

物理化学历年真题参考答案

编写说明

本资料为北航 2002—2009 年物理化学考研真题参考答案，其中 02-07 年的答案为网上购买，由王晓芳侯琴王焕芳等整理成电子版，0809 年的答案由董建江天陈贵勇等提供，由朱言言整理成电子版，最终汇总成本资料。由于时间有限，纰漏颇多，祈请指正，答案仅供参考。如发现答案错误或者对本资料有什么建议，请联系朱言言 zhuyanyanbuaa@126.com 以及时更正。祝愿大家取得好成绩。

3601 大班考研资料整理小组

2009 年 11 月 20 日

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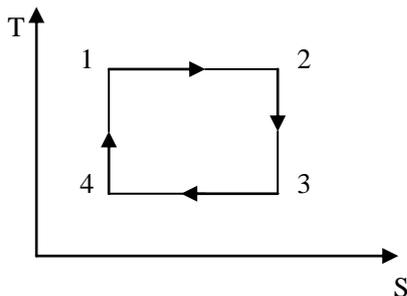
北航 2002 年硕士研究生入学考试试题答案参考

一、选择题

1.D 2.C 3.B 4.C 5.A 6.A 7.C 8.D 9.D 10.C

二、解答题

1.

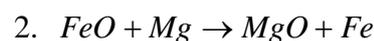


1→2 为等温可逆膨胀, 熵增过程

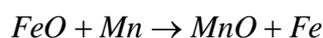
2→3 为绝热可逆膨胀, 恒熵过程

3→4 为等温可逆压缩, 熵减过程

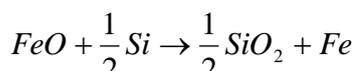
4→1 为绝热可逆压缩, 恒熵过程



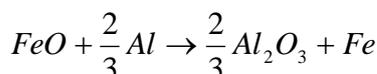
$$\Delta_r G_{m,1}^\theta = -569.57 + 244.34$$



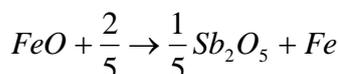
$$\Delta_r G_{m,2}^\theta = -363.20 + 244.34$$



$$\Delta_r G_{m,3}^\theta = \frac{1}{2} \times (-805.00) + 244.34$$



$$\Delta_r G_{m,4}^\theta = \frac{1}{3} \times (-1576.41) + 244.34$$



$$\Delta_r G_{m,5}^\theta = \frac{1}{5} \times (-838.90) + 244.34$$

通过比较, $\Delta_r G_{m,i}^\theta$ 最小, 因而选用 Mg 将使反应进行更为彻底, 从热力学角度考虑 Mg 最佳。

3. 使 $[Na_2B_4O_7 \cdot 10H_2O(s)]$ 不变质, 必须使 $P_{H_2O} > 912 Pa$ 使 $[Na_2B_4O_7 \cdot 10H_2O(s)]$ 多余的水分除去, 必须使 $P_{H_2O} < 2314 Pa$ 即, 使 $912 Pa < P_{H_2O} < 2314 Pa$ 由以上条件, 可选出最适合的干燥剂有 $NaBr \cdot 2H_2O(s)$ 和 $NaCl$

4. $\therefore [\sum \nu_B (\frac{\partial H_B}{\partial T})_P]_{\text{反应物}} < [\sum \nu_B (\frac{\partial H_B}{\partial T})_P]_{\text{产物}}$

$$\therefore \sum \nu_B (\frac{\partial H_B}{\partial T})_P = [\sum \nu_B (\frac{\partial H_B}{\partial T})_P]_{\text{产物}} - [\sum \nu_B (\frac{\partial H_B}{\partial T})_P]_{\text{反应物}} > 0$$

$$\therefore \sum \nu_B (\frac{\partial H_B}{\partial T})_P = \sum \nu_B C_{p,m}(B) > 0 \quad \text{即 } \Delta_r G_{p,m} > 0 \quad (\text{基尔霍夫定律})$$

$$\Delta_r H_m^\theta(T) = \Delta_r H_m^\theta(298K) + \int_{298}^T \Delta_r C_{p,m} dT$$

(1) 当 $\Delta H_m^\theta(298K) > 0$ 时, 又 $T > 298K$, $\Delta_r C_{p,m} > 0$, $\therefore \Delta_r H_m^\theta(T) > 0$

(2) 当 $\Delta H_m^\theta(298K) < 0$ 时, 随温度升高, $\Delta_r H_m^\theta(T)$ 逐渐变大, 开始时 $\Delta_r H_m^\theta(T) < 0$, 后经某一温度 $\Delta_r H_m^\theta(T) = 0$, 此后 $\Delta_r H_m^\theta(T) > 0$

三、计算题

1. 过程所做体积功 $W = -P\Delta V = -nRT = -8.314 \times 298 = -2.477kJ$

$$\Delta U = Q + W + W_r' \Rightarrow Q = \Delta U - W - W_r' = -180.3 - (-2.477) - (-144.0) = -33.823kJ$$

