

$$1. W = P_{\text{外}} \Delta V = P_{\text{外}} (V_2 - V_1) = P_{\text{外}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$$

$$= 50 \left(\frac{nRT}{50} - \frac{nRT}{100} \right) = \frac{1}{2} nRT = \frac{1}{2} \times 2.5 \times 300 \times 8.314 = 3117.75 \text{ J}$$

$$2. V_1 \rightarrow 10V_1 \quad W = 41.85 \text{ kJ} \quad P_1 = 202.65 \text{ kPa} \quad n = 2$$

$$(1) W = \int_{V_1}^{V_2} P_{\text{外}} dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \frac{V_2}{V_1} = nRT \ln 10 = 41.85 \text{ kJ}$$

$$P_1 V_1 = nRT$$

$$V_1 = \frac{nRT}{P_1} = \frac{41.85 \times 10^3 \text{ J} / \ln 10}{202.65 \times 10^3 \text{ Pa}} = 8.97 \times 10^{-2} \text{ m}^3 = 89.7 \text{ L}$$

$$(2) nRT \ln 10 = 41.85 \times 10^3$$

$$T = \frac{41.85 \times 10^3}{2 \times 8.314 \times \ln 10} = 1093 \text{ K}$$

$$3. n = 1 \text{ mol} \quad V_1 = 50 \text{ L} \quad V_2 = 100 \text{ L} \quad T_1 = T_2 = 373 \text{ K} \quad \text{at } W$$

$$(1) \text{ 恒温可逆膨胀}$$

$$W = \int P_{\text{外}} dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \frac{V_2}{V_1} = 2.15 \text{ kJ}$$

$$(2) \text{ 向真空膨胀}$$

$$W = \int P_{\text{外}} dV = 0$$

$$(3) \text{ 绝热可逆膨胀}$$

$$W = P_2 \Delta V = \frac{nRT_2}{V_2} (V_2 - V_1) = \frac{1 \times 8.314 \times 373}{100 \text{ L}} (100 - 50) = 1550 \text{ J}$$

$$(4) P' \rightarrow 75 \text{ kPa} \quad P_2 = 100 \text{ kPa}$$

$$W = \frac{P_1 V_1}{\gamma} (75 - 50) + \frac{P_1 V_1}{\gamma} (100 - 75) = 1809 \text{ J}$$

4. 忽略液体体积

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

$$\begin{aligned}\Delta U &= \Delta H - \Delta(PV) = \Delta H - nRT \\ &= 40.67 \times 10^3 - 1 \times 8.314 \times 373.15 \\ &= 37.57 \times 10^3 \text{ J} \cdot \text{mol}^{-1}\end{aligned}$$

$$5. \quad \Delta H = \Delta U + \Delta(PV)_{nRT}$$

$$\begin{aligned}&= -P_2 \times 10^3 + (-2) \times 8.314 \times 298.15 \\ &= -96.96 \times 10^3 \text{ J} \cdot \text{mol}^{-1}\end{aligned}$$

$$6. \quad T = 273.15 \text{ K} \quad P_1 = 5 \times 101325 \text{ Pa} \quad V_1 = 2 \text{ L} \\ P_2 = P_1 = 101325 \quad V_2 = 10 \text{ L}$$

$$W = P_{\text{外}} \Delta V = 101325 \times (10 - 2) = 810.5 \text{ J}$$

$$\Delta U = \Delta H = 0 \Rightarrow \text{恒温理想气体}$$

$$\Delta = W = 810.5 \text{ J}$$

$$7. \quad n = 2 \quad C_{V,m} = 20.79 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad T_1 = 323 \text{ K} \quad V_1 = 100 \text{ L} \\ T_2 = 423 \text{ K} \quad V_2 = 150 \text{ L}$$

