

## 物理化学期末考题(A)答案 2001-01-12

一 (30 分)

1  $(275.6 \times 10^{-4})$

2  $(5.25 \times 10^{-4})$

3  $(0.51), (5.81 \times 10^{-3})$

4  $Pb|PbSO_4(s)|SO_4^{2-}(a_{SO_4^{2-}})||Pb^{2+}(a_{Pb^{2+}})|Pb$

5  $(0.14 \text{ mol} \cdot \text{kg}^{-1})$

6  $(q = q^0 e^{-\varepsilon_0/kT})$

7  $(\sum g_i e^{-\varepsilon_i/kT} = e^{-\varepsilon_0/kT} \sum g_i e^{-\varepsilon_i^0/kT})$

8  $(0.356)$

9  $(\sigma_{s-g} > \sigma_{l-g} + \sigma_{l-s})$

10  $(\frac{-c}{RT} \frac{d\sigma}{dc})$  (正)

11  $(6.315)$

12  $(20)$

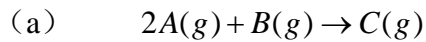
13 (发生反应的分子数/吸收的光量子数)

14 (高度分散的多相热力学不稳定系统)

15 (大于)(散射)

二 (29 分)

1 (20 分)



t=0  $2P_{B0} \quad P_{B0} \quad 0$

t  $2P_B \quad P_B \quad P_{B0} - P_B$

0 时刻:  $3P_{B0} = 40. \text{kPa}, \quad P_{B0} = 13.33. \text{kPa}$

t=50s:  $P_{\text{总}} = P_{B0} - P_B + 3P_B = P_{B0} + 2P_B = 26.7 \text{kPa}, \quad \text{则} \quad P_B = 6.685 \text{kPa}$

已知速率方程:  $\frac{-dP_B}{dt} = kP_A P_B = 2kP_B^2$

积分:  $\frac{1}{P_B} - \frac{1}{P_{B0}} = 2kt \quad (1)$

代入已知数据得:  $k = 7.46 \times 10^{-4} \text{ kPa}^{-1} \text{ s}^{-1}$

$$t=150s \text{ 时: } P_B = \frac{1}{2kt + \frac{1}{P_{B0}}} = 3.35kPa$$

$$P_{\text{总}} = P_{B0} + 2P_B = 20.0kPa$$

$$(b) \quad t=25s, \quad P_{B0}=13.33kPa, \quad P_B=6.685kPa$$

$$\text{由 (1) 式} \quad k_2 = k_1 \frac{t_1}{t_2} = 7.46 \times 10^{-4} \times \frac{50}{25} = 2k_1$$

$$\ln \frac{k_2}{k_1} = \frac{-20 \times 10^3}{8.314} \left( \frac{1}{T_2} - \frac{1}{300} \right)$$

$$T_2 = 328.4K$$

2 (9 分)

$$(a) \text{ CH}_4 \text{ 生成速率: } \frac{dC_{CH_4}}{dt} = k_2 C_{CH_3\cdot} C_{H_2} + k_3 C_{C_2H_6} C_{H\cdot} \quad (1)$$

稳态法处理中间产物  $CH_3\cdot$ ,  $H\cdot$

$$\begin{cases} \frac{dC_{CH_3\cdot}}{dt} = k_1 C_{C_2H_6} + k_3 C_{C_2H_6} C_{H\cdot} - k_2 C_{CH_3\cdot} C_{H_2} - k_4 C_{CH_3\cdot}^2 = 0 \\ \frac{dC_{H\cdot}}{dt} = k_2 C_{CH_3\cdot} C_{H_2} - k_3 C_{C_2H_6} C_{H\cdot} = 0 \end{cases}$$

$$\text{则} \quad \begin{cases} k_1 C_{C_2H_6} = k_4 C_{CH_3\cdot}^2 \\ k_2 C_{CH_3\cdot} C_{H_2} = k_3 C_{C_2H_6} C_{H\cdot} \end{cases} \quad \text{代入 (1) 式}$$

$$\frac{dC_{CH_4}}{dt} = \frac{2k_2 k_1}{k_4} C_{C_2H_6}^{1/2} C_{H_2} \quad (2)$$

