北京科大2004年考研物理化学试题解　(李汝雄教授做参考答案)

一、选择题(20分)

1. D　2. C　3. A　4. B　5. B

6. B　7. A　8. C　9. D　10. B

二、填空题(20分)

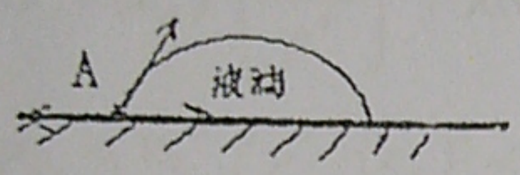
1. <

2. 20

3. –2080.5 J

4. 1，1

5. 低

6. 

7. 23116 J，-172749 J，-133576 J

8. 1.194，0.2089

三、计算题(110分)

1. (14分)

$H_2S(g)+2Ag(s)=Ag_2S(s)+H_2(g)$

(1) $p_{H_2}=\frac{1}{2}p^{\theta}$　$P_{H_2S}=\frac{1}{2}p^{\theta}$　$J_p=\frac{p_{H_2}}{p_{H_2S}}=1$

$$\Delta_r G_m^{\theta}=-40.25+32.93=-7.32kJ\cdot mol^{-1}$$

$$K^{\theta}=\exp\left(-\frac{\Delta_r G_m^{\theta}}{RT}\right)=\exp\left(\frac{7320}{8.314\times 298}\right)=19.19$$

$J_p < K^{\theta}$，可以生成 Ag_2S

(2) 当 $J_p=K^{\theta}$ 时，$J_p=\frac{P_{H_2}}{P_{H_2S}}=\frac{p(1-y_{H_2S})}{py_{H_2S}}=19.19$　解得 $y_{H_2S}=0.459$

H_2S 的百分数低于 $y_{H_2S}<0.459$ 才不致发生腐蚀。

2. (14分，单考生仅做(1)题)

(1) $p_1^{\cdot}=13706\ Pa$　$p_2^{\cdot}=39346\ Pa$

$$p_1 = py_1 \qquad p_2 = py_2$$

$$x_1 = 0.6 \qquad x_2 = 0.4$$

乙醇(1): $\gamma_1 = \dfrac{p_1}{p_1^{\cdot} x_1} = \dfrac{34291 \times (1 - 0.7446)}{13706 \times 0.6} = 1.065$

氯仿(2): $\gamma_2 = \dfrac{p_2}{p_2^{\cdot} x_2} = \dfrac{34291 \times 0.7446}{39343 \times 0.4} = 1.622$

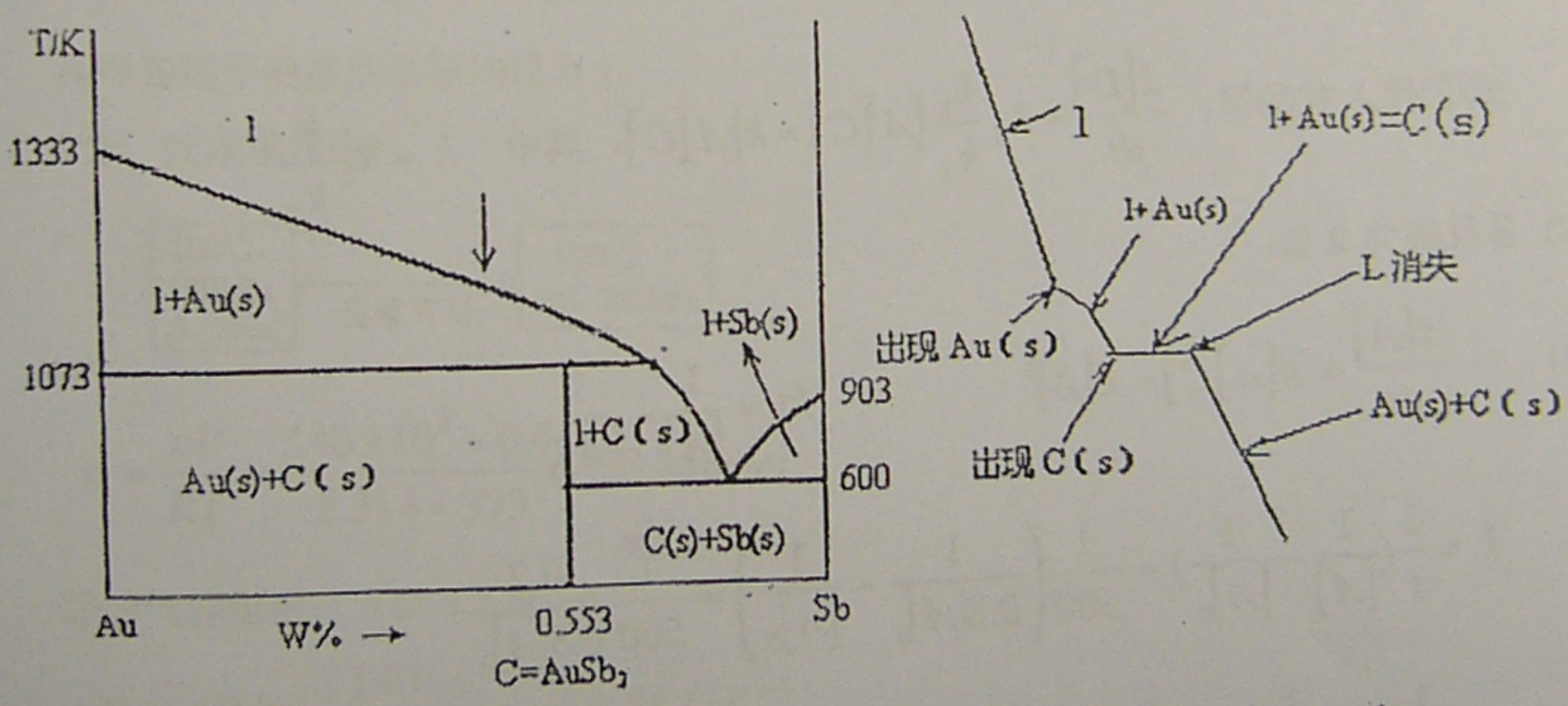
(2) $x_2 = 0.01$ 时，氯仿服从亨利定律：$p_2 = Kx_2$

