

普化作业参考答案

第一章 物态

P 38

2、(a) $P = 760 + 200 = 960 \text{ mmHg}$

(b) $P = 250 \text{ mmHg}$

4、已知：以 Hg 为计压计时，1 atm 为 0.76 m

$$P = \frac{F}{S} = \frac{mg}{S} = \frac{\rho Vg}{S} = \frac{\rho \square Sh \square g}{S} = \rho gh$$

$$\therefore \frac{h_{\text{水}}}{h_{\text{Hg}}} = \frac{\rho_{\text{Hg}}}{\rho_{\text{水}}}$$

$$\therefore h_{\text{水}} = \frac{\rho_{\text{Hg}}}{\rho_{\text{水}}} \times h_{\text{Hg}} = \frac{13.5951}{1} \times 0.76 = 10.33 \text{ m}$$

(注：也可以用 $P = \rho gh$ 直接计算)

P45

1、(a) $P_1 V_1 = P_2 V_2$

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{96.3 \text{ kPa} \times 22 \text{ L}}{73.3 \text{ L}} = 28.9 \text{ L}$$

$$(b) \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2},$$

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{96.3 \text{ kPa} \times 22 \text{ L} \times (273.15 - 23) \text{ K}}{0.3 \text{ kPa} \times (273.15 + 18) \text{ K}} \\ = 6068 \text{ L}$$

3、解： $P > 11.5 \text{ MPa}$ 时放气

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_1}{T_2},$$

$$P_2 = \frac{P_1}{T_1} T_2 = \frac{10}{(273.15 - 10)} \times (273.15 + 35) = 11.7 \text{ MPa} > 11.5 \text{ MPa}$$

(自动操作过)

P 48

1、(a)

$$p_{\text{总}} = \frac{nRT}{V} = \frac{0.065 \times 8.314 \times 273.15}{0.5} = 295.2 \text{ kPa}$$

$$p_{\text{H}_2} = \frac{0.015}{0.065} \times 295.2 = 68.1 \text{ kPa}$$

$$p_{\text{He}} = \frac{0.02}{0.065} \times 295.2 = 90.8 \text{ kPa}$$

$$p_{\text{H}_2} = \frac{0.03}{0.065} \times 295.2 = 136.2 \text{ kPa}$$

3、20 摄氏度时空气和水蒸气的总物质的量

$$n_{20} = \frac{101.6 \times 1}{8.314 \times (273.15 + 20)} = 0.0417 \text{ mol}$$

-10 摄氏度时空气和水蒸气的总物质的量

$$n_{-10} = \frac{80.9 \times 1}{8.314 \times (273.15 - 10)} = 0.0370 \text{ mol}$$

$$n_{\text{H}_2\text{O}} = 0.0417 - 0.0370 = 0.0047 \text{ mol}$$

$$m_{\text{H}_2\text{O}} = 0.0047 \times 18 = 0.0846 \text{ g}$$

5、(a) 解：对于 N_2 ，反应前后无 n 的变化

$$\text{则 } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2},$$

$$P_1 = \frac{P_2 V_2 T_1}{V_1 T_2}$$

$$= \frac{110 \text{ kPa} \times 150 \text{ ml} \times (273.15 + 25)}{500 \text{ ml} \times (273.15 + 50)}$$

$$= 30.447 \text{ kPa}$$

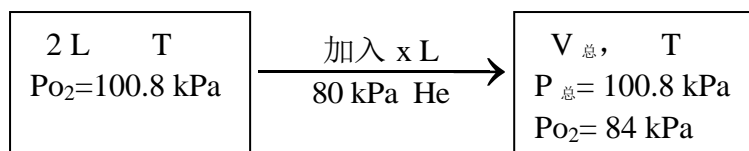
$$(b) P_i V = n_i R T$$

$$n_{\text{SO}_2} = \frac{P_i V}{RT} = \frac{79.553 \text{ kPa} \times 0.5 \text{ L}}{8.314 \text{ kPa} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298.15 \text{ K}}$$

$$= 0.01605 \text{ mol}$$

$$W_{\text{SO}_2} = 0.01605 \times 64 = 1.027 \text{ g}$$

7、解：



$$\text{对 } \text{O}_2: P_1 V_1 = P_2 V_2$$

$$P_{\text{O}_2 \text{始}} V_{\text{始}} = P_{\text{O}_2 \text{终}} V_{\text{总}}$$

$$100.82 \times 2 = 84 V_{\text{总}}$$

$$V_{\text{总}} = 2.4 \text{ L}$$

$$P_1 = \frac{P_2 V_2 T_1}{V_1 T_2}$$

对He: $P_1V_1 = P_2V_2$

$$80 \times x = (100.8 - 84) \times 2.4$$

$$x = 0.504 \text{ L}$$

10、

$$n_{\text{O}_2} = \frac{(101.3 - 2.6) \times 18}{8.314 \times (273.15 + 22)} = 0.724 \text{ mol}$$

$$n_{\text{KClO}_3} = \frac{2}{3} n_{\text{O}_2} = 0.483 \text{ mol}$$

$$m_{\text{KClO}_3} = 0.483 \times 122.5 = 59.17 \text{ g}$$

P 234

2、 $P_{\text{水}} V_{\text{水}} = n_{\text{水}} RT$

$$P = \frac{n_{\text{水}} RT}{V_{\text{总}}} = \frac{\frac{7.3}{18} \times 8.314 \times (273.15 + 80)}{25}$$

$$= 47.63 \text{ kPa}$$

5、(a) $P_{\text{乙醇}} = 7.83 \text{ kPa}$

(b)

$10 \text{ L} \quad P_{\text{乙}} = 100.8 \text{ kPa}$ $P_{\text{空}} = ?$ $P_{\text{总}} = 100 \text{ kPa}$

$0.5 \text{ L} \quad P_{\text{乙}} = 100.8 \text{ kPa}$ $P_{\text{空}} = ?$ $P_{\text{总}} = ?$
--

10L 时, $P_{\text{空}} = 100 - 7.83 = 92.17 \text{ kPa}$

$$P_{\text{空}} V_{\text{空}} = P_{\text{空}}' V_{\text{空}}'$$

$$P_{\text{空}}' = \frac{92.17 \times 10}{0.5} = 1843.4 \text{ kPa}$$

$$P_{\text{总}} = P_{\text{空}}' + P_{\text{乙}} = 1843.4 + 7.83 = 1851.23 \text{ kPa}$$

8、(a)解: $\lg P = -\frac{A}{T} + B$

$$\therefore \lg P = -\frac{1572}{T} + 7.644$$

$$0^\circ\text{C} \text{ 时, } \lg P = -\frac{1572}{273.15} + 7.644 = 1.8889$$

$$P = 77.42 \text{ mmHg}$$

$$40^\circ\text{C} \text{ 时, } \lg P = -\frac{1572}{313.15} + 7.644 = 2.624$$

$$P = 420.7 \text{ mmHg}$$

$$(b) A = + \frac{\Delta H_{\text{vap}}}{2.303R}$$

$$\Delta H_{\text{vap}} = +2.303R \Delta A$$

$$= +2.303 \times 8.314 \times 1572$$

$$= 30099 J / mol = 30.1 kJ / mol$$

P241

4. (a) 以上，画图可知

(b) 有，固相 \rightarrow 气相

P244

2. (a) 液体

(b) 气相

(c) 固相

(d) 气相

3. (a) 液态

(b) 气态

(c) 有，在 51.8 MPa、647.15 K 发生。

4. 解：(a) $P_{H_2} = 6.99 \text{ kPa}$

(b) 已标明为固态氢，所以一定会发生气-固相变

P276

$$3、\text{解：} C = \frac{n_{\text{质}}}{1.0 \text{ dm}^3 \text{ 溶液}}$$

$$= \frac{35.7 / 58.45}{135.7 \text{ g} / 1.2 \text{ cm}^{-3}}$$

$$= \frac{0.61 \text{ mol}}{0.1131 \text{ dm}^3 (113.1 \text{ cm}^3)}$$

$$= 5.39 \text{ mol/L}$$

7、解：25 °C: KCl 38.0g/100g

75 °C: 155.0g/100g

$$25 \text{ °C: } \frac{38}{38+100} \times 100\% = 27.54\%$$

$$75 \text{ °C: } \frac{155}{155+100} \times 100\% = 60.78\%$$

75 °C, 100g 饱和溶液中含水: $100 \times (1 - 60.78\%) = 39.22 \text{ g}$

$$100 \times 60.78\% - (100 - x) \times 27.54\% = x$$

$$\text{所以 } 39.22 \times \frac{155}{100} - 39.22 \times \frac{38}{100} = 45.89 \text{ g}$$

9、解：根据Herry定律：

$$K_c = \frac{P}{C} = \frac{101.3 \text{ kPa}}{0.034 \text{ mol/L}} = 2974.41 \text{ kPa} \cdot \text{mol}^{-1} \cdot \text{L}$$

在大气中

$$C = \frac{P_i}{K_c} = \frac{30 \times 10^{-3} \text{ kPa}}{2974.41 \text{ kPa} \cdot \text{mol}^{-1} \cdot \text{L}} = 1 \times 10^{-5} \text{ mol/L}$$

$$\text{也可以: } C_i = \frac{P_i}{K_c}, C_i' = \frac{P_i'}{K_c}$$

$$\frac{C_i}{C_i'} = \frac{P_i}{P_i'}$$

$$C_i = \frac{P_i}{P_i'} \cdot C_i' = \frac{30}{101.3 \times 10^3} \times 0.034 \text{ mol/L}$$

$$= 1 \times 10^{-5} \text{ mol/L}$$

P260

$$3、b_A = 2.47 \text{ mol} \cdot \text{kg}^{-1}$$

查表10-5得知：苯的 $K_b = 2.53 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$

$$K_f = 4.9 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$$

$$\Delta T_b = K_b \cdot b_A = 2.53 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 2.47 \text{ mol} \cdot \text{kg}^{-1} = 6.25 \text{ K}$$

$$T_b' = 80.1 + 6.25 = 86.35$$

$$\Delta T_f = K_f \cdot b_A = 4.9 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \times 2.47 \text{ mol} \cdot \text{kg}^{-1} = 12.1 \text{ K}$$

$$T_f' = T_f - \Delta T_f = 5.5 - 12.1 = -6.6 \text{ } ^\circ\text{C}$$

4、解：根据表10-5

$$b_A = \frac{\Delta T_f}{K_f} = \frac{[0 - (-4.02) \text{ K}]}{1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}} = 2.16 \text{ mol} \cdot \text{kg}^{-1}$$

$$b_A = n_A = \frac{W_A}{M_A}$$

$$W_A = b_A M_A = 2.16 \times 60 = 129.6 \text{ g} / \text{kg 溶剂}$$

$$\frac{129.6}{129.6 + 1000} \times 100\% = 11.47\%$$

$$1200 \times 11.47\% = 137.64 \text{ g}$$

$$(b) \Delta T_f = b_A K_f$$

$$b_A = \frac{\Delta T_f}{K_f} = \frac{1.1 \text{ K}}{1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}} = 0.59 \text{ mol} \cdot \text{kg}^{-1}$$

6、解：根据凝固点下降

$$\begin{aligned} M_A &= \frac{1000 K_f W_{\text{质}}}{W_{\text{剂}} \Delta T_f} \\ &= \frac{1000 \times 4.9 \times 1g}{8.5g \times (5.5 - 3.37)K} \\ &= 270.6 \text{ g/mol} \end{aligned}$$

设分子式为 $C_xH_yO_z$

$$\frac{12x}{271} = 80.78\% \Rightarrow x=18$$

$$\frac{y}{271} = 13.56\% \Rightarrow y=36$$

$$\frac{16z}{271} = 5.66\% \Rightarrow z=1$$

所以，分子式为： $C_{18}H_{36}O$

7、

$$T_f - T_f' = K_f \times b$$

$$b = 0.24 \text{ mol/kg}$$

$$n = b \times w = 0.24 \times 25.0 \times 10^{-3} = 6.1 \times 10^{-3} \text{ mol}$$

$$M = \frac{m}{n} = 262 \text{ g/mol}$$

分子式 $(C_6H_5)_3P$

$$\begin{aligned} 9、\text{解：} M_{\text{质}} &= \frac{W_{\text{质}} \times R \times T}{\pi \times V_{\text{溶液}}} \\ &= \frac{6.85g \times 8.314 \times 293.15K}{467kPa \times \frac{(100 + 6.85) \times 10^{-3}}{1.024 \text{ dm}^3}} \\ &= \frac{16695.156}{467 \times 0.1043} = 343 \text{ g/mol} \end{aligned}$$

P266

2、

$$M_{C_8H_{18}}=114$$

$$M_{C_9H_{20}}=128$$

$$(a) \chi_{C_8H_{18}} = \frac{\frac{200}{114}}{\frac{200}{114} + \frac{300}{128}} = \frac{1.7544}{1.7544 + 2.3438} = 0.428$$

$$\chi_{C_9H_{20}} = \frac{\frac{300}{128}}{\frac{200}{114} + \frac{300}{128}} = 0.572$$

$$(b) P_{C_8H_{18}} = P^\ominus \chi_{C_8H_{18}} = 13.3 \times 0.428 = 5.69 \text{ kPa}$$

$$P_{C_9H_{20}} = P^\ominus \chi_{C_9H_{20}} = 5.3 \times 0.572 = 3.03 \text{ kPa}$$

$$(c) \chi'_{C_8H_{18}} = \frac{P_{C_8H_{18}}}{P_{\text{总}}} = \frac{5.69}{5.69 + 3.03} = 0.653$$

$$\chi'_{C_9H_{20}} = \frac{P_{C_9H_{20}}}{P_{\text{总}}} = \frac{3.03}{5.69 + 3.03} = 0.347$$