$$(b) \text{ 由 (2) 式} \quad k = \frac{2k_2 k_1}{k_4}$$

$$\ln k = \ln 2 + \ln k_2 + \ln k_1 - \ln k_4$$

$$\frac{d \ln k}{dT} = \frac{d \ln k_2}{dT} + \frac{d \ln k_1}{dT} - \frac{d \ln k_4}{dT} = \frac{Ea}{RT^2}$$

$$\therefore Ea = E_2 + E_1 - E_4$$

三 (12 分)

$$1 \quad (a) \quad \because \quad \Gamma = \Gamma_{\infty} \frac{bp}{1+bp}$$

$$\therefore \frac{82.5}{93.8} = \frac{13.375b}{1+13.375b} \quad b = 0.546 \text{ kPa}^{-1}$$

$$(b) \quad P = \frac{\Gamma}{b(\Gamma_{\infty} - \Gamma)} = \frac{73.58}{0.546(93.8 - 73.58)} = 6.665 \text{ kPa}$$

2.  $\text{BaSO}_4$  的胶团结构:  $\{(\text{BaSO}_4)_m \cdot n\text{SO}_4^{2-} \cdot 2(n-x)\text{Na}^+\}^{2x-} \cdot 2x\text{Na}^+$

电泳实验中胶粒向正极移动

$\therefore$  是负胶团,  $\therefore \text{AlCl}_3$  聚沉值最小。

四 (11 分)

$$1 \quad (6 \text{ 分}) \quad q_t = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V$$

$$\text{其中 } V = \frac{8.314 \times 298.15}{10^5} = 0.0248 \text{ m}^3$$

$$m = \frac{3.0 \times 10^{-3}}{6.023 \times 10^{23}} = 4.98 \times 10^{-26} \text{ kg}$$

$$q_t = 3.94 \times 10^{30}$$

$$S_{m,t} = R \ln \frac{q_t}{L} + \frac{5}{2} R = 151.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

2 (5 分)

$$1 \text{ mol 理想气体向真空膨胀, 其 } \Delta S = R \ln \frac{V_2}{V_1}$$

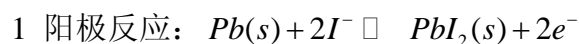
由玻兹曼熵定理:  $S = k \ln \Omega$

$$\Delta S = k \ln \Omega_2 - k \ln \Omega_1$$

$$= k \ln \frac{\Omega_2}{\Omega_1}$$

$$\therefore \left( \frac{V_2}{V_1} \right)^L = \frac{\Omega_2}{\Omega_1}$$

五 (18 分)



阴极反应:  $2AgI(s) + 2e^- \rightleftharpoons 2Ag(s) + 2I^-$

电池反应:  $Pb(s) + 2AgI(s) \rightleftharpoons PbI_2(s) + 2Ag(s)$

2.

$$E = E^\theta - \frac{0.05916}{2} \lg \frac{a_{Ag} a_{PbI_2}}{a_{Pb} a_{AgI}} = E^\theta = E_+^\theta - E_-^\theta = -0.152 + 0.3657 = 0.2137V$$

$$\Delta_r G_m = -2FE = -2 \times 96485 \times 0.2137 = -41.24 kJ \cdot mol^{-1}$$

$$\Delta_r S_m = 2F \left( \frac{\partial E}{\partial T} \right)_p = -2 \times 96485 \times 1.38 \times 10^{-4} = -26.63 J \cdot K^{-1} \cdot mol^{-1}$$

$$\Delta_r H_m = \Delta_r G_m + T \Delta_r S_m = -49.18 kJ \cdot mol^{-1}$$

$$Q_r = T \Delta_r S_m = -7.49 kJ$$

3. 电池反应:  $PbI_2(s) \rightleftharpoons 2I^- + Pb^{2+}$

阳极反应:  $Pb(s) \rightleftharpoons Pb^{2+} + 2e^-$

阴极反应:  $PbI_2(s) + 2e^- \rightleftharpoons 2I^- + Pb(s)$

$$E^\theta = \frac{0.05916}{2} \lg k_{sp} = E_+^\theta - E_-^\theta = -0.3657 + 0.126 = -0.2379V$$

$$k_{sp} = 7.87 \times 10^{-9}$$