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etapa județeană/a municipiului București
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Clasa a XII-a

Varianta 1

BAREM DE EVALUARE ȘI DE NOTARE

Orice modalitate corectă de rezolvare a cerințelor se va puncta corespunzător.

Subiectul I 20 puncte

A) 10 puncte

a)

$$\Delta_c H_{\text{CH}_3\text{OH}(l)}^0 = -a \text{ kJ/mol}$$

$$\Delta_c H_{\text{C}_6\text{H}_6(l)}^0 = -4,5a \text{ kJ/mol}$$

$$n_{\text{CH}_3\text{OH}} = 2x \text{ moli} \Rightarrow m_{\text{CH}_3\text{OH}} = 64 \cdot 10^{-3} x \text{ kg} \dots \text{ se degajă} \dots 2xa \text{ kJ}$$

$$n_{\text{C}_6\text{H}_6} = 3x \text{ moli} \Rightarrow m_{\text{C}_6\text{H}_6} = 234 \cdot 10^{-3} x \text{ kg} \dots \text{ se degaja} \dots 13,5xa \text{ kJ}$$

$$m_{\text{am}} = 298 \cdot 10^{-3} x \text{ kg} \dots \text{ se degajă} \dots Q = 15,5x \text{ kJ}$$

$$Q = q \cdot m \Rightarrow 15,5xa = 37450 \cdot 298 \cdot 10^{-3} x \Rightarrow a = \frac{37450 \cdot 298 \cdot 10^{-3}}{15,5} = 720$$

$$\Delta_c H_{\text{CH}_3\text{OH}(l)}^0 = -a = -720 \text{ kJ/mol}$$

$$\Delta_c H_{\text{C}_6\text{H}_6(l)}^0 = -4,5a = -3240 \text{ kJ/mol}$$

(3 p)

$$n_{\text{CH}_3\text{OH}} = n_{\text{C}_6\text{H}_6} = 1 \text{ mol} \Rightarrow m_{\text{am}} = 110 \text{ g} = 0,11 \text{ kg} \dots \text{ se degajă} \dots (720 + 3240) \text{ kJ}$$

$$q = \frac{3960}{0,11} = 36000 \text{ kJ/kg}$$

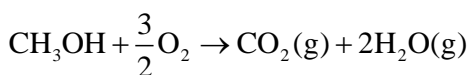
(2 p)

b)

$$q_i = \frac{1000}{M} \cdot |\Delta_c H| \Rightarrow q_i = \frac{1000}{32} \cdot 720 = 22500 \text{ kJ/kg}$$

$$q_s = q_i + n \cdot 44, \text{ unde } n - \text{ numărul de moli de apă care rezultă la arderea unui kg de metanol}$$

(2 p)



$$m_{\text{CH}_3\text{OH}} = 1 \text{ kg} \Rightarrow n_{\text{H}_2\text{O}(\text{g})} = \frac{2}{32} \text{ kmoli} = 62,5 \text{ moli}$$

$$q_s = q_i + n \cdot 44 = 22500 + 62,5 \cdot 44 = 25250 \text{ kJ/kg}$$

(3 p)

B) 10 puncte

$$|Q_{\text{cedat}}| = Q_{\text{primit}}$$

$$n_{\text{NaOH}} = 0,1 \text{ moli} \Rightarrow Q_{\text{primit}} = 0,1 \cdot 41300 = 4130 \text{ J}$$

$$\text{a)} \quad Q = (C + m_s \cdot c) \cdot \Delta t \Rightarrow \Delta t = \frac{Q}{C + m_s \cdot c} = \frac{4130}{3 + 150 \cdot 4,18} = 6,55^\circ$$

$$\Delta t = t - t_i \Rightarrow t = t_i + \Delta t = 26,55^\circ \text{ C}$$

(4 p)

b)

$$n_{\text{NaOH}} = 0,1 \text{ moli} \Rightarrow n_{\text{H}_2\text{O}(\text{formata})} = 0,1 \text{ moli} \Rightarrow \Delta_{\text{neutr}} H = 0,1 \cdot (-57,25) = -5,725 \text{ kJ} = -5725 \text{ J}$$

$$Q_{\text{primit}} = 5725 \text{ J}$$

$$Q = (C + m_{\text{sf}} \cdot c) \cdot \Delta t \Rightarrow \Delta t = \frac{Q}{C + m_{\text{sf}} \cdot c}$$

$$n_{\text{HCl}} = 0,1 \text{ moli} \Rightarrow V_s = 0,1 \text{ L soluție HCl} \Rightarrow m_s = 100 \text{ g soluție HCl}$$

$$m_{\text{sf}} = 150 + 100 = 250 \text{ g soluție NaCl}$$

(4 p)

$$\Delta t = t_f - t_i = \frac{5725}{3 + 250 \cdot 4,18} = 5,46^\circ \Rightarrow t_f = 25,46^\circ \text{ C}$$

