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

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

$= 3117.75\,J$

2. $V_1 \to 10V_1 \quad W = 41.85\,kJ \quad P_1 = 202.65\,kPa \quad n = 2$

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

$P_1V_1 = nRT$

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

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

$T = 41.85 \times 10^3 / 2 \times 8.314 \times \ln 10 = 1093\,K$

3. $n = 1\,mol \quad V_1 = 50\,L \quad V_2 = 100\,L \quad T_1 = T_2 = 373\,K$ 求 W

(1) 等温可逆膨胀

$W = \int P\,dV = \int_{V_1}^{V_2} \frac{nRT}{V}\,dV = nRT\ln\frac{V_2}{V_1} = 2.15\,kJ$

(2) 向真空膨胀

$W = \int P_{外}\,dV = 0$

(3) 恒外压 P_2

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

$= 1550\,J$

(4) $P' \to 75\,L \quad P_2 = 100\,L$

$W = \frac{RT}{75}(75 - 50) + \frac{RT}{100}(100 - 75) = 1809\,J$

4. 忽略液体水的体积

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

$\Delta U = \Delta H - \Delta(pV) = \Delta H - nRT$

$= 40.67\times10^3 - 1\times8.314\times373.15$

$= 37.57\times10^3\ J\cdot mol^{-1}$

5. $\Delta H = \Delta U + \Delta(pV)$

$\Delta(pV) = nRT$

$= -P2\times10^3 + (-2)\times8.314\times298.15$

$= -96.96\times10^3\ J$

6. $T=273.15k \quad P_1=5\times101325Pa \quad V_1=2L$

$P_2=P_{外}=101325 \quad V_2=10L$

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

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

$Q=W=810.5J$

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

$\Delta S = \int_{T_1}^{T_2}\frac{nC_{v,m}}{T}dT + \int_{V_1}^{V_2}\frac{nRT}{T\cdot V}dV$

$= 2\times20.79\times\ln\frac{423}{323} + 2\times8.314\times\ln\frac{150}{100}$

$= 2\times5.61 + 6.74 = 17.96\ J\cdot K^{-1}$

$\int dS = \int\frac{\delta Q_r}{T} = \int\frac{du+\delta w_r}{T} = \int\frac{Cv}{T}du + \int\frac{pdv}{T}$

$n=0.5\,mol$

8. $T_0=300K$ $P_0=101325Pa$ —①等温可逆膨胀→ $V_1=30L$ $T_1=300K$ —②恒容升温→ $T_2=600K$ $V_2=30L$

求 $W, Q, \Delta U, \Delta H, \Delta S$. $C_V=20.79\,J\cdot K^{-1}\cdot mol^{-1}$

① 等温 $\Delta U_1=0J$ $\Delta H_1=0J$

$$Q_1=W_1=\int_{V_0}^{V_1}pdV=\int_{V_0}^{V_1}\frac{nRT}{V}dV=0.5\times8.314\times300\ln\frac{30L}{12.3L}=1112J$$

$$V_0=\frac{nRT_0}{P_0}=\frac{0.5\times8.314\times300}{101325}=12.3L$$

$$\Delta S_1=\frac{Q_r}{T}=\frac{1112J}{300K}=3.7\,J/K$$

② $W_2=\int pdV=0$

~~$Q_2=Q_V=nC_V\ln\frac{T_2}{T_1}=0.5\times20.78\ln\frac{600}{300}=7.2\,J\cdot K^{-1}$~~

$$\Delta U_2=Q_V=Q_2=\int_{T_1}^{T_2}nC_VdT=C_V(T_2-T_1)=20.79\times0.5\times(600-300)=3118.5J$$

$$\Delta H_2=\Delta U+\Delta(pV)=\Delta U+(nRT_2-nRT_1)=3118.5+0.5\times8.314\times(600-300)=3118.5+1247.1=4365.6J$$

$$\Delta S_2=nC_V\ln\frac{T_2}{T_1}=0.5\times20.78\ln\frac{600}{300}=7.2\,J\cdot K^{-1}$$

∴ $W=W_1+W_2=1112J$

$Q=Q_1+Q_2=1112+3118.5=4230.5J$

$\Delta U=Q-W=3118.5J$

$\Delta H=\Delta H_1+\Delta H_2=4365.6J$

$\Delta S=\Delta S_1+\Delta S_2=3.7+7.2=10.9\,J/K$

或者 $\Delta S=nC_V\ln\frac{T_2}{T_0}+nR\ln\frac{V_2}{V_0}$

$=0.5\times20.79\ln\frac{600}{300}+0.5\times8.314\ln\frac{30}{12.3}$

$=7.2+3.7=10.9\,J/K$ (状态函数，仅跟始态和终态有关)