2. 由反应截距的单位 $dm^3 \cdot mol^{-1}$ 可判断此反应为二级反应, 且 $\frac{1}{c_{A,0}} = 2$

$$\text{其反应速率方程为 } \frac{1}{c_A} - \frac{1}{c_{A,0}} = kt$$

$$\text{当 } t = 8s, c_A = \frac{3}{4}c_{A,0} \text{ 代入得 } k = \frac{1}{12} \approx 0.0833 dm^3 \cdot mol^{-1} \cdot s^{-1}$$

3. $\Delta S_{sys} = \sum_B \nu_B S_B^\theta = 248.53 - 205.03 - 32.55 = 10.95 J \cdot mol^{-1} \cdot K^{-1}$

$$Q = \Delta_r H_m = \sum_B \nu_B H_B^\theta = -296.9 - 0.3 = -297.2 kJ \cdot mol^{-1}$$

$$\Delta S_{amb} = -\frac{Q}{T} = \frac{297200}{298} = 997.32 J \cdot mol^{-1} \cdot K^{-1}$$

$$\Delta S_{iso} = \Delta S_{sys} + \Delta S_{amb} = 10.45 + 997.32 = 1007.77 J \cdot mol^{-1} \cdot K^{-1}$$

$$\Delta_r G_m = \Delta_r H_m - T\Delta S = -297.2 - 298 \times (10.95 \times 10^{-3}) = -300.46 kJ \cdot mol^{-1}$$

$$K^\theta = \exp \frac{-\Delta_r G_m}{RT} = \exp \frac{-30046 \times 10^3}{8.314 \times 298} = \exp^{121.27} \approx 4.653 \times 10^{52}$$

四、选做题

1. $S(\text{斜方}) \rightarrow S(\text{单斜}) \quad \Delta_r S_m = 37.78 - 36.65 = 1.13 J \cdot mol^{-1} \cdot K^{-1}$

$$\begin{aligned} \text{据克拉佩龙方程 } \frac{dT}{dp} &= \frac{T\Delta_\alpha^\beta V_m}{\Delta_\alpha^\beta H_m} = \frac{\Delta_\alpha^\beta V_m}{\Delta_\alpha^\beta H_m / T} = \frac{\Delta_\alpha^\beta V_m}{\Delta_\alpha^\beta S_m} \\ &= \frac{4.5 \times 10^{-7}}{1.13} = 3.98 \times 10^{-7} K \cdot Pa^{-1} \end{aligned}$$

2. 阳: $2Cl^- = Cl_2 + 2e^- \quad -1.36V$

阴: $MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O \quad 1.23V$

电池反应: $4H^+ + 4Cl^- + MnO_2 \rightarrow Mn^{2+} + 2Cl_2 + 2H_2O$

(1) $E^\theta = 1.23 - (-1.36) = 2.59V$

$$\Delta_r G_m^\theta = -zFE = -2 \times 2.59 \times 96485 = -499.8 kJ \cdot mol^{-1} < 0$$

\therefore 可能制得氯气。

$$\begin{aligned}
 (2) E &= E^\theta - \frac{0.05916}{2} \lg \frac{a^2(\text{Cl}^-) \cdot a(\text{Mn}^{2+})}{a^4(\text{Cl}^-) \cdot a^4(\text{H}^+)} \cdot \frac{P_{\text{Cl}_2}}{P^\theta} \\
 &= E^\theta - \frac{0.05916}{2} \lg \frac{a(\text{Mn}^{2+})}{a^2(\text{Cl}^-) \cdot a^4(\text{H}^+)} \\
 &= E^\theta - \frac{0.05916}{2} \lg \frac{1}{12 \times 11^2 \times 12 \times 11^4} \\
 &= 2.59 + 0.25 = 2.84\text{V}
 \end{aligned}$$

$$\Delta_r G_m = -zFE = -2 \times 96485 \times 2.84\text{V} = -548.034\text{kJ} \cdot \text{mol}^{-1} < 0$$

∴ 可能制出氯气

3. (1) 人工降雨是用人工的方法在潮湿空气中布洒小固体微粒，增大雨滴开始凝结的曲率半径，使其饱和蒸汽压降低而易液化。

(2) 喷洒农药时，在农药中加入少量表面活性剂，加入表面活性剂可以降低农药的表面张力，增大其在植物枝叶上的吸附，增强杀虫效果。

北航 2004 年硕士研究生入学考试试题答案参考

一. 1.-3256.6KJ 2. $\frac{5}{3}$ 3. $w < 0, Q < 0, \Delta V < 0$ 4.S 5.O₂ 6. $\frac{a_{\text{B}}}{x_{\text{B}} - 1}$