$$K = \frac{P_2}{x_2} = \frac{14159 \times 0.7446}{0.01} = 58618\ Pa$$

$x_2 = 0.4$ 时，$a_2 = \dfrac{p_2}{K} = \dfrac{34291 \times 0.7446}{58618} = 0.4356$

$$\gamma_2 = \frac{a_2}{x_2} = \frac{0.4356}{0.4} = 1.089$$

3. (17 分)



4. (6 分)

$$\ln \frac{p_r}{p} = \frac{2M\sigma}{RT\rho r} = \frac{2 \times 18 \times 10^{-3} \times 0.0589}{8.314 \times 373 \times 1.0 \times 10^3 \times (-0.5 \times 10^{-6})} = -1.368 \times 10^{-3}$$

$$p_r = 101325 \times 0.9986 = 101187 Pa$$

5. (9 分)

(1) C=0.1mol · l^{-1} 时，$\dfrac{d\sigma}{dC} = -0.0131 \times \dfrac{19.62}{1 + 19.62C} = -0.08677$

$$\Gamma = -\frac{C}{RT}\frac{d\sigma}{dC} = -\frac{0.1}{8.314\times 293}(-0.08677) = 3.562\times 10^{-6}\,mol\cdot m^{-2}$$

(2) $\Gamma = -\dfrac{C}{RT}\dfrac{d\sigma}{dC} = \dfrac{C}{RT}\dfrac{0.0131\times 19.62}{1+19.62C}$ ①　　$\Gamma = \Gamma_\infty \dfrac{bC}{1+bC}$ ② $= \dfrac{C}{RT}\dfrac{0.0131\times 19.62}{1+19.62c}$　b

比较式①、②得饱和吸附量：$\Gamma_\infty = \dfrac{0.0131}{RT} = 5.378\times 10^{-6}\,mol\cdot m^{-2}$　　$\therefore \Gamma_\infty = \dfrac{0.0131}{RT}\dfrac{19.62c}{1+\underbrace{19.62c}_{b}}$

(3) 每个分子所占的面积：$a_m = \dfrac{1}{L\Gamma_\infty} = \dfrac{1}{6.022\times 10^{23}\times 5.378\times 10^{-6}} = 3.088\times 10^{-19}\,m^2$

6、(18 分，单考生仅做(1)(2)(3)题)

定容下，反应 A+C=D 为一气相反应，其机理为：

① $A \xrightarrow{k_1} B$

② $B \xrightarrow{k_2} A$

③ $B + C \xrightarrow{k_3} D$

其中步骤①和步骤②能很快达平衡，而步骤③反应速率很慢。

(1) $\dfrac{d[D]}{dt} = k_3[B][C]$ ①

$k_1[A] = k_2[B]$　　$[B] = \dfrac{k_1}{k_2}[A]$ ②

式②代入式①得：$\dfrac{d[D]}{dt} = k_3\dfrac{k_1}{k_2}[A][C] = k[A][C]$，其中 $k = k_3\dfrac{k_1}{k_2}$