(2 p)

Subiectul II 25 puncte

A) 10 puncte

Aplicând legea lui Hess în ciclurile date, rezultă:

$$\text{a)} \quad U_{\text{KI}(\text{s})}^0 + \Delta_{\text{diz}} H_{\text{KI}(\text{s})}^0 = \Delta_{\text{hidr}} H_{\text{K}^+(\text{aq})}^0 + \Delta_{\text{hidr}} H_{\text{I}^-(\text{aq})}^0$$

$$\Rightarrow U_{\text{KI}(\text{s})}^0 = \Delta_{\text{hidr}} H_{\text{K}^+(\text{aq})}^0 + \Delta_{\text{hidr}} H_{\text{I}^-(\text{aq})}^0 - \Delta_{\text{diz}} H_{\text{KI}(\text{s})}^0 = -647,35 \text{ kJ/mol} \quad (5 \text{ p})$$

$$\text{b)} \quad \Delta_f H_{\text{KI}(\text{s})}^0 = \Delta_{\text{subl}} H_{\text{K}(\text{s})}^0 + \frac{1}{2} \Delta_{\text{subl}} H_{\text{I}_2(\text{s})}^0 + \frac{1}{2} \Delta_{\text{disoc}} H_{\text{I}_2(\text{g})}^0 + I_{\text{K}(\text{g})} + A_{\text{I}(\text{g})} + U_{\text{KI}(\text{s})}^0$$

$$\Rightarrow A_{\text{I}(\text{g})} = \Delta_f H_{\text{KI}(\text{s})}^0 - \Delta_{\text{subl}} H_{\text{K}(\text{s})}^0 - \frac{1}{2} \Delta_{\text{subl}} H_{\text{I}_2(\text{s})}^0 - \frac{1}{2} \Delta_{\text{disoc}} H_{\text{I}_2(\text{g})}^0 - I_{\text{K}(\text{g})} - U_{\text{KI}(\text{s})}^0 = -295,2 \text{ kJ/mol} \quad (5 \text{ p})$$

B) 15 puncte

$$\text{a)} \quad (1) \quad \text{I}_{2(\text{s})} \rightarrow \text{I}_{(\text{g})}^+ + \text{I}_{(\text{g})}^- \quad \Delta H_1^0 = ?$$

$$\text{I}_{2(\text{s})} \rightarrow \text{I}_{2(\text{g})} \quad \Delta_{\text{subl}} H_{\text{I}_2(\text{s})}^0 = 62,8 \text{ kJ/mol}$$

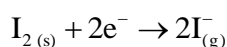
$$\text{I}_{2(\text{g})} \rightarrow 2\text{I}_{(\text{g})} \quad \Delta_{\text{disoc}} H_{\text{I}_2(\text{g})}^0 = 152,5 \text{ kJ/mol}$$

$$\text{I}_{(\text{g})} \rightarrow \text{I}_{(\text{g})}^+ + \text{e}^- \quad I_{\text{I}(\text{g})} = 1008,4 \text{ kJ/mol}$$

$$\text{I}_{(\text{g})} + \text{e}^- \rightarrow \text{I}_{(\text{g})}^- \quad A_{\text{I}(\text{g})} = -295,2 \text{ kJ/mol}$$

$$\Delta H_1^0 = \Delta_{\text{subl}} H_{\text{I}_2(\text{s})}^0 + \Delta_{\text{disoc}} H_{\text{I}_2(\text{g})}^0 + I_{\text{I}(\text{g})} + A_{\text{I}(\text{g})} = +928,5 \text{ kJ/mol} \quad (5 \text{ p})$$

b)



$$\text{I}_{2(\text{s})} \rightarrow \text{I}_{2(\text{g})} \quad \Delta_{\text{subl}} H_{\text{I}_2(\text{s})}^0 = 62,8 \text{ kJ/mol}$$

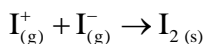
$$\text{I}_{2(\text{g})} \rightarrow 2\text{I}_{(\text{g})} \quad \Delta_{\text{disoc}} H_{\text{I}_2(\text{g})}^0 = 152,5 \text{ kJ/mol}$$



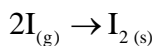
$$\Delta H^0 = \Delta_{\text{subl}} H_{\text{I}_2(\text{s})}^0 + \Delta_{\text{disoc}} H_{\text{I}_2(\text{g})}^0 + 2A_{\text{I}(\text{g})} = -375,1 \text{ kJ/mol} \quad (5 \text{ p})$$

c)

