



卓越考研北化定制辅导班

北化考研第一品牌！

卓越考研北化定制班优势：

- 阅卷名师公共课+北京化工大学老师专业课，高端专业对口的教学团队。
- 独家高分讲义+历年真题解析+点题押题试卷+内部复试资料，资料完善权威。
- 内部信息畅通，精准测评帮助考生选择最佳专业，初试保过，复试保录。
- 政治英语小班上课，专业课一对一辅导，集训营精细化管理，考研一次通过。

卓越考研北化物化辅导班

班型	学习时间	学费	班型特点
暑假强化班	7.15 ~ 8.25	2300 元	定制学习计划 + 北化物化老师 + 物化基础强化
周末强化班	10.1 ~ 12.1	2300 元	定制学习计划 + 北化物化老师 + 物化强化提高
国庆提高班	10.1 ~ 10.6	1280 元	北化物化老师 + 物化重点难点考点集中强化提高
冲刺点题班	11.19 ~ 11.21	1880 元	北化命题组老师 + 物化必考点串讲 + 内部点题
物化视频班	随报随学	680 元	北化老师内部课程，基础内容和知识点框架强化
个性保录班	随报随学	面 议	定制学习，基础 + 强化 + 押题 + 复试，签订保录协议

暑假班可免费试学一周，满意后再报名！

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数学作业纸

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08 年

2008

一. 选择题

1. B $pV_m = RT$ T 一定, 作 $pV_m - p$ 外推至 $p \rightarrow 0$ 得理想气体 R 值.
2. C. 绝热 $Q=0$ 铜瓶 $\Delta V=0 \Rightarrow W=0$
3. D
4. A
5. B. $\Delta G_m^\ominus = \Delta_r H_m^\ominus - T \Delta_r S_m^\ominus < 0$ $\Delta_r G_m^\ominus = -RT \ln K_f^\ominus < 0 \Rightarrow K^\ominus > 1$.
 $\Delta_r H_m^\ominus < 0$ 放热反应. $T \uparrow$ $K^\ominus \downarrow$.
6. B $S=4$, $R=2$ 有四种物质, 但有两个平衡关系. 一为化学平衡, 一为生成物间的比例关系 $C = S - R = 2$.
7. D. 自发过程 化学势降低 ($\Delta G < 0$). 根据依数性 T_f 降低. B 为非挥发组分 $p_A \downarrow$.
8. D
9. B. $E^\ominus(Cu^{2+}/Cu) < E^\ominus(O_2/H_2O)$
10. C. 速率常数与半衰期成反比.
11. D. 胶粒带电
12. A $\theta < 90^\circ$ 表示可以湿润.
13. B.
14. C.

2. (11) $pV_m - pb = RT$ (2). 由 (1) 可知: $z = 1 + \frac{pb}{RT}$ 其中 b 为常数
 $z = \frac{pV_m}{RT} = 1 + \frac{pb}{RT}$ 且 $b > 0$, 当 T 不变时 z 与 p 成正比. $p \uparrow$ 则 $z \uparrow$

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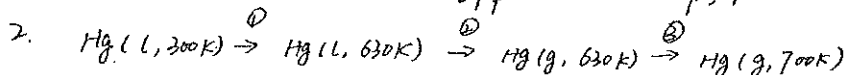
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$$(3) \mu_J - T = \left(\frac{\partial T}{\partial p} \right)_H = - \frac{\left(\frac{\partial H}{\partial p} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_p} = - \frac{1}{C_p} \left(\frac{\partial H}{\partial p} \right)_T = - \frac{1}{C_p} \left[V - T \left(\frac{\partial V}{\partial T} \right)_p \right]$$

对于 $p(V_m - b) = RT$ $V - T \left(\frac{\partial V}{\partial T} \right)_p = b > 0 \therefore \mu_J - T < 0$



过程 ①: $W_1 = 0$

$$\Delta S_1 = n C_{p,m} \ln \frac{T_2}{T_1} = 20.77 \text{ J/mol} \cdot \text{K}$$

过程 ②:

$$\Delta V_2 = \frac{nRT_2}{p} = \frac{8.314 \times 630}{100 \times 10^3} = 0.0523 \text{ m}^3$$

$$W_2 = p \Delta V_2 = 100 \times 10^3 \times 0.0523 = -5230 \text{ J}$$

过程 ③

$$\Delta S_2 = \frac{\Delta H}{T_2} = 103.04 \text{ J/mol} \cdot \text{K}$$

$$\Delta V_3 = \frac{nR(T_3 - T_2)}{p}$$

$$W_3 = p \Delta V_3 = nR(T_3 - T_2) = 8.314 \times 70 = -581.98 \text{ J}$$

$$\Delta S_3 = n C_{p,m} \ln \frac{T_3}{T_2} = 2.19 \text{ J/mol} \cdot \text{K}$$

$$W = \sum W_i = -5820.5 \text{ J}$$

$$\Delta S = \sum \Delta S_i = 125 \text{ J/mol} \cdot \text{K}$$

$$\therefore 1. K_1^\ominus = \frac{p^\ominus}{p_1} = \frac{100}{0.107} = 934.6$$

$$K_2^\ominus = \left(\frac{p^\ominus}{p_2} \right)^2 = \left(\frac{100}{0.747} \right)^2 = 1.79 \times 10^4$$

$$K_3^\ominus = \left(\frac{p^\ominus}{p_3} \right)^2 = \left(\frac{100}{1.04} \right)^2 = 9.24 \times 10^3$$

$$K^\ominus = K_1^\ominus K_2^\ominus K_3^\ominus = 1.548 \times 10^{11}$$

$$\Delta_r G_m^\ominus = -RT \ln K^\ominus = -63.876 \text{ kJ}$$

2. $\left(\frac{3.173}{100} \right)^{-5} = 3.109 \times 10^7 < K^\ominus$

\therefore 可以从左向右进行.

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10. 1. 由 Clausius - Clapeyron 方程可知

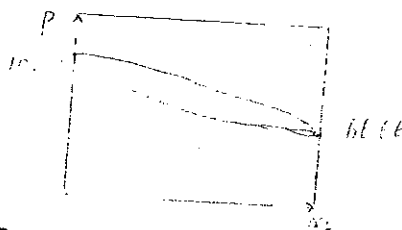
$$\Delta_{\text{vap}} H_m = 3637.1 \text{ R} = 30.24 \text{ kJ/mol}$$

$$\Delta_{\text{vap}} S_m = \frac{\Delta_{\text{vap}} H_m}{T} = 86.41 \text{ J/mol} \cdot \text{K}$$

2. 100 kPa 下 CCl_4 沸点为 350 K. 代入所给方程

$$C = \ln 10^5 + \frac{3637.1}{350} = 21.90$$

$$P_{\text{CCl}_4}^* = e^{-\frac{3637.1}{372.15} + 21.90} = 190.54 \text{ kPa}$$



3. $P_A + P_B = 100 \text{ kPa}$. $P_A = P_A^* X_A$ $P_B = P_B^* X_B = P_B^* (1 - X_A)$
 有 $X_A = 0.269$ $X_B = 0.731$

五. 1. 负极: $\text{H}_2(p_1) \rightarrow 2\text{H}^+(b) + 2e^-$

正极: $2\text{H}^+(b) + 2e^- \rightarrow \text{H}_2(p_2)$

电池反应: $\text{H}_2(p_1) \rightarrow \text{H}_2(p_2)$

2. $dG = -SdT + Vdp$

故有 $\left(\frac{\partial G}{\partial p}\right)_T = V$

$$\Delta_r G_m = \int_{p_1}^{p_2} V dp = \int_{p_1}^{p_2} \left(\frac{RT}{p} + \alpha p \right) dp = RT \ln \frac{p_2}{p_1} + \frac{\alpha}{2} (p_2^2 - p_1^2)$$

3. $T = 298 \text{ K}$ 时 $\Delta_r G_m = 8.314 \times 298 \ln 20^{-1} - 1.48 \times 10^{-5} \times 19 \times 10^5 = -7.45 \text{ kJ}$

$$\Delta S = -\left(\frac{\partial \Delta_r G_m}{\partial T}\right)_p = -8.314 \ln 20^{-1} = 24.9 \text{ J/mol} \cdot \text{K}$$

$$E = \frac{\Delta_r G_m}{-nF} = \frac{7.45 \times 10^3}{-2 \times 96485} = -0.038 \text{ V}$$

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11. 在恒容条件下, p 与 c 成正比

$$-\frac{dp_A}{dt} = k p_A^n$$

$$\int_{p_{A0}}^{p_A} -p_A^{-n} dp_A = \int_0^t k p dt$$

$$\frac{1}{n-1} (p_A^{-n+1} - p_{A0}^{-n+1}) = k p t$$

$$\text{当 } p_A = \frac{1}{2} p_{A0} \text{ 时}$$

$$-\frac{1}{2(n-1)} p_{A0}^{-n+1} = k p t$$

由于 p_{A0} 与 t 成反比 故 $n=2$.

