

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

$$P = \frac{F}{S} = \frac{mg}{S} = \frac{\rho V g}{S} = \frac{\rho \square S h \square g}{S} = \rho g h$$

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

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

(注：也可以用 $P = \rho g h$ 直接计算)

P 45

1、(a) $P_1 V_1 = P_2 V_2$

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

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

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

$$= 6068 \text{ L}$$

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 N₂，反应前后无 n 的变化

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

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

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

$$= 30.447 \text{ kPa}$$

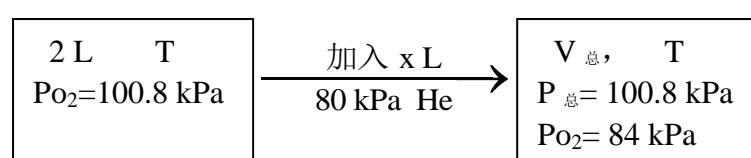
$$(b) P_i V = n_i R T$$

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

$$= 0.01605 \text{ mol}$$

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

7、解：



$$\text{对 O}_2: P_1 V_1 = P_2 V_2$$

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

$$100.82 \times 2 = 84 V_{\text{总}}$$

$$V_{\text{总}} = 2.4 \text{ L}$$

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

对He: $P_1V_1 = P_2V_2$

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

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

10、

$$n_{O_2} = \frac{(101.3 - 2.6) \times 18}{8.314 \times (273.15 + 22)} = 0.724 \text{ mol}$$

$$n_{KClO_3} = \frac{2}{3} n_{O_2} = 0.483 \text{ mol}$$

$$m_{KClO_3} = 0.483 \times 122.5 = 59.17 \text{ g}$$

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)

$$\begin{array}{l} 10 \text{ L } P_{\text{乙}} = 100.8 \text{ kPa} \\ P_{\text{空}} = ? \\ P_{\text{总}} = 100 \text{ kPa} \end{array}$$

$$\begin{array}{l} 0.5 \text{ L } P_{\text{乙}} = 100.8 \text{ kPa} \\ P_{\text{空}} = ? \\ P_{\text{总}} = ? \end{array}$$

10L 时, $P_{\text{空}} = 100 - 78.3 = 92.17 \text{ kPa}$

$$P_{\text{空}} V_{\text{空}} = P'_{\text{空}} V'_{\text{空}}$$

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

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

8、 (a) 解: $\lg P = -\frac{A}{T} + B$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

7、解: 25 °C: KCl 38.0g/100g

75 °C: 155.0g/100g

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

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

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：

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

在大气中

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

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、 $b_A = 2.47 \text{ mol/kg}^{-1}$

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

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

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

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

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

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

4、解：根据表10-5

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

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

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

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

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

(b) $\Delta T_f = b_A K_f$

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

6、解：根据凝固点下降

$$MA = \frac{1000 \times K_f \times W_{\text{质}}}{W_{\text{剂}} \times \Delta T_f}$$

$$= \frac{1000 \times 4.9 \times 1g}{8.5g \times (5.5 - 3.37)K}$$

$$= 270.6 \text{ g/mol}$$

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 $(C_6H_5)_3P$

9、解： $M_{\text{质}} = \frac{W_{\text{质}} \times R \times T}{\pi \times V_{\text{溶液}}}$

$$= \frac{6.85g \times 8.314 \times 293.15K}{467 \text{ kPa} \times \frac{(100 + 6.85) \times 10^{-3}}{1.024 \text{ dm}^3}}$$

$$= \frac{16695.156}{467 \times 0.1043} = 343 \text{ g/mol}$$

P266

2、

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

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

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

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

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

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

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

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

P272

3、查 P256 表 10-5

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

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

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

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

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

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

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

$$8、 C = \frac{n_{\text{质}}}{1L \cdot \text{溶液}} \\ = \frac{1L \times 1.005 \times 10^3 \times 0.86\% / 58.5}{1L} \\ = 8.643 / 58.5 = 0.148 \text{ mol/L}$$

$$\Pi = Icrt$$

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

$$= 7.53 \text{ atm}$$

第二章 热力学

P141

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

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

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 $P_1V_1 = P_2V_2$

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

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

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

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

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

\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)

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

$$= \Delta U + P_2V_2 - P_1V_1$$

$$= \Delta U = 0$$

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

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

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

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

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

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

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

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

$$= 7.55 \text{ KJ}$$

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

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

$$= 0.5946 \text{ KJ}$$

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

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

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

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

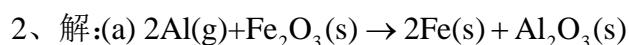
$$(d) \frac{n}{4} = \frac{q}{\Delta H^\ominus}$$

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

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

$$= 0.5086 \text{ KJ}$$

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



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

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

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

(c) ∵ 恒容反应

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

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



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

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

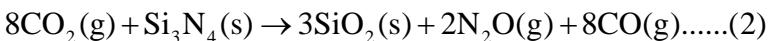
$$\Delta_r H_m^\ominus = \frac{7 \times (-393.51)}{-2754.57} + 3 \times (-285.83) - \Delta_f H_m^\ominus_{\text{C}_6\text{H}_5\text{COOH}(s)}$$

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

P154

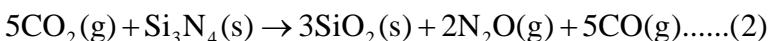


$$\Delta H_1 = 520.9 \text{ KJ/mol}$$



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

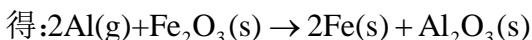
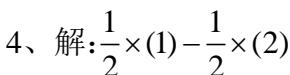
(1) × 3 + (2) 得:



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

$$= 520.9 \times 3 + 461.05$$

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



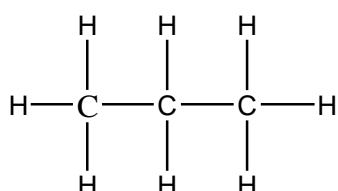
$$\Delta H^\ominus = \frac{1}{2} \Delta H_1^\ominus - \frac{1}{2} \Delta H_2^\ominus$$

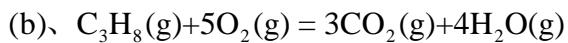
$$= \frac{1}{2} \times (-3351.4) - \frac{1}{2} \times (-1648.4)$$

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

P159

3、(a)





已知: B.E._{C-H} = 415 KJ/mol

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

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

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

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

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

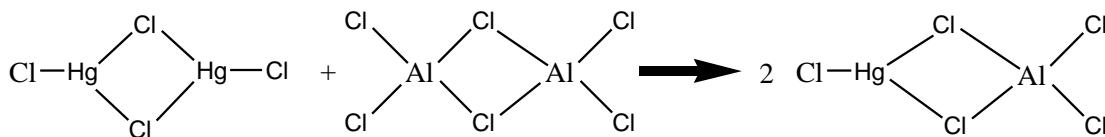
$$= 8\text{B.E.}_{\text{C-H}} + 2\text{B.E.}_{\text{C-C}} + 5\text{B.E.}_{\text{O=O}} - (3 \times 2\text{B.E.}_{\text{C=O}} + 4 \times 2\text{B.E.}_{\text{O-H}})$$

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

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

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

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

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

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

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

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

P179

2、(a) $\Delta S > 0$

(b) $\Delta S < 0$

(c) $\Delta S < 0$

(d) $\Delta S > 0$

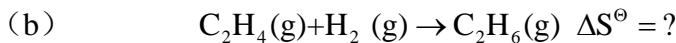
(e) $\Delta S < 0$



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

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

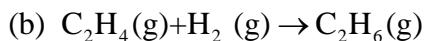
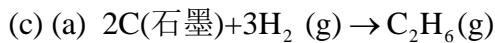
$$= -173.7 \text{ J/mol}\text{K}$$



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

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

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



对于反应(a)反应前后，气体分子数减小了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、

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

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

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

P181

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

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

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

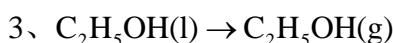
$$(b) \Delta G = 3.6 \times 0.737$$

$$= 2.653 \text{ KJ}$$

(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： $\Delta H = 38.7 \text{ KJ/mol}$

$$\Delta G = 0$$

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

体系吸热

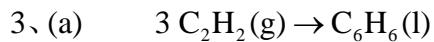
$$q = \Delta H = 38.7 \text{ kJ}$$

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

$$= 2.92 \text{ kJ (膨胀, 体系对环境做功)}$$

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

$$= 35.78 \text{ kJ}$$

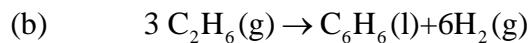
P186

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



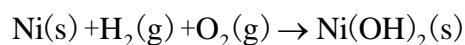
查表 ΔG_f^\ominus -32.89 124.5 0

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

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

不能自发发生

4、对 $\text{Ni(OH)}_2(\text{s})$



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

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

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

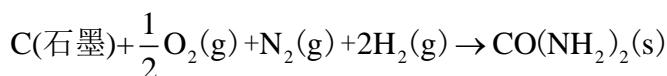
$$= 80 - 205.03 - 130.57 - 29.87$$

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

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

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

对 $\text{CO(NH}_2)_2(\text{s})$



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

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

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

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

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

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

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

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

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:

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

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

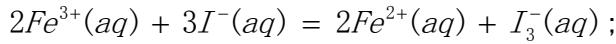
$$(c) Zn(s) + CO_2(g) = ZnO(s) + CO(g), K_p = \frac{P_{CO}}{P_{CO_2}}; \text{ 单位: 无量纲}$$

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

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

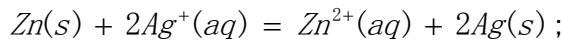
3. 解:

(a) .



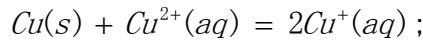
$$K_c = \frac{[Fe^{2+}]^2[I_3^-]}{[Fe^{3+}]^2[I^-]^3}; \text{ 单位: } (mol/L)^2$$

(b) .



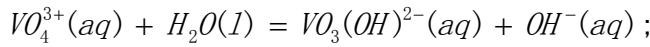
$$K_c = \frac{[Zn^{2+}]}{[Ag^+]^2}; \text{ 单位: } (mol/L)^{-1}$$

(c) .



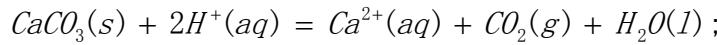
$$K_c = \frac{[Cu^+]^2}{[Cu^{2+}]}; \text{ 单位: } mol/L$$

(d) .



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

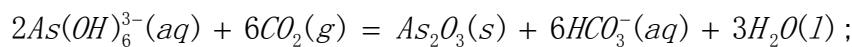
(e) .



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

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

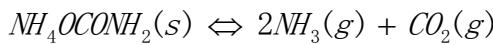
(f) .