(2) 总反应为 2 级；

(3) $-\dfrac{d[A]}{dt} = k[A][C] = k[A]^2$　　$kt = \dfrac{1}{[A]} - \dfrac{1}{[A]_0}$

$$k = \frac{1}{t}\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right) = \frac{1}{500}\left(\frac{1}{0.8[A]_0} - \frac{1}{[A]_0}\right) = \frac{1}{500}\frac{0.2}{0.8[A]_0}$$

$$k = \frac{1}{3000}\left(\frac{1}{x[A]_0} - \frac{1}{[A]_0}\right) = \frac{1}{500}\frac{0.2}{0.8[A]_0}$$　解得剩余的百分数为 $x = 0.6 = 60\%$

(4) $E_a = E_1 - E_2 + E_3$

$$\Delta H = \Delta U = E_1 - E_2 = 237 - 142 = 95kJ\cdot mol^{-1}$$

$$E_3 = E_a - (E_1 - E_2) = E_a - \Delta H = 120 - 95 = 25kJ\cdot mol^{-1}$$

7.(17分，单考生仅作(1)和(2)题)

电池 Pb(s)，$PbCl_2(s)|HCl\ (m=0.1mol\cdot kg^{-1})|H_2(0.1\ p^{\theta})$，Pt，

(1) 电池反应：$Pb+2HCl\ (m) \rightarrow PbCl_2(s)+H_2(0.1\ p^{\theta})$

(2) $$E=E^{\theta}-\frac{RT}{2F}\ln\frac{P_{H_2}/p^{\theta}}{a_+^2a_-^2}=(0-\varphi^{\theta})-\frac{RT}{2F}\ln\frac{0.1}{0.1^4}=0.144$$

$$\varphi^{\theta}(PbCl_2|Pb,\ Cl^{-1})=-0.144-\frac{8.314\times298}{2\times96485}\ln\frac{0.1}{0.1^4}=-0.2327V;$$

(3) 设计电池：$Pb(s)|Pb^{2+}\|Cl^-|PbCl_2(s)|Pb$，

电池反应：$PbCl_2(s)\rightarrow Pb^{2+}+2Cl^-$

$$E^{\theta}=\varphi^{\theta}(PbCl_2)-\varphi^{\theta}(Pb|Pb^{2+})=\frac{RT}{2F}\ln K_{sp}$$

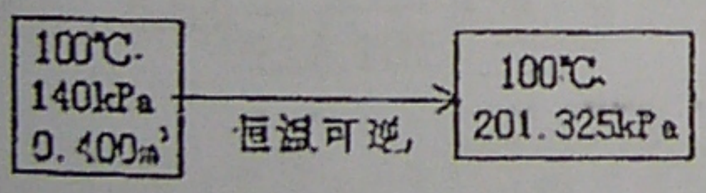
$$\ln K_{sp}=[\varphi^{\theta}(PbCl_2)-\varphi^{\theta}(Pb\ /|Pb^{2+})]\frac{2F}{RT}$$

$$=[-0.2327+0.126]\frac{2\times96485}{8.314\times298}=-0.1067$$

$$K_{sp}=0.8988=\frac{b_+b_-^2}{(b^{\theta})^3}=\frac{4b^3}{(b^{\theta})^3}\qquad b=0.608mol\cdot kg^{-1}$$

其中各离子的活度系数均视为1。

9.(15分，仅限单考生)