\therefore 为二级反应.

(2) 故式中化为:

$$\left(\frac{1}{p_A} - \frac{1}{p_{A0}}\right) = k p t$$

$$\text{当 } T = 967 \text{ K 时}$$

$$\frac{1}{p_{A0}} = k p t \quad k p = \frac{1}{p_{A0} t} = 1.68$$

$$\text{当 } T = 1030 \text{ K 时}$$

$$\frac{1}{9 p_{A0}} = k p' t \quad k p' = \frac{1}{9 p_{A0} t} = 1.$$

$$(3) \ln k_1 = -\frac{E_a}{R T_1}, \ln k_2 = -\frac{E_a}{R T_2}$$

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$E_a = R \ln \frac{k_1}{k_2} \cdot \frac{T_1 T_2}{T_1 - T_2} = 8.55 \times 10^5 \text{ J}$$

$$1. \quad u = NKT^2 \left(\frac{\partial \ln q}{\partial T} \right)_{v, N} = NKT^2 \left(\frac{\partial \ln \frac{2\pi m k T}{h^2}}{\partial T} \right)_{v, N}^{\frac{3}{2}}$$

$$= \frac{3}{2} NKT$$

$$u_m = \frac{3}{2} RT \quad \text{其中 } R = Nk.$$

2. 由 Gibbs 等温式:

$$(1) \quad \Gamma = -\frac{c}{RT} \frac{dV}{dc} = + \frac{AC}{RT} = \frac{V_0 - V}{RT}$$

$$(2) \quad V = \frac{1}{2} RT \Gamma = 0.0718 - 8.314 \times 298 \times 4.33 \times 10^{-6} = 0.0611 \text{ N.}$$

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09年.

一. 选择

1. C. $\Delta U = Q + W$ 刚性说明 $\Delta V = 0$ 故 $W = 0$. 绝热. $Q = 0 \therefore \Delta U = 0$.
2. D. 恒压过程有做功问题 B 无做功项, C 应为 $-p\Delta V$. $W = -p\Delta V$.
A 选项中应为 $C_{p,m}$
3. A. B 选项见做恒压要求, 由 H 定义即可推得. C 选项为过程方程.
D 选项为做功定义.
4. B. 处于相平衡状态.
5. C. 自发过程 $\Delta G < 0$
6. D. $\left(\frac{\partial A}{\partial V}\right)_T = \frac{A - G}{V} = \frac{-pV}{V} = -p < 0$.
7. D. 组成随压力改变
8. C. $S = k \ln \Omega$. k 为常数. Ω 为微观状态数. 与混乱程度有关.
9. B. 一级反应半衰期为常数. 与初始浓度无关.
10. A. 应为 $r_1 = r_{-1}$ 若 $A \rightarrow B$. $B \rightarrow A$ 反应级数相同. 则 $k_1 = k_{-1}$
11. C. 正吸附是表面活性物质在吸附剂表面吸附力加强的现象. $h_2 < h_1$ 表面张力
12. D. $m_{\pm} = (m_+^{v_+} m_-^{v_-})^{\frac{1}{v}}$ $v = v_+ + v_-$ 代入计算即可.
13. D. 视溶解度而定. 溶解度对其影响很大. 而 $\phi_{0.1}$ 不变.
14. C. 注意. " "
15. B
16. A. 催化剂不改变平衡状态.
17. D.
18. C
19. B $-2E_1^{\ominus} + E_2^{\ominus} = -2E_3^{\ominus}$
20. A

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二. 填空题

1. 136.5

~~170.2~~ 3
2837.2

$$P_1 T_1 = P_2 T_2 \quad T_2 = \frac{P_1 T_1}{P_2} = \frac{T_1}{2} = 136.5 \text{ K}$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} \frac{5}{2} R dT = 2837.2 \text{ J}$$

2. 1.56

$$P_B = P_B^* x_B \quad \Rightarrow \quad x_B = \frac{P_B}{P_B^*}$$

3. 大于 加入后, P 不变, V 变大, C 变小, 平衡正向移动 $\alpha_2 > \alpha_1$

4. 最大负

5. 增大, 减小.

6. 正极. Al^{3+} 价态高, 聚沉能力强, 说明胶粒带“-”电.

7. $\{AgCl\}_m n Ag^+, (n-x) NO_3^-, x NO_3^-$. $AgNO_3$ 过量, 首先吸附 Ag^+ .

8. 入射光的强度.

9. 气液相中各一半.

10. 10. 注意: 给的直径. $P_s = \frac{\gamma}{2r}$.

11. 760 等温吸附公式 $\theta = \frac{ap}{1+ap}$ 其中 $a = \frac{k_a}{k_d}$ 只是温度的函数

12. 2. $\phi = \frac{\text{反应物消耗}}{\text{吸收光子}}$ $\phi' = \frac{\text{生成物的变化}}{\text{吸收光子}}$ 二者可能不等.

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三. 综合题

$$1. (1) dU = TdS - PdV \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\frac{P}{V} - P = \frac{a}{V^2}$$

$$(2) dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{恒温过程 } dT = 0$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV \quad \Delta U = \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV = \int_{V_1}^{V_2} \frac{a}{V^2} dV = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$T \text{ 不变: } \left(p_1 + \frac{a}{V_1^2}\right)V_1 = \left(p_2 + \frac{a}{V_2^2}\right)V_2 \Rightarrow p_2 = p_1 \frac{V_1}{V_2} + \frac{a}{V_1 V_2} - \frac{a}{V_2^2}$$

$$W = -\Delta(pV) = p_1 V_1 - p_2 V_2 = p_1 V_1 - \left(p_1 \frac{V_1}{V_2} + \frac{a}{V_1 V_2} - \frac{a}{V_2^2}\right)V_2 = \left(\frac{1}{V_2} - \frac{1}{V_1}\right)a$$

$$Q = \Delta U - W = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) - a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) = 2a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$\text{可逆过程 } \Delta S = \frac{Q}{T_1} = \frac{2a}{T}\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$\Delta G = \Delta H - T\Delta S = \Delta U + \Delta(pV) - T\Delta S = 0$$

$$(3) \text{ 节流膨胀 绝热过程 } Q = 0 \quad \text{等焓过程 } \Delta H = 0$$

$$U \text{ 为状态函数 } \Delta U \text{ 仍为 } a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$W = \Delta U - Q = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$2. (1) \text{ 由 Clausius - Clapeyron 方程:}$$

$$\ln \frac{p_2}{p_1} = \frac{\Delta_{\text{vap}} H_m^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Rightarrow \text{已知}$$

$$p_2 = p_1 e^{\frac{\Delta_{\text{vap}} H_m^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = 101.325 \text{ e}^{\frac{8214}{8.314} \left(\frac{1}{332.15} - \frac{1}{363.15}\right)} = 129.1$$