7.3,4,1 8.正向 9.2.35KPa 10.<0,减小 11.4r_±²m³

12.正比, 反比 13. $\frac{1}{2}$ 14. $\frac{k_1}{k_2} = \frac{C_{\text{B},\text{e}}}{C_{\text{B},\text{e}}}$

二. 1. (1) 熵变与过程可逆与否无关，不能由可逆过程得出熵值不变。

(2) 只有在恒温恒压条件下， ΔG 才能最为系统做的非体积功，而且 G 本身是状态函数，而功是过程函数，因此二者不能等同。

(3) 只有在恒压不做非体积功时， ΔH 才能作为以热的方式与环境交换的能量，同样 H 是状态函数，而热是过程函数，因此二者不能等同。

2. $U_{\text{B}} = \left(\frac{\partial G}{\partial n_{\text{B}}}\right)_{T,P,n_c}$ ，它表示恒温恒压及其余组分不变时，在无限大的多组分体系中增加 1molB 所

引起的吉布斯自由能的变化，它表示组分 B 对体系总自由能的贡献。

任一组分的化学势在各相中相等时相平衡的条件。

反应物和生成物化学势的代数和相等是化学平衡的条件。

3. 温度一定时， $\Delta_r G_m^\ominus$ 与 K_p^\ominus 随标准状态的不同而不同。此时， $\Delta_r G_m^\ominus$ 与 K_p^\ominus 均是标准状态的量，而

标准状态一经决定， $\Delta_r G_m^\ominus$ ， K_p^\ominus 就随温度而变化。

$$4. \Delta T_f = K_f b_B = \frac{R(T_f^\ominus)^2 M_A}{\Delta_{\text{fus}} H_{m,A}^\ominus} \cdot b_B \quad \therefore \text{应选分子量大, 溶化焓小的溶剂。}$$

$$5. V^a = V_m^a \frac{bp}{1+bp} \text{-----朗格缪尔吸附等温方程}$$

低压时, $bp \ll 1$, 则吸附量与压力成正比。 $V^a = V_m^a bp$

压力大小适中时, 吸附量与平衡压力 P 成曲线关系

高压时, $bp \gg 1$, 则表明固体表面上吸附达到饱和状态, 吸附量达最大值, 此时 $V^a = V_m^a$

$$\text{三. 1. (1) } \lg k^\ominus = -\frac{2100}{T} + 4.67 \quad \therefore \frac{\ln k^\ominus}{\ln 10} = -\frac{2100}{T} + 4.67 \rightarrow \ln k^\ominus = -\frac{2100}{T} \ln 10 + 4.67 \ln 10$$

$$\frac{d \ln k^\ominus}{dT} = \frac{2100 \ln 10}{T^2} = \frac{\Delta_r H_m^\ominus}{RT^2} \rightarrow \Delta_r H_m^\ominus = 2100 \ln 10 \times R = 40.202 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m^\ominus = \Delta_f H_m^\ominus(\text{酯}) - 2\Delta_f H_m^\ominus(\text{醇}) \quad \therefore \Delta_f H_m^\ominus(\text{酯}) = \Delta_r H_m^\ominus + 2\Delta_f H_m^\ominus(\text{醇})$$

$$= 40.202 - 235.24 \times 2 = -430.478 \text{ kJ} \cdot \text{mol}^{-1}$$

$$(2) T=473 \text{ K}, k^\ominus = 10^{-\frac{2100}{473} + 4.67} = 1.7$$

$$\therefore \Delta_r G_m^\ominus = -RT \ln k^\ominus = -8.314 \times 473 \ln 1.7 = -2.085 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\therefore \Delta_r S_m^\ominus = \frac{\Delta_r H_m^\ominus - \Delta_r G_m^\ominus}{T} = \frac{40.202 + 2.085}{473} \times 10^3 = 89.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

2.(1) 假设冰全部融化, 末温为 t



$$m_1(l) = 1 \text{ kg} \quad m_1(s) = 0.5 \text{ kg} \quad \rightarrow Q = 0, dP = 0 \rightarrow m_2(l) = 1.5 \text{ kg}$$

$$t_1(l) = 25^\circ\text{C} \quad t_2(s) = -10^\circ\text{C} \qquad t$$

$$\Delta H = m_1(l) C_p(l) \{t - t_1(l)\} + m_1(s) C_p(s) \{0^\circ\text{C} - t_2(s)\} + m_1(s) \Delta_{\text{fus}} H + m_1(s) C_p(l) (t - 0^\circ\text{C})$$