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

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

7. 解:



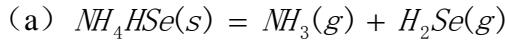
$$(a) 2x + x = 11.6 \Rightarrow x = 3.87kPa$$

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

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

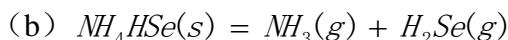
$$K^\theta = \left(\frac{PNH_3}{P^\theta} \right)^2 \frac{P_{CO_2}}{P^\theta} = 2.23 \times 10^{-4}$$

8. 解:



$$\text{平衡时: } P_{NH_3} = P_{H_2Se} = 1.86 / 2 = 0.93 \text{ kPa}$$

$$\Rightarrow K_p = 0.93 \text{ kPa} \times 0.93 \text{ kPa} = 0.86 \text{ kPa}^2$$

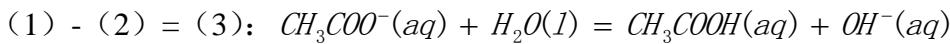
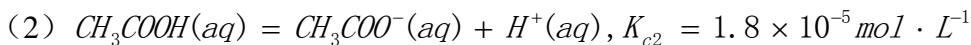
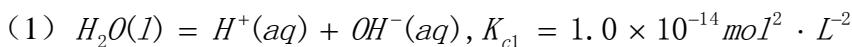


$$\text{平衡时: } 2.55 \text{ kPa}$$

$$K_p = P_{NH_3} \cdot P_{H_2Se} \Rightarrow P_{H_2Se} = K_p / P_{NH_3} = 0.86 \text{ kPa}^2 / 2.55 \text{ kPa} = 0.34 \text{ kPa}$$

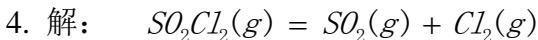
P296

6. 解:



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

P300



$$(a) \text{ 始: } P_{SO_2Cl_2} = \frac{nRT}{V} = \frac{\frac{3.714}{135} \times 0.082 \times 373}{1} = 0.842 \text{ atm} = 85.3 \text{ kPa}$$

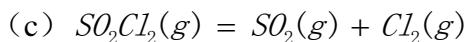
$$\text{平衡: } 85.3 - x \quad x \quad x$$

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

$$\therefore P_{SO_2} = P_{Cl_2} = 46.4 \text{ kPa} = 0.459 \text{ atm}; P_{SO_2Cl_2} = 85.3 - 46.4 = 38.9 \text{ kPa} = 0.383 \text{ atm}$$

$$(b) K_p = \frac{P_{SO_2} P_{Cl_2}}{P_{SO_2Cl_2}} = \frac{46.4 \times 46.4}{38.9} \text{ kPa} = 53.96 \text{ kPa} = 0.52 \text{ atm}$$

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



$$3.6 \times 10^{-4} \text{ mol/L} \quad 6.9 \times 10^{-3} \text{ mol/L}$$

$$K_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]}$$

$$\Rightarrow [SO_2] = \frac{K_c [SO_2Cl_2]}{[Cl_2]} = \frac{0.0174 \times 3.6 \times 10^{-4}}{6.9 \times 10^{-3}} = 9.1 \times 10^{-4} \text{ mol/L}$$

7. 解: $BBr_2(g) + I_2(g) = 2IBr(g)$

初: 5 kPa 4 kPa

平: 5-x 4-x 2x

$$K_p = \frac{P_{IBr}^2}{P_{BBr_2} P_{I_2}} = \frac{(2x)^2}{(5-x)(4-x)} = 322, \text{ 解得 } x = 3.84 \text{ kPa}$$

$$\therefore P_{BBr_2} = 5 - 3.84 = 1.16 \text{ kPa}, P_{I_2} = 4 - 3.84 = 0.16 \text{ kPa}$$

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

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: $500 + \frac{1}{2}x \quad 200 - x$

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

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

(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:

(a) $NH_4HS(s) = NH_3(g) + H_2S(g)$

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

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

(b) $NH_4HS(s) = NH_3(g) + H_2S(g)$

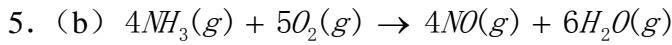
新平衡: 76 kPa x

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

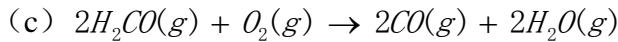
$$\therefore P_{H_2S} = x = 14.7 \text{ kPa} = 0.145 \text{ atm}$$

第四章 动力学

P473

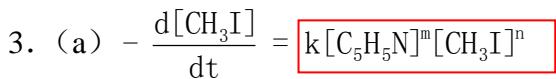


$$\nu = -\frac{d[NH_3]}{4dt} = -\frac{d[O_2]}{5dt} = \frac{d[NO]}{4dt} = \frac{d[H_2O]}{6dt}$$



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

P478



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

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

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

解得: $n = 1, m = 1, k = 75$

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

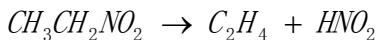
(c) $\nu = k[C_5H_5N][CH_3I]$
 $= 75 \times 5.0 \times 10^{-5} \times 2.0 \times 10^{-5} = 7.5 \times 10^{-8} mol^{-1} \cdot L \cdot s^{-1}$

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

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

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

8. 解:



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

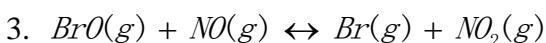
$$\text{解得 } P = \boxed{1.015 KPa}$$

9. 解: 一级反应

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

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

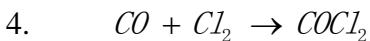
P489



\therefore 是基元反应

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

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



解: 因为(3)是速率控制步骤, 所以

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

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

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

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

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

6. 用稳态近似:

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

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

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

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

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

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

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

P495

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

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

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

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

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

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

(b) 根据 k 单位可判定反应为二级反应,

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

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

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) $\text{C}_5\text{H}_5\text{NH}^-$ $\text{C}_5\text{H}_5\text{NH}^+$

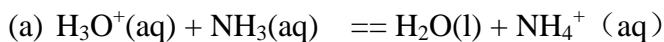
(c) HCO_3^-

(d) $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^-$ $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+$