9. $\Delta S = nC_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$

$= 0.5\times 20.1 \ln\frac{400}{298.15} + 0.5\times 8.314 \times \ln\frac{nRT_2/p}{nRT_1/p}$

$= 2.95 + 0.5\times 8.314 \ln\frac{400}{298.15} = 2.95 + 1.22 = 4.17 (J\cdot K^{-1})$

10. $\Delta G = 0$ 恒温恒压下的可逆过程

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

11. $2SO_2(g) + O_2(g) = 2SO_3(g)$

$\Delta_f G_m^\ominus$ -300.19 0 -371.1 $kJ\cdot mol^{-1}$

$\Delta_r G_m^\ominus = 2\times(-371.1) - 2\times(-300.19) = -141.8 J$ kJ

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

$\therefore K = e^{-\frac{\Delta_r G_m^\ominus}{RT}} = e^{57.2} = 7.0\times 10^{24}$

$J = \frac{(P_{SO_3}/p^\ominus)^2}{(P_{SO_2}/p^\ominus)^2 (P_{O_2}/p^\ominus)} = \frac{(1000/101325)^2}{(\frac{1000}{101325})^2 (\frac{1000}{101325})} = 101.325 << K$

∴ 反应朝生成SO3的方向进行。

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

$= (-604.06 - 394.36 + 1128.8)\times 10^3 + RT\ln\frac{101.325}{101325}$

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

$= 113.3\times 10^3$ J

12. $CaW_3(s) = WO_2(g) + CaO(s)$

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

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

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

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

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

298.15K 时 $\Delta H > 0$ ∴ 反应为吸热.

若希望 298.15 反应发生, 可以减小体系中 WO_2 的压力实现. 即抽真空.

14. $HAc = H^+ + Ac^-$

$\Delta_f G_m^\ominus$ -396.6 0 -369.4 $\Delta_r G_m^\ominus = -369.4 + 396.6 = 27.2$ kJ

$K_a = e^{-27.2 \times 10^3 / 298.15 \times 8.314} = e^{-10.97} = 1.72 \times 10^{-5}$

15. $N_2(g) + 3H_2(g) = 2NH_3(g)$

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

$K = e^{-(-33 \times 10^3)/298.15 \times 8.314} = e^{13.31} = 6.0 \times 10^5$

② $J = \dfrac{(\frac{2}{6})^2}{(\frac{2}{6})^3(\frac{1}{6})} = \dfrac{16}{3} < K$ 反应朝正方向进行. 即生成 NH_3

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

$\ln \dfrac{K_2}{6.0 \times 10^5} = -\dfrac{-92220}{8.314}\left(\dfrac{1}{450} - \dfrac{1}{298.15}\right) = -12.55$

$K_2 = 2.13$

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

④ $J = \dfrac{16}{3} > K = 2.13$ ∴ 反应朝左进行. 即 NH_3 分解

⑤ $J = \dfrac{(\frac{4}{6})^2}{(\frac{6}{6})^3(\frac{2}{6})} = \dfrac{4}{3} < K(450K) = 2.13$ ∴ 反应朝左进行即生成 NH_3

16. $HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$

$0.26-x$ $\quad x \quad x$

$$K_a = 2.95\times10^{-8} = \frac{[H_3O^+][ClO^-]}{[HClO]} = \frac{x^2}{0.06-x}$$

$\therefore X = [H_3O^+] = 4.2\times10^{-5}\ mol\cdot L^{-1}$

$$\alpha = \frac{x}{0.06} = \frac{4.2\times10^{-5}}{0.06} = 7\times10^{-4} = 0.07\%$$

17. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$0.3-x$ $\quad x \quad x$

$$K_b = 1.77\times10^{-5} = \frac{x^2}{0.3-x}$$ 得 $[OH^-] = x = 2.3\times10^{-3}\ mol\cdot L^{-1}$

$pH = 14 - \lg 2.3\times10^{-3} = 11.4$

100 ml 中加入 1.07 g NH_4Cl

$$C_{NH_4Cl} = \frac{1.07}{53.5}/0.1 = 0.2\ mol\cdot L^{-1}$$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$0.3-x$ $\quad 0.2+x \quad x$

$$K_b = 1.77\times10^{-5} = \frac{x(0.2+x)}{0.3-x}$$

$[OH^-] = x = 2.65\times10^{-5}\ mol/L$

$pH = 14 - \lg 2.65\times10^{-5} = 9.4$

说明 NH_4Cl in 加入，抑制了 NH_3 in 电离，平衡向左移动，导致 pH ↓.
（同离子效应）

18. (1) PbI_2 $\quad K_{sp} = 8.49\times10^{-9}$

$$J = \frac{0.01}{2}\times\left(\frac{0.01}{2}\right)^2 = 1.25\times10^{-7} > K_{sp}$$ ↓沉淀

