2004年硕士生无机化学试题答案 438

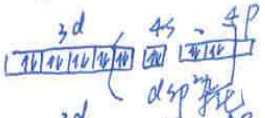
一. 60分

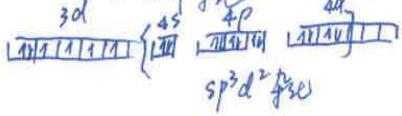
1. < 2. 0.5 3. > > 4. sp^2. sp^3. sp^3d. 平面正三角形. 三角锥形. T形
5. $4d^5 5s^1$. 五. ⅦB. 6 6. 27.2 7. 2.5, 1 8. 取向力. 诱导力. 色散力. 氢
9. $H_2O > NaHCO_3 > Na_2CO_3$ 10 增大. Zn 11. O≡O 2 顺
12. SiO_2 KCl H_2O CCl_4 CO_2 13 $CuI\downarrow + I_2$ $Co^{3+} + I_2$ 14 π_3^4 π_4^6. π_5^6
15. 4.0×10^{-3} 6.0×10^{-3} 16 $Ni(en)_3^{2+}$
17. +2 6 二水合乙二胺四乙酸合铁(II)酸钠
18 (1) < (2) < (3) > (4) > (5) > (6) > (7) > (8) > (9) > (10) <
(11) > > (12) > (13) < (14) < (15) < (16) >
19 TiO^{2+} MnO_4^{2-} $NiCl_2$ $SbOCl\downarrow$ 20 HAc

二. 6×5 = 30分

1. (1) $2Mn^{2+} + 5NaBiO_3 + 14H^+ = 2MnO_4^- + 5Bi^{3+} + 5Na^+ + 7H_2O$
$2MnO_4^- + 3Mn^{2+} + 2H_2O = 5MnO_2 + 4H^+$
(2) $Cr^{3+} + 4OH^- = Cr(OH)_4^-$ 亮绿色溶液. $2Cr(OH)_4^- + 3H_2O_2 + 2OH^- = 2CrO_4^{2-} + 4H_2O$ 黄色溶液.

2. $Fe(CN)_6^{3-}$: Fe^{3+} $3d^5$. ∵低自旋. $\Delta_o > P$. ∴ $d\varepsilon^5$
$Fe(H_2O)_6^{2+}$: Fe^{2+} $3d^6$ ∵ 与 " " $\Delta_o < P$. ∴ $d\varepsilon^4 d\gamma^2$

3. $Ni(CN)_4^{2-}$: Ni^{2+} $3d^8$. ∵ $\mu = 0$. ∴ $n = 0$. 

平面正方形. 逆磁.
CoF_6^{3-}: Co^{3+} $3d^6$ ∵ $\mu = 5.76$. ∴ $n = 0$ 

正八面体. 顺

4. $SnCl_2 + H_2O = Sn(OH)Cl\downarrow + HCl$
$H_3BO_3 + H_2O = [B(OH)_4]^- + H^+$
$PCl_3 + 2H_2O = H_3PO_3 + 3HCl$

5. ∵ Cu^+ $3d^{10}$ 为 18e 构型. 极化力 > Na^+ 8e 构型. ∴ CuCl 共价成份多. 向分子晶体过

三、2.5×4=10分

1. $Cu_2O + H_2SO_4(稀) = CuSO_4 + Cu + H_2O$

2. $2Co(OH)_3 + 6HCl = 2CoCl_2 + 3Cl_2 + 6H_2O$

3. $3I_2 + 6NaOH = 5NaI + NaIO_3 + 3H_2O$

4. $4Ag + 8CN^- + O_2 + 2H_2O = 4Ag(CN)_2^- + 4OH^-$

四、1. 6分 (1) $\Delta H^\theta = \Delta G^\theta + T\Delta S^\theta = 178\ kJ\cdot mol^{-1}$ $T_{min} = \frac{\Delta H^\theta}{\Delta S^\theta} = \frac{178\times10^3}{160} = 1112.5K$

(2) $\lg K^\theta_{298} = \frac{-\Delta G^\theta}{2.303RT} = -22.7836$ $K^\theta_{298} = 1.65\times10^{-23}$

$K^\theta = P_{CO_2}/P^\theta$ $\therefore P_{CO_2} = 1.65\times10^{-23}\times101.3 = 1.66\times10^{-21}\ kPa$

2. 6分 混合后 $C_{Ag^+} = 0.05M$. $C_{CN^-} = 0.20M$ $C_{I^-} = 0.02M$

$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$ $\frac{0.050}{0.1^2x} = 1.3\times10^{21}$. $\therefore C_{Ag^+} = 3.85\times10^{-21}M$

x $0.20-0.050\times2$ 0.050

$=0.10$

$Q = 3.85\times10^{-21}\times0.02 < 8.3\times10^{-17}$. $\therefore$ 无AgI↓.

3. 5分. $\varphi_{PbSO_4/Pb} = -0.126 + \frac{0.059}{2}\lg(1.3\times10^{-4}) = -0.24\ V$

4. 5分 $CaF_{2(s)} + 2H^+ \rightleftharpoons Ca^{2+} + 2HF$. $K^\theta = \frac{C_{Ca^{2+}}\cdot C^2_{HF}}{C^2_{H^+}} = \frac{K^\theta_{sp}}{K^{\theta2}_{HF}} = 0.012$

5. 5分 $NH_4HS_{(s)} \rightleftharpoons NH_3 + H_2S$ $\frac{x(50.6+x)}{P^{\theta2}} = K^\theta$ $P_{H_2S} = 16.8\ kPa$. $P_{NH_3} =$

$P_平/kPa$ $50.6+x$ x

6. 6分 (1) $Cr(OH)_3 + OH^- \rightleftharpoons Cr(OH)_4^-$ $\frac{0.01}{x} = 10^{-0.40}$ $\therefore C_{OH^-} = 0.025M$. $pH = 12.40$

$C_平/M$ x 0.01

(2) $Cr^{3+} + 4OH^- \rightleftharpoons Cr(OH)_4^-$ $K^\theta_f = \frac{[Cr(OH)_4^-]}{[Cr^{3+}][OH^-]^4} = \frac{K^\theta}{K^\theta_{sp}} = 6.3\times10^{29}$

7. 5分 $HCl + NH_3 \rightleftharpoons NH_4Cl + H_2O$ $[OH^-] = 1.8\times10^{-5}$ $pH = 9.26$

0.06 0.06

8. 6分. $[H^+]_1 = \sqrt{cK^\theta_{a1}} = 6.5\times10^{-5}M$. $[H^+]_2 = K^\theta_{a2} = 4.7\times10^{-11}M$ $[H^+]_{H_2O} = [OH^-] = \frac{1\times10^{-14}}{6.5\times10^{-5}}$

9. 6分. $0.77-0.56 = 0.21 = 0.86 + \frac{0.059}{2}\lg K^\theta_{Zn}$. $\therefore K^\theta_{Zn} = 9.2\times10^{-23}$