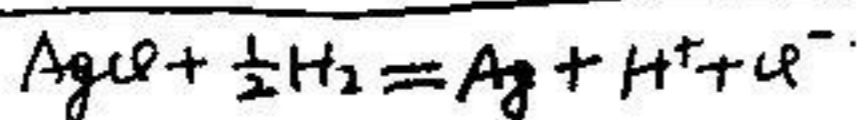
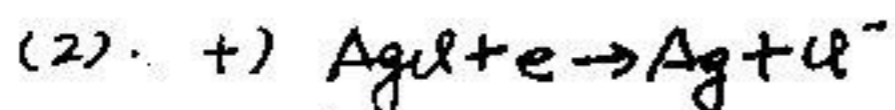


解: (1) $AgCl$ 的 K_{sp} 为 1.76×10^{-10} , $AgCl = Ag^+ + Cl^-$ 在平衡时, \therefore 将 $AgCl$ 放入水中

电池有: $Ag | Ag^+ || Cl^- | AgCl, Ag$ $\therefore \Delta_r G_m^\ominus = -zF E^\ominus = -RT \ln K_{sp}$

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

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



$$E = E^\ominus - \frac{RT}{zF} \ln \frac{a_{H^+} a_{Cl^-}}{P_{H_2}} = 0.2224 - \frac{8.314 \times 298}{96500} \ln \frac{a_{\pm}^2}{1}$$

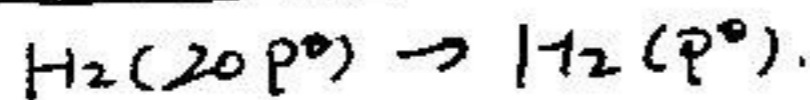
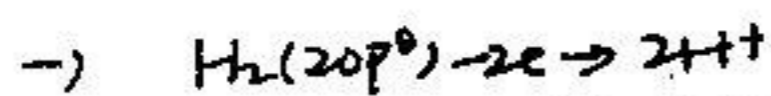
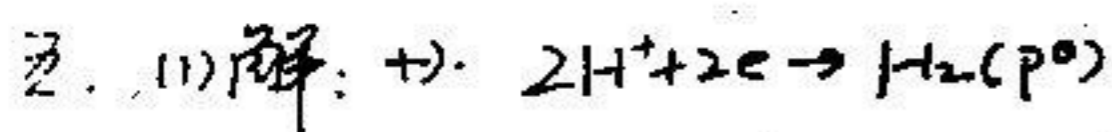
$$= 0.2224 - \frac{2 \times 8.314 \times 298}{96500} \ln m_{\pm}$$

$$m_{\pm} = \sqrt{1 \times 1} = 1$$

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

$$\lg \gamma_{\pm} = -A |z_+ z_-| \sqrt{I} = -0.509 \times 1 = -0.509, \quad \gamma_{\pm} = 0.3097$$

$$\therefore E = 0.2224 - \frac{2 \times 8.314 \times 298}{96500} \ln 0.3097 \times 1 = 0.1623 \text{ V}$$



$$\Delta G = \int_{20p^\ominus}^{p^\ominus} V dp = \int_{20p^\ominus}^{p^\ominus} \frac{RT}{p} dp = RT \ln \frac{p^\ominus}{20p^\ominus} = 8.314 \times 293 \ln \frac{1}{20} = -7297.6$$

$$\therefore E = \frac{-\Delta G}{zF} = \frac{7297.6}{2 \times 96500} = 0.0378 \text{ V}$$

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

$$= -\frac{8.314}{2 \times 96500} \times \ln \frac{1}{20} = 1.29 \times 10^{-4} \text{ V/K}$$

$$\Delta S_m = zF \left(\frac{\partial \bar{z}}{\partial T} \right)_p = 2 \times 96500 \times \left(\frac{\partial \bar{z}}{\partial T} \right)_p = 2498 \text{ J/K} \cdot \text{mol}$$

$$\begin{aligned} \Delta_r H_m &= -z\bar{z} + zF T \left(\frac{\partial \bar{z}}{\partial T} \right)_p = -2 \times 96500 \times 1.29 \times 0.0378 \\ &\quad + 2 \times 96500 \times 293 \times 1.29 \times 10^{-4} = -7295.4 + 7297.6 \\ &= 2.2 \text{ J/mol} \end{aligned}$$

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

$$\therefore r = k P_A^\alpha P_B^\beta = k' P_A^\alpha \quad \ln P_A \sim t \text{ 为直线. } \therefore |\alpha| = 1.$$