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_2} \frac{n C_{V,m}}{T} dT + \int_{V_1}^{V_2} \frac{nR}{T} dV \\ &= 2 \times 20.79 \times \ln \frac{423}{323} + 2 \times 8.314 \times \ln \frac{150}{100} \\ &= 2 \times 5.61 + 6.74 = 17.96 \text{ J} \cdot \text{K}^{-1}\end{aligned}$$

$$\int ds = \int \frac{\delta Q_r}{T} = \int \frac{du + \delta w_r}{T} = \int \frac{C_V}{T} du + \int \frac{P dv}{T}$$

$$n = 0.5 \text{ mol}$$

$$8. \quad T_0 = 302 \text{ K} \quad \text{①} \quad V_1 = 30 \text{ L} \quad \text{②} \quad T_2 = 600 \text{ K}$$

$$P_0 = 101325 \text{ Pa} \quad \xrightarrow{\text{等温膨胀}} \quad T_1 = 300 \text{ K} \quad \xrightarrow{\text{恒容升温}} \quad V_2 = 30 \text{ L}$$

$$\text{求 } W, Q, \Delta U, \Delta H, \Delta S.$$

$$C_V = 20.79 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\text{① 等温 } \Delta U_1 = 0 \text{ J} \quad \Delta H_1 = 0 \text{ J}$$

$$Q_1 = W_1 = \int_{V_0}^{V_1} p dV = \int_{V_0}^{V_1} \frac{nRT}{V} dV = 0.5 \times 8.314 \times 300 \ln \frac{30 \text{ L}}{12.3 \text{ L}} = 1112 \text{ J}$$

$$V_0 = \frac{nRT_0}{P_0} = \frac{0.5 \times 8.314 \times 300}{101325} = 12.3 \text{ L}$$

$$\Delta S_1 = \frac{Q_1}{T} = \frac{1112 \text{ J}}{300 \text{ K}} = 3.7 \text{ J/K}$$

$$\text{② } W_2 = \int p dV = 0$$

$$Q_2 = Q_V = n C_V \ln \frac{T_2}{T_1} = 0.5 \times 20.79 \ln \frac{600}{300} = 7.2 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta U_2 = Q_V = Q_2 = \int_{T_1}^{T_2} n C_V dT = C_V (T_2 - T_1) = 20.79 \times 0.5 \times (600 - 300) = 3118.5 \text{ J}$$

$$\Delta H_2 = \Delta U + \Delta(pV)$$

$$= \Delta U + (nRT_2 - nRT_1)$$

$$= 3118.5 + 0.5 \times 8.314 \times (600 - 300) = 3118.5 + 1247.1 = 4365.6 \text{ J}$$

$$\Delta S_2 = n C_V \ln \frac{T_2}{T_1} = 0.5 \times 20.79 \ln \frac{600}{300} = 7.2 \text{ J} \cdot \text{K}^{-1}$$

$$\therefore W = W_1 + W_2 = 1112 \text{ J}$$

$$Q = Q_1 + Q_2 = 1112 + 3118.5 = 4230.5 \text{ J}$$

$$\Delta U = Q - W = 3118.5 \text{ J}$$

$$\Delta H = \Delta U + \Delta H_2 = 4365.6 \text{ J}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = 3.7 + 7.2 = 10.9 \text{ J/K}$$

$$\text{或者 } \Delta S = n C_V \ln \frac{T_2}{T_0} + n R \ln \frac{V_2}{V_0}$$

$$= 0.5 \times 20.79 \ln \frac{600}{300} + 0.5 \times 8.314 \ln \frac{30}{12.3}$$

