DST 2021

A) 1) $C_4H_{10(g)} + \frac{13}{2} O_{2(g)} \rightarrow 4\,CO_{2(g)} + 5\,H_2O_{(g)}$

(1)

2) $\Delta_r H^\circ_{298} = \Delta_{comb} H^\circ_{298} = 4 \Delta_f H^\circ_{298}\, CO_{2(g)} + 5 \Delta_f H^\circ_{298}\, H_2O_{(g)}$
$- \Delta_f H^\circ_{298}\, C_4H_{10}(g) - \frac{13}{2} \times 0$
$= -2655{,}8$ kJ/mol.

(1)

3) $m_{butane} =$ [redacted] $2{,}61$ g

(1)

$\rightarrow n_{butane} =$ [redacted] $= \frac{2{,}61}{58} = 0{,}045$ mole

$Q_P = n_{butane} \times \Delta_{comb} H^\circ_{298, C_4H_{10}(g)} =$ [redacted]

$Q_P = -119{,}51$ kJ

4) $H_2O(l), 298K \xrightarrow{\Delta H_1} H_2O(l), 373K$.

(1)

$-Q_P = \Delta H_1 = \frac{m_{H_2O}}{M_{H_2O}} \times C_p^\circ\, H_2O(l) \times \Delta T$

AN $m_{H_2O} = \frac{119{,}51 \times 18}{75{,}2\ 10^{-3} \times 75} = 381{,}42$ g.

5) $H_2O(l), 298K \xrightarrow{\Delta H'_1} H_2O(l), 373K \xrightarrow{\Delta H_2} H_2O(gaz), 373K$.

(1)

$-Q_P = \Delta H'_1 + \Delta H_2$
$= \frac{m_{H_2O}}{M_{H_2O}} \left(C_p^\circ\, H_2O(l) \times \Delta T + \Delta H_{vap}\, H_2O, 373 \right)$

AN $m_{H_2O} = \frac{119{,}51 \times 18}{75{,}2\,10^{-3} \times 75 + 40{,}62} = 46{,}50$ g

B) $N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)}$

$\left.\begin{matrix} p = 1\,atm \\ T = 300K \end{matrix}\right] \rightarrow \alpha = 0{,}2$

$t=0$	n_0	0	
$t+dt$	$n_0(1-\alpha)$	$2n_0\alpha$	$n_{tot} = n_0(1+\alpha)$

(1) $K = \dfrac{a_{NO_2}^2}{a_{N_2O_4}} = \dfrac{(P_{NO_2}/p°)^2}{(P_{N_2O_4}/p°)} = \dfrac{P_{NO_2}^2}{P_{N_2O_4}} \cdot \dfrac{1}{p°}$

avec $P_{N_2O_4} = \dfrac{n_0(1-\alpha)}{n_0(1+\alpha)} \cdot P_{tot} = \dfrac{1-\alpha}{1+\alpha} P_{tot}$

$P_{NO_2} = \dfrac{2n_0\alpha}{n_0(1+\alpha)} P_{tot} = \dfrac{2\alpha}{1+\alpha} P_{tot}$.

2 $\rightarrow K = \dfrac{4\alpha^2}{1-\alpha^2} \dfrac{P_{tot}}{p°}$

(2) (1) AN $K = \dfrac{4 \cdot 0{,}2^2}{1-0{,}2^2} \dfrac{101325}{100000} \rightarrow K = 0{,}1689$

(3) $\dfrac{4\alpha^2}{1-\alpha^2} = \dfrac{Kp°}{P_{tot}} = 0{,}1689 \times \dfrac{100000}{0{,}05 \times 101325} = 3{,}3333 = C$

(1) $\rightarrow 4\alpha^2 = (1-\alpha^2) \cdot C \rightarrow \alpha = \sqrt{\dfrac{C}{4+C}} \rightarrow \alpha = 0{,}6742$

Rq $p\downarrow \rightarrow \alpha\uparrow$

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(4) $n_0 = \dfrac{46}{92} = 0{,}5$ mole.