P272

3、查 P256 表 10-5

$$\text{水: } K_b = 0.512 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$$

$$K_f = 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$$

$$b_{NaCl} = \frac{21.2 / 58.5 \times 1000}{135} = 2.68 \text{ mol} \cdot \text{kg}^{-1}$$

$$\Delta T_b = i \cdot k_b \cdot b = 2 \times 0.512 \times 2.68 = 2.74 \text{ K}$$

$$\text{正常沸点: } 100 + 2.74 = 102.74 \text{ } ^\circ\text{C}$$

$$\Delta T_f = i \cdot k_f \cdot b = 2 \times 1.86 \times 2.68 = 9.97 \text{ K}$$

$$\text{正常凝固点: } 0 - 9.97 = -9.97 \text{ } ^\circ\text{C}$$

$$8、C = \frac{n_{\text{质}}}{1\text{L溶液}}$$

$$= \frac{1\text{L} \times 1.005 \times 10^3 \times 0.86\% / 58.5}{1\text{L}}$$

$$= 8.643 / 58.5 = 0.148 \text{ mol/L}$$

$$\Pi = i c r t$$

$$= 2 \times 0.148 \text{ mol/L} \times 0.08206 \text{ atm} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (273.15 + 37) \text{ K}$$

$$= 7.53 \text{ atm}$$

第二章 热力学

P141

$$\begin{aligned} 1、W &= P_{\text{外}} \Delta V \\ &= -5000 \text{ kPa} \times (974 - 542) \text{ L} \\ &= -2.16 \times 10^6 \text{ J} \end{aligned}$$

$$4、q_{\text{冰}} = \frac{3}{4} q_{\text{水}} = \frac{3}{4} \times 4.18 \times 100 = 313.5 \text{ J}$$

P146

2、体系从环境吸热： $q=4.53\text{KJ}$

膨胀，体系对环境做功： $W=2.74\text{KJ}$

$$\Delta U = q - W = 4.53 - 2.74 = 1.79 \text{ KJ}$$

10、解： 可通过 $PV=nRT$ 分别计算出 V_1 , V_2

也可以 $P_1 V_1 = P_2 V_2$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$W = nRT \ln \frac{V_2}{V_1}$$

$$= nRT \ln \frac{P_1}{P_2}$$

$$= \frac{54}{40} \times 8.314 \times 400 \ln \frac{150}{400}$$

$$= -4403.5 \text{ J}$$

\therefore 等温可逆过程，

$$\therefore \Delta U = 0, \Delta T = 0$$

$$W = q$$

$q = -4403.5 \text{ J}$ (体系对环境放热)

$$\Delta H = \Delta U + \Delta PV$$

$$= \Delta U + P_2 V_2 - P_1 V_1$$

$$= \Delta U = 0$$

P152

1、解： $\text{Br}_2(\text{l}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{NaBr}(\text{aq}) + \text{NaBrO}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

体系向环境放热 $q < 0$

$$\Delta_r H_m^\ominus = \frac{q}{n} = -\frac{(121.3 - 2.34) \text{ J}}{2.88 \times 10^{-3} \text{ mol}}$$

$$= -4.13 \times 10^4 \text{ J/mol}$$

$$= -41.3 \text{ KJ/mol}$$

5、 $\text{C}_6\text{H}_6(\text{l}) + 7.5\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$

$$\Delta_c H_{m\text{C}_6\text{H}_6(\text{l})}^\ominus = \Delta_r H_m^\ominus = \Delta U + \Delta nRT$$

$$= \frac{-11.14 \times 3.008}{0.7928/78} + \Delta nRT \quad (q < 0)$$

$$= -3296.8 - 1.5 \times 8.314 \times 2.98 \times 10^{-3}$$

$$= -3300.5 \text{ KJ/mol}$$

$$6、\text{解： (a) } \frac{n}{1} = \frac{q}{\Delta H^{\ominus}}$$

$$\Delta H = q = n \Delta H^{\ominus}$$

$$= \frac{1}{40} \times 302 \text{ KJ/mol}$$

$$= 7.55 \text{ KJ}$$

$$(b) \frac{n}{2} = \frac{q}{\Delta H^{\ominus}}$$

$$\Delta H = q = \frac{1/28}{2} \times 33.3$$

$$= 0.5946 \text{ KJ}$$

$$(c) \frac{n}{1} = \frac{q}{\Delta H^{\ominus}}$$

$$\Delta H = q = n \Delta H^{\ominus}$$

$$= \frac{1}{160} \times (-683)$$

$$= -4.27 \text{ KJ}$$

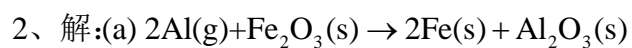
$$(d) \frac{n}{4} = \frac{q}{\Delta H^{\ominus}}$$

$$\Delta H = q = \frac{n}{4} \Delta H^{\ominus}$$

$$= \frac{1/232}{4} \times 472$$

$$= 0.5086 \text{ KJ}$$

P155



$$\Delta_f H_m^{\ominus} \quad 0 \quad -824.2 \quad 0 \quad -1675.7$$

$$\Delta_r H_m^{\ominus} = 1 \times (-1675.7) + 2 \times 0 - [2 \times 0 + 1 \times (-824.2)]$$

$$= -1675.7 + 824.2$$

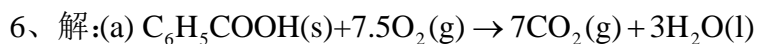
$$= -851.5 \text{ KJ/mol}$$

$$(b) q = \Delta H = n \Delta_r H_m^{\ominus}$$

$$= \frac{3.21}{160} \times (-851.5)$$

$$= -17.08 \text{ KJ}$$

放出热量： 17.08 KJ



(b) $\Delta U^\ominus = \frac{q}{n}$ 放热反应 $q < 0$

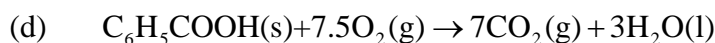
$$= -\frac{9.382 \times 2.15}{0.8/122}$$

$$= -3076.12 \text{ KJ/mol}$$

(c) ∵ 恒容反应

$$\Delta H^\ominus = \Delta U^\ominus + \Delta nRT = -3076.12 - 0.5 \times 8.314 \times 298 \times 10^{-3}$$

$$= 3077.36 \text{ KJ/mol}$$



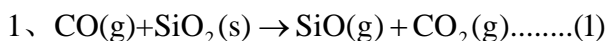
$$\Delta_f H_m^\ominus \quad ? \quad 0 \quad -393.51 \quad -285.83$$

$$\Delta_f H_m^\ominus = -3077.76 \text{ KJ/mol}$$

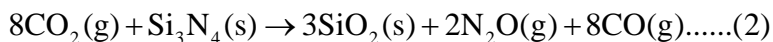
$$\Delta_f H_m^\ominus = \frac{7 \times (-393.51)}{-2754.57} + 3 \times (-285.83) - \Delta_f H_m^\ominus_{\text{C}_6\text{H}_5\text{COOH}(\text{s})}$$

$$\Delta_f H_m^\ominus_{\text{C}_6\text{H}_5\text{COOH}(\text{s})} = -534.7 \text{ KJ/mol}$$

P154

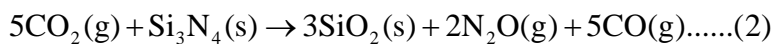


$$\Delta H_1 = 520.9 \text{ KJ/mol}$$



$$\Delta H_2 = 461.05 \text{ KJ/mol}$$

(1) × 3 + (2) 得:

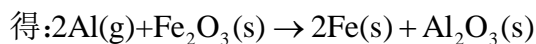


$$\Delta H = \Delta H_1 \times 3 + \Delta H_2$$

$$= 520.9 \times 3 + 461.05$$

$$= 2023.75 \text{ KJ/mol}$$

4、解: $\frac{1}{2} \times (1) - \frac{1}{2} \times (2)$



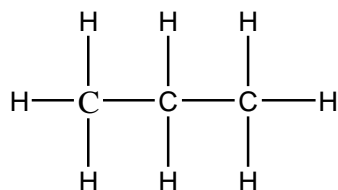
$$\Delta H^\ominus = \frac{1}{2} \Delta H_1^\ominus - \frac{1}{2} \Delta H_2^\ominus$$

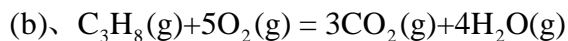
$$= \frac{1}{2} \times (-3351.4) - \frac{1}{2} \times (-1648.4)$$

$$= -851.5 \text{ KJ/mol}$$

P159

3、 (a)





已知: $\text{B.E.}_{\text{C-H}} = 415 \text{ KJ/mol}$

$\text{B.E.}_{\text{O=O}} = 498 \text{ KJ/mol}$

$\text{B.E.}_{\text{C=O}} = 725 \text{ KJ/mol}$

$\text{B.E.}_{\text{O-H}} = 463 \text{ KJ/mol}$

$\text{B.E.}_{\text{C-C}} = 344 \text{ KJ/mol}$

$$\Delta H^\ominus = \sum \text{B.E.}(\text{反应物}) - \sum \text{B.E.}(\text{生成物})$$

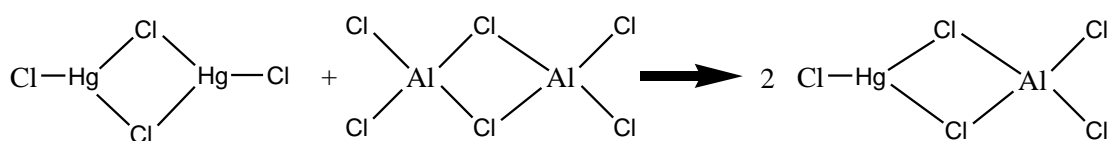
$$= 8\text{B.E.}_{\text{C-H}} + 2\text{B.E.}_{\text{C-C}} + 5\text{B.E.}_{\text{O=O}} - (3 \times 2\text{B.E.}_{\text{C=O}} + 4 \times 2\text{B.E.}_{\text{O-H}})$$

$$= 8 \times 415 + 2 \times 344 + 5 \times 498 - 6 \times 725 - 8 \times 463$$

$$= 3320 + 688 + 2490 - 4350 - 3704$$

$$= -1556 \text{ KJ/mol}$$

5、若此络合物结构为此时，



反应的

$$\Delta H = \sum \text{B.E.}(\text{反应物}) - \sum \text{B.E.}(\text{生成物})$$

$$= [6\text{B.E.}_{\text{Hg-Cl}} + 8\text{B.E.}_{\text{Al-Cl}}] - [2 \times 3\text{B.E.}_{\text{Hg-Cl}} + 2 \times 4\text{B.E.}_{\text{Al-Cl}}]$$

$$= [6\text{B.E.}_{\text{Hg-Cl}} + 8\text{B.E.}_{\text{Al-Cl}}] - [6\text{B.E.}_{\text{Hg-Cl}} + 8\text{B.E.}_{\text{Al-Cl}}]$$

$$= 0$$

$\therefore \Delta H$ 值会很小

若以b结构反应时

$$\Delta H = [4\text{B.E.}_{\text{Hg-Cl}} + \text{B.E.}_{\text{Hg-Hg}} + 8\text{B.E.}_{\text{Al-Cl}}] - [6\text{B.E.}_{\text{Hg-Cl}} + 8\text{B.E.}_{\text{Al-Cl}}]$$

$$= \text{B.E.}_{\text{Hg-Hg}} - 2\text{B.E.}_{\text{Hg-Cl}}$$

反应前后有键能和键的类型变化, $\therefore \Delta H$ 值不会很小

P176

$$1、S_{\text{溶}} = \Delta S = \frac{\Delta H}{T}$$

$$= \frac{35400 \text{ J/mol}}{(273.15 + 3410) \text{ K}}$$

$$= 9.6 \text{ J/mol} \cdot \text{K}$$

$$S_{3683.15 \text{ K}} = \Delta S = 9.6 \text{ J/mol} \cdot \text{K}$$

P179

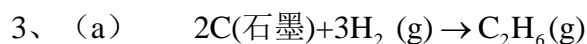
2、(a) $\Delta S > 0$

(b) $\Delta S < 0$

(c) $\Delta S < 0$

(d) $\Delta S > 0$

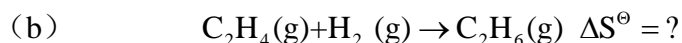
(e) $\Delta S < 0$



$$S^\ominus \text{ J/mol}\cdot\text{K} \quad 5.74 \quad 130.57 \quad 229.49$$

$$\Delta_f S^\ominus = \Delta_r S^\ominus = 229.49 - [3 \times 130.57 + 2 \times 5.74]$$

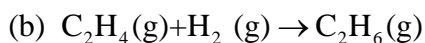
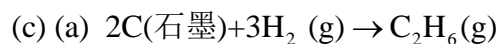
$$= -173.7 \text{ J/mol}\cdot\text{K}$$



$$S^\ominus \text{ J/mol}\cdot\text{K} \quad 219.45 \quad 130.57 \quad 229.49$$

$$\Delta S = 229.49 - 219.45 - 130.57$$

$$= -120.53 \text{ J/mol}\cdot\text{K}$$



对于反应(a)反应前后，气体分数减小了2mol，而反应(b)，反应前后气体分子数仅仅减少了1mol，所以反应(a)的 ΔS^\ominus 比反应(b)的 ΔS^\ominus 更负

4、

$$\Delta_f S^\ominus = 2S^\ominus_{(\text{NO}_2, \text{g})} + 2S^\ominus_{(\text{H}_2\text{O}, \text{l})} - (S^\ominus_{(\text{N}_2\text{H}_4, \text{l})} + 3S^\ominus_{(\text{O}_2, \text{g})})$$

$$= [2 \times 239.95 + 2 \times 69.91 - (121.21 + 3 \times 205.03)]$$

$$= -116.58 \text{ J/mol}\cdot\text{K}^{-1}$$

P181

1、 (a) $\Delta G = \Delta H - T\Delta S$

$$= 5.65 - 170 \times 28.9 \times 10^{-3}$$

$$= 0.737 \text{ KJ/mol}$$

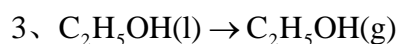
(b) $\Delta G = 3.6 \times 0.737$

$$= 2.653 \text{ KJ}$$

(c) 否

(d) $\Delta G = 0 = \Delta H - T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{5650}{28.9} = 195.5 \text{ K}$$



恒温，可逆过程：已知： $\Delta H = 38.7 \text{ KJ/mol}$

$$\Delta G = 0$$

$$\Delta S_{\text{体}} = \frac{\Delta H}{T} = \frac{38.7 \times 10^3}{78 + 273.15} = 110.2 \text{ J/mol}\cdot\text{K}$$