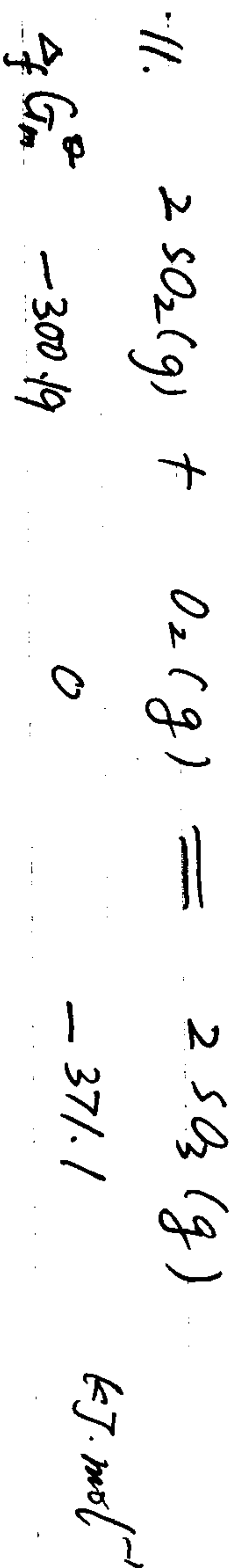
$$= 7.2 + 3.7 = 10.9 \text{ J/K}$$

(状态函数, 只跟始态和终态有关)

$$\begin{aligned}
 9. \Delta S &= n C_v \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1} \\
 &= 0.5 \times 20.1 \ln \frac{400}{298.15} + 0.5 \times 8.314 \times \ln \frac{n R T_2 / p}{n R T_1 / p} \\
 &= 2.95 + 0.5 \times 8.314 \ln \frac{400}{298.15} = 2.95 + 1.22 = 4.17 \text{ J} \cdot \text{K}^{-1}
 \end{aligned}$$

$$10. \Delta G = 0 \quad \text{恒温恒压无非体积功过程}$$

$$\Delta S = \frac{Q_r}{T} = \frac{6.008 \times 10^3}{273.15} = 22 \text{ J} \cdot \text{K}^{-1}$$



$$\Delta_r G_m^\ominus = 2 \times (-371.1) - 2 \times (-300.19) = -141.8 \text{ J} \cdot \text{mol}^{-1}$$

$$\Delta_f G_m^\ominus = -R T \ln K$$

$$\therefore K = e^{-\frac{\Delta_f G_m^\ominus}{R T}} = e^{57.2} = 7.0 \times 10^{24}$$

$$\begin{aligned}
 J &= \frac{(P_{\text{SO}_3}/p^\ominus)^2}{(P_{\text{SO}_2}/p^\ominus)^2 (P_{\text{O}_2}/p^\ominus)} = \frac{(1000/101325)^2}{\left(\frac{1000}{101325}\right)^2 \left(\frac{1000}{101325}\right)} = 101325 < K \\
 &\quad \text{反应朝生成 SO}_3 \text{ 方向进行。}
 \end{aligned}$$

$$13. \Delta_r G_m = \Delta_r G_m^\ominus + R T \ln \frac{p}{p^\ominus}$$

$$= (-604.06 - 394.36 + 1128.8) \times 10^3 + R T \ln \frac{101325}{101325}$$

$$= 130.38 \times 10^3 + (-17.12 \times 10^3)$$

$$= 113.26 \times 10^3 \text{ J}$$



$$\Delta_r H_m^\ominus = -393.51 - 635.09 - (-1206.9) = 178.3 \times 10^3 \text{ J}$$

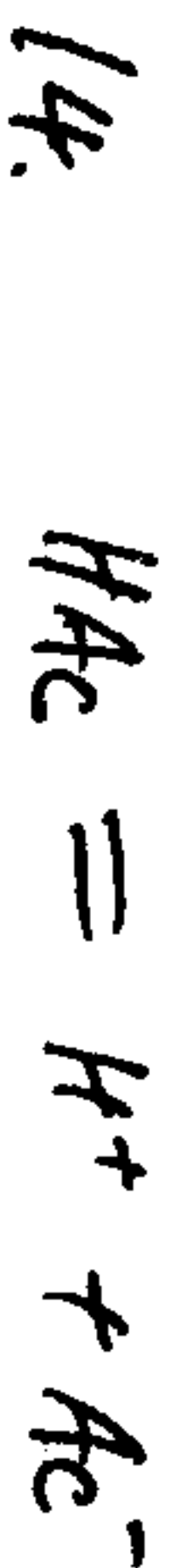
$$\Delta_r S_m^\ominus = 213.6 + 39.75 - 92.9 = 160.45 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta_r G_m^\ominus = -394.36 - 604.04 - (-1128.8) = 130.4 \times 10^3 \text{ J}$$