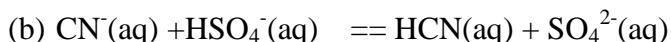
(e) $\text{NH}_3^+\text{CH}_2\text{COOH}$

P313

4、



酸 1 碱 2 碱 1 酸 2



碱 2 酸 1 酸 2 碱 1

B 酸 共轭碱

HSO_4^- SO_4^{2-}

HCN CN^-

P318

4、

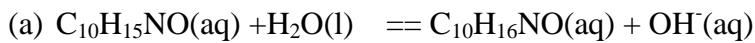
$$pH = 7.4 = -\lg[H_3O^+]$$

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

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

P320

1、



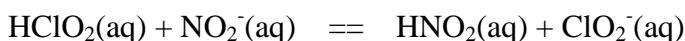
$$(b) K_a = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.4 \times 10^{-4}} = 7.14 \times 10^{-11}$$

(c) 对 NH_3 来讲, $K_{\text{bNH}_3} = 1.8 \times 10^{-5} < K_{\text{bC}_{10}\text{H}_{15}\text{NO}} = 1.4 \times 10^{-4}$

所以, 它的碱性比氨强

P320

3、



上式=(1)-(2)

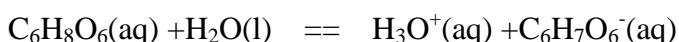
$$K = \frac{K_{a1}}{K_{a2}} = \frac{1.1 \times 10^{-2}}{4.55 \times 10^{-4}} = 23.9$$

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-X

X

X

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

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

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

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

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

P330

5、

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

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

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

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

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,

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

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

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

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

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

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、

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

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

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

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

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

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

也可以直接用

$$P_2 V_1 = n_2 RT$$

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

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

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

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

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

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

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

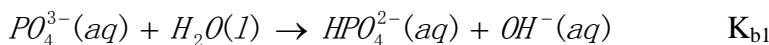
$$pH = -\lg[H_3O^+]$$

$$= 4 - \lg 1.47$$

$$= 3.83$$

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: $c - x \quad x \quad x$

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

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

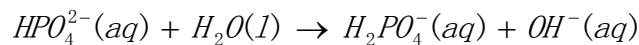
$$[OH^-] = \frac{-K_{b1} + \sqrt{K_{b1}^2 + 4K_{b1}c}}{2}$$

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

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{0.0309} = 3.24 \times 10^{-13}$$

$$[HPO_4^{2-}] = [OH^-] = 0.0309$$

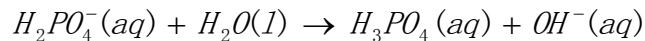
$$[PO_4^{3-}] = 0.050 - 0.0309 = 0.0191$$



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

$$K_{b2} = \frac{[H_2PO_4^-] \times [OH^-]}{[HPO_4^{2-}]} = [H_2PO_4^-]$$

$$[H_2PO_4^-] = K_{b2} = 1.61 \times 10^{-7}$$



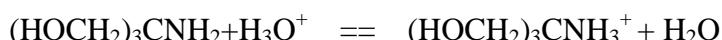
$$K_{b3} = \frac{K_w}{K_{a3}} = \frac{1 \times 10^{-14}}{7.5 \times 10^{-3}} = 1.33 \times 10^{-12}$$

$$K_{b3} = \frac{[H_3PO_4] \times [OH^-]}{[H_2PO_4^-]}$$

$$[H_3PO_4] = \frac{K_{b3}[H_2PO_4^-]}{[OH^-]} = \frac{1.33 \times 10^{-12} \times 1.61 \times 10^{-7}}{0.0309} = 6.93 \times 10^{-18}$$

P351

1、



$$[\text{OH}^-] = \text{Kb} \times \frac{C_{\text{共轭碱}}}{C_{\text{共轭酸}}}$$

$$pOH = pKb + \lg \frac{C_{\text{共轭碱}}}{C_{\text{共轭酸}}}$$

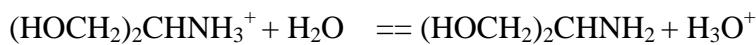
$$= 5.92 + \lg \frac{\frac{0.025}{2}}{\frac{0.05 - 0.025}{2}}$$

$$= 5.92$$

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

若改为 Bis, $\text{pKb}=8.8$, $\text{Kb}=1.58 \times 10^{-9}$

等 mol 反应最后, 生成强酸弱碱盐



$$0.025 - x \quad x \quad x$$

$$K_w = \frac{K_w}{K_b} = \frac{x^2}{0.025 - x} = 6.63 \times 10^{-6}$$

$$x = 3.98 \times 10^{-4}$$

$$\text{pH} = 3.4$$

P351

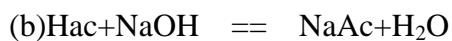
2、

(a)

$$[\text{H}_3\text{O}^+] = K_a \frac{C_a}{C_b} = 1.8 \times 10^{-5} \times \frac{\frac{0.050}{0.5}}{\frac{0.020}{0.5}}$$

$$= 4.5 \times 10^{-5}$$

$$\text{pH} = -\lg [\text{H}_3\text{O}^+] = -\lg (4.5 \times 10^{-5}) = 4.35$$



$$C_a = \frac{0.050}{0.5} - \frac{0.010}{0.5} = \frac{0.040}{0.5}, C_b = \frac{0.020}{0.5} + \frac{0.010}{0.5} = \frac{0.030}{0.5}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{C_a}{C_b} = 1.8 \times 10^{-5} \times \frac{\frac{0.040}{0.5}}{\frac{0.030}{0.5}}$$

$$= 2.4 \times 10^{-5}$$

$$\text{pH} = -\lg [\text{H}_3\text{O}^+] = -\lg (2.4 \times 10^{-5}) = 4.62$$

P351

4、

甲酸 $K_a = 1.77 \times 10^{-4}$

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

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

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

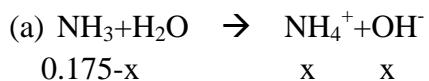
$$\frac{\frac{V * C_{\text{NaOH}}}{V + 0.5}}{0.5C_{\text{甲酸}} - V * C_{\text{NaOH}}} = 1.77$$

