PCl_3 + Cl_2$ (g).

t_0	n_0	0	0
t	$n_0(1-\alpha)$	αn_0	αn_0

$n_T = n_0(1+\alpha)$

$$K_T = \frac{a_{PCl_3}\, a_{Cl_2}}{a_{PCl_5}} = \left(\frac{\alpha \cancel{n_0}}{\cancel{n_0}(1+\alpha)} \frac{P_T}{P_0}\right)^2 \times \frac{\cancel{n_0}(1+\alpha)}{\cancel{n_0}(1-\alpha)} \frac{P_0}{P_T}$$

$$\Rightarrow \boxed{K_T = \frac{\alpha^2}{1-\alpha^2}\frac{P_T}{P_0} = \frac{\alpha^2}{1-\alpha^2}}$$ 2 car $P_T = P_0 = 1\text{bar}$

B-6) $(1-\alpha^2)K_T - \alpha^2 = 0 \Rightarrow \alpha = \sqrt{\dfrac{K_T}{1+K_T}}$

AN $\boxed{\alpha = 6{,}65\,10^{-4}}$. 1

1

B-7) α est très faible $\Rightarrow PCl_5$ peu dissocié donc très stable à 298K.

B-8) à $P = 2\text{bar}$: $K_T = \dfrac{\alpha^2}{1-\alpha^2} \times 2 \Rightarrow \alpha = \sqrt{\dfrac{K_T}{2+K_T}}$

AN $\boxed{\alpha = 4{,}70\,10^{-4}}$ 1

$P\uparrow \Rightarrow$ déplacement de l'équilibre dans le sens $\leftarrow$ pour s'opposer à $P\uparrow$. 1

c)

4

$$\begin{tikzcd} C(s) + 4\,H(g) \arrow[r, "\Delta_r H^\circ"] \arrow[d, "2\Delta_{r1} H^\circ"'] & CH_4(g) \\ C(s) + 2\,H_2(g) \arrow[ur, "\Delta_{r3} H^\circ"'] & \end{tikzcd}$$

$$\Delta_r H^\circ = 2\,\Delta_{r1} H^\circ + \Delta_{r3} H^\circ$$

$$2 \times (-437{,}6) + (-75{,}2)$$

$$\boxed{\Delta_r H^\circ = -950{,}4 \text{ kJ/mol}}$$