$$-RT \ln K = \Delta_r G_m^\ominus$$

$$K = e^{-\Delta_r G_m^\ominus / RT} = e^{-52.6} = 1.43 \times 10^{-23}$$

298.15K 时 $\Delta H > 0$ \therefore 反应为吸热。
若希望 298.15 反应发生，则减小体系中 CaO 的压力实现，即抽真空。



$$\Delta_r G_m^\ominus = -39.66 - 368.4 - (-277.0) = -369.4 \text{ kJ}$$

$$K_a = e^{-\Delta_r G_m^\ominus / RT} = e^{-10.87} = 1.72 \times 10^{-5}$$



$$\textcircled{1} \Delta_r G_m^\ominus = 2 \times (-16.5) = -33 \text{ kJ}$$

$$K = e^{-\Delta_r G_m^\ominus / RT} = e^{13.31} = 6.0 \times 10^5$$

$$\textcircled{2} J = \frac{(\frac{2}{6})^2}{(\frac{2}{6})^3 (\frac{1}{6})} = \frac{16}{3} < K \quad \text{反应朝正方向进行即生成} \text{NH}_3$$

$$\textcircled{3} \Delta_r H_m^\ominus = 2 \times (-46.11) = -92.22 \text{ kJ}$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta_r H_m^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = -12.55$$

$$K_2 = 2.13$$

$$\Delta_r G_m^\ominus = -RT \ln K = -450 \times 8.314 \ln 2.13 = -2.8 \times 10^3 \text{ J}$$

$$\textcircled{4} J = \frac{16}{3} > K = 2.13 \quad \therefore \text{反应朝左进行即} \text{NH}_3 \text{分解}$$

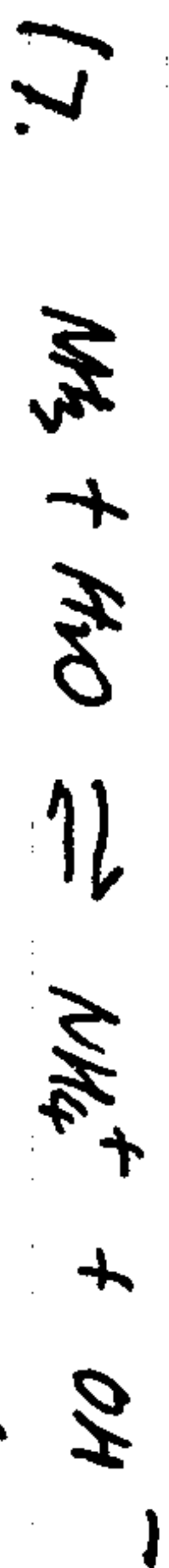
$$\textcircled{5} J = \frac{(\frac{4}{6})^2}{(\frac{2}{6})^3 (\frac{2}{6})} = \frac{4}{3} < K(450\text{K}) = 2.13 \quad \therefore \text{反应朝右进行即生成} \text{NH}_3$$



$$K_a = 2.95 \times 10^{-8} = \frac{[\text{H}_3\text{O}^+][\text{AlO}^-]}{[\text{HAlO}]} = \frac{x^2}{0.06-x}$$

$$\therefore x = [\text{H}_3\text{O}^+] = 4.2 \times 10^{-5} \text{ mol/L}$$

$$\alpha = \frac{x}{0.06} = \frac{4.2 \times 10^{-5}}{0.06} = 7 \times 10^{-4} = 0.07\%$$