第二次实验. $P_{A,0} = P_{B,0} \therefore P_A = P_B$

$$r = k P_A^\alpha P_A^\beta = k P_A^{\alpha+\beta} \quad \text{又因: } \ln P_A \sim t \text{ 为直线,}$$

$$\therefore \alpha + \beta = 1 \quad \text{即 } \beta = 0$$

$$\therefore \text{第一次实验中半衰期为 } 10 \text{ s. } \therefore k' = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{10} = 6.93 \times 10^{-2} \text{ s}^{-1}.$$

$$\text{从第二次实验知. } k' = k P_B^\beta \quad \therefore k = \frac{k'}{P_B^\beta} = k' = 6.93 \times 10^{-2} \text{ s}^{-1} \quad (\beta = 0).$$

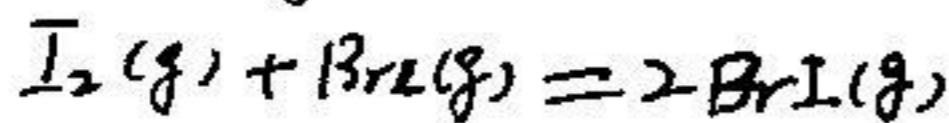
(2) 为第三次实验时 $r = k P_A P_B^0 = k P_A$.

当 $P_B = 0.5 P_{B,0}$ 时. $P_A = 9.95 \times 10^3 \text{ Pa}$.

$$\therefore t = \frac{1}{k} \ln \frac{P_{A,0}}{P_A} = \frac{1}{6.93 \times 10^{-2}} \ln \frac{1.00 \times 10^4}{9.95 \times 10^3} = 0.072 \text{ s}.$$

七. 解: 当体系达到平衡时体系 Br₂ 的总压力为 4660.95 Pa

设 I₂ 的转化率为 α .



| | | |
|---------|-------------------|--------------|
| $t=0$ 时 | 0.1 | 0 |
| | 0.1(1- α) | 0.2 α |

$$\therefore 75588.45 - 4660.95 = \frac{[0.1(1-\alpha) + 0.2\alpha] \cdot RT}{\sqrt{2}}$$

解得 $\alpha = 0.752$

$$\therefore P_{I_2} = \frac{0.1(1-\alpha)RT}{\sqrt{2}} = 10050.86 \text{ Pa} \quad P_{H_2} = \frac{0.2\alpha RT}{\sqrt{2}} = 60895.7 \text{ Pa}$$

$$\therefore K_p = \frac{P_{B_2}^2}{P_{A_2} P_{I_2}} = 79.16$$

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

$$\therefore \Delta_r H_m^\ominus = \frac{R \ln \left(\frac{K_{p1}}{K_{p2}} \right)}{\frac{1}{T_1} - \frac{1}{T_2}} = -1.37 \times 10^4 \text{ J/mol}$$

八. 由于是平行反应: $-\frac{d[A]}{dt} = \frac{d[B]}{dt} + \frac{d[C]}{dt}$

$$\therefore R[A] = R_1[A] + R_2[A]$$

$$\therefore R = R_1 + R_2 \quad \text{两边求导数(对时间)}$$

$$\frac{dR}{dT} = \frac{dR_1}{dT} + \frac{dR_2}{dT}, \quad R \frac{d \ln R}{dT} = R_1 \frac{d \ln R_1}{dT} + R_2 \frac{d \ln R_2}{dT}$$

把指数代换: $R \frac{E}{RT^2} = R_1 \frac{E_1}{RT^2} + R_2 \frac{E_2}{RT^2}$

$$\therefore R_2 E = R_1 E_1 + R_2 E_2$$

$$\therefore E = \frac{R_1 E_1 + R_2 E_2}{R} = \frac{R_1 E_1 + R_2 E_2}{R_1 + R_2} \quad \text{证毕}$$

九. 解: (1) $Q = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \cdot V$

$$= \left[\frac{2 \times 3.14 \times 28 \times 10^{-3} \times 1.38 \times 10^{-23} \times 298}{6.023 \times 10^{23} \times (6.626 \times 10^{-34})^2} \right]^{3/2} \times 1.0 \text{ m}^3$$

$$= [273.46 \times 10^{19}]^{3/2} \times 1 = 1.43 \times 10^{32}$$

$$(2). \quad \textcircled{H} = \frac{h^2}{8\pi^2 I R} = \frac{(6.626 \times 10^{-34})^2}{8 \times 3.14^2 \times 1.394 \times 10^{-46} \times 1.38 \times 10^{-23}}$$

$$= 2.784 \times 10^0 = 2.784 \text{ (K)}.$$