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

$$V = 0.639L$$

P353

11、



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

$$x = 0.00177$$

$$\text{pOH} = 2.75$$

$$\boxed{\text{pH}=11.25}$$



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

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

$$\boxed{\text{pH}=9.25}$$

(c) 计量点时，先设全是 $[\text{NH}_4^+]$

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

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

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

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

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

$$\boxed{\text{pH}=5.22}$$

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

pH = 3.54

P355

30、

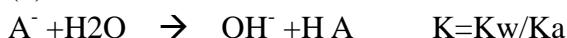
(a)未知酸为 50ml



$$X \quad [H^+] \quad 4x$$

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

(b)计量点时, 浓度为 0.05mol/L, 可认为生成 NaA

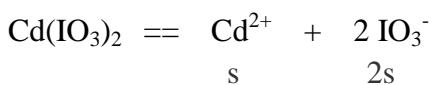


$$\frac{x^2}{0.05} = \frac{10^{-14}}{1.26 \times 10^{-4}}$$

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

pH=5.70

P359/3



$$s \quad 2s$$

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

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

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

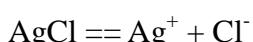
$$n_{AgCl} = \frac{1.8 \times 10^{-2}}{143.5} = 1.25 \times 10^{-4} \text{ mol / L}$$

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

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

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

P365/1



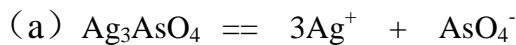
$$x = 0.5 - s$$

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

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

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

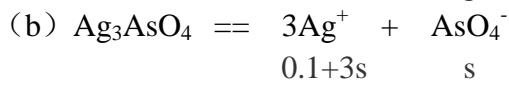
P365/2



$$s \quad \quad \quad s$$

$$K_{sp} = (3s)^3 s = 27s^4 = 1.0 \times 10^{-22}$$

$$\Rightarrow s = 1.39 \times 10^{-6} \text{ mol/L 即 } 6.43 \times 10^{-4} \text{ g/L}$$



$$0.1 + 3s \quad \quad \quad s$$

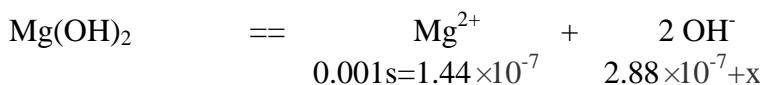
$$K_{sp} = (0.1)^3 s = 1.0 \times 10^{-22}$$

$$\Rightarrow s = 1.0 \times 10^{-19} \text{ mol/L 即 } 4.63 \times 10^{-17} \text{ g/L}$$

P365/5



$$\text{纯水中: } s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.2 \times 10^{-11}}{4}} = 1.44 \times 10^{-4}$$



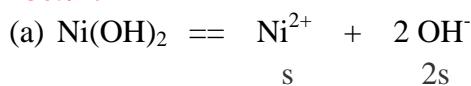
$$0.001s = 1.44 \times 10^{-7} \quad 2.88 \times 10^{-7} + x$$

$$K_{sp} = 1.44 \times 10^{-7} \times (2.88 \times 10^{-7} + x)^2 = 1.2 \times 10^{-11}$$

$$x = 9.13 \times 10^{-3}$$

$$[\text{OH}^-] = 9.13 \times 10^{-3} \text{ mol/L}$$

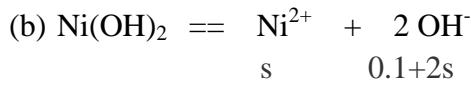
P365/10



$$s \quad \quad \quad 2s$$

$$K_{sp} = s(2s)^2 = 4s^3 = 1.6 \times 10^{-16}$$

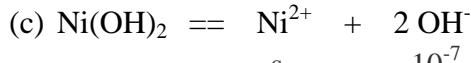
$$\Rightarrow s = 3.42 \times 10^{-6} \text{ mol/L}$$



$$s \quad \quad \quad 0.1 + 2s$$

$$K_{sp} = s \times (0.1 + 2s)^2 = 0.01s = 1.6 \times 10^{-16}$$

$$\Rightarrow s = 1.6 \times 10^{-14} \text{ mol/L}$$



$$s \quad \quad \quad 10^{-7}$$

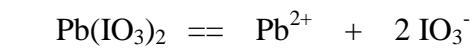
$$K_{sp} = s(10^{-7})^2 = 1.6 \times 10^{-16}$$

$$\Rightarrow s = 1.6 \times 10^{-2} \text{ mol/L}$$

P369/3

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

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



$$[\text{IO}_3^-] = 8.89 \times 10^{-2} - 2 \times 2.78 \times 10^{-2}$$

$$= 3.33 \times 10^{-2} \text{ mol/L}$$

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

P369/6

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

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



$$2.67 \times 10^{-2} - 0.5 \times 3.33 \times 10^{-2}$$

$$= 1.0 \times 10^{-2} \text{ mol/L}$$

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

P377/5

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

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

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

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

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

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



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

(a) 有 Ni(OH)_2 沉淀形成。

(b) 欲抑制沉淀的形成, 需满足 $Q_c \leq K_{\text{sp}}$

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

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

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

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

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

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

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。

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

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



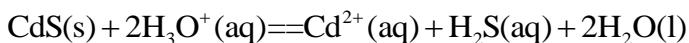
| | |
|-------|--------|
| 0.1 | 0.3 |
| x | 2x |
| 0.1-x | 0.3+2x |