Considerându-se procesele de recombinaire a fragmentelor rezultate în scindările (1) și (2):



$$\Delta H_1^{0'} = -\Delta H_1^0 = -(\Delta_{\text{subl}} H_{\text{I}_2(\text{s})}^0 + \Delta_{\text{disoc}} H_{\text{I}_2(\text{g})}^0 + I_{1 \text{ I}(\text{g})} + A_{\text{I}(\text{g})}) = -928,5 \text{ kJ/mol}$$



$$\Delta H_2^{0'} = -(\Delta_{\text{subl}} H_{\text{I}_2(\text{s})}^0 + \Delta_{\text{disoc}} H_{\text{I}_2(\text{g})}^0) = -215,3 \text{ kJ/mol} \quad (4 \text{ p})$$

Inversul procesului (1) este favorizat energetic, deoarece recombinarea fragmentelor este un proces puternic exoterm. (1 p)

Subiectul III **25 puncte**

a)

$$\text{Oxidare: } \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \quad \varepsilon_1 = \varepsilon_{\text{Zn}^{2+}/\text{Zn}}^0 + \frac{0,059}{2} \lg[\text{Zn}^{2+}] \quad (3 \text{ p})$$

$$\text{Reducere: } 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O} \quad \varepsilon_2 = \varepsilon_{\text{O}_2, \text{H}^+/\text{H}_2\text{O}}^0 + \frac{0,059}{2} \lg([\text{H}^+]^2 \cdot p_{\text{O}_2}^{1/2}) \quad (3 \text{ p})$$

$$[\text{Zn}^{2+}] = [\text{H}^+] = 1\text{M}, \quad P_{\text{O}_2} = 1 \text{ atm}$$

$$E = \varepsilon_2 - \varepsilon_1 = \varepsilon_{\text{O}_2, \text{H}^+/\text{H}_2\text{O}}^0 - \varepsilon_{\text{Zn}^{2+}/\text{Zn}}^0 = 1,229 - (-0,762) = 1,991 \text{ V} > 0 \quad (3 \text{ p})$$

⇒ dizolvarea zincului în soluția data are loc spontan (1 p)

b) În timpul dizolvării Zn, concentrația ionilor Zn^{2+} crește, iar cea a H^+ scade. Procesul încetează atunci când concentrațiile Zn^{2+} și H^+ ajung la astfel de valori încât forța electromotoare, E, este egală cu zero. (3 p)

$$E = \varepsilon_2 - \varepsilon_1 = \varepsilon_{\text{O}_2, \text{H}^+/\text{H}_2\text{O}}^0 - \varepsilon_{\text{Zn}^{2+}/\text{Zn}}^0 + \frac{0,059}{2} \lg \frac{[\text{H}^+]^2}{[\text{Zn}^{2+}]} = 0 \Rightarrow \varepsilon_{\text{O}_2, \text{H}^+/\text{H}_2\text{O}}^0 - \varepsilon_{\text{Zn}^{2+}/\text{Zn}}^0 = \frac{0,059}{2} \lg \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

$$\lg \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} = 67,49 \Rightarrow \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} = 3 \cdot 10^{67} \quad (3 \text{ p})$$

Pe baza raportului de mai sus, se pot evalua concentrațiile ionilor Zn^{2+} și H^+ atunci când procesul încetează. Scăderea concentrației H^+ este de două ori mai rapidă decât creșterea concentrației ionilor Zn^{2+} . Astfel, concentrațiile ionilor Zn^{2+} și H^+ sunt date de ecuațiile:

$$[\text{Zn}^{2+}] = 1 + \Delta C_{\text{Zn}^{2+}} \text{ și } [\text{H}^+] = 1 - \Delta C_{\text{H}^+} = 1 - 2\Delta C_{\text{Zn}^{2+}} \quad (4 \text{ p})$$

$$\frac{1 + \Delta C_{\text{Zn}^{2+}}}{(1 - 2\Delta C_{\text{Zn}^{2+}})^2} = 3 \cdot 10^{67} \Rightarrow (1 - 4\Delta C_{\text{Zn}^{2+}} + 4\Delta C_{\text{Zn}^{2+}}^2) \cdot n = 1 + \Delta C_{\text{Zn}^{2+}}, \text{ unde } n = 3 \cdot 10^{67}$$

$$4n\Delta C_{\text{Zn}^{2+}}^2 - (4n + 1)\Delta C_{\text{Zn}^{2+}} + n - 1 = 0$$

$$4n + 1 \cong 4n \text{ și } n - 1 \cong n$$

$$4n\Delta C_{\text{Zn}^{2+}}^2 - 4n\Delta C_{\text{Zn}^{2+}} + n = 0 \Rightarrow 2\Delta C_{\text{Zn}^{2+}} = 1 \Rightarrow \Delta C_{\text{Zn}^{2+}} = 0,5 \text{ și } \Delta C_{\text{H}^+} = 2\Delta C_{\text{Zn}^{2+}} = 1 \Rightarrow [\text{Zn}^{2+}] = 1,5\text{M} \quad (3 \text{ p})$$