体系吸热

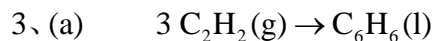
$$q = \Delta H = 38.7 \text{ kJ}$$

$$W = P\Delta v = nRT = 1 \times 8.314 \times (78 + 273.15)$$

$$= 2.92 \text{ kJ} \text{ (膨胀, 体系对环境做功)}$$

$$\Delta U = q - W = 38.7 - 2.92$$

$$= 35.78 \text{ kJ}$$

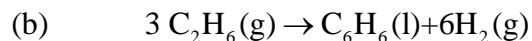
P186

查表 ΔG_f^\ominus 209.2 124.5

$$\Delta G_f^\ominus = 124.5 - 3 \times 209.2$$

$$= -503.1 \text{ kJ/mol} < 0$$

能自发发生

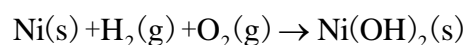
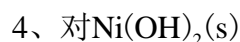


查表 ΔG_f^\ominus -32.89 124.5 0

$$\Delta G_f^\ominus = 124.5 - 3 \times (-32.89)$$

$$= 223.17 \text{ kJ/mol} > 0$$

不能自发发生



$$\Delta G_f^\ominus = \Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

其中 $\Delta H^\ominus = -538.1 \text{ kJ/mol}$, $T = 298 \text{ K}$

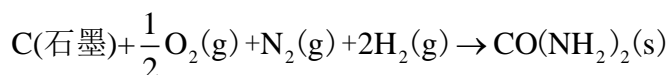
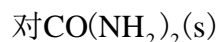
$$\Delta S^\ominus = S_{\text{Ni}(\text{OH})_2} - S_{\text{Ni}} - S_{\text{H}_2} - S_{\text{O}_2}$$

$$= 80 - 205.03 - 130.57 - 29.87$$

$$= -285.74 \text{ J/mol}$$

$$\Delta G_f^\ominus = \Delta G^\ominus = -538.1 - 298 \times (-285.74 \times 10^{-3})$$

$$= -452.95 \text{ kJ/mol}$$



$$\Delta G_f^\ominus_{\text{CO}(\text{NH}_2)_2} = \Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

已知 $\Delta H^\ominus = -333.2 \text{ kJ/mol}$, $T = 298 \text{ K}$

$$\Delta S^\ominus = S_{\text{CO}(\text{NH}_2)_2} - S_{\text{C}} - \frac{1}{2} S_{\text{O}_2} - S_{\text{N}_2} - 2S_{\text{H}_2}$$

$$= 104.6 - 5.74 - \frac{1}{2} \times 205.03 - 191.5 - 2 \times \frac{1}{2} 130.57$$

$$= -456.395 \text{ J/mol} \cdot \text{K}$$

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$= -333.2 - 298 \times (-456.395 \times 10^{-3})$$

$$= -197.2 \text{ kJ/mol}$$

P190

3、

$$(a)\Delta G = \Delta H - T\Delta S$$

$$\Delta H = [2 \times 0 + 3 \times (-393.51) - 2 \times (-842.87) + 3 \times 0]$$

$$= 505.21 \text{ KJ/mol}$$

$$T\Delta S = 298 \times [2 \times 32.64 + 3 \times 213.63 - (2 \times 75.90 + 3 \times 5.74)] \times 10^{-3}$$

$$= 160.07 \text{ KJ/mol}$$

$$\therefore \Delta G = 345.14 \text{ KJ/mol} > 0 \text{ 不能进行}$$

$$(b)\Delta G = \Delta H - T\Delta S \leq 0$$

$$T \geq \frac{\Delta H}{\Delta S} = 940.54 \text{ K}$$

第三章 化学平衡

P286

2. 解:

$$(a) 2H_2(g) + O_2(g) = 2H_2O(g), K_p = \frac{P_{H_2O}^2}{P_{H_2}^2 P_{O_2}}; K_c = \frac{[H_2O]^2}{[H_2]^2 [O_2]}$$

$$(b) Xe(g) + 3F_2(g) = XeF_6(g), K_p = \frac{P_{XeF_6}}{P_{Xe} P_{F_2}^3}; K_c = \frac{[XeF_6]}{[F_2]^3 [Xe]}$$

$$(c) CO(g) + Cl_2(g) = COCl_2(g), K_p = \frac{P_{COCl_2}}{P_{CO} P_{Cl_2}}; K_c = \frac{[COCl_2]}{[CO] [Cl_2]}$$

$$(d) 2Cl_2(g) + O_2(g) = 2Cl_2O(g), K_p = \frac{P_{Cl_2O}^2}{P_{Cl_2}^2 P_{O_2}}; K_c = \frac{[Cl_2O]^2}{[Cl_2]^2 [O_2]}$$

$$(e) N_2(g) + O_2(g) + Br_2(g) = 2NOBr(g), K_p = \frac{P_{NOBr}^2}{P_{N_2} P_{O_2} P_{Br_2}}; K_c = \frac{[NOBr]^2}{[N_2] [O_2] [Br_2]}$$

5. 解:

$$(a) CO(g) + H_2O(g) = H_2(g) + CO_2(g), K_p = \frac{P_{H_2} P_{CO_2}}{P_{CO} P_{H_2O}}$$

$$(b) CO(g) + H_2O(g) = H_2(g) + CO_2(g)$$

$$10 \text{ kPa} \quad 10 \text{ kPa} \quad P_{H_2} \quad 70 \text{ kPa}$$

$$K_p = \frac{P_{H_2} P_{CO_2}}{P_{CO} P_{H_2O}} = 3.6 \Rightarrow P_{H_2} = 5.14 \text{ kPa}$$

P293

2. 解:

$$(a) 8H_2(g) + S_8(s) = 8H_2S(g), K_p = \frac{P_{H_2S}^8}{P_{H_2}^8}; \text{无量纲}$$

$$(b) C(s) + H_2O(l) + Cl_2(g) = COCl_2(g) + H_2(g), K_p = \frac{P_{COCl_2} P_{H_2}}{P_{Cl_2}}; \text{单位: kPa}$$

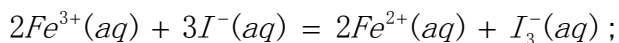
$$(c) Zn(s) + CO_2(g) = ZnO(s) + CO(g), K_p = \frac{P_{CO}}{P_{CO_2}}; \text{单位: 无量纲}$$

$$(d) MgSO_4(s) = Mg(s) + SO_3(g), K_p = P_{SO_3}; \text{单位: kPa}$$

$$(e) 3C_2H_2(g) = C_6H_6(l), K_p = \frac{1}{P_{C_2H_2}^3}; \text{单位: (kPa)}^{-3}$$

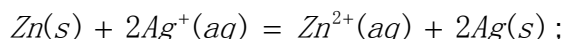
3. 解:

(a) .



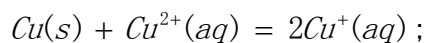
$$K_c = \frac{[Fe^{2+}]^2[I_3^{-}]}{[Fe^{3+}]^2[I^{-}]^3}; \text{ 单位: } (mol/L)^2$$

(b) .



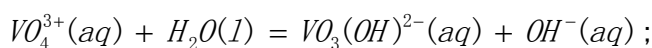
$$K_c = \frac{[Zn^{2+}]}{[Ag^{+}]^2}; \text{ 单位: } (mol/L)^{-1}$$

(c) .



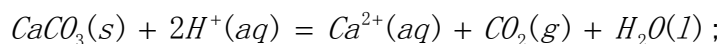
$$K_c = \frac{[Cu^{+}]^2}{[Cu^{2+}]}; \text{ 单位: } mol/L$$

(d) .



$$K_c = \frac{[VO_3(OH)^{2-}][OH^{-}]}{[VO_4^{3+}]}; \text{ 单位: } mol/L$$

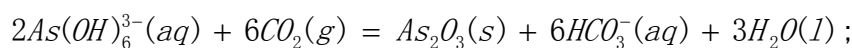
(e) .



$$K = \frac{[Ca^{2+}]P_{CO_2}}{[H^{+}]^2}; \text{ 单位: } atm \cdot (mol/L)^{-1} \text{ 或 } kPa \cdot (mol/L)^{-1}$$

$$\text{或 } K_c = \frac{[Ca^{2+}][CO_2]}{[H^{+}]^2}; \text{ 单位: 无量纲}$$

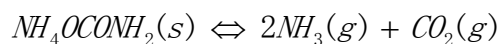
(f) .



$$K_c = \frac{[HCO_3^{-}]^6}{[As(OH)_6^{3-}]^2[CO_2]^6}; \text{ 单位: } (mol/L)^{-2}$$

$$\text{或 } K = \frac{[HCO_3^{-}]^6}{[As(OH)_6^{3-}]^2 P_{CO_2}^6}; \text{ 单位: } (mol/L)^4 \cdot kPa^{-6} \text{ 或 } (mol/L)^4 \cdot atm^{-6}$$

7. 解:



$$2x \quad x$$

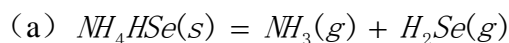
$$(a) \quad 2x + x = 11.6 \Rightarrow x = 3.87 kPa$$

$$\therefore P_{NH_3} = 2 \times 3.87 = 7.74 kPa, P_{CO_2} = 3.87 kPa$$

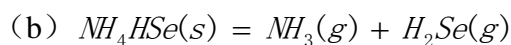
$$(b) \quad K_p = P_{NH_3}^2 \cdot P_{CO_2} = 7.74^2 \times 3.87 = 231.8 kPa^3$$

$$K^\theta = \left(\frac{P_{NH_3}}{P^\theta} \right)^2 \frac{P_{CO_2}}{P^\theta} = 2.23 \times 10^{-4}$$

8. 解:



平衡时: $P_{\text{NH}_3} = P_{\text{H}_2\text{Se}} = 1.86 / 2 = 0.93 \text{ kPa}$
 $\Rightarrow K_p = 0.93 \text{ kPa} \times 0.93 \text{ kPa} = 0.86 \text{ kPa}^2$

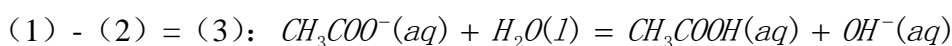
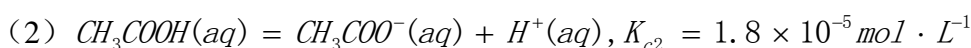
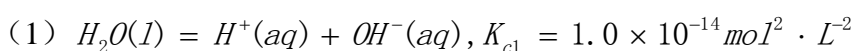


平衡时: 2.55 kPa

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{Se}} \Rightarrow P_{\text{H}_2\text{Se}} = K_p / P_{\text{NH}_3} = 0.86 \text{ kPa}^2 / 2.55 \text{ kPa} = 0.34 \text{ kPa}$$

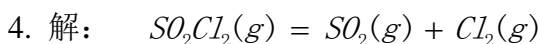
P296

6. 解:



$$\therefore K_{c3} = \frac{K_{c1}}{K_{c2}} = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10} \text{ mol} \cdot \text{L}^{-1}$$

P300



$$(a) \text{始: } P_{\text{SO}_2\text{Cl}_2} = \frac{nRT}{V} = \frac{3.714 / 135 \times 0.082 \times 373}{1} = 0.842 \text{ atm} = 85.3 \text{ kPa}$$

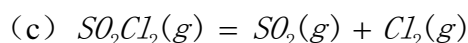
平衡: 85.3-x x x

$$85.3 - x + x + x = 131.7, \text{解得 } x = 46.4$$

$$\therefore P_{\text{SO}_2} = P_{\text{Cl}_2} = 46.4 \text{ kPa} = 0.459 \text{ atm}; P_{\text{SO}_2\text{Cl}_2} = 85.3 - 46.4 = 38.9 \text{ kPa} = 0.383 \text{ atm}$$

$$(b) K_p = \frac{P_{\text{SO}_2} P_{\text{Cl}_2}}{P_{\text{SO}_2\text{Cl}_2}} = \frac{46.4 \times 46.4}{38.9} \text{ kPa} = 53.96 \text{ kPa} = 0.52 \text{ atm}$$

$$K_c = K_p (RT)^{-\Delta n} = 53.96 \text{ kPa} \cdot (8.314 \times 373)^{-1} = 0.0174 \text{ mol} / \text{L}$$



3.6×10⁻⁴ mol/L 6.9×10⁻³ mol/L

$$K_c = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]}$$

$$\Rightarrow [\text{SO}_2] = \frac{K_c [\text{SO}_2\text{Cl}_2]}{[\text{Cl}_2]} = \frac{0.0174 \times 3.6 \times 10^{-4}}{6.9 \times 10^{-3}} = 9.1 \times 10^{-4} \text{ mol/L}$$

7. 解: $Br_2(g) + I_2(g) = 2IBr(g)$

初: 5 kPa 4 kPa

平: 5-x 4-x 2x

$$K_p = \frac{P_{IBr}^2}{P_{Br_2} P_{I_2}} = \frac{(2x)^2}{(5-x)(4-x)} = 322, \text{ 解得 } x = 3.84 \text{ kPa}$$

$$\therefore P_{Br_2} = 5 - 3.84 = 1.16 \text{ kPa}, P_{I_2} = 4 - 3.84 = 0.16 \text{ kPa}$$

$$P_{IBr} = 2 \times 3.84 = 7.68 \text{ kPa}$$

P306

4. 解: $P_4(g) = 2P_2(g)$

(a) 初: 500 kPa 200 kPa

$$Q = \frac{P_{P_2}^2}{P_{P_4}} = \frac{(200 \text{ kPa})^2}{(500 \text{ kPa})} = 80 \text{ kPa} > K, \therefore \text{反应逆向进行, 由右向左趋于平衡}$$

(b) 初: 500 kPa 200 kPa

终: 500+x 200-2x

或: $500 + \frac{1}{2}x$ 200-x

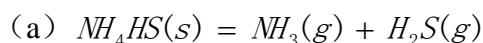
$$K_p = \frac{(200-x)^2}{500 + \frac{1}{2}x} = 62, \text{ 解得 } x = 22 \text{ kPa}$$

$$\therefore P_{P_4} = 500 + 22 / 2 = 511 \text{ kPa}, P_{P_2} = 200 - 22 = 178 \text{ kPa}$$

(c) 体系体积增加, 相当于压强减小, 反应朝着分子数增加的方向进行, 说明 P4 分解

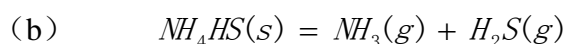
P309

25. 解:



平: $P_{NH_3} = P_{H_2S} = P_{\text{总}} / 2 = 33.4 \text{ kPa}$

$$K_p = P_{NH_3} \cdot P_{H_2S} = 33.4 \times 33.4 = 1115.56 (\text{kPa})^2$$



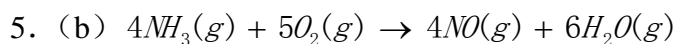
新平衡: 76 kPa x

$$K_p = P_{NH_3} \cdot P_{H_2S} = 76 \times x = 1115.56, \text{ 解得 } x = 14.7 \text{ kPa}$$

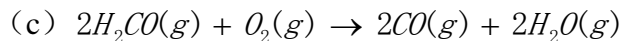
$$\therefore P_{H_2S} = x = 14.7 \text{ kPa} = 0.145 \text{ atm}$$

第四章 动力学

P473



$$\nu = -\frac{d[NH_3]}{4dt} = -\frac{d[O_2]}{5dt} = \frac{d[NO]}{4dt} = \frac{d[H_2O]}{6dt}$$



$$\nu = -\frac{d[H_2CO]}{2dt} = -\frac{d[O_2]}{dt} = \frac{d[CO]}{2dt} = \frac{d[H_2O]}{2dt}$$

P478

3. (a) $-\frac{d[CH_3I]}{dt} = k[C_5H_5N]^m[CH_3I]^n$

(b) $\lg \nu = \lg k + m \lg [C_5H_5N] + n \lg [CH_3I]$

$$\lg 7.5 \times 10^{-7} = \lg k + m \lg 1.0 \times 10^{-4} + n \lg 1.0 \times 10^{-4}$$

$$\lg 3.0 \times 10^{-6} = \lg k + m \lg 2.0 \times 10^{-4} + n \lg 2.0 \times 10^{-4}$$

$$\lg 6.0 \times 10^{-6} = \lg k + m \lg 2.0 \times 10^{-4} + n \lg 4.0 \times 10^{-4}$$

解得: $n = 1, m = 1, k = 75$

\therefore 反应为二级反应, k 单位为: $mol^{-1} \cdot L \cdot s^{-1}$

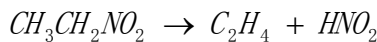
(c) $\nu = k[C_5H_5N][CH_3I]$
 $= 75 \times 5.0 \times 10^{-5} \times 2.0 \times 10^{-5} = 7.5 \times 10^{-8} mol^{-1} \cdot L \cdot s^{-1}$

6. 解: 已知 $P_0=100 \text{ kPa}$, $P=50 \text{ kPa}$, $k=2.2 \times 10^{-5} s^{-1}$

$$\ln \frac{P}{P_0} = -kt \Rightarrow \ln \frac{1}{2} = -2.2 \times 10^{-5} \times t, \text{ 解得 } t = 31507s$$

$$\text{或: } t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} = 31507s$$

8. 解:



$$\ln \frac{c}{c_0} = -kt \Rightarrow \ln \frac{P}{7.9} = -1.9 \times 10^{-4} \times 3 \times 3600 = -2.052$$

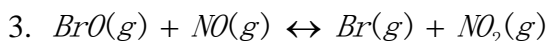
$$\text{解得 } P = 1.015KPa$$

9. 解: 一级反应

$$\ln \frac{c}{c_0} = -kt \Rightarrow \ln \frac{0.0016}{0.0096} = -k \times 340$$

$$\text{解得 } k = 5.27 \times 10^{-3} s^{-1}$$

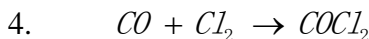
P489



\therefore 是基元反应

$$\therefore k_{\text{平}} = \frac{k_+}{k_-} \Rightarrow k_- = \frac{k_+}{k_{\text{平}}} = \frac{1.3 \times 10^{10} L \cdot mol \cdot s^{-1}}{5 \times 10^{10}} = 0.26 L \cdot mol \cdot s^{-1}$$

$$\therefore k = 0.26 L \cdot mol \cdot s^{-1}$$



解: 因为(3)是速率控制步骤, 所以

$$\frac{d[COCl_2]}{dt} = k_3[ClCO][Cl_2]$$

$$\text{对 (1)} \frac{[Cl]^2}{[Cl_2]} = K_1 = \frac{k_1}{k_{-1}} \Rightarrow [Cl] = \sqrt{\frac{k_1}{k_{-1}}} [Cl_2]$$

$$\text{对 (2)} \frac{[ClCO]}{[Cl][CO]} = K_2 = \frac{k_2}{k_{-2}} \Rightarrow [ClCO] = \frac{k_2}{k_{-2}} [Cl][CO] = \frac{k_2}{k_{-2}} \sqrt{\frac{k_1}{k_{-1}}} [Cl_2] \cdot [CO]$$

$$\frac{d[COCl_2]}{dt} = k_3[ClCO][Cl_2] = k_3 \frac{k_2}{k_{-2}} \sqrt{\frac{k_1}{k_{-1}}} [Cl_2] \cdot [CO][Cl_2] = k[Cl_2]^{\frac{2}{3}}[CO]$$

$$\text{其中 } k = k_3 \frac{k_2}{k_{-2}} \left(\frac{k_1}{k_{-1}} \right)^{\frac{1}{2}}$$

6. 用稳态近似:

$$\frac{d_{N_2}}{dt} = k_4[NH_3NO^+]$$

设中间体 $[NH_3NO^+]$ 生成和消耗的速率相等,

$$k_4[NH_3NO^+] = k_3[NH_3][NO^+] \Rightarrow [NH_3NO^+] = \frac{k_3}{k_4}[NH_3][NO^+]$$

$$\frac{k_1}{k_{-1}} = \frac{[NO^+]}{[HNO_2][H^+]} \Rightarrow [NO^+] = \frac{k_1}{k_{-1}}[HNO_2][H^+]$$

$$\frac{k_2}{k_{-2}} = \frac{[NH_3][H^+]}{[NH_4^+]} \Rightarrow [NH_3] = \frac{k_2[NH_4^+]}{k_{-2}[H^+]}$$

$$\text{代入 } \frac{d_{N_2}}{dt} = k_4 \frac{k_3}{k_4}[NH_3][NO^+] = k_3 \frac{k_1}{k_{-1}}[HNO_2][H^+] \frac{k_2[NH_4^+]}{k_{-2}[H^+]}$$

$$= K[HNO_2][NH_4^+], \text{ 其中 } K = k_3 \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}}$$

或者用速率控制步骤

$$\frac{d_{N_2}}{dt} = v_3 = k_4 \frac{k_3}{k_4}[NH_3][NO^+]$$

$$\frac{k_1}{k_{-1}} = \frac{[NO^+]}{[HNO_2][H^+]} \Rightarrow [NO^+] = \frac{k_1}{k_{-1}}[HNO_2][H^+]$$

$$\frac{k_2}{k_{-2}} = \frac{[NH_3][H^+]}{[NH_4^+]} \Rightarrow [NH_3] = \frac{k_2[NH_4^+]}{k_{-2}[H^+]}$$

$$\text{代入 } v = k_3 \frac{k_1}{k_{-1}}[HNO_2][H^+] \frac{k_2[NH_4^+]}{k_{-2}[H^+]} = k_3 \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}}[HNO_2][NH_4^+]$$

$$= K[HNO_2][NH_4^+]$$

P495

2. 解: (a) $\lg \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$

$$T_1 = 273 + 30 = 303 \text{ K}, T_2 = 313 \text{ K}$$

$$k_1 = 1.94 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

$$E_a = 161 \text{ kJ/mol}$$

$$\Rightarrow \lg \frac{k_2}{1.94 \times 10^4} = \frac{161 \times 10^3}{2.303 \times 8.314} \left(\frac{313 - 303}{313 \times 303} \right) = 0.8866$$

$$\Rightarrow k_2 = 1.49 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

(b) 根据 k 单位可判定反应为二级反应,

$$t_{1/2} = \frac{1}{k[A]_0}, t_{\frac{1}{2}, 303K} = \frac{1}{k_{303K}[A]_0}$$

$$\therefore \frac{t_{\frac{1}{2}, 313K}}{t_{\frac{1}{2}, 303K}} = \frac{k_{303K}}{k_{313K}} \Rightarrow t_{\frac{1}{2}, 313K} = \frac{1.94 \times 10^4}{1.49 \times 10^5} \times 1 \times 10^4 = 1.3 \times 10^3 \text{ s}$$

P495

5.

$$\Delta E = E_a - E_a'$$

$$E_a' = E_a - \Delta E$$

$$= 3.5 - (-66.8)$$

$$= 70.3 \text{ KJ/mol}$$

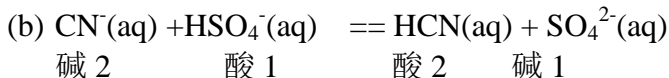
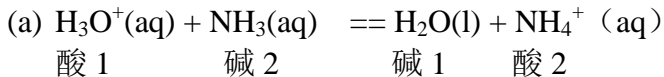
第五章 酸碱、沉淀、络合平衡**P313**

1、

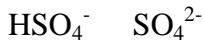
B 酸 (a) HI (f) NH_4^+ B 碱 (b) CH_3COO^- (d) PO_4^{3-} (e) ClO_2^- 二者均可 (c) H_2PO_4^- 2、(a) SO_4^{2-} (b) HCOO^- (c) H_2PO_4^- H_2PO_2^- (d) OH^- (e) $\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ 3、(a) H_2SO_3 (b) $\text{C}_5\text{H}_5\text{NH}^-$ $\text{C}_5\text{H}_5\text{NH}^+$ (c) HCO_3^- (d) $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^-$ $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+$ (e) $\text{NH}_3^+\text{CH}_2\text{COOH}$

P313

4、



B 酸	共轭碱
H_2O	OH^-
H_2S	HS^-
H_2SO_4	HSO_4^-
H_2SO_3	HSO_3^-
H_2CO_3	HCO_3^-
$\text{H}_2\text{C}_2\text{O}_4$	HC_2O_4^-
H_2PO_4^-	HPO_4^{2-}
H_2PO_3^-	HPO_3^{2-}
$\text{H}_2\text{P}_2\text{O}_7^{4-}$	$\text{HP}_2\text{O}_7^{3-}$
$\text{H}_2\text{SiO}_4^{2-}$	HSiO_4^{3-}
H_2SiO_3^-	HSiO_3^{2-}
H_2SiO_2	HSiO_2^-
H_2SiO	HSiO^-
H_2Si	HSi^-
H_2Si^{2-}	HSi^{3-}
H_2Si^{3-}	HSi^{4-}
H_2Si^{4-}	HSi^{5-}
H_2Si^{5-}	HSi^{6-}
H_2Si^{6-}	HSi^{7-}
H_2Si^{7-}	HSi^{8-}
H_2Si^{8-}	HSi^{9-}
H_2Si^{9-}	HSi^{10-}
$\text{H}_2\text{Si}^{10-}$	HSi^{11-}
$\text{H}_2\text{Si}^{11-}$	HSi^{12-}
$\text{H}_2\text{Si}^{12-}$	HSi^{13-}
$\text{H}_2\text{Si}^{13-}$	HSi^{14-}
$\text{H}_2\text{Si}^{14-}$	HSi^{15-}
$\text{H}_2\text{Si}^{15-}$	HSi^{16-}
$\text{H}_2\text{Si}^{16-}$	HSi^{17-}
$\text{H}_2\text{Si}^{17-}$	HSi^{18-}
$\text{H}_2\text{Si}^{18-}$	HSi^{19-}
$\text{H}_2\text{Si}^{19-}$	HSi^{20-}
$\text{H}_2\text{Si}^{20-}$	HSi^{21-}
$\text{H}_2\text{Si}^{21-}$	HSi^{22-}
$\text{H}_2\text{Si}^{22-}$	HSi^{23-}
$\text{H}_2\text{Si}^{23-}$	HSi^{24-}
$\text{H}_2\text{Si}^{24-}$	HSi^{25-}
$\text{H}_2\text{Si}^{25-}$	HSi^{26-}
$\text{H}_2\text{Si}^{26-}$	HSi^{27-}
$\text{H}_2\text{Si}^{27-}$	HSi^{28-}
$\text{H}_2\text{Si}^{28-}$	HSi^{29-}
$\text{H}_2\text{Si}^{29-}$	HSi^{30-}
$\text{H}_2\text{Si}^{30-}$	HSi^{31-}
$\text{H}_2\text{Si}^{31-}$	HSi^{32-}
$\text{H}_2\text{Si}^{32-}$	HSi^{33-}
$\text{H}_2\text{Si}^{33-}$	HSi^{34-}
$\text{H}_2\text{Si}^{34-}$	HSi^{35-}
$\text{H}_2\text{Si}^{35-}$	HSi^{36-}
$\text{H}_2\text{Si}^{36-}$	HSi^{37-}
$\text{H}_2\text{Si}^{37-}$	HSi^{38-}
$\text{H}_2\text{Si}^{38-}$	HSi^{39-}
$\text{H}_2\text{Si}^{39-}$	HSi^{40-}
$\text{H}_2\text{Si}^{40-}$	HSi^{41-}
$\text{H}_2\text{Si}^{41-}$	HSi^{42-}
$\text{H}_2\text{Si}^{42-}$	HSi^{43-}
$\text{H}_2\text{Si}^{43-}$	HSi^{44-}
$\text{H}_2\text{Si}^{44-}$	HSi^{45-}
$\text{H}_2\text{Si}^{45-}$	HSi^{46-}
$\text{H}_2\text{Si}^{46-}$	HSi^{47-}
$\text{H}_2\text{Si}^{47-}$	HSi^{48-}
$\text{H}_2\text{Si}^{48-}$	HSi^{49-}
$\text{H}_2\text{Si}^{49-}$	HSi^{50-}
$\text{H}_2\text{Si}^{50-}$	HSi^{51-}
$\text{H}_2\text{Si}^{51-}$	HSi^{52-}
$\text{H}_2\text{Si}^{52-}$	HSi^{53-}
$\text{H}_2\text{Si}^{53-}$	HSi^{54-}
$\text{H}_2\text{Si}^{54-}$	HSi^{55-}
$\text{H}_2\text{Si}^{55-}$	HSi^{56-}
$\text{H}_2\text{Si}^{56-}$	HSi^{57-}
$\text{H}_2\text{Si}^{57-}$	HSi^{58-}
$\text{H}_2\text{Si}^{58-}$	HSi^{59-}
$\text{H}_2\text{Si}^{59-}$	HSi^{60-}
$\text{H}_2\text{Si}^{60-}$	HSi^{61-}
$\text{H}_2\text{Si}^{61-}$	HSi^{62-}
$\text{H}_2\text{Si}^{62-}$	HSi^{63-}
$\text{H}_2\text{Si}^{63-}$	HSi^{64-}
$\text{H}_2\text{Si}^{64-}$	HSi^{65-}
$\text{H}_2\text{Si}^{65-}$	HSi^{66-}
$\text{H}_2\text{Si}^{66-}$	HSi^{67-}
$\text{H}_2\text{Si}^{67-}$	HSi^{68-}
$\text{H}_2\text{Si}^{68-}$	HSi^{69-}
$\text{H}_2\text{Si}^{69-}$	HSi^{70-}
<	