=0

$$\rightarrow t = \frac{m_1(l) C_p(l) t_1(l) + m_1(s) C_p(s) t_2(s) - m_1(s) \Delta_{\text{fus}} H}{\{m_1(s) + m_1(l)\} \times C_p(l)}$$

$$= \frac{1000 \times 4.184 \times 25 + 500 \times 2 \times (-10) - 0.5 \times 10^3 \times 6.003 \times 10^3 \times 18}{(1000 + 500) \times 4.184}$$

$$= -11.5^\circ\text{C}$$

水至融化，而 $t < 0^\circ\text{C}$ ，假设不合理

设有 $x\text{kg}$ 冰融化，则冰水末态温度为 0°C

$$\therefore m_2(\text{l}) = x + 1, m_2(\text{s}) = 0.5 - x$$

$$\Delta H = m_1(\text{l})C_p(\text{l})\{0^\circ\text{C} - t_1(\text{l})\} + m_1(\text{s})C_p(\text{s})\{0^\circ\text{C} - t_1(\text{s})\} + x\Delta_{\text{fus}}H \times 18 = 0$$

$$\rightarrow x = \frac{m_1(\text{l})C_p(\text{l}) \times 25 - m_1(\text{s})C_p(\text{s}) \times 10}{\Delta_{\text{fus}}H \times 18} = \frac{1000 \times 4.184 \times 25 - 500 \times 2 \times 10}{6.003 \times 10^3 \times 18}$$

$$= 0.28\text{kg}$$

$$\therefore m_2(\text{l}) = 0.28 + 1 = 1.28\text{kg} \quad m_2(\text{s}) = 0.5 - 0.28 = 0.22\text{kg}$$

$$(2)\Delta S_1 = m_1(\text{l})C_p(\text{l})\ln\frac{273}{298} + C_p(\text{s})m_1(\text{s})\ln\frac{273}{263}$$

$$= 1000 \times 4.184 \ln\frac{273}{298} + 500 \times 2 \ln\frac{273}{263} = -329.29\text{J} \cdot \text{K}^{-1}$$

$$\Delta S_2 = \frac{\Delta_{\text{fus}}H}{T} = \frac{280 \times 6.003 \times 10^3 \times 18}{273} = 342.05\text{J} \cdot \text{K}^{-1}$$

$$\therefore \Delta S = \Delta S_1 + \Delta S_2 = 12.76\text{J} \cdot \text{K}^{-1}$$

3.(1)根据速率常数形式可知

$$A = 5.4 \times 10^{11}\text{s}^{-1} \quad E_a = 122.59\text{kJ} \cdot \text{mol}^{-1}$$

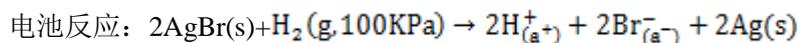
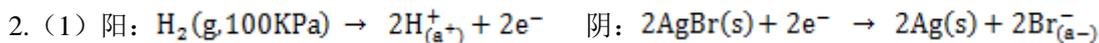
$$(2)T = 150 + 273 = 423\text{K}$$

$$k = 5.4 \times 10^{11} \exp\left(-\frac{122.59 \times 10^3}{8.314 \times 423}\right) = 3.92 \times 10^{-4}\text{s}^{-1}$$

$$P_{A,0} = 100\text{KPa} \quad P_A = 100 - 40 = 60\text{KPa}$$

$$\ln\frac{C_{A,0}}{C_A} = \ln\frac{P_{A,0}}{P_A} = \ln\frac{100}{60} = kt \rightarrow t = \frac{1}{k} \ln\frac{100}{60} = \frac{1}{3.92 \times 10^{-4}} \ln\frac{100}{60} = 130\text{s}$$

四. 1. 见试卷



$$E = \varphi^\ominus(\text{Br}^- \setminus \text{AgBr} \setminus \text{Ag}) - \varphi^\ominus(\text{Ag}^+ \setminus \text{Ag}) - 0.05916 \lg \frac{a_{\text{Br}^-} a_{\text{Ag}^+}}{1} = 0$$

$$\rightarrow \varphi^\ominus(\text{Br}^- \setminus \text{AgBr} \setminus \text{Ag}) = \varphi^\ominus(\text{Ag}^+ \setminus \text{Ag}) + 0.05916 \lg k_{\text{sp}}^\ominus$$

$$= 0.7996 + 0.05916 \lg 4.79 \times 10^{-13} = 0.071 \text{V}$$

补充: 二.6. 用伏特表测的是端电压, 与电动势的大小不相等, 当把伏特计与电池接通后, 必须有适量的电流通过才能使伏特计显示, 这样发生化学反应溶液的浓度不断改变, 另外电池本身有内阻, 因此不可直接用伏特计测量, 使用对消法可以使电动势测定在无电流的情况下进行, 各物质的活度保持不变, 使外阻很大而内阻可以忽略不计, 这时 $U \approx E$

北航 2005 年硕士研究生入学考试试题答案参考

一、填空题

1. 500R

$$2. C_p - C_v = nTV \partial v^2 / R_T \quad \text{或} \quad C_p - C_v = \left[\left(\frac{\partial v}{\partial v} \right)_T + P \right] \left(\frac{\partial v}{\partial T} \right)_P$$