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

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

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

注：另一种算法：设 CdS 的溶解度为 x (设小数)



| | | |
|---------------|----------|------------|
| 0.5 | 0 | 0.1 |
| 0.5-2x | x | 0.1 |

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

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

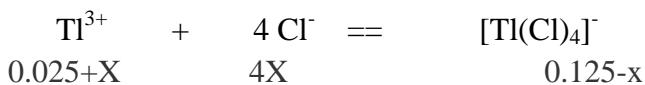
P393-5

- (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) 碘化五羰基合锝 (I)
- (c) 五氰合锰 (IV) 酸钾

P405-1



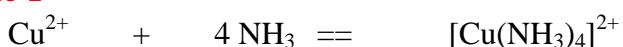
$$\frac{(0.025+x)(4x)^4}{0.125-x} = K_{\text{不稳}} = 10^{-18}$$

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

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

$$[\text{Tl}(\text{Cl})_4]^- = 0.125$$

P405-2



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

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

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

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

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

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

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

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

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

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

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

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

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

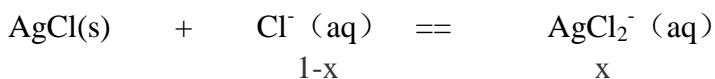
$$[\text{K}^+] = x = 5.46 \times 10^{-8} \text{ mol/L}$$

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

P412-1

纯水中: $s = 1.26 \times 10^{-5}$

1molNaCl 中



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

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

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

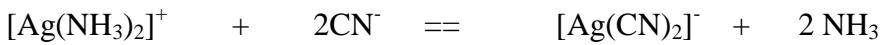
[CoClBr(en)] 没有几何异构体，也没有光学异构体

P418-15

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

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

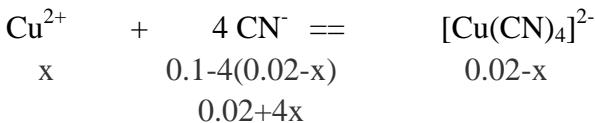
(c) $Q = Q^\circ = \frac{1 \times 1}{6^2} = 2.8 \times 10^{-2} \gg K^\circ$ 则平衡向逆向移动

P418-16

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

$$\Delta G = -RT \ln K_f = -8.314 \times 298 \times \ln 1.18 \times 10^{14}$$

$$= -80.28 \text{ kJ/mol}$$

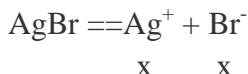
P418-19

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

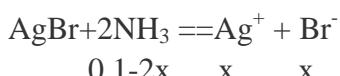
$$X = 6.25 \times 10^{-26}$$

P418-23

纯水中：



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



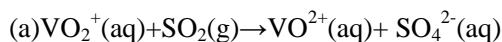
$$\frac{x^2}{(0.1 - 2x)^2} = 7.7 \times 10^{-13} \times 1.1 \times 10^7$$

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

第六章 氧化还原

P423

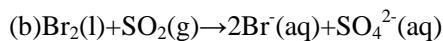
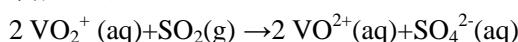
5、



氧化 $\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}$

还原 $2\text{H}^+ + \text{VO}_2^+ + \text{e} \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$

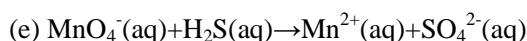
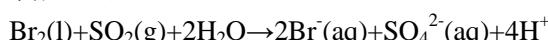
氧化+还原 $\times 2$



氧化 $\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}$

还原 $\text{Br}_2 + 2\text{e} \rightarrow 2\text{Br}^-$

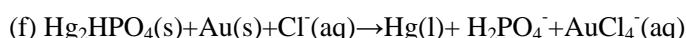
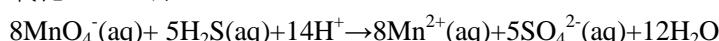
氧化+还原



氧化 $\text{H}_2\text{S} + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}$

还原 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

氧化 $\times 5$ +还原 $\times 8$



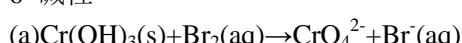
氧化: $\text{Au} + 4\text{Cl}^- \rightarrow \text{AuCl}_4^- + 3\text{e}$

还原: $\text{Hg}_2\text{HPO}_4(\text{s}) + \text{H}^+ + 2\text{e} \rightarrow 2\text{Hg}(\text{l}) + \text{H}_2\text{PO}_4^-$

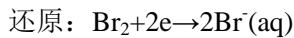
氧化 $\times 2$ +还原 $\times 3$



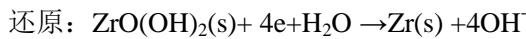
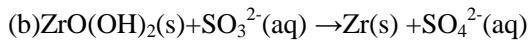
6 碱性



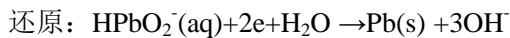
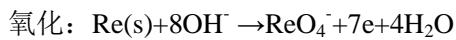
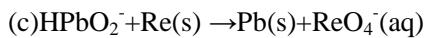
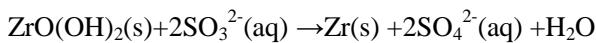
氧化: $\text{Cr(OH)}_3 + 5\text{OH}^- \rightarrow \text{CrO}_4^{2-} + 3\text{e} + 4\text{H}_2\text{O}$



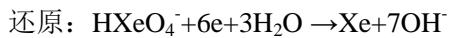
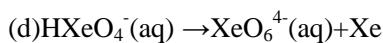
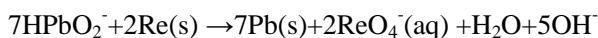
氧化 $\times 2+$ 还原 $\times 3$