$$(2) p_B = p_B^* x_B \quad p_A = p_A^* x_A \quad p_{\text{总}} = p_A + p_B \quad x_A + x_B = 1$$

$$\text{则有: } x_B = 0.66$$

$$y_B = \frac{p_B}{p_{\text{总}}} = \frac{p_B^* x_B}{p_{\text{总}}} = 0.38$$



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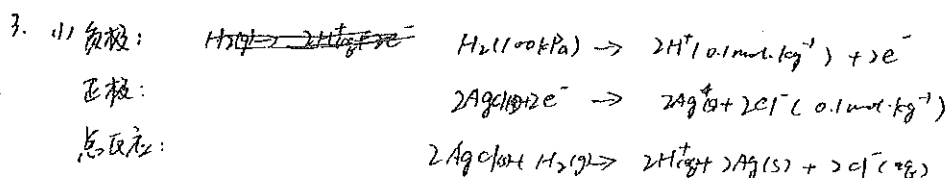
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(3) ~~$n_A(g) + n_B(g) = n(g)$~~ 由(2)可知 ~~$n_A(g) = n_A$~~

$$\begin{cases} n_A(g) + n_{A(l)} = n_A \\ n_B(g) + n_{B(l)} = n_B \end{cases} \Rightarrow \begin{cases} n_A(g) = n_A - n_{A(l)} \\ n_B(g) = n_B - n_{B(l)} \end{cases}$$

则有: $\begin{cases} 0.62n_g + 0.34n_l = 5 \\ 0.38n_g + 0.66n_l = 5 \end{cases}$ 得: $\begin{cases} n_g = 5.7 \\ n_l = 4.3 \end{cases}$



(2) $\Delta_r H_m = -zEF + zFT \left(\frac{\partial E}{\partial T} \right)_P$

1A 时有 $E = \left[\Delta_r H_m + zFT \left(\frac{\partial E}{\partial T} \right)_P \right] / zF = 0.2985V$

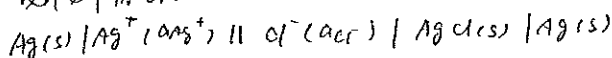
由于 H 电极处于标准态 $E_{H^+/H_2} = 0V$

$E_{AgCl/Ag} = E + E_{H^+/H_2} = E = 0.2985V$

$E_{AgCl/Ag} = E^\ominus_{AgCl/Ag} - \frac{RT}{zF} \ln a(Cl^-)$

$E^\ominus_{AgCl/Ag} = E_{AgCl/Ag} + \frac{RT}{zF} \ln a(Cl^-) = 0.2985 + \frac{0.314 \times 298}{96000} \ln 0.1 \times 0.7$
 $= 0.2886V$

(3) 在 25°C 时设计如下原电池:



$E^\ominus = \varphi^\ominus_{右} - \varphi^\ominus_{左} = 0$

$\Delta_r G_m^\ominus = -zE^\ominus F = -RT \ln K_{sp}$

$\Rightarrow K_{sp} = \exp \left(\frac{zE^\ominus F}{RT} \right)$

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$$4. (1) -\frac{dp}{dt} = k_p p^2$$

$$\frac{1}{p} - \frac{1}{p_0} = k_p t$$

$$\frac{1}{2} p = \frac{p_0}{2} \text{ 时 } t = \frac{1}{k_p p_0} \Rightarrow k_p = \frac{1}{p_0 t} = \frac{1}{40 \times 118} = 1.096 \times 10^{-4} \text{ kPa}^{-1} \cdot \text{s}^{-1}$$

$$k = A e^{-\frac{E_a}{RT}} \Rightarrow \frac{k_1}{k_2} = e^{-\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \Rightarrow k_2 = k_1 e^{-\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

$$k_2 = 1.096 \times 10^{-4} e^{-\frac{250.8 \times 10^3}{8.314} \times \left(\frac{1}{1300} - \frac{1}{1200} \right)} = 7.579 \times 10^{-4} \text{ kPa}^{-1} \cdot \text{s}^{-1}$$

(2) 当 $t = 1000 \text{ s}$ 时

$$\frac{1}{p} - \frac{1}{p_0} = k_p t \Rightarrow p = \left(k_p t + \frac{1}{p_0} \right)^{-1} = 9.92 \text{ kPa}$$

$$p_B = p_C = p_0 - p_A = 30.08 \text{ kPa}$$

$$p_{\text{总}} = 2p_B = 70.06 \text{ kPa}$$

5 (1)

$$\gamma = \frac{T}{\Theta_T} = \frac{300}{2.68} = 111.9$$

$$U_{m,r} = NKT^2 \left(\frac{\partial \ln g_r}{\partial T} \right)_{v,N} = NKT = 300 \times 8.314 = 2.494 \text{ kJ} \cdot \text{mol}^{-1}$$

$$S_{m,r} = NK \ln g_r + NKT \left(\frac{\partial \ln g_r}{\partial T} \right)_{v,N} = 339.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

(2) $\frac{AP}{p_0} = 1$ 不可简化

$$\therefore RT \ln \frac{p_r}{p_0} = \frac{\gamma M}{R' p}$$

$$\gamma = \frac{R' p R T \ln \frac{p_r}{p_0}}{2M} = \frac{1.5 \times 10^{-9} \times 10^3 \times 8.314 \times 298 \ln 2}{2 \times 18} = 7.16 \times 10^{-6}$$

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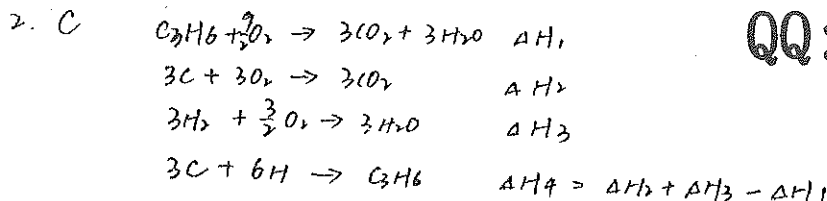
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10年

一. 选择题

1. B. 可参照 van der Waals 方程



3. D. 将蒸气与理想气体处理, 由 Clausius - Clapeyron 方程: $\ln p = -\frac{\Delta_{\text{vap}}H_m}{R} + \dots$
易知

4. C. 可证明 $(\frac{\partial U}{\partial p})_T = 0$.

5. C. 在这个体系中存在两个平衡, 且相互独立. $\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$
 $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$ $C = S - R = 5 - 2 = 3$.

6. C. 由 Raoult 定律: $P_A = P_A^* x_A = 50 \times (1 - 0.15) = 42.5 \text{ Pa}$
 $P_B = \frac{P_A}{y_A} y_B = \frac{42.5}{0.89} \times 0.11 = 5.25 \text{ Pa}$
 $K_{\text{AB}} = \frac{P_B}{x_B} = 47.8$.

7. C

8. A. 体积变大, 气体浓度变A, 平衡向正向移动.

9. A. KI 过量, 胶粒带负电, 异相电荷价数越小, 聚沉能力弱

10. D. 无法确定

11. C $h = \frac{2\gamma}{R\rho g}$

12. C

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13. A. k 单位为 min^{-1} 为一级反应. $t_{1/2} = \frac{\ln 2}{k}$

14. B

15. C.

二. 简答题

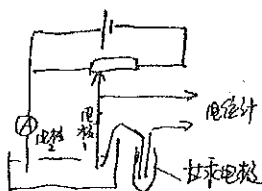
1. $=$; $<$ 可逆相变 $\Delta G = 0$; 自发过程 $\Delta G < 0$

$$2. \left(\frac{\partial T}{\partial p}\right)_H = - \frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = - \frac{1}{C_p} \left(\frac{\partial H}{\partial p}\right)_T = \mu_{J-T}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = -\mu_{J-T} C_p = -1.07 \times 10^{-5} \times 36.61 = 3.92 \times 10^{-4} \text{ Pa}^{-1} \cdot \text{mol}^{-1}$$

3. 偏摩尔量即为多组分系统中, 某一广度性质随着其中一种组成变化的变化率. 化学势则是该系统中表征能量的物理量在其特征函数不变时, 其随其组成变化的变化率.