3. W、C

$$4. T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

5. 负

$$6. < 0 \quad > 0 \quad > 0$$

7. < > =

$$8. M_A < M_B$$

9. < 0 减小

10. 吸、增、 ∂ -HgS11. $a_1 > a_2$ Pb(Hg)(a_1) — Pb(Hg)(a_2)

12. 52.89 KJ/mol ~ 105.79 KJ/mol

二、简答题

1. 不能。 $\Delta_r G_m = 0$ 表明在反应条件下该反应达到了平衡, 而 $\Delta_r G_m^\ominus(T)$ 是反应物和生成物各自处于标准态时的反应的摩尔吉布斯函数变。 $\Delta_r G_m^\ominus(T) = \sum_B \nu_B \mu_B^\ominus$, $\Delta_r G_m^\ominus(T)$ 仅与反应物和生成物标准

态时的化学势有关。 $\Delta_r G_m = 0$ $\Delta_r G_m^\ominus(T)$ 不一定为零, 则由公式 $K^\ominus(T) = \exp\left(-\frac{\Delta_r G_m^\ominus(T)}{RT}\right)$ 可知 K^\ominus

(T) 不一定为 1。

2. (1) 理想液态混合物任一组分的化学势

$$\begin{aligned}\mu_B(l, T, p) &= \mu_B(g) = \mu_B^\theta(g) + RT \ln \frac{P_B^* x_B}{p^\theta} \\ &= \mu_B^\theta(g) + RT \ln \frac{P_B^*}{p^\theta} + RT \ln x_B = \mu_B^\theta(l, T, p) + RT \ln x_B\end{aligned}$$

$$\therefore \mu_B^\theta(l, T, p) = \mu_B^\theta(g) + RT \ln \frac{P_B^*}{p^\theta}$$

(2) 理想稀溶液中溶剂的化学势

$$\mu_B(l, T, p) = \mu_B(g) = \mu_B^\theta(g) + RT \ln \frac{p_B}{p^\theta} = \mu_B^\theta(g) + RT \ln \frac{p_B^* x_B}{p^\theta}$$

$$\text{同理 } \mu_B^\theta(l, T, p) = \mu_B^\theta(g) + RT \ln \frac{p_B^*}{p^\theta}$$

(3) 理想稀溶液中溶质的化学势 (溶质具有挥发性)

$$\mu_B(l, T, p) = \mu_B(g) = \mu_B^\theta(g) + RT \ln \frac{k_{c,B} \cdot C_B}{p^\theta} = \mu_B^\theta(g) + RT \ln \left(\frac{k_{c,B} \cdot C_B^\theta \cdot C_B / C_B^\theta}{p^\theta} \right)$$

$$= \mu_B^\theta(g) + RT \ln \frac{k_{c,B} \cdot C_B^\theta}{p^\theta} + RT \ln (C_B / C_B^\theta) = \mu_B^\theta(l, T, p) + RT \ln (C_B / C_B^\theta)$$

$$\therefore \mu_B^\theta(l, T, p) = \mu_B^\theta(g) + RT \ln \frac{k_{c,B} \cdot C_B^\theta}{p^\theta}$$

$$3. (1) \text{ 克拉佩龙方程: } \frac{dp}{dT} = \frac{\Delta_{fus} H_m}{T \Delta_s V_m}$$

若压力改变后, 熔点改变不大时, 克拉佩龙方程可变为 $\Delta T = T_1 \frac{\Delta_{fus} V_m}{\Delta_{fus} H_m}$ 。

熔化过程 $\Delta_{fus} H_m > 0$, 所以, 当熔化后体积增大, 即 $\Delta_{fus} V_m > 0$, 增大压力, 熔点升高; 当熔化后体积缩小, 即 $\Delta_{fus} V_m < 0$, 增大压力, 熔点降低。

$$(2) \text{ 克-克方程: } \frac{d \ln p}{dT} = \frac{\Delta_{vap} H_m}{RT^2} \text{ 或 } \frac{d \ln p}{dT} = \frac{\Delta_{sub} H_m}{RT^2}$$

$$\therefore \Delta_{vap} H_m > 0, \Delta_{sub} H_m > 0$$

$$\therefore \frac{d \ln p}{dT} > 0$$

所以凝聚态饱和蒸汽压随温度升高而升高。

1. 该电池不能构成可逆电池。
因为 此电极反应为

阳: $\text{H}_2(\text{P}_1) \rightarrow 2\text{H}^+(\text{m}_1) + 2\text{e}^-$

阴: $2\text{H}^+(\text{m}_2) + 2\text{e}^- \rightarrow \text{H}_2(\text{p}_2)$

电池反应: $\text{H}_2(\text{P}_1) + 2\text{H}^+(\text{m}_2) \rightarrow 2\text{H}^+(\text{m}_1) + \text{H}_2(\text{p}_2)$