P318

4、

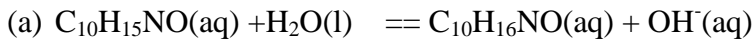
$$pH = 7.4 = -\lg[H_3O^+]$$

$$[H_3O^+] = 10^{-7.4} = 3.98 \times 10^{-8}$$

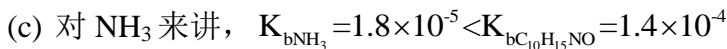
$$[OH^-] = K_w / [H_3O^+] = \frac{2.4 \times 10^{-14}}{3.98 \times 10^{-8}} = 6.03 \times 10^{-7}$$

P320

1、



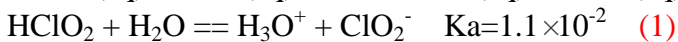
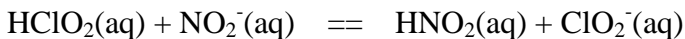
$$\text{(b) } K_a = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.4 \times 10^{-4}} = 7.14 \times 10^{-11}$$



所以，它的碱性比氨强

P320

3、



上式=(1)-(2)

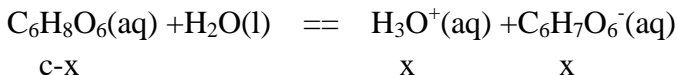
$$K = \frac{K_{a1}}{K_{a2}} = \frac{1.1 \times 10^{-2}}{4.55 \times 10^{-4}} = 23.9$$

所以 HClO_2 是较强的 B 酸，而其共轭碱 ClO_2^- 是较弱的 B 碱

HNO_2 是较弱的 B 酸, 而其共轭碱 NO_2^- 是较强的 B 碱

P330

2、



$$C = \frac{0.5 / 176}{0.1} = 0.0284 \text{ mol} / L$$

$$\frac{C}{K_a} = \frac{0.0284}{8 \times 10^{-5}} = 355 < 400$$

$$K_a = \frac{x^2}{c - x} = 8 \times 10^{-5}$$

$$x = 1.47 \times 10^{-3}$$

$$pH = -\lg[H_3O^+] = 2.83$$

P330

5、

$$C = \frac{0.1}{1.00} = 0.100 \text{ mol} / L$$

$$\frac{C}{K_a} < 400$$

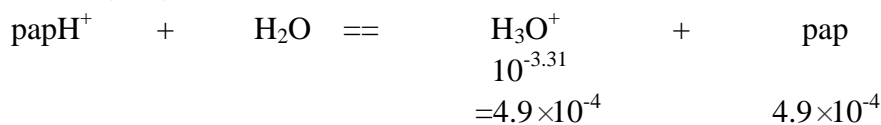
$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a C}}{2} = \frac{-0.033 + \sqrt{0.033^2 + 4 \times 0.033 \times 0.100}}{2} = 0.04327$$

$$pH = -\lg 0.04327 = 1.36$$

P330

6、

papH⁺Cl在水中完全电离



$$0.205 - 4.9 \times 10^{-4}$$

$$K_a = \frac{(4.9 \times 10^{-4})^2}{0.205 - 4.9 \times 10^{-4}} = 1.17 \times 10^{-6}$$

P330

10、

两者完全反应生成 CH₃COONa, CH₃COONa 在水中完全电离, 为 CH₃COO⁻
CH₃COO⁻是一元弱碱,

$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.68 \times 10^{-10}$$

$$\frac{C}{K_b} \geq 400$$

$$[OH^-] = \sqrt{K_b C} = \sqrt{5.68 \times 10^{-10} \times 0.0500} = 5.33 \times 10^{-6}$$

$$pOH = -\lg[OH^-] = -\lg(5.33 \times 10^{-6}) = 5.27$$

$$pH = 14 - pOH = 14 - 5.27 = 8.73$$

P346

1、

$$K_{a1} \ll K_{a2}$$

$$\frac{C}{K_{a1}} = \frac{0.01}{1.26 \times 10^{-3}} = 7.93 < 400$$

$$[H_3O^+] = \frac{-K_{a1} + \sqrt{K_{a1}^2 + 4K_{a1}C}}{2}$$

$$= \frac{-1.26 \times 10^{-3} + \sqrt{(1.26 \times 10^{-3})^2 + 4 \times 1.26 \times 10^{-3} \times 0.01}}{2}$$

$$= 2.98 \times 10^{-3}$$

$$[ph^{2-}] = K_{a2} = 3.1 \times 10^{-6}$$

$$[Hph^-] = [H_3O^+] = 2.98 \times 10^{-3}$$

$$[H_2ph] = \frac{[H_3O^+][Hph^-]}{K_{a1}} = \frac{(2.98 \times 10^{-3})^2}{1.26 \times 10^{-3}} = 7.02 \times 10^{-3}$$

P346

3、

$$K_c = \frac{P_1}{C_1} \text{ 或 } K_c' = \frac{P_1}{C_1} = \frac{P_2}{C_2}$$

$$P_1 V_1 = n_1 RT \Rightarrow n_1 = \frac{101.3 \times 0.806 \times 10^{-3}}{8.314 \times 293}$$

$$n_1 = 3.35 \times 10^{-5}$$

$$C_1 = \frac{n_1}{V_1} = \frac{3.35 \times 10^{-5}}{10^{-3}} = 3.35 \times 10^{-2}$$

$$\frac{P_1}{C_1} = \frac{P_2}{C_2} \Rightarrow$$

$$C_2 = \frac{C_1}{P_1} P_2 = 5.03 \times 10^{-2}$$

也可以直接用

$$P_2 V_1 = n_2 RT$$

$$n_2 = 5.03 \times 10^{-5} \text{ mol}$$

$$c_2 = 5.03 \times 10^{-5} \text{ mol/L}$$

$$[H_2CO_3] = 5.03 \times 10^{-2} \text{ mol/L}$$

$$K_{a1} = 4.3 \times 10^{-7}$$

$$K_{a2} = 4.8 \times 10^{-11}$$

$$K_{a1} \gg K_{a2} \quad \frac{C_{H_2CO_3}}{K_{a1}} > 400$$

$$[H_3O^+] = \sqrt{cK_{a1}} = \sqrt{5.03 \times 10^{-2} \times 4.3 \times 10^{-7}} = 1.47 \times 10^{-4}$$

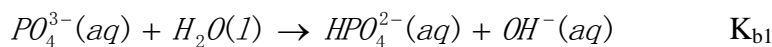
$$pH = -\lg[H_3O^+]$$

$$= 4 - \lg 1.47$$

$$= 3.83$$

P347

4、

 H_3PO_4 的 $K_{a1}=7.5\times 10^{-3}$, $K_{a2}=6.2\times 10^{-8}$, $K_{a3}=2.0\times 10^{-13}$ Na_3PO_4 是三元弱碱, 当一元弱碱处理。 PO_4^{3-} 的 $c=0.05\text{mol/L}$ 平衡时: $c-x$ x x

$$K_{b1} = \frac{K_w}{K_{a3}} = \frac{1 \times 10^{-14}}{2.0 \times 10^{-13}} = 0.05$$

$$\frac{C}{K_{b1}} < 400$$

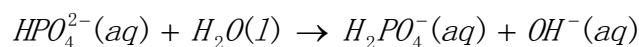
$$[\text{OH}^-] = \frac{-K_{b1} + \sqrt{K_{b1}^2 + 4K_{b1}c}}{2}$$

$$= \frac{-0.05 + \sqrt{0.05^2 + 4 \times 0.05 \times 0.050}}{2} = 0.0309$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{0.0309} = 3.24 \times 10^{-13}$$

$$[\text{HPO}_4^{2-}] = [\text{OH}^-] = 0.0309$$

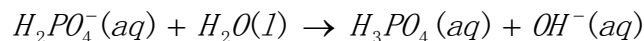
$$[\text{PO}_4^{3-}] = 0.050 - 0.0309 = 0.0191$$



$$K_{b2} = \frac{K_w}{K_{a2}} = \frac{1 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.61 \times 10^{-7}$$

$$K_{b2} = \frac{[\text{H}_2\text{PO}_4^-] \times [\text{OH}^-]}{[\text{HPO}_4^{2-}]} = [\text{H}_2\text{PO}_4^-]$$

$$[\text{H}_2\text{PO}_4^-] = K_{b2} = 1.61 \times 10^{-7}$$



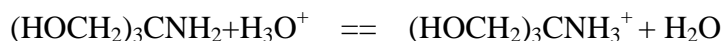
$$K_{b3} = \frac{K_w}{K_{a3}} = \frac{1 \times 10^{-14}}{7.5 \times 10^{-3}} = 1.33 \times 10^{-12}$$

$$K_{b3} = \frac{[\text{H}_3\text{PO}_4] \times [\text{OH}^-]}{[\text{H}_2\text{PO}_4^-]}$$

$$[\text{H}_3\text{PO}_4] = \frac{K_{b3}[\text{H}_2\text{PO}_4^-]}{[\text{OH}^-]} = \frac{1.33 \times 10^{-12} \times 1.61 \times 10^{-7}}{0.0309} = 6.93 \times 10^{-18}$$

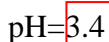
P351

1、

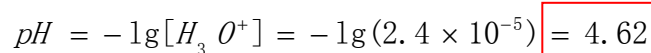


$$\text{pH} = 14 - 5.92 = 8.08$$

等 mol 反应最后, 生成强酸弱碱盐



2、

$$pH = -\lg[H_3O^+] = -\lg(4.5 \times 10^{-5}) = 4.35$$


4、

$$\text{甲酸 } K_a = 1.77 \times 10^{-4}$$

$$pH = pK_a + \lg \frac{C_{\text{共轭碱}}}{C_{\text{共轭酸}}}$$

$$\lg \frac{C_{\text{共轭碱}}}{C_{\text{共轭酸}}} = 4 - pK_a = 0.25$$

$$\frac{C_{\text{共轭碱}}}{C_{\text{共轭酸}}} = 1.77$$

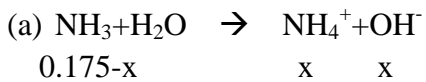
$$\frac{\frac{V * C_{NaOH}}{V + 0.5}}{0.5C_{\text{甲酸}} - \frac{V * C_{NaOH}}{V + 0.5}} = 1.77$$

$$\frac{0.05V}{0.1 * 0.5 - 0.05V} = 1.77$$

$$V = 0.639L$$

P353

11、



$$1.8 \times 10^{-5} = K_b = \frac{x^2}{0.175 - x}$$

$$x = 0.00177$$

$$pOH = 2.75$$

$$pH = 11.25$$



$$[\text{NH}_3] = [\text{NH}_4^+]$$

$$[\text{H}_3\text{O}^+] = K_w / K_b$$

$$pH = 9.25$$

(c) 计量点时，先设全是 $[\text{NH}_4^+]$

$$V_{HCl} = \frac{V_{NH_3} C_{NH_3}}{C_{HCl}} = \frac{140.0 * 0.175}{0.106} = 231.1$$

$$V_{\text{总}} = 231.1 + 140 = 371.1$$

$$C_{NH_4Cl} = \frac{140.0 * 0.175}{371.1} = 0.066$$

$$\frac{x^2}{0.066} = \frac{10^{-14}}{1.8 * 10^{-5}}$$

$$x = 6.06 \times 10^{-6}$$

$$pH = 5.22$$

$$(d) C_{HCl} = \frac{1 \times 0.106}{372.1} = 0.0002849$$

$$pH = 3.54$$

P355

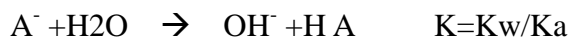
30、

(a)未知酸为 50ml



$$K_a = \frac{4x \times [H^+]}{x} = 4 \times 10^{-4.5} = 1.26 \times 10^{-4}$$

(b)计量点时，浓度为 0.05mol/L，可认为生成 NaA

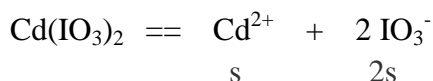


$$\frac{x^2}{0.05} = \frac{10^{-14}}{1.26 \times 10^{-4}}$$

$$x = 1.99 \times 10^{-6} \quad pH = 8.30 \quad pOH = 5.70$$

$$pH = 5.70$$

P359/3



$$[IO_3^-] = 2 \times 1.79 \times 10^{-3} = 3.58 \times 10^{-3} \text{ mol/L}$$

$$K_{sp} = [Cd^{2+}][IO_3^-]^2 = 4s^3 = 2.29 \times 10^{-8}$$

P359/4



$$[Pb^{2+}] = \frac{0.00896 \div 557}{0.4} = 4.02 \times 10^{-5}$$

$$[IO_3^-] = 2 \times 4.02 \times 10^{-5} = 8.04 \times 10^{-5}$$

$$K_{sp} = 4.02 \times 10^{-5} \times (8.04 \times 10^{-5})^2 = 2.6 \times 10^{-13}$$