4.



首先测量1的极化曲线, 借助2电极, 将其接成一个电解池. 调节外电路中的电阻, 来改变通过电极的电流. 当待测电极上有电流时, 其电极电势可随电流变化. 另一个电极(标准电极)与待测电极组成原电池, 用电压计测电压. 每变一次电流, 记录其对应电压即可.

5. 设其为 n 级反应. C_A^{1-n} 应与 t 成正比. 作 \ln 改变 n 值作图即可.

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三. 综合题

1. ① 双原子气体 $C_v = \frac{5}{2}R$ $C_p = \frac{7}{2}R = \frac{C_p}{C_v} = \frac{7}{5}$

由理想气体状态方程 $pV = nRT$ 可知在 A 状态下: $p_1 = \frac{nRT}{V} = 101.3 \text{ kPa}$

由绝热过程方程: $p_1 V_1^\gamma = p_2 V_2^\gamma$ $V_2 = \left(\frac{p_1 V_1^\gamma}{p_2} \right)^{\frac{1}{\gamma}} = 40.13 \text{ dm}^3$

$$T_2 = \frac{p_2 V_2}{nR} = 244.53 \text{ K}$$

$$W = C_v(T_2 - T_1) = \frac{5}{2}R(T_2 - T_1) = -1114.5 \text{ J}$$

$$\Delta U = Q + W = W = -1114.5 \text{ J}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + p_2 V_2 - p_1 V_1 = -1559.3 \text{ J}$$

$$\Delta S_{\text{系统}} = \int \frac{\delta Q}{T} = 0$$

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② $\frac{T_2}{V_2} = \frac{T_3}{V_3} \Rightarrow V_3 = \frac{V_2 T_3}{T_2} = 48.93 \text{ dm}^3$

$$W = -p \Delta V = 50.66 \times (48.93 - 40.13) = -445.8 \text{ J}$$

$$\Delta U = n \int_{T_2}^{T_3} C_{p,m} dT = C_v(T_3 - T_2) = \frac{5}{2}R(T_3 - T_2) = 1114.5 \text{ J}$$

$$Q = \Delta U - W = 1560.3 \text{ J}$$

$$\Delta H = n \int_{T_2}^{T_3} C_{p,m} dT = \frac{7}{2}R(T_3 - T_2) = 1560.3 \text{ J}$$

$$\Delta S_{\text{系统}} = \frac{Q}{T} = \int_{T_1}^{T_2} \frac{n C_{p,m}}{T} dT = C_{p,m} \ln \frac{T_2}{T_1} = \frac{7}{2}R \ln \frac{T_2}{T_1} = 5.77 \text{ J/K}$$

③ 节流膨胀是一个等焓过程 $\Delta H = 0$. 因为焓值为状态函数, 理想气体的

焓值又仅与状态有关: $T_1 = T_4$ $V_4 = \frac{nRT_4}{p_4} = 48.93 \text{ dm}^3$

由于过程绝热 $Q = 0$ $\Delta U = W = p_1 V_1 - p_4 V_4 = -1114.5 \text{ J}$

$$\Delta S_{\text{系统}} = \int \frac{\delta Q}{T} = 0$$

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$$2. (1) \left(\frac{\partial \ln K^\ominus}{\partial T} \right)_P = \frac{\Delta_r H_m^\ominus}{RT^2} \Rightarrow \Delta_r H_m^\ominus = \left(\frac{\partial \ln K^\ominus}{\partial T} \right)_P RT^2 = -41.9 \text{ kJ/mol}$$

$$\Delta G_m^\ominus = \Delta H_m^\ominus - T \Delta S_m^\ominus = -RT \ln K^\ominus \Rightarrow \ln K^\ominus = \frac{T \Delta S_m^\ominus - \Delta H_m^\ominus}{RT} = 11.5$$

$$K^\ominus = e^{11.5} = 9.87 \times 10^4$$

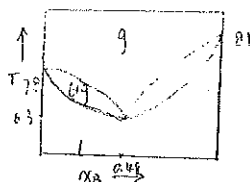
$$(2) \ln K^{\ominus'} = \frac{T' \Delta_r S_m^\ominus - \Delta_r H_m^\ominus}{RT'} = 4.68$$

$$K^{\ominus'} = e^{4.68} = 107.8$$

(3)

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3. (1)



各区域的自由度为2;
线上的自由度为1;
交点处的为0.

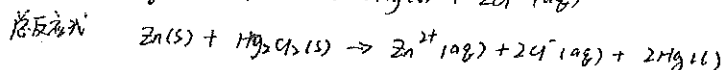
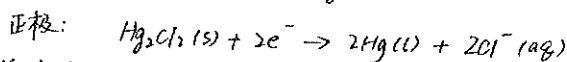
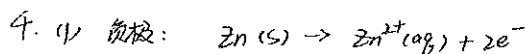
(2) 对 Raoult 定律产生很大的正偏差

$$(3) y_B = 0.65 \quad x_B = 0.92$$

$$\begin{cases} 0.65 n_g + 0.92 n_l = 0.85 n_{\text{总}} \\ n_g + n_l = n_{\text{总}} \end{cases}$$

$$\text{得} \begin{cases} n_g = 2.6 \text{ mol} \\ n_l = 7.4 \text{ mol} \end{cases} \begin{cases} n_{B(g)} = 1.69 \text{ mol} \\ n_{B(l)} = 6.81 \text{ mol} \end{cases}$$

(4) 塔顶: B 纯组分 塔底: A、B 共沸物.



$$E = E^\ominus - \frac{RT}{2F} \ln(a_{\text{Zn}^{2+}} \cdot a_{\text{Cl}^-}^2)$$

$$(2) E^\ominus = E^\ominus_{\text{Hg}_2\text{Cl}_2/\text{Hg}} - E^\ominus_{\text{Zn}^{2+}/\text{Zn}} = 1.031$$

$$a_{\pm} = (a_{\text{Zn}^{2+}} \cdot a_{\text{Cl}^-}^2)^{\frac{1}{3}} = e^{\frac{(E^\ominus - E)F}{RT}} = 0.00015$$

$$b_{\pm} = (b_+ b_-^2)^{\frac{1}{3}} = 0.00018$$

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$$(3) \Delta G = -zEF = -RT \ln K^\ominus$$

$$\ln K^\ominus = \frac{zEF}{RT} = \frac{2 \times 1.031 \times 96000}{8.314 \times 298} = 79.9$$

$$(2) K^\ominus = 5 \times 10^{34}$$

$$(4) \Delta_r H_m^\ominus = -zEF + 2FT \left(\frac{\partial E}{\partial T} \right)_p = -2 \times 1.031 \times 96000 + 2 \times 96000 \times$$

$$\left(\frac{\partial E}{\partial T} \right)_p = \frac{\Delta_r H_m^\ominus}{2FT} + \frac{E}{T} = 0.0068 \text{ V} \cdot \text{K}^{-1}$$

$$5. (1) \frac{d[P]}{dt} = k_2 [A^*] \quad (1)$$

$$\frac{d[A^*]}{dt} = k_1 [A]^2 - k_{-1} [A^*] [A] - k_2 [A^*] = 0$$

$$[A^*] = \frac{k_1 [A]^2}{k_{-1} [A] + k_2}$$

$$\text{代入 (1) 中: } \frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1} [A] + k_2}$$

$$(2) \text{ 当 } k_{-1} [A] \gg k_2 \text{ 时}$$

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1} [A]} = \frac{k_1 k_2}{k_{-1}} [A] \quad \text{为一级反应}$$

$$\text{当 } k_{-1} [A] \ll k_2 \text{ 时}$$

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2}{k_2} = k_1 [A]^2 \quad \text{为二级反应}$$

$$(3) \text{ 在 } [A] \text{ 很小时分别测定 } T_1 \text{ 和 } T_2 \text{ 下的反应速率, 并计算出 } k_1 \text{ 和 } k_2$$

$$\text{则 } k_1 = e^{-\frac{E_a}{RT_1}} \quad k_2 = e^{-\frac{E_a}{RT_2}}$$

$$E_a = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{k_2}{k_1}$$

$$6. (1) \Delta G = \delta_{L-S} + \gamma_{H-L} - \gamma_{H-S} = 0.3870 + 0.02239 - 0.4865 = -0.07511 < 0$$

