四：解：(1) AgCl的 K_{sp} 为反应 $AgCl = Ag^+ + Cl^-$ 的平衡常数. ∴ 将其设计成电池有：$Ag|Ag^+||Cl^-|AgCl,Ag$ ∴ $\Delta_r G_m^\ominus = -zFE^\ominus = -RT\ln K_{sp}$.

$$\therefore E^\ominus = \frac{RT}{zF}\ln K_{sp} = \frac{8.314\times 298}{96500}\ln 1.76\times10^{-10} = -0.577$$

$$\therefore \varphi_{AgCl/Ag} = 0.7991 - 0.577 = 0.2224\,V.$$

(2)
$$\begin{aligned} &+)\ AgCl + e \rightarrow Ag + Cl^- \\ &-)\ \tfrac{1}{2}H_2 - e \rightarrow H^+ \\ \hline &AgCl + \tfrac{1}{2}H_2 = Ag + H^+ + Cl^- \end{aligned}$$

$$E = E^\ominus - \frac{RT}{zF}\ln\frac{a_{H^+}a_{Cl^-}}{P_{H_2}^{1/2}} = 0.2224 - \frac{8.314\times298}{96500}\ln\frac{a_\pm^2}{1}$$

$$= 0.2224 - \frac{2\times8.314\times298}{96500}\ln \gamma_\pm m_\pm.$$

$$m_\pm = \sqrt[2]{1^2\times1} = 1$$

$$I = \frac{1}{2}\sum m_i z_i^2 = \frac{1}{2}(1\times1^2 + 1\times1^2) = 1.$$

$$\lg\gamma_\pm = -A|z_+ z_-|\sqrt{I} = -0.509\times1 = -0.509.\quad \gamma_\pm = 0.3097.$$

$$\therefore E = 0.2224 - \frac{2\times8.314\times298}{96500}\ln 0.3097\times1 = 0.1623\,V.$$

三. (1) 解：
$$\begin{aligned} &+)\ 2H^+ + 2e \rightarrow H_2(p^\ominus) \\ &-)\ H_2(20p^\ominus) - 2e \rightarrow 2H^+ \\ \hline &H_2(20p^\ominus) \rightarrow H_2(p^\ominus). \end{aligned}$$

$$\Delta G = \int_{20p^\ominus}^{p^\ominus} V\,dp = \int\frac{RT}{p}dp = RT\ln\frac{p^\ominus}{20p^\ominus} = 8.314\times293\ln\frac{1}{20} = -7297.6.$$

$$\therefore E = \frac{-\Delta G}{zF} = \frac{7297.6}{2\times96500} = 0.0378\,V.$$

(2)
$$E = -\frac{\Delta G}{zF} = -\frac{RT}{zF}\ln\frac{p^\ominus}{20p^\ominus}.\quad \therefore \left(\frac{\partial E}{\partial T}\right)_p = -\frac{R}{zF}\ln\frac{p^\ominus}{20p^\ominus}$$

$$= -\frac{8.314}{2\times96500}\times\ln\frac{1}{20} = 1.29\times10^{-4}\,V/K.$$

∴ $\Delta_r S_m = zF(\frac{\partial E}{\partial T})_p = 2\times96500\times(\frac{\partial E}{\partial T})_p = 24.9$ J/K.mol

$\Delta_r H_m = -zFE + zFT(\frac{\partial E}{\partial T})_p = -2\times96500\times\cancel{\ }\times0.0378$

$+2\times96500\times293\times1.29\times10^{-4} = -7295.4 + 7297.6$

$= 2.21$ J/mol

六. 解(1): 根据第一次实验. $p_{B,0} >> p_{A,0}$　$p_B \approx p_{B,0}$ 认为不变

∴ $r = k p_A^{\alpha} p_B^{\beta} = k' p_A^{\alpha}$.　$\ln p_A \sim t$ 为直线. 则 $\alpha = 1$.