P359/6

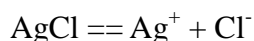
$$n_{AgCl} = \frac{1.8 \times 10^{-2}}{143.5} = 1.25 \times 10^{-4} \text{ mol/L}$$

$$C_{AgCl} = \frac{1.25 \times 10^{-4}}{1} = 1.25 \times 10^{-4}$$

$$[Ag^+] = [Cl^-] = 1.25 \times 10^{-4}$$

$$K_{sp} = 1.56 \times 10^{-8}$$

P365/1



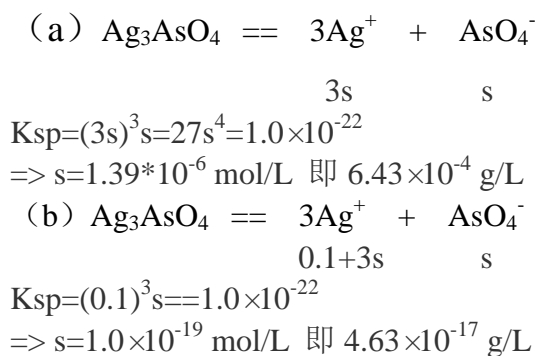
$$x \quad 0.5-x$$

$$K_{sp}=x(0.15+x)=1.6 \times 10^{-10}$$

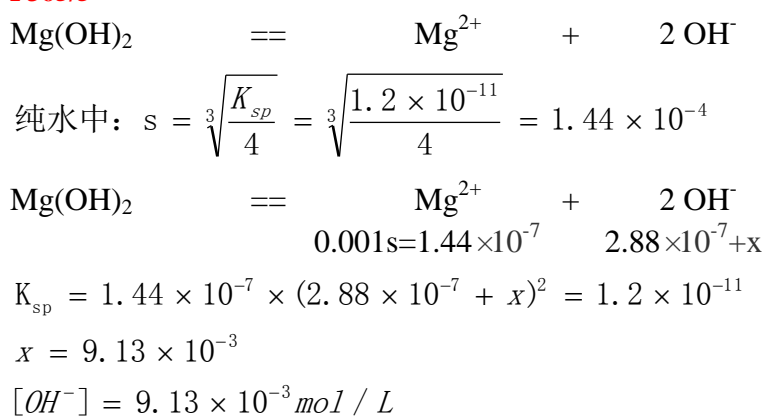
解得 $x=1.07 \times 10^{-9} \text{ mol/L}$

则 $m=1.07 \times 10^{-9} \times 0.1 \times 143.5=1.53 \times 10^{-8} \text{ g}$

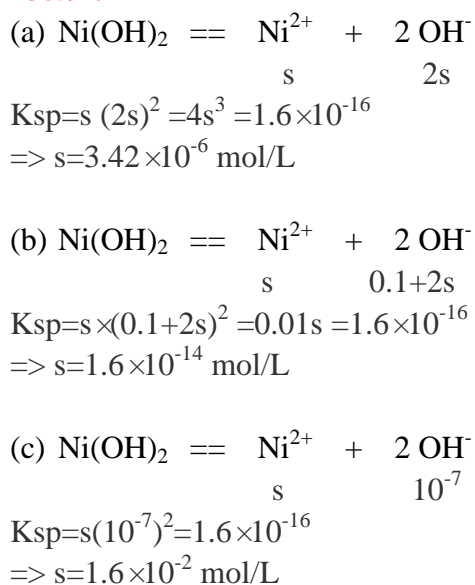
P365/2



P365/5



P365/10



P369/3

$$[Pb^{3+}] = \frac{0.05 \times 0.05}{0.09} = 2.78 \times 10^{-2} \text{ mol/L}$$

$$[IO_3^-] = \frac{0.2 \times 0.04}{0.09} = 8.89 \times 10^{-2}$$

$$\begin{aligned} Pb(IO_3)_2 &== Pb^{2+} + 2 IO_3^- \\ [IO_3^-] &= 8.89 \times 10^{-2} - 2 \times 2.78 \times 10^{-2} \\ &= 3.33 \times 10^{-2} \text{ mol/L} \end{aligned}$$

$$[Pb^{2+}] = \frac{K_{sp}}{[IO_3^-]^2} = 2.34 \times 10^{-10} \text{ mol/L}$$

P369/6

$$[Sr^{2+}] = \frac{0.08 \times 0.04}{0.12} = 2.67 \times 10^{-2}$$

$$[F^-] = \frac{0.05 \times 0.08}{0.12} = 3.33 \times 10^{-2}$$

$$\begin{aligned} Sr^{2+} + 2F^- &--> SrF_2 \\ 2.67 \times 10^{-2} - 0.5 \times 3.33 \times 10^{-2} \\ &= 1.0 \times 10^{-2} \text{ mol/L} \end{aligned}$$

$$[F^-] = \sqrt{\frac{K_{sp}}{[Sr^{2+}]}} = \sqrt{\frac{2.8 \times 10^{-9}}{1.0 \times 10^{-2}}} = 5.29 \times 10^{-4} \text{ mol/L}$$

P377/5

NH_4^+ 的 $K_a = 5.6 \times 10^{-10}$, NH_4NO_3 的摩尔质量:80.04g/mol

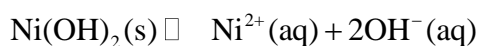
$$C_{\text{Ni}^{2+}} = \frac{0.0100 \times 40.0}{10.0 + 40.0} = 0.008(\text{mol/L})$$

$$C_{\text{NH}_3} = \frac{0.100 \times 10.0}{10.0 + 40.0} = 0.020(\text{mol/L})$$

$$K_b = K_w / K_a = 1 \times 10^{-14} / 5.6 \times 10^{-10} = 1.79 \times 10^{-5}$$

$$C_{\text{NH}_3} \geq 400K_b$$

$$[\text{OH}^-] = \sqrt{K_b C_{\text{NH}_3}} = \sqrt{1.79 \times 10^{-5} \times 0.020} = 5.98 \times 10^{-4}$$



$$Q_c = C_{\text{Ni}^{2+}} C_{\text{OH}^-}^2 = 0.008 \times (5.98 \times 10^{-4})^2 = 2.86 \times 10^{-9} > K_{sp}$$

(a) 有 $\text{Ni}(\text{OH})_2$ 沉淀形成。

(b) 欲抑制沉淀的形成, 需满足 $Q_c \leq K_{sp}$

$$\text{即 } C_{\text{Ni}^{2+}} C_{\text{OH}^-}^2 \leq K_{sp}, \quad C_{\text{OH}^-} \leq \sqrt{\frac{K_{sp}}{C_{\text{Ni}^{2+}}}} \quad (1)$$

加入 NH_4NO_3 后, NH_4NO_3 与 NH_3 形成缓冲溶液。

$$C_{\text{H}_3\text{O}^+} = \frac{K_a C_a}{C_b}, \quad C_{\text{OH}^-} = \frac{K_w}{C_{\text{H}_3\text{O}^+}} = \frac{K_w C_b}{(K_a C_a)}, \text{代入(1)式得:}$$

$$\frac{K_w C_b}{K_a C_a} \leq \sqrt{\frac{K_{sp}}{C_{\text{Ni}^{2+}}}}$$

$$C_a \geq \frac{K_w C_b \times \sqrt{\frac{C_{\text{Ni}^{2+}}}{K_{sp}}}}{K_a} = \frac{1 \times 10^{-14} \times 0.020 \times \sqrt{\frac{0.008}{1.6 \times 10^{-16}}}}{5.6 \times 10^{-10}} = 2.525(\text{mol/L})$$

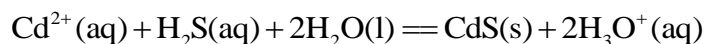
$$m = C_a V_M \geq 2.525 \times 0.05 \times 80.04 = 10.1(\text{g})$$

需要在上述混合溶液中加 ≥ 10.1 克固体硝酸铵才能抑制沉淀的形成。

$$\text{注: 恰好没有沉淀形成时, } [\text{OH}^-] = \sqrt{\frac{K_{sp}}{C_{\text{Ni}^{2+}}}} = \sqrt{2} \times 10^{-7} \text{ mol/L}$$

$$\text{形成的缓冲溶液中, } c_{\text{NH}_4^+} = \frac{K_b C_{\text{NH}_3}}{[\text{OH}^-]} = 2.53 \text{ mol/L}$$

P380-5



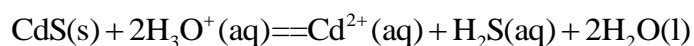
0.1	0.3
x	2x
0.1-x	0.3+2x

$$K_{sp,a} = \frac{[\text{Cd}^{2+}][\text{H}_2\text{S}]}{[\text{H}_3\text{O}^+]^2} = \frac{(0.1-x) \times 0.1}{(0.3+2x)^2} = 8 \times 10^{-7}$$

$$x = 0.1 - 2 \times 10^{-6}$$

$$[\text{Cd}^{2+}] = 2 \times 10^{-6} \quad [\text{H}_3\text{O}^+] = 0$$

注：另一种算法：设 CdS 的溶解度为 x (设小数)



$$\begin{array}{ccc} 0.5 & 0 & 0.1 \\ 0.5-2x & x & 0.1 \end{array}$$

$$K_{\text{sp},a} = \frac{[\text{Cd}^{2+}][\text{H}_2\text{S}]}{[\text{H}_3\text{O}^+]^2} = \frac{x \times 0.1}{(0.5 - 2x)^2} = 8 \times 10^{-7}$$

可得 $x = 2 \times 10^{-6}$

即 $[\text{Cd}^{2+}] = 2 \times 10^{-6} \text{ mol/L}$

$[\text{H}^+] = 0.5 \text{ mol/L}$

P393-4

(a) V +2

(b) Mo +2

(c) Co +2

(d) Ni 0

(e) Re +3

(f) Fe +3

P393-5

(a) $\text{Na}_2[\text{Zn}(\text{OH})_4]$

(b) $[\text{CoCl}_2(\text{en})_2]\text{NO}_3$

(c) $[\text{PtBr}(\text{H}_2\text{O})_3]\text{Cl}$

(d) $[\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_4]\text{Br}_2$

(e) $\text{K}_2[\text{Co}(\text{NCS})_4]$

(f) $\text{Na}_3[\text{VF}_6]$

(g) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$

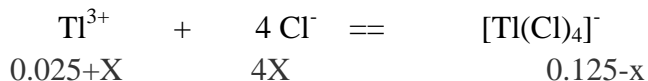
P393-6

(a) 四异硫氰根*二氨合铬(III)酸铵

(b) 碘化五羰基合钨(I)

(c) 五氰合锰(IV)酸钾

P405-1



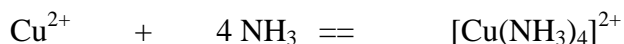
$$\frac{(0.025 + x)(4x)^4}{0.125 - x} = K_{\text{不稳}} = 10^{-18}$$

$$x = 1.18 \times 10^{-5}$$

$$[\text{Ti}^{3+}] = 0.025$$

$$[\text{TiCl}_4] = 0.125$$

P405-2



$$\begin{array}{ccc} X & 1.5-4(0.1-x) & 0.1-x \\ & 1.1+4x & \end{array}$$

$$\frac{0.1-x}{(1.1+4x)^4 \times x} = 2.1 \times 10^{13}$$

$$X = 3.25 \times 10^{-15}$$

$$[\text{Cu}^{2+}] = 3.25 \times 10^{-15}$$

$$[\text{NH}_3] = 1.1$$

$$[\text{Cu}(\text{NH}_3)]^{2+} = \beta_1 [\text{Cu}^{2+}][\text{NH}_3] = 7.15 \times 10^{-11}$$

$$[\text{Cu}(\text{NH}_3)_2]^{2+} = \beta_2 [\text{Cu}^{2+}][\text{NH}_3]^2 = 3.78 \times 10^{-7}$$

$$[\text{Cu}(\text{NH}_3)_3]^{2+} = \beta_3 [\text{Cu}^{2+}][\text{NH}_3]^3 = 4.76 \times 10^{-4}$$

$$[\text{Cu}(\text{NH}_3)_4]^{2+} = 0.1$$

P405-4

$\text{K}^+ + 18\text{-冠-6} = \text{K 配合物}$

$$x \quad 0.26+x+y \quad 0.02-x \quad K_K = 1.41 \times 10^6$$

$\text{Cs}^+ + 18\text{-冠-6} = \text{Cs 配合物}$

$$y \quad 0.26+x+y \quad 0.02-y \quad K_{\text{Cs}} = 2.75 \times 10^4$$

$$\frac{0.02-x}{x(0.26+x+y)} = 1.41 \times 10^6$$

$$\frac{0.02-y}{y(0.26+x+y)} = 2.75 \times 10^4$$

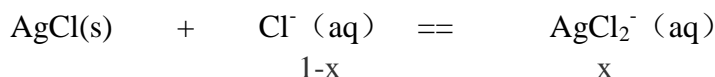
$$[\text{K}^+] = x = 5.46 \times 10^{-8} \text{ mol/L}$$

$$[\text{Cs}^+] = y = 2.80 \times 10^{-6} \text{ mol/L}$$

P412-1

纯水中: $s = 1.26 \times 10^{-5}$

1molNaCl 中



$$k = K_{sp} \cdot \beta_2 = \frac{x}{1-x} = 1.76 \times 10^{-5}$$

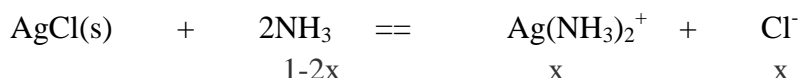
$$X = 1.76 \times 10^{-5} > 1.26 \times 10^{-5}$$

在 0.1molNaCl 中

$$k = \frac{x}{0.1-x} = 1.76 \times 10^{-5}$$

$$X = 1.76 \times 10^{-6} < 1.26 \times 10^{-5}$$

P412-2



$$\frac{x^2}{(1-2x)^2} = K_{sp} \times K_f = 1.6 \times 10^{-10} \times 1.1 \times 10^7$$

$$X = 0.039$$

$$m_{\text{AgCl}} = 143.5 \times 0.039 = 5.6 \text{ g}$$

P418-10

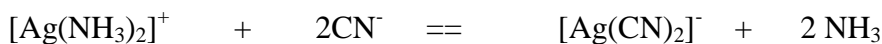
八面体构型

P418-11**[CoCl₂(en)]** 没有几何异构体, 也没有光学异构体**[CoClBr(en)]** 没有几何异构体, 也没有光学异构体**P418-15**

$$(a) \Delta G = \Delta G_1 - \Delta G_2 = -41.4 + 55.6 = 14.2 \text{ KJ/mol}$$

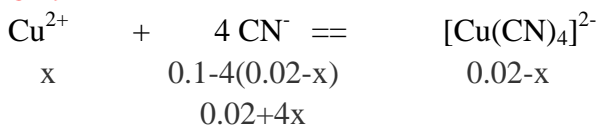
$$(b) \Delta G = RT \ln K^\ominus \quad K^\ominus = 3.25 \times 10^{-3}$$

$$(c) Q = \frac{1 \times 1}{6^2} = 2.8 \times 10^{-2} > K^\ominus \quad \text{则平衡向逆向移动}$$