∴ 可以铺展

$$(2) S_{\text{表面积}} = 4\pi \left(\frac{d}{2} \right)^2 = \pi d^2 = 3.14 \times 10^{-6} \text{ m}^2$$

$$W_i = (\delta_{\text{汞-空气}} + \delta_{\text{汞-2油}}) S = (0.3870 - 0.4865) \times 3.14 \times 10^{-6} = -0.311$$

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一. 选择题

1. A. 超临界流体的定义

2. C

3. C. 只有分子和下标相乘为能量量纲的才能用麦克斯韦关系式。

4. B 低温有利于反应, 说明是放热反应。高压有利于反应, 说明是体积减小的反应。

5. A $C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$ a ① $C + O_2 \rightarrow CO_2$ b ② $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ c

$5C + 6H_2 \rightarrow C_5H_{12}$? ③ ① + ② - ③ \Rightarrow ④ $\Rightarrow \Delta H = 5b + 6c -$

6. A. 其它组分不改变

7. D

8. D. n_D 越大, 折光率越大。混合系统的折光率与组成是线性关系

9. D A 中应为浓度不大且完全溶解的条件下成立。B 应在 $C < 0.001 \text{ mol/L}$ 时
C 应为开始时增大, 而后减小

10. C. 与所态的 δ 成反比。

11. D. $r = \frac{k_2 a_1 P_A}{1 + K A P_A}$ 反应级数还与压力有关

12. A 观察可知半衰期与初始浓度的平方成反比。为二级反应

13. B $g_r = \frac{T}{\Theta_r}$

14. C $\frac{\Delta P}{P_0} = \frac{2\gamma M}{R T R P}$ 液滴越小, 蒸气压越大

15. C 由 K_A 单位可知为二级反应。 $-\frac{dCA}{dt} = K_A C A^2$ 积分: $\frac{1}{CA} - \frac{1}{CA_0} = k t$

二. 简答题

$$1. \mu_{J-T} = \left(\frac{\partial T}{\partial p} \right)_H = - \frac{\left(\frac{\partial H}{\partial p} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_p} = - \frac{1}{C_{p,m}} \left(\frac{\partial H}{\partial p} \right)_T$$

$$dH = T ds + v dp \Rightarrow \left(\frac{\partial H}{\partial p} \right)_T = T \left(\frac{\partial s}{\partial p} \right)_T + v = -T \left(\frac{\partial v}{\partial T} \right)_p + v$$

$$\text{代入原式: } \mu_{J-T} = - \frac{1}{C_{p,m}} \left[-T \left(\frac{\partial v}{\partial T} \right)_p + v \right] = \frac{1}{C_{p,m}} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right]$$

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$$7. (1) \quad g = g_t \cdot g_r \cdot g_v = \left(\frac{2\pi m k T}{h} \right)^{\frac{3}{2}} V \cdot \frac{T}{\sigma \Theta_r} \cdot \frac{e^{-\frac{\Theta_v}{T}}}{1 - e^{-\frac{\Theta_v}{T}}}$$

$$U = NkT^2 \left(\frac{\partial \ln g}{\partial T} \right)_{V, N}$$

(2) 对于理想气体, 只考虑 g_t .

$$U = NkT^2 \left(\frac{\partial \ln g_t}{\partial T} \right)_{V, N} = NkT^2 \frac{\partial \ln \left(\frac{2\pi m k T}{h} \right)^{\frac{3}{2}} V}{\partial T}$$

$$= \frac{3}{2} NkT.$$

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2. $P_B = P_B^* x_B$ Raoult 定律 $y_B = \frac{P_B}{P_{\text{总}}} = \frac{P_B^* x_B}{P_{\text{总}}}$

3. $\Delta T_b = K_b m \Rightarrow K_b = \frac{0.143}{1.43 \times 10^{-1}} = 1^\circ \text{C} \cdot \text{kg/mol}$

$m' = \frac{\Delta T_b}{K_b} = \frac{0.125}{1} = 0.125 \text{ mol/kg}$

$m' = \frac{\frac{m}{M}}{m_{\text{溶剂}}} = \frac{\frac{m}{M}}{m_{\text{溶剂}}} = \frac{8}{M(8+400) \times 10^{-3}} \rightarrow \text{得 } M = 26.11 \text{ g/mol}$

4. 杠杆规则 $n_1(x_A - x_1) = n_2(x_2 - x_A)$

5. 在电场的作用下, 固液之间发生电动现象时, 相对运动边界处与溶液本体之间的电势差称为电动电势。

有显著影响。

6. 毛细管中液面高度从大到小依次为: Na_2SO_4 溶液, 水, 洗衣粉, 加入 Na_2SO_4 后, 水的表面张力变大, 液面上升, 而洗衣粉为表面活性物质, 加入后水的表面张力减弱。

7. 实际电解过程中, 所加电压大于两极反电动势的部分称为超电势。从能耗的角度来说对电极反应很不利。

8. $\sum_i g_i e^{-\epsilon_i/kT} = Z$, $g = g_t \cdot g_r \cdot g_e \cdot g_n$

全配分函数为其它独立运动的配分函数之积

三 (1) 由 Clausius - Clapeyron 方程: $\ln p = -\frac{\Delta_{\text{vap}} H_m^\ominus}{RT} + C$ 可知

$p^* = \exp \left[-\frac{\Delta_{\text{vap}} H_m}{R} \left(\frac{1}{T^*} - \frac{1}{T} \right) \right] p = 142.7 \text{ kPa}$

绝热可逆过程的过程方程: $p^{1-\gamma} T^\gamma = C$ 其中 $\gamma = \frac{C_p}{C_v}$

而 $C_p - C_v = nR$ 由题可知 $C_p = 33.58 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ $C_v = 25.27 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

$\gamma = \frac{C_p}{C_v} = \frac{33.58}{25.27} = 1.33$

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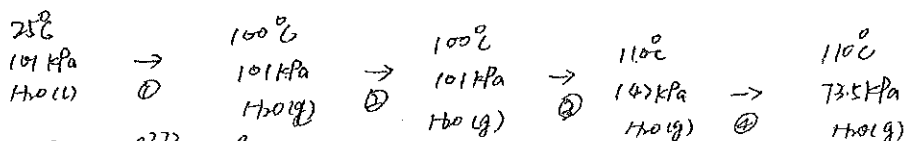
$$p_2^{1-\gamma} T_2^{\gamma} = p_3^{1-\gamma} T_3^{\gamma} \Rightarrow T_3 = \left(\frac{p_2}{p_3}\right)^{\frac{1-\gamma}{\gamma}} T_2 = 2^{-0.25} T_2 = 322 \text{ K.}$$

(2) 从 110°C 147 kPa 至 49°C 73.5 kPa 的过程中

$$\Delta H' = n \int_{T_2}^{T_3} C_{p,m} dT = 33.58 \times (49 - 110) = -2.05 \text{ kJ}$$

$$\Delta H_{\text{总}} = \Delta H + \Delta H' = 44.6 \text{ kJ}$$

~~ΔH~~



$$\Delta S_1 = n \int_{298}^{373} \frac{75.29}{T} dT = 75.29 \ln \frac{373}{298} = 16.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta S_2 = \frac{\Delta_{\text{vap}} H_m}{T} = \frac{40.67 \times 10^3}{373} = 109 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta S_3 = nR \ln \frac{p_2}{p_3} + \int_{T_2}^{T_3} \frac{n C_{p,m}}{T} dT = 8.314 \ln \frac{101}{147} + 33.58 \ln \frac{373}{298} = -2.23 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta S_4 = 0 \quad (\text{绝热可逆})$$

$$\Delta S = \sum_{i=1}^4 \Delta S_i = 123.67 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