第二次实验. $p_{A,0} = p_{B,0}$ ∴ $p_A = p_B$

$r = k p_A^{\alpha} p_A^{\beta} = k p_A^{(\alpha+\beta)}$.　又因: $\ln p_A \sim t$ 为直线,

则 $\alpha + \beta = 1$.　即 $\beta = 0$

∵ 第一次实验中 半衰期为 10s. ∴ $k' = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{10}$

$= 6.93\times10^{-2}$ s $^{-1}$.

从原始假设. $k' = k p_B^{\beta}$.　∴ $k = \frac{k'}{p_B^{\beta}} = k' = 6.93\times10^{-2}$ s $^{-1}$

($\beta = 0$).

(2). 当第三次实验时 $r = k p_A p_B^0 = k p_A$.

当 $p_B = 0.5 p_{B,0}$ 时. $p_A = 9.95\times10^3$ Pa.

∴ $t = \frac{1}{k}\ln\frac{p_{A0}}{p_A} = \frac{1}{6.93\times10^{-2}}\ln\frac{1.00\times10^4}{9.95\times10^3} = 0.072$ s.

七. 解: 当体系达平衡时体系中 Br_2 的压力总保持在 4660.95 Pa

设 I_2 的转化率为 α.

$I_2(g) + Br_2(g) = 2BrI(g)$

t=0时　0.1　　　　0

　　$0.1(1-\alpha)$　　0.2α

$\because$ $75588.45-4660.95=\dfrac{[0.1(1-\alpha)+0.2\alpha]}{V}\cdot RT$

简单整理得，$\alpha=0.752$

$\therefore$ $P_{I_2}=\dfrac{0.1(1-\alpha)RT}{V}=10050.86Pa$. $P_{HI}=\dfrac{0.2\alpha RT}{V}=60895.7Pa$.

$\therefore$ $K_p=\dfrac{P_{HI}^2}{P_{H_2}P_{I_2}}=79.16$.

(2). $T_1=487K$. $K_{p1}=79.16$ $T_2=387K$. $K_{p2}=190$

$\therefore$ $\Delta_r H_m^\circ=\dfrac{R\ln(K_{p2}/K_{p1})}{1/T_1-\frac{1}{T_2}}=-1.37\times10^4 J/mol$.

八. 对于其平行反应：$-\dfrac{d[A]}{dt}=\dfrac{d[B]}{dt}+\dfrac{d[C]}{dt}$.

$\therefore$ $k[A]=k_1[A]+k_2[A]$

$\therefore$ $k=k_1+k_2$. 两边求导数对T得 .

$\dfrac{dk}{dT}=\dfrac{dk_1}{dT}+\dfrac{dk_2}{dT}$, $k\dfrac{d\ln k}{dT}=k_1\dfrac{d\ln k_1}{dT}+k_2\dfrac{d\ln k_2}{dT}$.

根据阿氏公式. $k\dfrac{E}{RT^2}=k_1\dfrac{E_1}{RT^2}+k_2\dfrac{E_2}{RT^2}$

$\therefore$ $kE=k_1E_1+k_2E_2$

$\therefore$ $E=\dfrac{k_1E_1+k_2E_2}{k}=\dfrac{k_1E_1+k_2E_2}{k_1+k_2}$. 证毕.

九. 解: (1). $q_t=(\dfrac{2\pi mkT}{h^2})^{\frac{3}{2}}\cdot V$

$=\left[\dfrac{2\times3.14\times28\times10^{-3}\times1.38\times10^{-23}\times298}{6.023\times10^{23}\times(6.626\times10^{-34})^2}\right]^{\frac{3}{2}}\times1.00$

$=[273.46\times10^{19}]^{\frac{3}{2}}\times1=1.43\times10^{32}$.

(2). $\Theta_r = \frac{h^2}{8\pi^2 I k} = \frac{(6.626\times10^{-34})^2}{8\times3.14^2\times1.394\times10^{-46}\times1.38\times10^{-23}}$

$= 2.784\times10^0 = 2.784(K)$.