(1) $P_0 = n_0\dfrac{RT}{V} \rightarrow P_0 = 62355\,Pa = 0{,}6154\,atm$.

(5) $P_{tot} = n_0(1+\alpha)\frac{RT}{V} = (1+\alpha)P_0$

$$K = \frac{4\alpha^2}{1-\alpha^2}\frac{P_{tot}}{P^\circ} = \frac{4\alpha^2}{1-\alpha^2}\frac{(1+\alpha)P_0}{P^\circ} = \boxed{\frac{4\alpha^2}{1-\alpha}\frac{P_0}{P^\circ} = \underset{K}{\underline{0{,}1689}}}$$

Donc $\frac{4\alpha^2}{1-\alpha} = \frac{K P^\circ}{P_0} = 0{,}2745 = C$

$\Rightarrow 4\alpha^2 + \alpha C - C = 0$ $\Delta = 4.4675$

$\alpha = (-c + \sqrt{\Delta})/8$

(1) $\Rightarrow \alpha = 0{,}2298 \simeq 0{,}23$

(6) $P_{tot} = (1+\alpha)P_0 = 76\,689{,}7\ Pa = 0{,}7569\ atm$

(1) $P_{N_2O_4} = \frac{1-\alpha}{1+\alpha}P_{tot} = (1-\alpha)P_0 = 48\,025{,}8\ Pa = 0{,}4740\ atm$

(1) $P_{NO_2} = \frac{2\alpha}{1+\alpha}P_{tot} = 2\alpha P_0 = 28\,658{,}4\ Pa = 0{,}2829\ atm$

Rq $T = 300K$

$P = 1\ atm$	$\alpha = 0{,}2$	$K = 0{,}1689$
" $0{,}61\ atm$	" $0{,}23$	
" $0{,}05$	" $0{,}67$	

c) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ (gaz)

n ($t=0$: n_0 | 0 | 0 ; $t+dt$: $n_0 - \xi$ | ξ | ξ

c ($t=0$: n_0/V | 0 | 0 ; $t+dt$: $(n_0-\xi)/V$ | ξ/V | ξ/V

(1) à $t=0$ $P_0 = n_0 \frac{RT}{V}$

à $t+dt$ $P = (n_0 + \xi) \frac{RT}{V}$

à t_∞ $P_\infty = 2 n_0 \frac{RT}{V}$ car $\xi_{max} = n_0$ (réaction totale)

(1) $\Rightarrow P_\infty = 2P_0 \Rightarrow P_0 = P_\infty/2 = 0{,}693$ atm

(2) à tout instant :

$P_{SO_2Cl_2} = (n_0 - \xi)\frac{RT}{V}$ et $P = (n_0+\xi)\frac{RT}{V}$

$= (2n_0)\frac{RT}{V} - (n_0+\xi)\frac{RT}{V}$

(1) $= 2P_0 - P$

(3) à $t = 40$ minutes $P_{SO_2Cl_2} = 2 \cdot 0{,}693 - 1{,}008$

(1) $= 0{,}378$ atm

(4) à $t = 40$ min $P_{SO_2Cl_2} = \frac{n_{SO_2Cl_2}}{V} RT \Rightarrow [SO_2Cl_2] = \frac{n_{SO_2Cl_2}}{V} = \frac{P_{SO_2Cl_2}}{RT}$

(1) $\Rightarrow [SO_2Cl_2] = 7{,}4 \frac{mol}{m^3} = 7{,}4$ mmol/l

(5) <u>Cinétique d'ordre 1</u> $v = -\frac{dC}{dt} = kC^1$ avec $C = [SO_2Cl_2]$

$\Rightarrow \ln\frac{C_0}{C} = kt$ et $\frac{C_0}{C} = \frac{P_0}{P_{SO_2Cl_2}} = \frac{P_0}{2P_0 - P}$

(2) $\Rightarrow$ $k = \frac{1}{t}\ln\left(\frac{P_0}{2P_0 - P_{totale}}\right)$

(6) Calcul de $k \Rightarrow k = 0{,}015$ min^{-1} $\forall t$ cqfd.

(1)