~~ΔG~~

$$\Delta G = \Delta H - T \Delta S = \Delta H - (T_3 S_3 - T_1 S_1)$$

$$S_3 = \Delta S + S_1 = 69.91 + 123.67 = 193.58 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta G = 44.6 \times 10^3 - (322 \times 193.58 - 298 \times 69.91) = 3.1 \text{ kJ}$$

(3) 不可以 体系不是等温、等压的。

四 (1) $\Phi = 2$ 固相和气相. $C = S - R = 4 - 2 = 2$ 有 4 个物种, 两个平衡:
一是化学平衡, 二是组成物间的比例关系. $f' = C - \Phi + 1 = 1$ 温度已定

(2) ~~假设~~ 假设均为理想气体, 满足分压定律

$$p(\text{H}_2\text{O}) = \frac{p}{2} \quad p(\text{CO}_2) = \frac{p}{2} \quad K^\ominus = \frac{p(\text{H}_2\text{O}) p(\text{CO}_2)}{p^\ominus p^\ominus} = \frac{1}{4} \left(\frac{p}{p^\ominus}\right)^2$$

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$$(3) \quad \frac{d(\frac{\Delta_r G_m^\ominus}{T})}{dT} = -\frac{\Delta_r H_m^\ominus}{T^2} \quad \text{而} \quad \Delta_r G_m^\ominus = -RT \ln K^\ominus$$

$$\text{则有} \quad \frac{d \ln K^\ominus}{dT} = \frac{\Delta_r H_m^\ominus}{RT^2} \quad \text{积分有:} \quad \ln K^\ominus = \frac{-\Delta_r H_m^\ominus}{RT} + I' \quad (\Delta_r H_m^\ominus \text{视为})$$

$$\text{当 } T = T_1 \text{ 时 } K_1^\ominus = \frac{1}{4} \frac{P_1^2}{P^\ominus^2} = \frac{1}{4} \times \left(\frac{15.9}{100}\right)^2 = 6.32 \times 10^{-3}$$

$$\text{当 } T = T_2 \text{ 时 } K_2^\ominus = \frac{1}{4} \frac{P_2^2}{P^\ominus^2} = \frac{1}{4} \times \left(\frac{9.74}{100}\right)^2 = 2.38 \times 10^{-1}$$

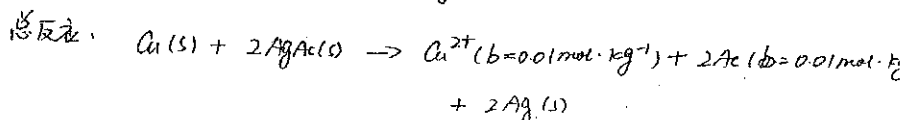
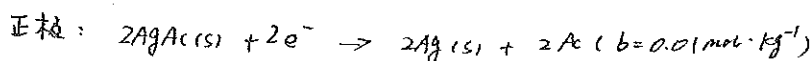
$$\ln \frac{K_1^\ominus}{K_2^\ominus} = -\frac{\Delta_r H_m^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{得} \quad \Delta_r H_m^\ominus = \frac{R \cdot \frac{T_1 T_2}{T_1 - T_2} \ln \frac{K_1^\ominus}{K_2^\ominus}}{1} = 128$$

(4) 由(3)可知, 只须确定积分常数 I' 即可.

$$\text{当 } T = T_1 = 343 \text{ K 时 } K^\ominus = 6.32 \times 10^{-3} \text{ 代入得 } I' = -49.9$$

$$\ln \frac{1}{4} \left(\frac{P}{P^\ominus}\right)^2 = -\frac{128 \times 10^3}{8.314} \cdot \frac{1}{T} - 49.9$$

~~ln P~~



$$(2) \quad \Delta_r G_m^\ominus = -zEF = -2 \times 96000 \times 0.327 = -62.78 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m^\ominus = \Delta_r G_m^\ominus + T \Delta_r S_m^\ominus = -zEF + zFT \left(\frac{\partial E}{\partial T}\right)_P = -62.78$$

$$= -2 \times 96000 \times 0.327 + 2 \times 96000 \times 298 \times 2 \times 10^{-4} = -62.78 + 11.32 = -51.46$$

$$(3) \quad I = \frac{1}{2} \sum m_B z_B^2 = \frac{1}{2} (0.01 \times 2^2 + 0.02 \times 1^2) = 0.03 \text{ mol} \cdot \text{kg}^{-1}$$

$$\gamma_{\pm} = \exp(-A |z_+ z_-| \sqrt{I}) = e^{-0.509 \times 2 \times \sqrt{0.03}} = 0.84$$

$$m_{\pm} = (0.01^2 \cdot 0.02)^{\frac{1}{2}} = 0.013 \text{ mol} \cdot \text{kg}^{-1}$$

数学作业纸

班级:

姓名:

编号:

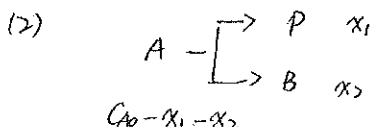
第 20 页

$$E = E^{\ominus} - \frac{RT}{2F} \ln a(A_2^{2+}) a(A_2O)^2 = E^{\ominus} - \frac{RT}{2F} \ln a_2^2$$

$$E^{\ominus} = E + \frac{RT}{2F} \ln a_2 = 0.327 + \frac{8.314 \times 298 \times 3}{2 \times 96000} \ln 0.011 = 0.152 \text{ V.}$$

7. (1) $-\frac{dCA}{dt} = k_1$ 由反应速率常数的单位可知这两个反应均为二级反应.

$$-\frac{dCA}{dt} = k_1 CA^2 + k_2 CA^2 = (k_1 + k_2) CA^2$$



$$r_1 = \frac{dx_1}{dt} = k_1 (CA_0 - x_1 - x_2)^2 \quad \dots \textcircled{1}$$

$$r_2 = \frac{dx_2}{dt} = k_2 (CA_0 - x_1 - x_2)^2 \quad \dots \textcircled{2}$$

$$r = r_1 + r_2 = \frac{dx}{dt} = (k_1 + k_2) (CA_0 - x)^2 \quad \text{其中 } x = x_1 + x_2$$

$$\textcircled{1} / \textcircled{2} \quad \frac{dx_1}{dt} / \frac{dx_2}{dt} = \frac{k_1}{k_2}$$

∵ 反应时间相同 ∴ 有 $\frac{k_1}{k_2} = \frac{x_1}{x_2}$.