参加反应的离子只有阳离子, 而此种情况对阳离子不可逆, 因而构不成可逆电池。

可调整如下: $\text{Pt}|\text{H}_2(\text{p}_1)|\text{HCl}(\text{m})|\text{H}_2(\text{p}_2)|\text{Pt}$ 或 $\text{Pt}, \text{H}_2(\text{p})|\text{HCl}(\text{m}_1)||\text{H}_2(\text{m}_2)|\text{H}_2(\text{p}), \text{Pt}$

2. 处在管左端的液体受热而温度升高, 使液体的表面张力变小, 同时毛细管本身被加热而发生膨胀而使弯曲液面曲率半径稍微变大, 两者均导致附加压力 ΔP 减小, 因而原有平衡被破坏, 再有, 附加压力的方向指向气体, 当左端附加压力减小, 对水柱而言, 便是水柱左端的压力大而右端压力小, 于是水柱向右移动。

3. E_a 越大表示越不易活化

由阿伦尼乌斯方程 $\frac{d \ln p}{dT} = \frac{E_a}{RT^2}$ 知, E_a 越大, $\frac{d \ln p}{dT}$ 越大, 所以反应受温度的影响也越大。

三、计算题

1. (1) $2\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) + \text{C}(\text{石墨}) \rightarrow \text{CH}_3\text{OH}(\text{l})$

$$\Delta_r H_m^\theta = \sum_B \nu_B \Delta_f H_m^\theta = -238.7 \text{ KJ/mol}$$

$$\Delta_r S_m^\theta = \sum_B \nu_B S_m^\theta = -2 \times 130.57 - \frac{1}{2} \times 205.03 - 5.74 + 127.0 = -242.395 \text{ J/mol}$$

$$\therefore \Delta_f G_m^\theta(\text{CH}_3\text{OH}, \text{l}) = \Delta_r G_m^\theta = \Delta_r H_m^\theta - T \Delta_r S_m^\theta$$

$$= -238.7 - 298.15 \times (-242.395) \times 10^{-3} = -166.43 \text{ KJ} \cdot \text{mol}^{-1}$$

- (2) $\text{CH}_3\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{g})$

$$\Delta_{\text{vap}} H_m^\theta = \Delta_f H_m^\theta(\text{CH}_3\text{OH}, \text{g}) - \Delta_f H_m^\theta(\text{CH}_3\text{OH}, \text{l})$$

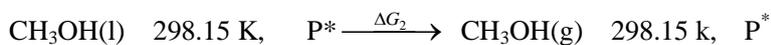
$$= -200.7 - (-238.7) = 38 \text{ KJ} \cdot \text{mol}^{-1}$$

- (3) 设计可逆过程



$\downarrow \Delta G_1$

$\uparrow \Delta G_3$



$$\Delta_{\text{vap}}H_m^\theta = 38\text{KJ} \cdot \text{mol}^{-1}$$

$$\Delta_rS_m^\theta = 239.7 - 127.0 = 112.7\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta G = \Delta_{\text{vap}}H_M^\theta - T\Delta S_M^\theta = 38 - 298.15 \times 112.7 \times 10^{-3} = 4.4\text{KJ} \cdot \text{mol}^{-1}$$

$$\Delta G_1 = 0$$

$$\Delta G_2 = 0$$

$$\Delta G_3 = -T\Delta S_3 = -RT \ln \frac{p^*}{p^\theta} = RT \ln \frac{p^\theta}{p^*}$$

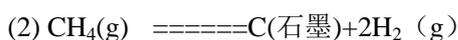
$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 = RT \ln \frac{p^\theta}{p^*}$$

$$p^* = p^\theta \exp\left(-\frac{\Delta G}{RT}\right) = 100 \exp\left(-\frac{4.4 \times 10^3}{8.314 \times 298.15}\right) = 16.95\text{KP}$$

2. (1) $T = 500 + 273.15 = 773.15\text{K}$

$$\Delta_rG_m^\theta = 90165 - 109.56 \times 773.15 = 5458.686\text{KJ} \cdot \text{mol}^{-1}$$

$$K^\theta = \exp\left(-\frac{\Delta_rG_m^\theta}{RT}\right) = \exp\left(-\frac{5458.686}{8.314 \times 773.15}\right) = 0.428$$



| | | | | |
|----|------------|-----------|-----------|--------------|
| 开始 | 1 | 0 | 0 | |
| 平衡 | $1-\alpha$ | 2α | 2α | 总 $1+\alpha$ |

$$\therefore K^\theta = \frac{\left\{ \frac{2\alpha}{1+\alpha} \cdot p_{\text{总}} / p^\theta \right\}^2}{\left\{ \frac{1-\alpha}{1+\alpha} \cdot p_{\text{总}} / p^\theta \right\}} = \frac{4\alpha^2}{1-\alpha^2} p_{\text{总}} / p^\theta$$

当 $p_{\text{总}} = p^\theta$ 时 $\frac{4\alpha^2}{1-\alpha^2} = 0.428 \Rightarrow \alpha = 0.31$