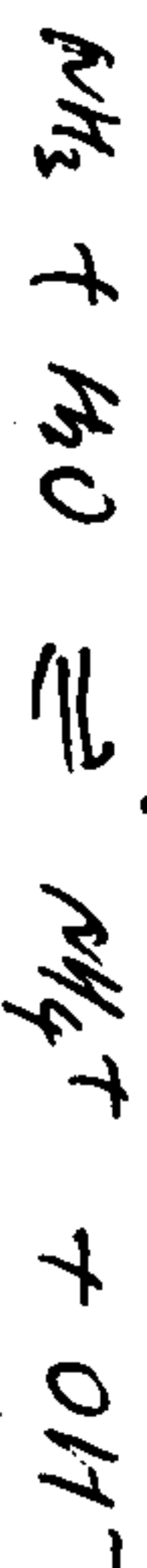


$$K_b = 1.77 \times 10^{-5} = \frac{x^2}{0.3-x} \quad \lg [\text{OH}^-] = x = 2.3 \times 10^{-3} \text{ mol/L}$$

$$\text{pH} = 14 - \lg 2.3 \times 10^{-3} = 11.4$$

100 ml 中 加入 1.07 g NH_4Cl

$$C_{\text{NH}_4\text{Cl}} = \frac{1.07}{53.5} / 0.1 = 0.2 \text{ mol/L}$$



$$K_b = 1.77 \times 10^{-5} = \frac{x(0.2+x)}{0.3-x}$$

$$[\text{OH}^-] = x = 2.65 \times 10^{-5} \text{ mol/L}$$

$$\text{pH} = 14 - \lg 2.65 \times 10^{-5} = 9.4$$

说明 NH_4Cl 的加入, 抑制了 NH_3 的电离, 平衡向左移动, 导致 $\text{pH} \downarrow$.
(同离子效应)



$$I = \frac{0.01}{2} \times \left(\frac{0.01}{2}\right)^2 = 1.25 \times 10^{-7} > K_{sp} \quad \downarrow \text{沉淀}$$



$$I = \frac{0.05}{20+30} \times 20 \times \frac{0.5}{20+30} \times 30 > K_{sp} \quad \downarrow$$



$$I = 0.01 \times \frac{0.535 \times 10}{53.5} = 10^{-3} > K_{sp} \quad \downarrow$$

19. $Pb(NO_3)_2$ 与 Na_2S 混合, 其中 $Pb^{2+} = 0.2 \text{ mol/L}$

(1) $K_{sp} = 8.49 \times 10^{-9} = 0.2 \times x^2$

$[Z^{-}] = x = 2.06 \times 10^{-4} \text{ mol/L}$

(2) $(6.0 \times 10^{-2})^2 x = 8.49 \times 10^{-9}$

$[Pb^{2+}] = x = 2.36 \times 10^{-6} \text{ mol/L}$

20. (1) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$\frac{0.1}{2} - x \quad x \quad x$

$K_b = 1.77 \times 10^{-5} = \frac{x^2}{\frac{0.1}{2} - x} \quad \therefore [OH^-] = x = 1.32 \times 10^{-4} \text{ mol/L}$

$J = \frac{0.5}{2} \times x^2 = 2.17 \times 10^{-7} > K_{sp} = 5.61 \times 10^{-12} \quad \downarrow \text{有沉淀}$

(2) 混合液不沉淀

$K_{sp} = 5.61 \times 10^{-12} = \frac{0.5}{2} \times [OH^-]^2 \quad \therefore [OH^-] = 4.74 \times 10^{-6} \text{ mol/L}$

$K_b = 1.77 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3 \cdot H_2O]} = \frac{4.74 \times 10^{-6} \times x}{0.1/2}$