当 $CA = (1 - 0.9) CA_0 = 0.1 CA_0$ 时.

$$C_p = \frac{k_1}{k_1 + k_2} \cdot 0.9 CA_0 = \frac{9k_1}{10(k_1 + k_2)} CA_0$$

$$(3) \quad k_1 = A_1 e^{-\frac{E_1}{RT}}$$

$$k_2 = A_2 e^{-\frac{E_2}{RT}}$$

$$K = k_1 + k_2 = A_3 e^{-\frac{E_0}{RT}}$$

$$\therefore E_2 = -RT \ln \left(\frac{A_2}{A_1} e^{-\frac{E_0}{RT}} - \frac{A_1}{A_2} e^{-\frac{E_1}{RT}} \right)$$

北京化工大学 2012年 物化试题答案

一、选择题

1. C 2. C 3. B 4. A 5. A 6. C
 7. D 8. A 9. A 10. D 11. B 12. B
 13. C 14. C

二、简答题

1. (1) $\alpha = \frac{PV_m}{RT} = \frac{10.086 \times 10^4 \times 0.26 \times 10^{-3}}{8.314 \times 200} = 0.161 < \alpha = 1$

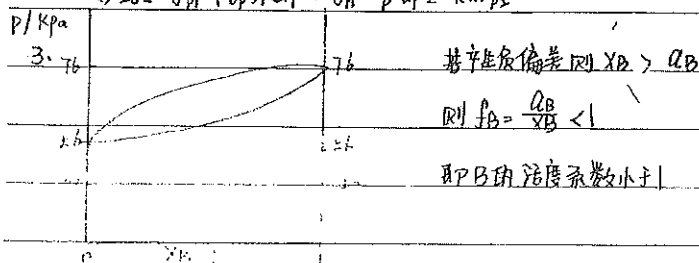
∴ 该气体与理想气体相比易于压缩

(2) 偏离理想气体用主要因素: 真实气体分子间有相互作用力且分子本身占有体积

2. $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$

∵ $V_m = \frac{RT}{P} + \alpha$ ∴ $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P = -\frac{R}{P}$

∴ $\Delta S = \int_{P_1}^{P_2} (\frac{\partial S}{\partial P})_T dP = \int_{P_1}^{P_2} -\frac{R}{P} dP = R \ln \frac{P_1}{P_2}$



4. (1) ① 放热反应 $\Delta_r H_m^0 < 0$, 即开高温度 K^0 减小, 平衡向着反应物方向移动

② 吸热反应 $\Delta_r H_m^0 > 0$, 即开高温度 K^0 变大, 平衡向着生成物方向移动

(2) $K_y = \prod (y_B)^{v_B} = (\frac{P_B}{P})^{-a} (\frac{P_B}{P})^b (\frac{P_C}{P})^c (\frac{P_D}{P})^d = P^{a+b-c-d} \frac{P_C^c P_D^d}{P_A^a P_B^b}$

∴ $\ln K_y = (a+b-c-d) \ln P + c \ln P_C + d \ln P_D - a \ln P_A - b \ln P_B$

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$$\Rightarrow \left(\frac{\partial \ln K_f}{\partial p} \right)_T = \frac{a+b-c-d}{p} + \frac{c}{p_c} + \frac{d}{p_d} - \frac{a}{p_A} - \frac{b}{p_B}$$

5. (1) 因为 NaOH 溶液会与空气中的 CO_2 反应, 使浓度变低, 所以配制 NaOH 溶液后立即测量

(2) K_0 会产生负偏差, K_2 产生负偏差

6. 可以, 可得到 AgBr 的正溶胶, 过剩的 $AgNO_3$ 则起到稳定剂的作用。

胶团结构: $\left[AgBr \right]_m \cdot n Ag^+ \cdot (n-x) NO_3^- \cdot x NO_3^-$

7. (1) Langmuir 模型的特点:

① 单分子层吸附 ② 固体表面是均匀的 ③ 被吸附在固体表面上的分子无相互作用力

④ 吸附平衡是动态平衡

$$(2) \theta_A = \frac{b p_A}{1 + b p_A} \quad \text{且} \quad P_A = P_{YA}$$

$$\Rightarrow \theta_A = \frac{b P_{YA}}{1 + b P_{YA}}$$

$$8. \textcircled{1} \begin{cases} E_{v1} = 15 kT \\ g_{v1} = 1 \end{cases} \Rightarrow g_v = 1 \times e^{-\frac{E_{v1}}{kT}} = 3.06 \times 10^{-7}$$

$$\textcircled{2} E_{v1} = 15 kT \quad \text{且} \quad T = 300$$

$$\Rightarrow 15 \times 300 \times 1.381 \times 10^{-23} = (V + \frac{1}{2}) \times 6.626 \times 10^{-34} \times \nu$$

$$\text{解得 } \nu = 9684504$$

$$\Rightarrow \theta_v = \frac{h \nu}{k} = \frac{6.626 \times 10^{-34} \times 9684504}{1.381 \times 10^{-23}} = 4.65 \times 10^4 K$$

三. 综合题

1. (1) ① 该过程为循环过程。② H, S, G 均为状态函数

$$\Rightarrow \Delta U = 0 \quad \Delta H = 0 \quad \Delta S = 0 \quad \Delta G = 0$$

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$$① A \rightarrow B: W_1 = \Delta U_1 = \int_{T_1}^{T_2} n C_{V,m} dT = \int_{200}^{100} 1 \times \frac{5}{2} \times 8.314 dT = -1.2471 \text{ kJ}$$

$$Q_1 = 0$$

$$② B \rightarrow C: Q_2 = \Delta U_2 = n C_{V,m} (T_2 - T_1) = 1 \times \frac{5}{2} \times 8.314 \times (200 - 100) = 1.2471 \text{ kJ}$$

$$W_2 = 0$$

$$③ C \rightarrow A: \text{因 } A \rightarrow B \text{ 为绝热可逆过程 } \rightarrow \gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{\frac{5}{2}R}{\frac{5}{2}R} = \frac{5}{3}$$

$$\rightarrow T_A P_A^{(1-\gamma)/\gamma} = T_B P_B^{(1-\gamma)/\gamma} \rightarrow \text{代入数据求解得 } \frac{P_A}{P_B} = 5.66$$

$$\text{因 } B \rightarrow C \text{ 为等容过程 } \rightarrow \frac{P_B}{P_C} = \frac{T_B}{T_C} = \frac{100}{200} = \frac{1}{2}$$

$$\rightarrow \frac{P_A}{P_C} = \frac{P_A}{P_B} \cdot \frac{P_B}{P_C} = 5.66 \times \frac{1}{2} = 2.83$$

$$\rightarrow Q_3 = W_3 = nRT \ln \frac{V_A}{V_C} = -nRT \ln \frac{P_C}{P_A} = -1 \times 8.314 \times 200 \times \ln 2.83 = -1.730 \text{ kJ}$$

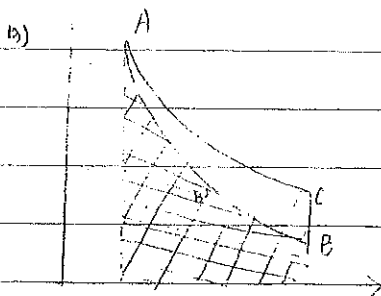
$$\rightarrow Q = Q_1 + Q_2 + Q_3 = 0 + 1.2471 + (-1.730) = -0.4829 \text{ kJ}$$

$$W = W_1 + W_2 + W_3 = -1.2471 + 0 + 1.730 = 0.4829 \text{ kJ}$$

$$\Delta U = \Delta H = \Delta S = \Delta G = 0$$

$$② \text{ 熵是状态函数 } \rightarrow \Delta S = 0 \text{ 又 } A \rightarrow B \text{ 为绝热可逆过程 } \rightarrow \Delta S_{A \rightarrow B} = 0$$

$$\rightarrow \Delta S_{B \rightarrow C} + \Delta S_{C \rightarrow A} = 0 \rightarrow \Delta S_{B \rightarrow C} = -\Delta S_{C \rightarrow A} = \Delta S_{A \rightarrow C}$$



左斜线未与右斜线相交区域

即为两过程体积功差值

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$$2. \quad (1) \quad J_p = \frac{\left[\frac{p_{CO_2}}{p^\ominus} \right]^2}{\left[\frac{p_{CO}}{p^\ominus} \right] \left[\frac{p_{H_2}}{p^\ominus} \right]^2} = \frac{100^2 \times 100}{5 \times 1^2} = 2 \times 10^5 < K^\ominus = 2.23 \times 10^7$$