当 $p_{\text{总}} = 1/2 p^\theta$ 时 $\frac{4\alpha^2}{1-\alpha^2} \times 0.5 = 0.428 \Rightarrow \alpha = 0.42$

$$\frac{d[\text{CH}_4]}{dt} = k_2[\text{CH}_3\bullet][\text{CH}_3\text{CHO}]$$

3. (1) $\frac{d[\text{CH}_3\bullet]}{dt} = k_1[\text{CH}_3\text{CHO}] - k_2[\text{CH}_3\bullet][\text{CH}_3\text{CHO}] + k_3[\text{CH}_3\text{CO}\bullet] - k_4[\text{CH}_3\bullet]^2 = 0$

$$\frac{d[\text{CH}_3\text{CO}\bullet]}{dt} = k_2[\text{CH}_3\bullet][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}\bullet] = 0$$

$$\text{上两式相加得到 } k_1[\text{CH}_3\text{CHO}] = k_4[\text{CH}_3\bullet]^2 \Rightarrow [\text{CH}_3\bullet] = \left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} [\text{CH}_3\text{CHO}]^{\frac{1}{2}}$$

$$\therefore \frac{d[\text{CH}_4]}{dt} = k_2 \left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} [\text{CH}_3\text{CHO}]^{\frac{3}{2}} = k[\text{CH}_3\text{CHO}]^{\frac{1}{2}}$$

对上式两边取对数并求导

$$\frac{d \ln k}{dT} = \frac{d \ln k_2}{dT} + \frac{1}{2} \frac{d \ln k_1}{dT} - \frac{1}{2} \frac{d \ln k_4}{dT}$$

$$\therefore \frac{E_a}{RT^2} = \frac{E_{a,2}}{RT^2} + \frac{1}{2} \frac{E_{a,1}}{RT^2} - \frac{1}{2} \frac{E_{a,4}}{RT^2}$$

$$\therefore E_a = E_{a,2} + \frac{1}{2}(E_{a,1} - E_{a,4})$$

四、选做题

1. (1) 利用克拉佩龙方程

$$\frac{dT}{dp} = \frac{T \Delta_{fus} V_m}{\Delta_{fus} H_m} = \frac{T \left(\frac{1}{p_V} - \frac{1}{p_g} \right)}{\Delta_{fus} H_m} = \frac{273.15(1/0.9998 - 1/0.9168) \times 10^{-6}}{333.5} = -7.42 \times 10^{-8} \text{ k} \cdot \text{Pa}^{-1}$$

$$\text{由 } \ln \frac{T_2}{T_1} = \frac{\Delta V}{\Delta H} (P_2 - P_1)$$

$$(2) \ln \frac{272.8}{273.15} = \frac{\left(\frac{1}{0.9998} - \frac{1}{0.9618} \right) \times 10^{-6}}{333.5} (P_2 - 101315)$$

$$\Rightarrow P_2 = 4803625 \text{ Pa}$$

2. (1) 阳: $2\text{Sb} + 3\text{H}_2\text{O} \rightarrow \text{Sb}_2\text{O}_3 + 6\text{H}^+(a_{\text{H}^+}) + 6\text{e}^-$

阴: $3\text{Hg}_2\text{Cl}_2 + 6\text{e}^- \rightarrow 6\text{Hg} + 6\text{Cl}^-$

电池反应: $2\text{Sb} + 3\text{H}_2\text{O} + 3\text{Hg}_2\text{Cl}_2 \rightarrow \text{Sb}_2\text{O}_3 + 6\text{Hg} + 6\text{H}^+ + 6\text{Cl}^-$

$$E = E^\theta - \frac{0.05916}{6} \lg \{a_{\text{H}^+}\}^6 \cdot \{a_{\text{Cl}^-}\}^6 = E^\theta - 0.05916 \lg a_{\text{H}^+} \cdot a_{\text{Cl}^-}$$

$$E' = E^\theta - 0.05916 \lg a_{\text{H}^+}' \cdot a_{\text{Cl}^-}'$$

$$E' - E = -0.05916 \lg \frac{a_{\text{H}^+}'}{a_{\text{H}^+}} = 0.05916 (\text{PH}' - \text{PH})$$

$$\therefore \text{PH}' = \text{PH} + \frac{E' - E}{0.05916} = 5.96$$

$$\therefore a_{\text{H}^+} = 1.098 \times 10^{-6}$$

北航 2006 年硕士研究生入学考试试题答案参考

一、选择题

1.A 2.B 3.A 4.D 5.D 6.C 7.D 8.D 9.B 10.A 11.B 12.D
13.B 14.A 15.C 16.C 17.C 18.A 19.B 20.A

二、解答题

1. CS_2 液态可在常温下稳定存在而不分解, $\Delta_r G_m^\theta$ 只反应可能性, 而不能说明现实性

$\text{CS}_2 \text{液} \rightarrow \text{C} + 2\text{S}$, $\Delta_r G_m^\theta = -\Delta_f G_m^\theta < 0$, 只能说明 CS_2 有分解的可能性, 而实际上, CS_2 分解的速率极小, 可以忽略。