⇒ $[\text{H}^+] = 0$, adică „dizolvarea” Zn încetează atunci când tot HCl s-a consumat în proces. (2 p)

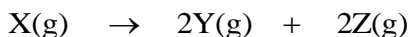
Subiectul IV **30 puncte**

a)

Fie α - gradul de disociere al reactantului X.

$$\alpha = \frac{C_{X(\text{react})}}{C_{0(X)}} = \frac{P_{X(\text{react})}}{P_0} \Rightarrow P_{X(\text{react})} = \alpha \cdot P_0 \Rightarrow P_X = P_0 - P_{X(\text{react})} = (1 - \alpha) \cdot P_0, \text{ unde } P_X - \text{presiunea parțială a}$$

reactantului X la momentul t.



| Momentul | P_X | P_Y | P_Z | P |
|------------------------|--------------------------|---------------------|---------------------|---------------------------|
| t = 0 | P_0 | - | - | |
| t | $(1 - \alpha) \cdot P_0$ | $2\alpha \cdot P_0$ | $2\alpha \cdot P_0$ | $(1 + 3\alpha) \cdot P_0$ |
| t $\rightarrow \infty$ | 0 | $2P_0$ | $2P_0$ | $4P_0$ |

$$\ln \frac{C_{0(X)}}{C_X} = \ln \frac{P_0}{P_X} = \ln \frac{P_0}{(1 - \alpha)P_0} = k \cdot t \Rightarrow \ln \frac{1}{1 - \alpha} = k \cdot t \Rightarrow \alpha = 1 - e^{-k \cdot t}$$

La momentul t: $P = (1 + 3\alpha) \cdot P_0 \Rightarrow P = P_0 + 3(1 - e^{-k \cdot t})P_0 \Rightarrow P = 4P_0 - 3P_0 \cdot e^{-k \cdot t}$

$$\Rightarrow e^{-k \cdot t} = \frac{4P_0 - P}{3P_0} \Rightarrow e^{k \cdot t} = \frac{3P_0}{4P_0 - P} \Rightarrow k \cdot t = \ln \frac{3P_0}{4P_0 - P}$$

$$\Rightarrow k = \frac{1}{t} \ln \frac{3P_0}{4P_0 - P} \quad \text{(6 p)}$$

t = 200 s $\Rightarrow k_1^{(1)} = 10^{-3} \text{ s}^{-1}$

t = 400 s $\Rightarrow k_1^{(2)} = 10^{-3} \text{ s}^{-1}$

t = 600 s $\Rightarrow k_1^{(3)} = 9,99 \cdot 10^{-4} \text{ s}^{-1}$

t = 800 s $\Rightarrow k_1^{(4)} = 10^{-3} \text{ s}^{-1}$

t = 1200 s $\Rightarrow k_1^{(5)} = 10^{-3} \text{ s}^{-1}$

$k_1^{(1)} = k_1^{(2)} = k_1^{(3)} = k_1^{(4)} = k_1^{(5)} = k \Rightarrow$ rezultă că reacția este de ordinul 1. (5 p)

b) Constanta de viteză, la 298 K, este $\Rightarrow k = 10^{-3} \text{ s}^{-1}$ (1 p)

n = 1 $\Rightarrow t_{1/2} = \frac{\ln 2}{k} = \frac{0,693}{10^{-3}} = 693 \text{ s}$ (3 p)

c) La momentul t = 15 min de la începutul reacției

$P = 4P_0 - 3P_0 \cdot e^{-k \cdot t} = (4 - 3 \cdot e^{-k \cdot t})P_0 = 834 \text{ Torr}$ (3 p)

$P_\infty = 4P_0 = 1200 \text{ Torr}$ (3 p)

d) $\ln \frac{P_0}{P_X} = \ln \frac{P_0}{(1 - \alpha)P_0} = k \cdot t \Rightarrow \ln \frac{1}{1 - \alpha} = k \cdot t \Rightarrow k = \frac{1}{t} \ln \frac{1}{1 - \alpha}$

La t = 800 s $\Rightarrow k' = \frac{1}{800} \ln \frac{1}{1 - 0,9} = 2,878 \cdot 10^{-3} \text{ s}^{-1}$ (4 p)

$$k' = A \cdot e^{-\frac{E_a}{RT}}$$

$$k = A \cdot e^{-\frac{E_a}{RT}}$$

$$\ln \frac{k'}{k} = -\frac{E_a}{RT'} + \frac{E_a}{RT} \Rightarrow \frac{R}{E_a} \ln \frac{k'}{k} = -\frac{1}{T'} + \frac{1}{T} \Rightarrow \frac{1}{T'} = \frac{1}{T} - \frac{R}{E_a} \ln \frac{k'}{k} \Rightarrow T' = 403,74 \text{ K (5 p)}$$

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