(2) $BaCO_3$ $\quad K_{sp} = 2.56\times10^{-9}$

$$J = \frac{0.05}{20+30}\times20 \times \frac{0.5}{20+30}\times30 > K_{sp}$$ ↓

(3) $K_{sp} = 1.77\times10^{-10}$

$$J = 0.01\times\frac{0.535\times10}{53.5} = 10^{-3} > K_{sp}$$ ↓

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

(1) $K_{sp} = 8.49\times10^{-9} = 0.2 \times X^2$

$[I^-] = X = 2.06\times10^{-4}\ mol/L$

(2) $(6.0\times10^{-2})^2 X = 8.49\times10^{-9}$

$[Pb^{2+}] = X = 2.36\times10^{-6}\ mol/L$

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

$\frac{0.1}{2} - X \qquad X \qquad X$

$K_b = 1.77\times10^{-5} = \dfrac{X^2}{\frac{0.1}{2} - X}$ ∴ $[OH^-] = X = 9.32\times10^{-4}\ mol/L$

$J = \frac{0.5}{2} \times X^2 = 2.17\times10^{-7} > K_{sp} = 5.61\times10^{-12}$ ↓有沉淀

(2) 恰好不完全

$K_{sp} = 5.61\times10^{-12} = \frac{0.5}{2} \times [OH^-]^2$ ∴ $[OH^-] = 4.74\times10^{-6}\ mol/L$

$K_b = 1.77\times10^{-5} = \dfrac{[NH_4^+][OH^-]}{[NH_3\cdot H_2O]} = \dfrac{4.74\times10^{-6}\times X}{0.1/2}$

∴ $[NH_4^+] = X = 0.187\ mol/L$

↓为溶液中浓度

∴ 加入 NH_4Cl $2\times0.187\times53.5 = 20g$

21. $Mg(OH)_2$ $K_{sp} = 5.61\times10^{-12}$

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

得 $X = 1.12\times10^{-4}\ mol/L$

(2) $[Mg^{2+}] = 1.12\times10^{-4}\ mol/L$ $[OH^-] = 2.24\times10^{-4}\ mol/L$

(3) 加入 0.01 mol/L NaOH

$K_{sp} = [Mg^{2+}][OH^-]^2 = X\cdot(0.01+2X)^2$ $X = [Mg^{2+}] = 5.61\times10^{-8}\ mol/L$

$[OH^-] = 0.01\ mol/L$

(4) 0.01 mol/L $MgCl_2$ $K_{sp} = 0.01\,[OH^-]^2$ ∴ $[OH^-] = 2.4\times10^{-5}\ mol/L$

溶解 $Mg(OH)_2 = 1.2\times10^{-5}\ mol/L$

23. (1) =,= (2) = = = >> (3)(大)(正) 16) K_1^2/K_2 Date No.

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

$$HAc = H^+ + Ac^-$$
$$0.1-X \quad X \quad 0.1+X$$

$$K_a = 1.76\times10^{-5} = \frac{X(0.1+X)}{0.1-X}$$

$[H^+]$

$\therefore X = 1.76\times10^{-5}\ mol/L$

$$pH = -\lg X = 4.75$$

② 向①中加入 0.01 mol NaOH

$$HAc = H^+ + Ac^-$$
$$0.1-0.01-X \quad X \quad 0.1+0.01+X$$

$$K_a = 1.76\times10^{-5} = \frac{X(0.11+X)}{(0.09-X)}$$

$$\therefore [H^+] = X = 1.44\times10^{-5}\ mol/L$$

$$pH = -\lg X = 4.84$$

③ 1L 0.1mol/L HAc 中加入 0.01mol NaOH 固体

$$HAc = H^+ + Ac^-$$
$$0.1-0.01-X \quad X \quad 0.01+X$$

$$K_a = 1.76\times10^{-5} = \frac{X(0.01+X)}{0.09-X}$$

$$\therefore X = 1.58\times10^{-4}\ mol/L = [H^+]$$

$$pH = -\lg X = 3.8$$

$$HAc \rightleftharpoons H^+ + Ac^-$$
$$0.1-X \quad X \quad X$$

$$K_a = 1.76\times10^{-5} = \frac{X^2}{0.1-X}$$

$\therefore [H^+] = X = 1.3\times10^{-3}\ mol/L$

$pH = -\lg X = 2.9$

通过以上计算我们知道，当 HAc 与其盐 NaAc 组成缓冲溶液时，往其中加入少量 NaOH 对溶液 pH 的值改变小，从 4.75 → 4.84（缓冲溶液）。

加入固体 NaOH，pH 从 2.9 → 3.8 有较大改变。