$$n=\frac{pV}{RT}=\frac{140\times10^3\times0.4}{8.314\times373}=18.058mol$$

理想气体恒温：$\Delta U=\Delta H=0$

$$\Delta S=nR\ln\frac{140}{201.325}=-54.54J\cdot K^{-1}$$

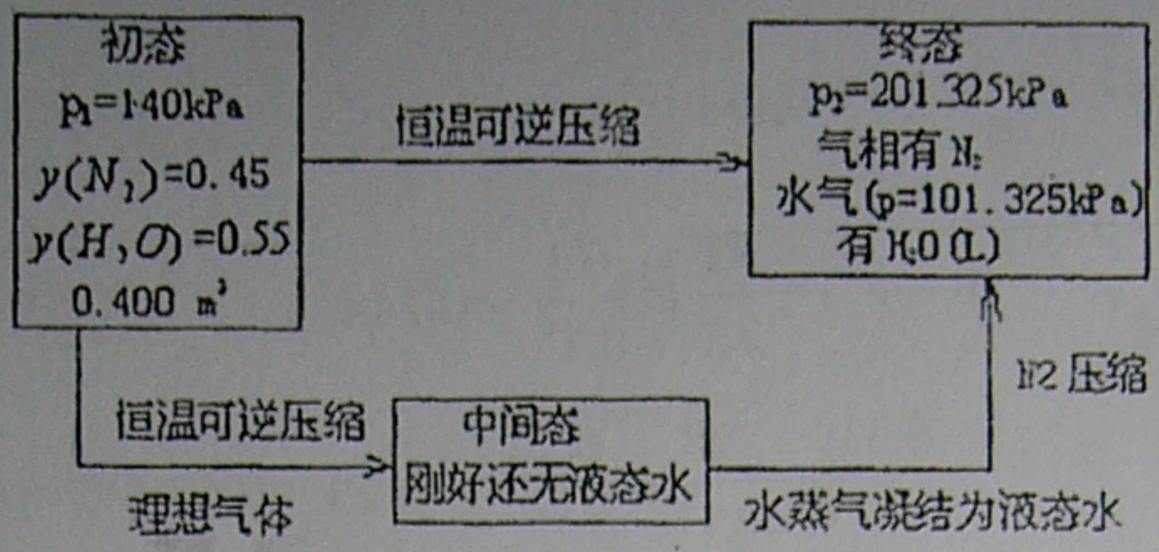
$$Q=T\Delta S=-20343\ J$$

$$W=-Q=20343\ J$$

$$\Delta G=\Delta H-T\Delta S=0-373.15\times(-54.54)=20343\ J$$

$$\Delta A=\Delta U-T\Delta S=20343\ J$$

8、(15 分，仅限统考生做)　均为 100℃



步骤分析：初态气相中水蒸气未饱和，故首先为理想气体恒温可逆压缩至出现第 1 滴水前，为中间态；然后 N_2 压缩同时水蒸气凝结为液态水，至终态。故分两步，第二步是非联步，如图。

状态计算：

初态：$n=\dfrac{pV}{RT}=\dfrac{140\times10^3\times0.4}{8.314\times373}=18.058mol$，

$P_{N_2}=py_{N_2}=63kPa$　　$P_{H_2O}=77kPa$

$n_{N_2}=8.126mol$　　$n_{H_2O}=9.932mol$

中间态：应为水气压力刚到 p^0，$p_{H_2O}=101.325kPa$，$V=\dfrac{77}{101.325}\times0.4=0.304m^3$

$p=140\times\dfrac{101.325}{77}=184.23kPa$　　$P_{N_2}=82.90kPa$

$n_{N_2}=8.126mol$　　$n_{H_2O}(g)=9.932mol$

终态：$p_{H_2O}=101.325kPa$　　$P_{N_2}=100kPa$

$V=\dfrac{82.9}{100}\times0.304=0.252m^3$　　$n_{N_2}=8.126mol$

$n_{H_2O}(g)=\dfrac{101.325}{100}\times8.126=8.234mol$

$n_{H_2O}(L)=9.932-8.234=1.698mol$

第 1 步：理想气体恒温可逆压缩：$\Delta U_1=\Delta H_1=0$

$\Delta S_1=nR\ln\dfrac{p_1}{p_2}=18.058\times8.314\times\ln\dfrac{140}{184.23}=-41.22J\cdot K^{-1}$

$Q_1=T\Delta S_1=-15381\ J$　　$W_1=-Q_1=15381\ J$

第2步：对 N_2：$\Delta U_{N2} = \Delta H_{N2} = 0$

$$\Delta S_{N2} = n_{N2} R \ln \frac{P_2}{P_3} = 8.126 \times 8.314 \times \ln \frac{82.90}{100} = -12.67 J \cdot K^{-1}$$

$$Q_{N2} = T\Delta S_{N2} = -4728 J \qquad W_{N2} = 4728 J$$

对 H_2O（g）→H_2O（L）：$n_{H_2O} = 1.698 mol$ n

$$\Delta H_{H2O} = 1.698 \times (-40670) = -69058 J$$

$$\Delta U_{H2O} = \Delta H + pV_s = -69058 + 1.698 \times 80314 \times 373.15 = -63790 J$$

$$\Delta S_{H2O} = \frac{\Delta H}{T} = \frac{-69058}{373.15} = -185.07 J \cdot K^{-1}$$

$$Q_{H2O} = \Delta H = -69058 J$$

$$W_{H2O} = \Delta U - Q = -63790 + 69058 = 5268 J$$

总过程的：$\Delta U = \Delta U_{H2O} = -63790 J$

$$\Delta H = \Delta H_{H2O} = -69058 J$$

$$Q = Q_1 + Q_{N2} + Q_{H2O} = -15381 - 69058 - 4728 = -89167 J$$

$$W = W_1 + W_{N2} + W_{H2O} = 15381 + 5268 + 4728 = 25377 J$$

$$\Delta S = -41.22 - 185.07 - 12.67 = -238.96 J \cdot K^{-1}$$

$$\Delta G = \Delta H - T\Delta S = -69058 - 373.15 \times (-238.96) = 20110 J$$

$$\Delta A = \Delta U - T\Delta S = -63790 - 373.15 \times (-238.96) = 25378 J$$