P418-16

$$K = \frac{K_f[\text{Ag}(\text{CN})_2]^-}{K_f[\text{Ag}(\text{NH}_3)_2]^+} = 1.18 \times 10^{14}$$

$$\Delta G = -RT \ln K = -8.314 \times 298 \times \ln 1.18 \times 10^{14} \\ = -80.28 \text{ KJ/mol}$$

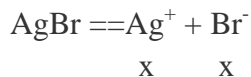
P418-19

$$K = \frac{0.02 - x}{(0.02 + 4x)^4 \times x} = 2 \times 10^{30}$$

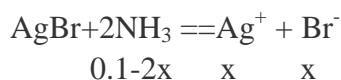
$$x = 6.25 \times 10^{-26}$$

P418-23

纯水中:



$$x = \sqrt{K_{sp}} = \sqrt{7.7 \times 10^{-13}} = 8.77 \times 10^{-7} \text{ mol/L}$$



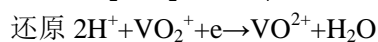
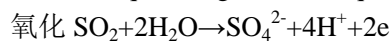
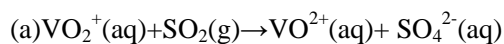
$$\frac{x^2}{(0.1 - 2x)^2} = 7.7 \times 10^{-13} \times 1.1 \times 10^7$$

$$\text{解得 } x = 2.89 \times 10^{-4}$$

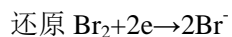
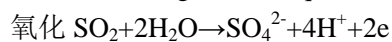
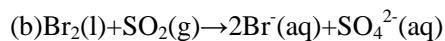
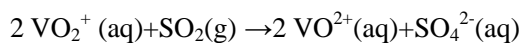
第六章 氧化还原

P423

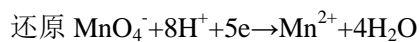
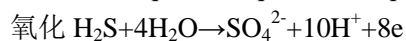
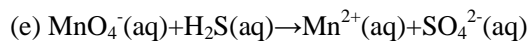
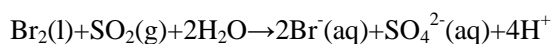
5、



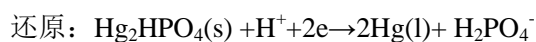
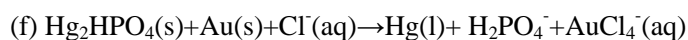
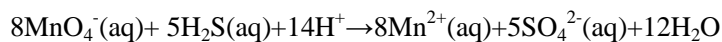
氧化+还原 $\times 2$



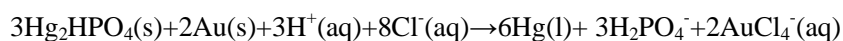
氧化+还原



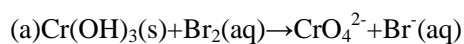
氧化 $\times 5$ +还原 $\times 8$



氧化 $\times 2$ +还原 $\times 3$

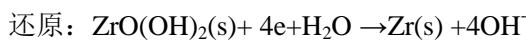
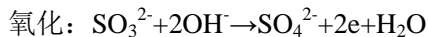
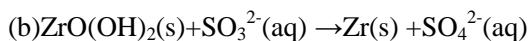


6 碱性

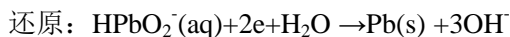
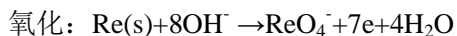
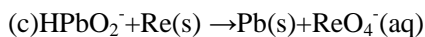
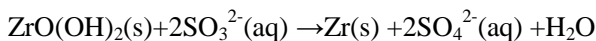


还原: $\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$

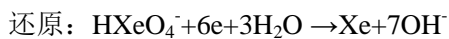
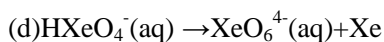
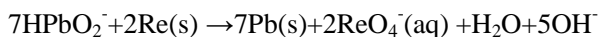
氧化 $\times 2$ + 还原 $\times 3$



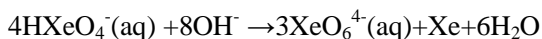
氧化 $\times 2$ + 还原



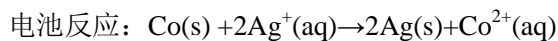
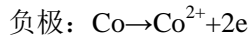
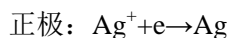
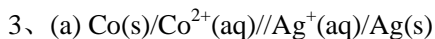
氧化 $\times 2$ + 还原 $\times 7$



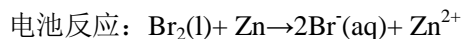
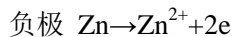
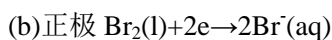
氧化 $\times 3$ + 还原



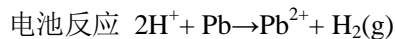
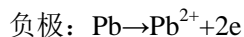
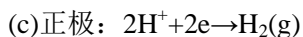
P433 标明物质状态



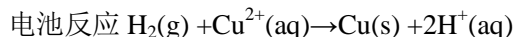
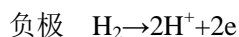
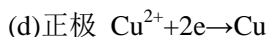
负极材料 Co



负极材料 Zn



负极材料 Pb



负极材料 Pt

$$\text{已知 } \square \varepsilon_1^\ominus = E_{H^+/H_2}^\ominus - E_{Zn^{2+}/Zn}^\ominus = 0.763V$$

$$\square \varepsilon_2^\ominus = E_{Ti^+/Ti}^\ominus - E_{Zn^{2+}/Zn}^\ominus = 0.427V$$

$$\square \varepsilon_3^\ominus = E_{Zn^{2+}/Zn}^\ominus - E_{Sc^{3+}/Sc}^\ominus = 1.32V$$

$$\because E_{H^+/H_2}^\ominus = 0$$

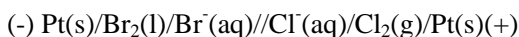
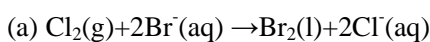
$$\therefore E_{Zn^{2+}/Zn}^\ominus = -0.763V$$

$$\text{代入 } \square \varepsilon_2^\ominus, E_{Ti^+/Ti}^\ominus - (-0.763) = 0.427$$

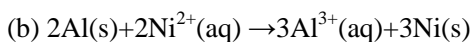
$$\therefore E_{Ti^+/Ti}^\ominus = -0.336V$$

$$\text{代入 } \square \varepsilon_3^\ominus, E_{Sc^{3+}/Sc}^\ominus = -2.083V$$

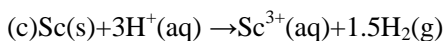
8、



$$\square \varepsilon^\ominus = E_{Cl_2/Cl^-}^\ominus - E_{Br_2/Br^-}^\ominus = 1.3583 - 1.065 = 0.2933V$$



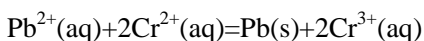
$$\square \varepsilon^\ominus = E_{Ni^{2+}/Ni}^\ominus - E_{Al^{3+}/Al}^\ominus = -0.23 - (-1.076) = 0.846V$$



$$\square \varepsilon^\ominus = E_{H^+/H_2}^\ominus - E_{Sc^{3+}/Sc}^\ominus = 0 - (-2.08) = 2.08V$$

P440

4、



$$E_{\text{池}} = E_{\text{池}}^\ominus - \frac{0.059}{n} \lg \frac{[Cr^{3+}]^2}{[Pb^{2+}][Cr^{2+}]^2}$$

$$E_{\text{池}} = 0.41 - 0.1263 - \frac{0.059}{2} \lg \frac{(0.003)^2}{0.15 \times (0.2)^2}$$

$$= 0.367V$$

6、



$$E_{\text{池}} = E_{\text{池}}^\ominus - \frac{0.059}{2} \lg [Cu^{2+}][Br^-]^2 = 1.065 - 0.3402 - \frac{0.059}{2} \lg [Br^-]^2$$

$$-0.2382 = \frac{0.059}{2} \lg [Br^-]^2$$

$$[Br^-] = 9.18 \times 10^{-5} \text{ mol/L (用0.05917计算, 结果为} 9.43 \times 10^{-5} \text{)}$$

P454

3、

电池反应 $I_2 + H_2 + H_2O \rightarrow 2I^- + 2H_3O^+$

$$E_{\text{池}} = E_{\text{池}}^{\ominus} - \frac{0.059}{2} \lg [H_3O^+]^2 [I^-]^2$$

$$0.814 = 0.5355 - 0 + 0.059 pH$$

$$pH = 4.72$$

4、

电池反应 $2Ag^+ + H_2 \rightarrow 2Ag + 2H^+$

$$E_{\text{池}} = E_{\text{池}}^{\ominus} - \frac{0.059}{2} \lg \frac{[H^+]^2}{[Ag^+]^2 P_{H_2}}$$

$$1.03 = 0.7996 - 0 - \frac{0.059}{2} \lg [H^+]^2$$

$$pH = 3.91$$

$$[H^+] = 1.24 \times 10^{-4} \text{ mol/L}$$

$phcooH + H_2O \rightarrow phcoo^- + H_3O^+$

$$K_a = \frac{[H_3O^+][phcoo^-]}{[phcooH]}$$

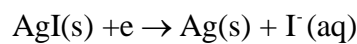
$$= \frac{1.24 \times 10^{-4} \times 0.05}{0.1}$$

$$= 6.2 \times 10^{-5}$$

7、(a)



(1)+(2)



$$E = E_{AgI/Ag}^{\ominus} - \frac{0.059}{1} \lg [I^-]$$

$$\text{由(1)知, } E = E_{Ag^+/Ag}^{\ominus} - \frac{0.059}{1} \lg \frac{1}{[Ag^+]}$$

$$\text{由(2)知, } [Ag^+] = \frac{K_{sp}}{[I^-]}$$

$$E = E_{Ag^+/Ag}^{\ominus} - \frac{0.059}{1} \lg \frac{[I^-]}{K_{sp}}$$

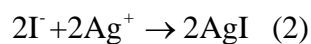
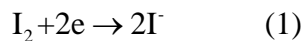
$$= E_{Ag^+/Ag}^{\ominus} - \frac{0.059}{1} \lg \frac{1}{K_{sp}} - \frac{0.059}{1} \lg [I^-]$$

$$\therefore E_{AgI/Ag}^{\ominus} = E_{Ag^+/Ag}^{\ominus} - \frac{0.059}{1} \lg \frac{1}{K_{sp}}$$

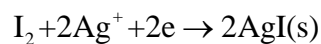
$$= 0.7996 - \frac{0.059}{1} \lg \frac{1}{1.5 \times 10^{-16}}$$

$$= -0.134V$$

(b)



(1)+(2)



$$E = E_{I_2/AgI}^{\ominus} - \frac{0.059}{2} \lg \frac{1}{[Ag^+]^2}$$

$$\text{由 (1) 知, } E = E_{I_2/I^-}^{\ominus} - \frac{0.059}{2} \lg [I^-]^2$$

$$\text{由 (2) 知, } [I^-]^2 = \frac{K_{sp}^2}{[Ag^+]^2}$$

$$\therefore E = E_{I_2/I^-}^{\ominus} - \frac{0.059}{2} \lg \frac{K_{sp}^2}{[Ag^+]^2}$$

$$E = E_{I_2/I^-}^{\ominus} - \frac{0.059}{2} \lg K_{sp}^2 - \frac{0.059}{2} \lg \frac{1}{[Ag^+]^2}$$

$$\therefore E_{I_2/AgI}^{\ominus} = E_{I_2/I^-}^{\ominus} - \frac{0.059}{2} \lg K_{sp}^2$$

$$= 0.5355 - 0.059 \lg K_{sp}$$

$$= 1.47V$$

9、(a)

$$\Delta \varepsilon_{\text{池}}^{\ominus} = E_{\text{正}}^{\ominus} - E_{\text{负}}^{\ominus}$$

$$= E_{H^+/H_2}^{\ominus} - E_{Pb^{2+}/Pb}^{\ominus}$$

$$= 0 - (-0.1263)$$

$$= 0.1263$$

(b)

$$E_{\text{池}} = E_{\text{池}}^{\ominus} - \frac{0.059}{2} \lg \frac{[Pb^{2+}]P_{H_2}}{[H_3O^+]^2}$$

$$0.22 = 0.1263 - \frac{0.059}{2} \lg [Pb^{2+}]$$

$$[Pb^{2+}] = 6.66 \times 10^{-4}$$

(c)

$$K_{sp} = [Pb^{2+}][Cl] = 6.66 \times 10^{-4} \times (0.15)^2$$

$$= 1.5 \times 10^{-5}$$

11、

$$Au^+(aq) + e \rightleftharpoons Au(s) \quad E_{Au^+/Au}^\ominus = 1.68 \quad (1)$$

$$Au(CN)_2^-(aq) + e \rightleftharpoons Au(s) + 2CN^-(aq) \quad E_{Au(CN)_2^-/Au}^\ominus = -0.6 \quad (3)$$

$$(3) \text{ 分解为: } Au(CN)_2^- \rightleftharpoons Au^+(aq) + 2CN^-(aq) \quad (2)$$

$$(1) \text{ 式 } \Delta G_1^\ominus = -nFE^\ominus = -1 \times 96500 \times 1.68 = -162.12 \text{ KJ/mol}$$

$$(3) \text{ 式 } \Delta G_3^\ominus = -nFE^\ominus = -1 \times 96500 \times (-0.6) = 57.9 \text{ KJ/mol}$$

$$(1) + (2) = (3)$$

$$(2) = (3) - (1)$$

$$\Delta G_2^\ominus = \Delta G_3^\ominus - \Delta G_1^\ominus = 57.9 + 162.12$$

$$\Delta G = -\Delta G_2 = -220 \text{ KJ/mol} = 220.02 \text{ KJ/mol}$$

$$\Delta G^\ominus = -RT \ln K_{\text{稳}}$$

$$-220.02 = -8.314 \times 298 \ln K_{\text{稳}}$$

$$K_{\text{稳}} = 3.69 \times 10^{38} \text{ 或 } 4.4 \times 10^{38}$$

也可以, 从(3)式

$$E = E_{Au(CN)_2^-/Au}^\ominus - 0.059 \lg \frac{[CN^-]^2}{[Au(CN)_2^-]}$$

$$\text{从(1), } E = E_{Au^+/Au}^\ominus - 0.059 \lg \frac{1}{[Au^+]}$$

$$\text{从(2) } \frac{1}{K_{\text{稳}}} = \frac{[Au^+][CN^-]^2}{[Au(CN)_2^-]}$$

$$E = E^\ominus - 0.059 \lg \frac{[CN^-]^2 K_{\text{稳}}}{[Au(CN)_2^-]}$$

$$= E - 0.059 \lg K_{\text{稳}} - 0.059 \lg \frac{[CN^-]^2}{[Au(CN)_2^-]}$$

$$E_{Au(CN)_2^-/Au}^\ominus = E_{Au^+/Au}^\ominus - 0.059 \lg K_{\text{稳}}$$

$$-0.6 = 1.68 - 0.059 \lg K_{\text{稳}}$$

$$K_{\text{稳}} = 4.41 \times 10^{38} = -220.457 \text{ KJ/mol}$$

$$\Delta G^\ominus = -RT \ln K_{\text{稳}}$$

$$= -8.314 \times 298 \times 4.41 \times 10^{38}$$

$$= -220.02 \text{ KJ/mol}$$

c

12、

$$(1) \text{Co}^{3+}(\text{aq}) + e \rightarrow \text{Co}^{2+}(\text{aq}) \quad \varepsilon^{\ominus} = 1.92\text{V}$$