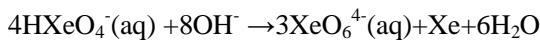
氧化 $\times 2+$ 还原



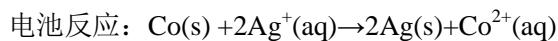
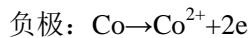
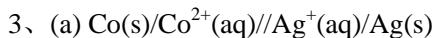
氧化 $\times 2+$ 还原 $\times 7$



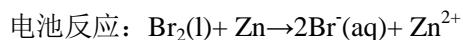
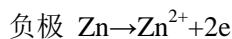
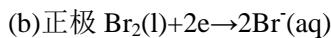
氧化 $\times 3+$ 还原



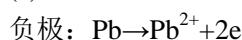
P433 标明物质状态



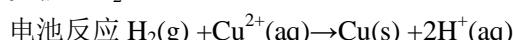
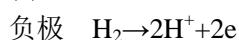
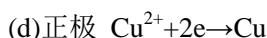
负极材料 Co



负极材料 Zn



负极材料 Pb



负极材料 Pt

$$\text{已知 } \square\epsilon_1^\Theta = E_{H^+/H_2}^\Theta - E_{Zn^{2+}/Zn}^\Theta = 0.763\text{V}$$

$$\square\epsilon_2^\Theta = E_{Tl^+/Tl}^\Theta - E_{Zn^{2+}/Zn}^\Theta = 0.427\text{V}$$

$$\square\epsilon_3^\Theta = E_{Zn^{2+}/Zn}^\Theta - E_{Sc^{3+}/Sc}^\Theta = 1.32\text{V}$$

$$\therefore E_{H^+/H_2}^\Theta = 0$$

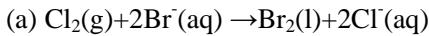
$$\therefore E_{Zn^{2+}/Zn}^\Theta = -0.763\text{V}$$

$$\text{代入}\square\epsilon_2^\Theta, E_{Tl^+/Tl}^\Theta - (-0.763) = 0.427$$

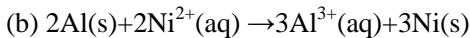
$$\therefore E_{Tl^+/Tl}^\Theta = -0.336\text{V}$$

$$\text{代入}\square\epsilon_3^\Theta, E_{Sc^{3+}/Sc}^\Theta = -2.083\text{V}$$

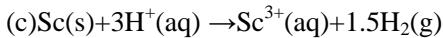
8、



$$\square\epsilon^\Theta = E_{Cl_2/Cl^-}^\Theta - E_{Br_2/Br^-}^\Theta = 1.3583 - 1.065 = 0.2933\text{V}$$



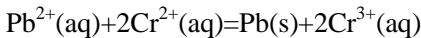
$$\square\epsilon^\Theta = E_{Ni^{2+}/Ni}^\Theta - E_{Al^{3+}/Al}^\Theta = -0.23 - (-1.076) = 0.846\text{V}$$



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

P440

4、



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

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

$$= 0.367\text{V}$$

6、



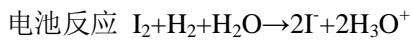
$$E_{\text{池}} = E_{\text{池}}^\Theta - \frac{0.059}{2} \lg [Cu^{2+}][Br^-]^2 = 1.065 - 0.3402 - \frac{0.059}{2} \lg [Br^-]^2$$

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

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

P454

3、

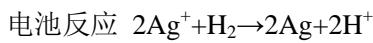


$$E_{\text{池}} = E_{\text{池}}^\Theta - \frac{0.059}{2} \lg [H_3\text{O}^+]^2 [I^-]^2$$

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

$$pH = 4.72$$

4、

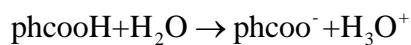


$$E_{\text{池}} = E_{\text{池}}^\Theta - \frac{0.059}{2} \lg \frac{[H^+]^2}{[\text{Ag}^+]^2 P_{\text{H}_2}}$$

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

$$pH = 3.91$$

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

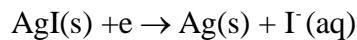


$$\begin{aligned} K_a &= \frac{[H_3\text{O}^+][\text{phcoo}^-]}{[\text{phcooH}]} \\ &= \frac{1.24 \times 10^{-4} \times 0.05}{0.1} \\ &= 6.2 \times 10^{-5} \end{aligned}$$

7、(a)



(1)+(2)



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

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

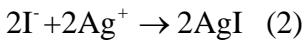
$$\text{由(2)知, } [\text{Ag}^+] = \frac{K_{sp}}{[I^-]}$$

$$\begin{aligned} E &= E_{\text{Ag}^+/\text{Ag}}^\Theta - \frac{0.059}{1} \lg \frac{[I^-]}{K_{sp}} \\ &= E_{\text{Ag}^+/\text{Ag}}^\Theta - \frac{0.059}{1} \lg \frac{1}{K_{sp}} - \frac{0.059}{1} \lg [I^-] \end{aligned}$$

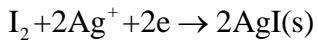
$$\begin{aligned} \therefore E_{\text{AgI/Ag}}^\Theta &= E_{\text{Ag}^+/\text{Ag}}^\Theta - \frac{0.059}{1} \lg \frac{1}{K_{sp}} \\ &= 0.7996 - \frac{0.059}{1} \lg \frac{1}{1.5 \times 10^{-16}} \end{aligned}$$

$$= -0.134 \text{ V}$$

(b)



(1)+(2)



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

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

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

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

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

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

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

$$= 1.47V$$

9、(a)

$$\Delta\epsilon_{池}^\Theta = E_{正}^\Theta - E_{负}^\Theta$$

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

$$= 0 - (-0.1263)$$

$$= 0.1263$$

(b)

