Pauta Interrogación 2 2° Semestre 2020

1. a) H_2X 1,0 $Ka_1 = 10^{-2}$ 1,0
$Ka_2 = 10^{-7}$ 1,0

b) 100 mL H_2X 0,45 M + 150 mL Hg^{2+} 0,05 M

$C_{H_2X} = \frac{0,45M \cdot 100mL}{250mL} = 0,18M$ 1,0

$C_{Hg} = \frac{0,05M \cdot 150mL}{250mL} = 0,03M$ 1,0

$H_2X + H_2O \rightleftharpoons HX^- + H_3O^+$ Ka_1
$HX^- + H_2O \rightleftharpoons X^{2-} + H_3O^+$ Ka_2

$Hg^{2+} + X^{2-} \rightleftharpoons HgX$ k_1
$HgX + X^{2-} \rightleftharpoons HgX_2^{2-}$ k_2
$HgX_2^{2-} + X^{2-} \rightleftharpoons HgX_3^{4-}$ k_3

$Hg^{2+} + 3X^{2-} \rightleftharpoons HgX_3^{4-}$ K_f } 2,0

$K_f = \frac{[HgX_3^{4-}]}{[Hg^{2+}][X^{2-}]^3} = 1,58 \cdot 10^{47}$ 2,0

BM: $C_{Hg} = [Hg^{2+}] + [HgX] + [HgX_2^{2-}] + [HgX_3^{4-}]$
$C_{X^{2-}} = [H_2X] + [HX^-] + [X^{2-}] + [HgX] + 2[HgX_2^{2-}] + 3[HgX_3^{4-}]$
$C_L = [H_2X] + [HX^-] + [X^{2-}]$ } 1,0

Aproximación: $[HgX_3^{4-}] \gg [Hg^{2+}]; [HgX]; [HgX_2^{2-}]$ } 1,0

$\therefore C_{Hg} = [HgX_3^{4-}] = 0{,}03\ M$

$C_{H_2X} = C_L + 3[HgX_3^{4-}]$

$\therefore C_L = C_{H_2X} - 3[HgX_3^{4-}] = 0{,}18 - 3 \cdot 0{,}03 = 0{,}09\ M$ 2,0

$\alpha_0 = \frac{[H_2X]}{C_L}$; $\alpha_1 = \frac{[HX^-]}{C_L}$; $\alpha_2 = \frac{[X^{2-}]}{C_L}$

$\alpha_0 + \alpha_1 + \alpha_2 = 1$

$\alpha_0 = \frac{[H_3O^+]^2}{[H_3O^+]^2 + K_{a_1}[H_3O^+] + K_{a_1}K_{a_2}} = \frac{10^{-17}}{10^{-17} + 3{,}16 \cdot 10^{-11} + 10^{-9}} = 9{,}7 \cdot 10^{-9}$ 1,0

$\alpha_2 = \frac{K_{a_1}K_{a_2}}{[H_3O^+]^2} \cdot \alpha_0 = \frac{10^{-9}}{10^{-17}} \cdot 9{,}7 \cdot 10^{-9} = 0{,}97$ 1,0

$\therefore [X^{2-}] = \alpha_2 \cdot C_L = 0{,}97 \cdot 0{,}09 = 0{,}0873\ M$ 2,0

$\therefore [Hg^{2+}] = \frac{[HgX_3^{4-}]}{K_f [X^{2-}]^3} = \frac{0{,}03}{1{,}58 \cdot 10^{47} \cdot (0{,}0873)^3} = 2{,}85 \cdot 10^{-46}\ M$ 2,0

Chequeo: $5\%\ [HgX_3^{4-}] \geq [HgX_2^{2-}]$

$[HgX_2^{2-}] = \frac{[HgX_3^{4-}]}{k_3 [X^{2-}]} = \frac{0{,}03}{5 \cdot 10^{18} \cdot 0{,}0873} = 6{,}86 \cdot 10^{-20}\ M$

$\therefore \quad 5\%\ 0{,}03 \geq 6{,}86 \cdot 10^{-20}$

$1{,}5 \cdot 10^{-3} \geq 6{,}86 \cdot 10^{-20}$ ✓

} 1,0

2. a) $Cr(OH)_3$ $pKps = 30,2$ $\therefore Kps = 10^{-30,2} = 6,31 \cdot 10^{-31}$ 3

$Kps = [Cr^{3+}][OH^-]^3 = s(3s)^3 = 27s^4$

$\therefore s = \sqrt[4]{\frac{Kps}{27}} = \sqrt[4]{\frac{6,31 \cdot 10^{-31}}{27}} = 1,24 \cdot 10^{-8}$ M 1,0