$\therefore [NH_4^+] = x = 0.187 \text{ mol/L}$

\downarrow 为混合液中的离子

\therefore 加入 $MgCl_2 \quad 2 \times 0.187 \times 53.5 = 20 \text{ g}$

21. $Mg(OH)_2 \quad K_{sp} = 5.61 \times 10^{-12}$

(1) 水中溶解度 $K_{sp} = [Mg^{2+}][OH^-]^2 = x \cdot (2x)^2$

1g $x = 1.12 \times 10^{-4} \text{ mol/L}$

(2) $[Mg^{2+}] = 1.12 \times 10^{-4} \text{ mol/L} \quad [OH^-] = 2.24 \times 10^{-4} \text{ mol/L}$

(3) 加入 0.01 mol/L NaOH

$K_{sp} = [Mg^{2+}][OH^-]^2 = x \cdot (0.01 + 2x)^2 \quad x[Mg^{2+}] = 5.61 \times 10^{-8} \text{ mol/L}$
 $[OH^-] = 0.01 \text{ mol/L}$

(4) $0.01 \text{ mol/L MgCl}_2 \quad K_{sp} = 0.01 [OH^-]^2 \quad \therefore [OH^-] = 2.4 \times 10^{-5} \text{ mol/L}$

~~混合液~~ $Mg(OH)_2 = 1.2 \times 10^{-5} \text{ mol/L}$

23. (1) =, = (2) = = >> (3) (大) (E) 16) K_1^2/K_2

Date

No.

22. ① 1L 含 0.1 mol HAc 和 0.1 mol NaAc 的 pH



$$K_a = 1.76 \times 10^{-5} = \frac{x(0.1+x)}{0.1-x}$$

$$\therefore \overset{[H^+]}{x} = 1.76 \times 10^{-5} \text{ mol/L}$$

$$pH = -\lg x = 4.75$$

② 向①中加入 0.01 mol NaOH



$$K_a = 1.76 \times 10^{-5} = \frac{x(0.11+x)}{(0.09-x)}$$

$$\therefore [H^+] = x = 1.44 \times 10^{-5} \text{ mol/L}$$

$$pH = -\lg x = 4.84$$

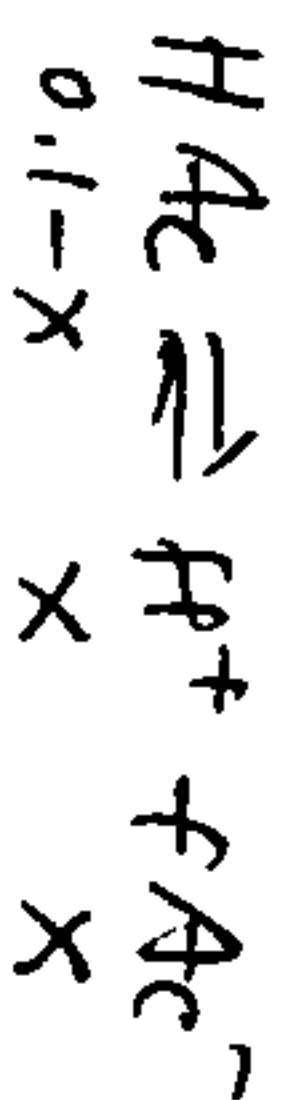
③ 1L 0.1 mol/L HAc 中加入 0.01 mol NaOH (固体)



$$K_a = 1.76 \times 10^{-5} = \frac{x(0.01+x)}{0.09-x}$$

$$\therefore x = 1.58 \times 10^{-4} \text{ mol/L} = [H^+]$$

$$pH = -\lg x = 3.8$$



$$K_a = 1.76 \times 10^{-5} = \frac{x^2}{0.1-x}$$

$$\therefore [H^+] = x = 1.3 \times 10^{-3} \text{ mol/L}$$

$$pH = -\lg x = 2.9$$

通过以上计算可知，当 HAc 与 NaAc 组成缓冲溶液时，

往其中加入少量 NaOH 时溶液 pH 变化较小，从 4.75 \rightarrow 4.84

(缓冲作用)。

加入 0.01 mol NaOH, pH 从 2.9 \rightarrow 3.8 变化较大。