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

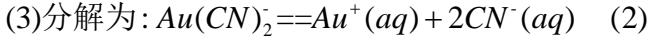
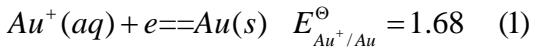
$$0.22 = 0.1263 - \frac{0.059}{2} \lg [Pb^{2+}]$$

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

(c)

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

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



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

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

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

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

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

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

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

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

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

也可以，从(3)式

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

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

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

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

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

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

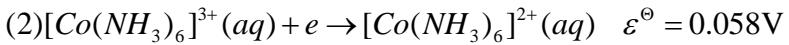
$$K_{\text{稳}} = 4.41 \times 10^{38} = -220.457 \text{ KJ/mol}$$

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

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

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

c



$$E = E_{[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}}^\Theta - 0.059 \lg \frac{[Co(NH_3)_6]^{2+}}{[Co(NH_3)_6]^{3+}}$$

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



$$[Co^{3+}] = \frac{[Co(NH_3)_6]^{3+}}{k_1[NH_3]^6}$$



$$[Co^{2+}] = \frac{[Co(NH_3)_6]^{2+}}{k_2[NH_3]^6}$$

$$E^\Theta = E_{Co^{3+}/Co^{2+}}^\Theta - 0.059 \lg \frac{k_1[Co(NH_3)_6]^{2+}}{k_2[Co(NH_3)_6]^{3+}} \\ = E_{Co^{3+}/Co^{2+}}^\Theta - 0.059 \lg \frac{k_1}{k_2} - 0.059 \lg \frac{[Co(NH_3)_6]^{2+}}{[Co(NH_3)_6]^{3+}}$$

$$E_{[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}}^\Theta = E_{Co^{3+}/Co^{2+}}^\Theta - 0.059 \lg \frac{k_1}{k_2}$$

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

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

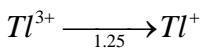
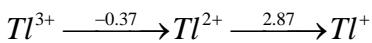
$$\frac{k_1}{k_2} > 1$$

$$\therefore k_1 > k_2$$

$[Co(NH_3)_6]^{3+}$ 更稳定

P464 /5

相当于



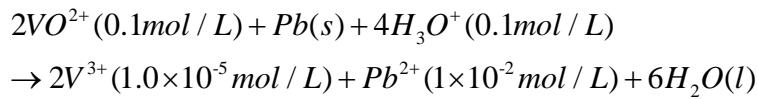
$$1 \times (-0.37) + 1 \times E_{Tl^{2+}/Tl^+}^\Theta = 2 \times 1.25$$

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

$$E_{\text{右}} > E_{\text{左}}$$

可以发生歧化反应

电池反应：



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

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

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

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

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

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

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) x

(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

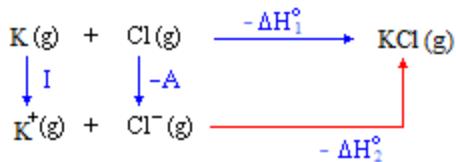
(e) Rb

(f) I

(g)Te
(h)Cl

P129/4

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



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

$$\Delta H_1^\circ = 452 \text{ kJ/mol}$$

P129/6

(a)

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

$$R = 9.46(\text{\AA})$$

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

(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($p_y p_z$)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

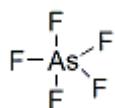
P121/2

| | | | |
|---------|-----|-----|--------------------------|
| (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 $KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$
 $F_2^+ KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$
 (b) F_2 键级为 1, F_2^+ 键级为 1.5
 (c) F_2^+ 有顺磁性
 (d) F_2^+ 键能较大

P156/2

- $O_2^+ KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$ 键级为 2.5
 $O_2^- KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$ 键级为 2
 $O_2^- KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$ 键级为 1.5
 $O_2^{2-} KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$ 键级为 1
 O_2^+, O_2^- 和 O_2^{2-} 有顺磁性
 $O_2^+ > O_2^- > O_2^{2-}$

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

P193

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

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

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

P199

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

P208

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，Cl₂(s)属于分子晶体，NaCl(s)属于离子晶体。

(b) Na(s)为金属离子与自由电子的作用，Cl₂(s)为分子间范德华力的作用，NaCl(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；Cl₂(s)为底心正交，分子；NaCl(s)为面心立方，离子。

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

Cl₂(s): (0,0,0) (1/2,1/2,0)

NaCl(s): (0,0,0) (1/2,1/2,0) (1/2,0,1/2) (0,1/2,1/2)

P258

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，H₂O, H₂S

8. BaH₂: 氢化钡，类盐型氢化物

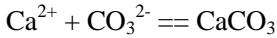
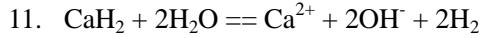
SiH₄: 甲硅烷，分子型氢化物

NH₃: 氨，分子型氢化物

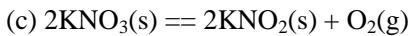
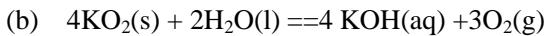
AsH₃: 砷化氢/氢化砷，分子型氢化物

PdH_{0.9}: 氢化钯，金属型氢化物

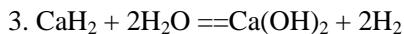
HI: 碘化氢，分子型氢化物



P265



P270



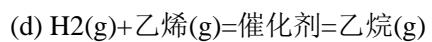
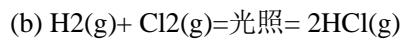
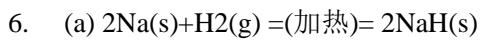
$$(a) 500\text{g CaH}_2 = 500/42 = 11.9 \text{ mol}$$

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

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

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

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



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