$$(2) [\text{Co}(\text{NH}_3)_6]^{3+}(\text{aq}) + e \rightarrow [\text{Co}(\text{NH}_3)_6]^{2+}(\text{aq}) \quad \varepsilon^{\ominus} = 0.058\text{V}$$

$$E = E_{[\text{Co}(\text{NH}_3)_6]^{3+}/[\text{Co}(\text{NH}_3)_6]^{2+}}^{\ominus} - 0.059 \lg \frac{[\text{Co}(\text{NH}_3)_6]^{2+}}{[\text{Co}(\text{NH}_3)_6]^{3+}}$$

$$E^{\ominus} = E_{\text{Co}^{3+}/\text{Co}^{2+}}^{\ominus} - 0.059 \lg \frac{[\text{Co}^{2+}]}{[\text{Co}^{3+}]}$$



$$[\text{Co}^{3+}] = \frac{[\text{Co}(\text{NH}_3)_6]^{3+}}{k_1[\text{NH}_3]^6}$$



$$[\text{Co}^{2+}] = \frac{[\text{Co}(\text{NH}_3)_6]^{2+}}{k_2[\text{NH}_3]^6}$$

$$E^{\ominus} = E_{\text{Co}^{3+}/\text{Co}^{2+}}^{\ominus} - 0.059 \lg \frac{k_1[\text{Co}(\text{NH}_3)_6]^{2+}}{k_2[\text{Co}(\text{NH}_3)_6]^{3+}}$$

$$= E_{\text{Co}^{3+}/\text{Co}^{2+}}^{\ominus} - 0.059 \lg \frac{k_1}{k_2} - 0.059 \lg \frac{[\text{Co}(\text{NH}_3)_6]^{2+}}{[\text{Co}(\text{NH}_3)_6]^{3+}}$$

$$E_{[\text{Co}(\text{NH}_3)_6]^{3+}/[\text{Co}(\text{NH}_3)_6]^{2+}}^{\ominus} = E_{\text{Co}^{3+}/\text{Co}^{2+}}^{\ominus} - 0.059 \lg \frac{k_1}{k_2}$$

$$0.058 = 1.92 - 0.059 \lg \frac{k_1}{k_2}$$

$$0.059 \lg \frac{k_1}{k_2} = 1.92 - 0.058$$

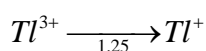
$$\frac{k_1}{k_2} > 1$$

$$\therefore k_1 > k_2$$

$[\text{Co}(\text{NH}_3)_6]^{3+}$ 更稳定

P464 /5

相当于



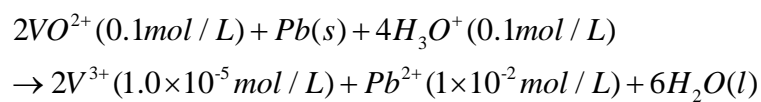
$$1 \times (-0.37) + 1 \times E_{\text{Tl}^{2+}/\text{Tl}^{+}}^{\ominus} = 2 \times 1.25$$

$$E_{\text{Tl}^{2+}/\text{Tl}^{+}}^{\ominus} = 2.5 + 0.37 = 2.87$$

$$E_{\text{右}} > E_{\text{左}}$$

可以发生歧化反应

电池反应:



$$E_{池} = E_{池}^{\ominus} - \frac{0.059}{2} \lg \frac{[Pb^{2+}][V^{3+}]^2}{[H_3O^+]^4[VO^{2+}]^2}$$

$$0.64 = E_{VO^{2+}/V^{3+}}^{\ominus} - (-0.126) - \frac{0.059}{2} \lg \frac{1 \times 10^{-2} \times (1.0 \times 10^{-5})^2}{(0.1)^4 \times (0.1)^2}$$

$$E_{VO^{2+}/V^{3+}}^{\ominus} = 0.640 - 0.126 - 0.177 = 0.337$$

$$E_{池}^{\ominus} = 0.337 + 0.126 = 0.463$$

$$\lg K^{\ominus} = \frac{nE_{池}^{\ominus}}{0.059} = \frac{2 \times 0.463}{0.059}$$

$$K^{\ominus} = 4.95 \times 10^{15}$$

第八章 原子的电子结构、化学键

P81/3

Li⁺: [He]

B: [He]2s²2p¹

C: [He]2s²2p²

O²⁻: [He]2s²2p⁶

Mg: [Ne]3s²

P: [Ne]3s²3p³

Fe: [Ar]3d⁶4s²

Se²⁻: [Ar]3d¹⁰4s²4p⁶

Te: [Kr]4d¹⁰5s²5p⁴

P81/5

V²⁺: [Ar]3d³

Cr³⁺: [Ar]3d³

Fe³⁺: [Ar]3d⁵

Zn²⁺: [Ar]3d¹⁰

Ag⁺: [Kr]4d¹⁰

Pt²⁺: [Xe]4f¹⁴5d⁸

P81/6

顺磁性: Be⁺, C⁻, Ne²⁺, Mg⁺, P²⁺, As⁺, I⁺

P81/9

(a) ×

(b) √

(c) ×

(d) ×

(e) 基态

(f) √

(g) ×

P88/1

(a) K > Na

(b) K > Ca

(c) Ca > Mg

(d) Ge > As

(e) Al = Ga

(f) I < Xe

P88/3

(a) Cs

(b) F

(c) K

(d) Po

(e) Rb

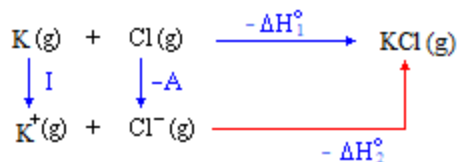
(f) I

(g)Te

(h)Cl

P129/4

$$E_{\text{吸引}} = -\Delta H_2^\circ = -\frac{Z_+ Z_- e^2}{4\pi\epsilon_0 r} = \frac{1 \times 1 \times 6.022 \times 10^{23} \times (1.602 \times 10^{-19})^2}{4 \times 3.14 \times 8.854 \times 10^{-12} \times 267 \times 10^{-12} \times 1000}$$
$$= -521 \text{ kJ/mol}$$



$$-\Delta H_1^\circ = I - A - \Delta H_2^\circ = 418 - 349 - 521 = -452 \text{ kJ/mol}$$
$$\Delta H_1^\circ = 452 \text{ kJ/mol}$$

P129/6

(a)

$$\frac{1389.4 \times 1 \times 1}{R(A)} = 146.8$$

$$R = 9.46(A)$$

$$R = 946 \text{ pm}$$

(b)

F的亲和能小于Cl

ΔE更大，因此距离更小

P112/3

(a) sp^3 正四面体

(b) sp^2 三角形

(c) sp 直线型

(d) sp^3 正四面体

(e) $\text{sp}^3 \text{d}^2$ 正八面体

P112/5

sp^2 杂化

P112/7

两端的C sp^2 杂化，中间的C sp 杂化，所以三个C在一条直线上。

中间C的两根 π 键轨道($\text{p}_y \text{p}_z$)相互垂直，所以两个 CH_2 基团平面互相垂直

P121/1

(a) 4 正四面体 正四面体

(b) 3 三角形 三角形

(c) 6 正八面体 正八面体

(d) 4 四面体 三角锥

(e) 5 三角双锥 T型

(f) 4 四面体 三角锥

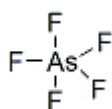
P121/2

(a) 5.5	八面体	四方锥	
(b) 4	四面体	V 型	夹角小于 109°
(c) 4	四面体	三角锥	夹角小于 109°
(d) 2	直线型	直线型	
(e) 4	四面体	V 型	夹角小于 109°
(f) 4	四面体	三角锥	夹角小于 109°
(g) 4	四面体	四面体	
(h) 6	八面体	四方锥	赤道上的 Xe-F 键向极方向的 Xe-F 靠拢

P121/8

- (a) sp^3 杂化 孤对电子的排斥力要比成键电子的排斥力大，成键电子间的夹角小于标准值
 (b) sp^2 杂化 孤对电子的排斥力要比成键电子的排斥力大，成键电子间的夹角小于标准值
 (c) sp^3 杂化 孤对电子的排斥力要比成键电子的排斥力大，成键电子间的夹角小于标准值

P121/9



指向两极的 As-F 键与三根 As-F 键呈 90° 夹角，而指向赤道的 As-F 键与两根 As-F 键呈 120° 夹角。两极的 As-F 键所受排斥力更大，因此键长更长。

指向两极的 As-F 键长 171.1pm，指向赤道的 As-F 键长 165.6pm

P156/1

$$(a) F_2 \quad KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$$

$$F_2^+ \quad KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$$

$$(b) F_2 \text{ 键级为 } 1, F_2^+ \text{ 键级为 } 1.5$$

$$(c) F_2^+ \text{ 有顺磁性}$$

$$(d) F_2^+ \text{ 键能较大}$$

P156/2

$$O_2^+ \quad KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1 \text{ 键级为 } 2.5$$

$$O_2 \quad KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2 \text{ 键级为 } 2$$

$$O_2^- \quad KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3 \text{ 键级为 } 1.5$$

$$O_2^{2-} \quad KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4 \text{ 键级为 } 1$$

$$O_2^+, O_2 \text{ 和 } O_2^- \text{ 有顺磁性}$$

$$O_2^+ > O_2 > O_2^- > O_2^{2-}$$

P156/5

- (a) F 键级为 1
 (b) N 键级为 2.5
 (c) O 键级为 1.5
 (d) O 键级为 2
 (e) B 键级为 1.5

(f) F 键级为 2

P158/2

$CF^+ KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4$ 键级为 3

$CF KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$ 键级为 2.5

CF^+ 键级更大，键长更短

P158/3

$NO^+ KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4$ 键级为 3

$NO KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$ 键级为 2.5

NO^+ 键级更大，键长更短，全部电子全部成对，不具有顺磁性

P158/4

(a) $NO(2.5) > NO^-(2)$

(b) $BN(2) < BO(2.5)$

(c) $NF(2) < NO(2.5)$

第二十一章 元素化学

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6、 $V=abcsin \beta =5.89 \times 10^{-22} \text{cm}^3$

9、 $\rho=4 \times M(\text{Au})/N_A \times a^3$

代入数据，得 $N_A=6.06 \times 10^{23} \text{mol}^{-1}$

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7、(a) $V=(2a)^3=1.794 \times 10^{-22} \text{cm}^3$

(b) $N=(nM(\text{NaCl})/\rho)/V=1.508 \times 10^{23}$

(c) $N_A=4N=6.032 \times 10^{23}$

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- 1、(a) 分子晶体
(b) 分子晶体
(c) 原子晶体
(d) 金属晶体
(e) 离子晶体

2、(a) Na(s)属于金属晶体， $\text{Cl}_2(\text{s})$ 属于分子晶体， $\text{NaCl}(\text{s})$ 属于离子晶体。

(b) Na(s)为金属离子与自由电子的作用， $\text{Cl}_2(\text{s})$ 为分子间范德华力的作用， $\text{NaCl}(\text{s})$ 为阴、阳离子之间的静电相互作用。

(c) Na(s)为体心立方，原子； $\text{Cl}_2(\text{s})$ 为底心正交，分子； $\text{NaCl}(\text{s})$ 为面心立方，离子。

(d) Na(s): (0,0,0) (1/2,1/2,1/2)

$\text{Cl}_2(\text{s})$: (0,0,0) (1/2,1/2,0)

$\text{NaCl}(\text{s})$: (0,0,0) (1/2,1/2,0) (1/2,0,1/2) (0,1/2,1/2)

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6. (1)类盐型氢化物: LiH , NaH , KH ,……

(2)金属型氢化物: PdH_x , ZrH_x

(3)分子型氢化物: 卤化氢, H_2O , H_2S

8. BaH_2 : 氢化钡, 类盐型氢化物

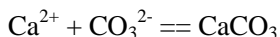
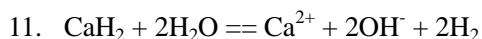
SiH_4 : 甲硅烷, 分子型氢化物

NH_3 : 氨, 分子型氢化物

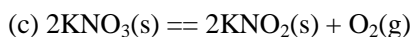
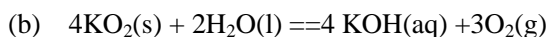
AsH_3 : 砷化氢/氢化砷, 分子型氢化物

$\text{PdH}_{0.9}$: 氢化钯, 金属型氢化物

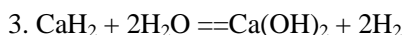
HI : 碘化氢, 分子型氢化物



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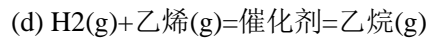
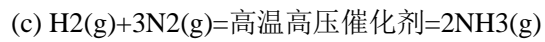
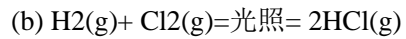
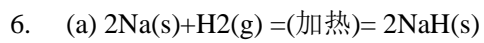
(a) $500\text{g CaH}_2 = 500/42 = 11.9\text{ mol}$

$n(\text{H}_2) = 23.8\text{mol}$

$V = nRT/P = 582.4\text{ (L)}$

(b) $n(\text{H}_2\text{O}) = 23.8\text{mol}$

$V(\text{H}_2\text{O}) = 23.8 \times 18/1 = 428.4\text{mL}$



8. 类盐型氢化物: (a)KH, (e)CaH₂,

金属型氢化物: (c)UH₃, (f)Pd₂H_x

分子型氢化物: (b)NH₃, (d)SiH₄