∴ 反应向着生成物的方向进行

(2) 当 $J_p > K^\ominus$ 时, 反应向着反应物方向进行

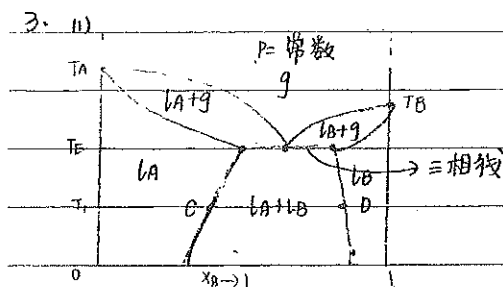
$$\text{此时 } J_p = \frac{\left[\frac{p_{CO_2}}{p^\ominus} \right]^2}{\left[\frac{p_{CO}}{p^\ominus} \right] \left[\frac{p_{H_2}}{p^\ominus} \right]^2} > K^\ominus$$

代入数据得 $p_{CO} = 1 \text{ kPa}$ $p_{H_2} = 5 \text{ kPa}$ $K^\ominus = 2.23 \times 10^7$ $p^\ominus = 100 \text{ kPa}$

可得 $p_{CO_2} > 1270.8 \text{ kPa}$

(3) 温度及系统总压不变, 加入惰性气, 各气体分压减小, 反应平衡将向左移动

温度及系统总压不变, 加入惰性气, 各气体分压不变, 反应平衡不变



(2) 对于C点, 溶剂为A, 溶质为B

$$\text{有 } p_A = p_A^\ominus x_A \quad \Rightarrow \quad p_A = (1-0.3) \times 0.760 = 0.532 \text{ kPa}$$

$$p_B = p_B^\ominus x_B \quad \Rightarrow \quad p_B = \frac{p_B^\ominus}{x_B} = \frac{10}{0.3} = \left(\frac{10}{3} P - 1.773 \right) \text{ kPa}$$

$$p = p_A + p_B$$

对于D点, 溶剂为B, 溶质为A

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$$\begin{cases} p_A = K_A x_A^D & \Rightarrow p_B = 19.9 \times 0.9 = 17.91 \text{ KPa} \end{cases}$$

$$\begin{cases} p_B = p_B^* x_B^D & \Rightarrow K_A = \frac{p_A}{x_A} = \frac{p - 17.91}{1 - 0.9} = (10p - 179.1) \text{ KPa} \end{cases}$$

$$p = p_A + p_B$$

4. (1) $E^{\theta} = 0.0713 \text{ V} - 4.99 \times 10^{-4} (T - 298) - 3.45 \times 10^{-6} T^2 + 2.056 \times 10^{-3} T - 0.7064$

$$\Rightarrow \Delta_r G_m^{\theta} = RT \left(\frac{\partial E^{\theta}}{\partial T} \right)_p$$

$$= RT [-4.99 \times 10^{-4} - 2 \times 3.45 \times 10^{-6} T + 2.056 \times 10^{-3}]$$

$$= 2 \times 96500 \times [-4.99 \times 10^{-4} - 2 \times 3.45 \times 10^{-6} \times 298 + 2.056 \times 10^{-3}]$$

$$= -96.35 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

(2) $I = \frac{1}{2} \sum b_i z_i^2 = \frac{1}{2} [b(x)^2 + b(x)^2] = b = 0.1000 \text{ mol} \cdot \text{kg}^{-1}$

$$\Rightarrow \lg \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I}$$

$$= -0.509 \times |1 \times 1| \times \sqrt{0.1000} = -5.09 \times 10^{-3}$$

$$\Rightarrow \gamma_{\pm} = 0.988$$

(3) $T = 298 \text{ K}, E^{\theta} = 0.07131 \text{ V}, E^{\theta} \{ \text{H}^+ | \text{H}_2(1013) \} = 0$

$$\Rightarrow E^{\theta} \{ \text{Br}^- | \text{AgBr(s)} | \text{Ag} \} = E^{\theta} \{ \text{Ag}^+ | \text{Ag} \} + \frac{RT}{F} \ln K_{sp}$$

$$= 0.799 + \frac{8.314 \times 298}{96500} \ln K_{sp}$$

$$= 0.07131 - 0$$

解得 $K_{sp} = 4.906 \times 10^{-13}$

(4) $K(\text{AgBr}) = K(\text{溶解}) - K(\text{沉淀})$

$$= 1.664 \times 10^{-5} - 5.471 \times 10^{-6} = 1.1143 \times 10^{-5} \text{ S} \cdot \text{m}^{-1}$$

$$K_{sp} = \frac{c(\text{Ag}^+) c(\text{Br}^-)}{c^{\ominus 2}} \quad \text{且} \quad c(\text{Ag}^+) = c(\text{Br}^-) = c(\text{AgBr})$$

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$$\therefore \text{代数据解得 } c(\text{AgBr}) = 7.004 \times 10^{-7} \text{ mol} \cdot \text{dm}^{-3} = 7.004 \times 10^{-4} \text{ mol} \cdot \text{m}^{-3}$$

$$\therefore \Lambda_m(\text{AgBr}) = \frac{\kappa(\text{AgBr})}{c(\text{AgBr})} = \frac{1.143 \times 10^{-3}}{7.004 \times 10^{-4}} = 0.159 \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

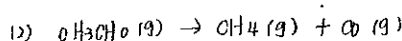
$$\therefore \Lambda_m(\text{Ag}^+) = \Lambda_m(\text{AgBr}) - \Lambda_m(\text{Br}^-) = 0.159 - 78.40 \times 10^{-4} = 8.06 \times 10^{-3} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

$$5. (1) n = 1 + \frac{\frac{19}{19.04} - \frac{19}{19.06}}{\frac{19}{19.06} - \frac{19}{19.08}} = 1 + \frac{\frac{19(19.08 - 19.04)}{19.06 \times 19.08}}{\frac{19(19.08 - 19.06)}{19.06 \times 19.08}} = 2$$

$$P = cRT \quad \therefore c_{\text{AgBr}} = \frac{P_{\text{AgBr}}}{RT}$$

$$\therefore t_{\text{H}^+} = \frac{1}{\kappa c_{\text{H}^+}} = \frac{RT}{\kappa P_{\text{H}^+}}$$

$$\therefore \kappa = \frac{RT}{t_{\text{H}^+} P_{\text{H}^+}} = \frac{8.314 \times 518}{48396 \times 410} = 2.17 \times 10^{-4} \text{ m}^2 \cdot \text{mol}^{-1} \cdot \text{S}^{-1}$$



$$t=0 \quad 5000 \quad 0 \quad 0$$

$$t=t \quad 5000-a \quad a \quad a \Rightarrow 5000+a=6000$$

$$\therefore a=1000 \quad \therefore P_A=5000-1000=4000 \text{ Pa}$$

该反应为一级反应

$$c_A - c_{A0} = \kappa t \quad \text{or} \quad RT \left[\frac{1}{P_A} - \frac{1}{P_{A0}} \right] = \kappa t$$

$$\therefore t = \frac{RT}{\kappa} \left(\frac{1}{P_A} - \frac{1}{P_{A0}} \right) = \frac{8.314 \times 518}{2.17 \times 10^{-4}} \times \left[\frac{1}{4000} - \frac{1}{5000} \right] = 992.3 \text{ S}$$

$$(3) \ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\therefore \ln \frac{(1+81\%)k_1}{k_1} = -\frac{E_a}{8.314} \times \left[\frac{1}{518+1} - \frac{1}{518} \right]$$

$$\therefore E_a = 174.09 \text{ kJ} \cdot \text{kmol}^{-1}$$

$$b. \frac{dC_A}{dt} = k_1 C_A$$

$$\frac{dC_A}{dt} = k_1 C_A - k_2 C_A - k_3 C_A - k_4 C_A = 0 \quad \therefore C_A = \frac{2k_1 C_{A2}}{k_2 + k_3 + k_4}$$

$$\therefore \frac{dC_A}{dt} = k_5 C_A = \frac{2k_1 k_5 C_{A2}}{k_2 + k_3 + k_4}$$