$Cd(OH)_2$ $pKps = 14,4$ $\therefore Kps = 10^{-14,4} = 3,98 \cdot 10^{-15}$

$Kps = [Cd^{2+}][OH^-]^2 = s(2s)^2 = 4s^3$

$\therefore s = \sqrt[3]{\frac{Kps}{4}} = \sqrt[3]{\frac{3,98 \cdot 10^{-15}}{4}} = 9,98 \cdot 10^{-6}$ M 1,0

$Zn(OH)_2$ $pKps = 14,8$ $\therefore Kps = 10^{-14,8} = 1,58 \cdot 10^{-15}$

$Kps = [Zn^{2+}][OH^-]^2 = s(2s)^2 = 4s^3$

$\therefore s = \sqrt[3]{\frac{Kps}{4}} = \sqrt[3]{\frac{1,58 \cdot 10^{-15}}{4}} = 7,34 \cdot 10^{-6}$ M 1,0

$\therefore$ Orden de Solubilidad: 1° $Cd(OH)_2$, 2° $Zn(OH)_2$, 3° $Cr(OH)_3$ } 3,0

b) $Cr(OH)_3$ $\quad K_{ps} = [Cr^{3+}][OH^-]^3$

$$[OH^-] = \sqrt[3]{\frac{K_{ps}}{[Cr^{3+}]}} = \sqrt[3]{\frac{6,3 \cdot 10^{-31}}{0,8}} = 9,24 \cdot 10^{-11}\ M \quad 1,0$$

$$\therefore [H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{9,24 \cdot 10^{-11}} = 1,08 \cdot 10^{-4}\ M \quad 1,0$$

1,0 $pH = 3,97$ (pH al cual comenzaría a precipitar $Cr(OH)_3$)

$Cd(OH)_2$ $\quad K_{ps} = [Cd^{2+}][OH^-]^2$

$$[OH^-] = \sqrt{\frac{K_{ps}}{[Cd^{2+}]}} = \sqrt{\frac{3,98 \cdot 10^{-15}}{0,3}} = 1,15 \cdot 10^{-7}\ M \quad 1,0$$

$$\therefore [H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1,15 \cdot 10^{-7}} = 8,68 \cdot 10^{-8}\ M \quad 1,0$$

1,0 $pH = 7,06$ (pH al cual comenzaría a pp $Cd(OH)_2$)

$Zn(OH)_2$ $\quad K_{ps} = [Zn^{2+}][OH^-]^2$

$$[OH^-] = \sqrt{\frac{K_{ps}}{[Zn^{2+}]}} = \sqrt{\frac{1,58 \cdot 10^{-15}}{0,5}} = 5,62 \cdot 10^{-8}\ M \quad 1,0$$

$$\therefore [H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{5,62 \cdot 10^{-8}} = 1,78 \cdot 10^{-7}\ M \quad 1,0$$

1,0 $pH = 6,75$ (pH al cual comenzaría a pp $Zn(OH)_2$)

∴ En el contenedor hay Cr^{3+} y Zn^{2+} 3,0
a pH = 3,97 comienza a pp Cr^{3+} y a pH = 6,75 Zn^{2+}
1,0 1,0

3. a) $Br^- + NO_3^- \rightleftharpoons Br_2 + NO$ 5

$2\,Br^- \rightleftharpoons Br_2 + 2\bar{e} \quad /\cdot 3$

$4H^+ + 3\bar{e} + NO_3^- \rightleftharpoons NO + 2H_2O \quad /\cdot 2$

$6\,Br^- \rightleftharpoons 3Br_2 + 6\bar{e}$

$8H^+ + 6\bar{e} + 2NO_3^- \rightleftharpoons 2NO + 4H_2O$

$8H^+ + 6Br^- + 2NO_3^- \rightleftharpoons 3Br_2 + 2NO + 4H_2O$ 5,0

$$\Delta E = \Delta E^0 - \frac{0,0592}{n} \log \frac{P_{Br_2}^3 \cdot P_{NO}^2}{[H^+]^8 [Br^-]^6 [NO_3^-]^2}$$

$$\Delta E = (0,956 - 1,065) - \frac{0,0592}{6} \log \frac{0,5^3 \cdot 0,3^2}{1^8 \cdot 0,02^6 \cdot 0,5^2} = -0,196\ V$$ 5,0

∴ La reacción, en las condiciones del diagrama, es no espontánea 5,0

b) $\log K_{eq} = \frac{\Delta E^0 \cdot n}{0,0592} = \frac{(0,956 - 1,065) \cdot 6}{0,0592} = -11,05$

$\therefore K_{eq} = 10^{-11,05} = 8,9 \cdot 10^{-12}$ 5,0