2. 绝热不可逆压缩时, $\Delta_{\text{iso}} S_1 = \Delta S_{\text{sys}} + \Delta S_{\text{amb}} = \Delta S_1 > 0$

绝热不可逆膨胀时, $\Delta_{\text{iso}} S_2 = \Delta S_{\text{sys}} + \Delta S_{\text{amb}} = \Delta S_2 > 0$

因为熵是一直增大的, 所以不可能以绝热不可逆过程膨胀回到始态。

3. 设在 P 压力下的熔点为 T_{fus} 对任一金属 A , $A(\text{s}) \rightarrow A(\text{l})$ 在熔点发生相变的吉布斯函数

$$\Delta G(T_{\text{fus}}) = 0。$$

$$\Delta G = G(\text{l}) - G(\text{s}) \quad \Delta S = S(\text{l}) - S(\text{s})$$

$$\text{因为} \left(\frac{\partial G}{\partial T} \right)_p = -S, \text{ 所以} \left(\frac{\partial \Delta G}{\partial T} \right)_p = -\Delta S,$$

$$\text{即} \Delta G(T) = \Delta G(T_{\text{fus}}) + \int_{T_{\text{fus}}}^T -\Delta S dT = -\int_{T_{\text{fus}}}^T \Delta S dT$$

当 $T > T_{\text{fus}}$ 时, $\Delta G(T) < 0$, 反应 $A(\text{s}) \rightarrow A(\text{l})$ 自发, 即在较高温度时, 液态稳定

当 $T < T_{\text{fus}}$ 时, $\Delta G(T) > 0$, 反应 $A(\text{l}) \rightarrow A(\text{s})$ 自发, 即在较低温度时, 固态稳定

4. 液面不会上升而会下降

$$\Delta P = \frac{2\delta}{r} = \frac{2\delta \cos \theta}{R} = \rho g h \Rightarrow h = \frac{2\delta \cos \theta}{\rho g R}$$

对上升部分加热时, δ 下降, 由于热膨胀性玻璃管 R 会稍变大
综合两种因素, h 会变小, 即液面会下降

5.

$$\frac{d \ln R}{dT} = \frac{E_a}{RT^2} \Rightarrow \ln R = -\frac{E_a}{RT} + \ln A$$

$$\therefore \ln R_+ = -\frac{E_{a,+}}{RT} + \ln A_+ \quad \text{且} \quad \ln R_- = -\frac{E_{a,-}}{RT} + \ln A_-$$

$$\because E_{a,+} > E_{a,-} \quad \text{而又有} \quad A_+ / A_- > 1, \therefore \ln A_+ > \ln A_-$$

高温时适宜正反应，低温时适宜逆反应

三、计算题

$$1. (1) \quad C=S-R-R'=4-1-2=1 \quad f=C-P+1=1-2+2=1$$

(2)

$$\therefore \Delta_r H_m^\theta = 167.87 \text{ kJ} \cdot \text{mol}^{-1} \quad \text{且} \quad \Delta_r S_m^\theta = 474.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\therefore \Delta_r G_m^\theta = \Delta_r H_m^\theta - T \Delta_r S_m^\theta = 167.87 - 298.15 \times 474.0 \times 10^{-3} = 26.5469 \text{ kJ} \cdot \text{mol}^{-1}$$

$$K_p^\theta = \exp\left(-\frac{\Delta_r G_m^\theta}{RT}\right) = \exp\left(-\frac{26.5469 \times 10^3}{8.314 \times 298.15}\right) = 2.233 \times 10^{-5}$$

$$K_p^\theta = \{P_{\text{NH}_3} / P^\theta\}^3 = 2.233 \times 10^{-5} \Rightarrow P_{\text{NH}_3} = 2.816 \text{ KPa}$$

$$\therefore P_{\text{总}} = 3P_{\text{NH}_3} = 8.448 \text{ KPa}$$

(3) 温度升高时， $\Delta_r G_m^\theta$ 降低， K_p^θ 变大，平衡总压变大

(4) 无关， $f=C-P+1=1-2+1=0$

平衡时总压只随温度变化，改变容器体积并不影响总压

2. (1) 甲苯(l) → 甲苯(g)

$$Q = \Delta_{\text{vap}} H_m = 361.9 \text{ J} \cdot \text{g}^{-1} \times 92.16 \text{ g} \cdot \text{mol}^{-1} = 33.35 \text{ kJ} \cdot \text{mol}^{-1}$$

$$w = -P\Delta V = -n(g)RT = -1 \times 8.314 \times 383 = -3.184 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H = 33.35 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G = 0$$

$$\Delta S = \frac{\Delta H}{T} = \frac{33.35 \times 10^3}{383} = 87.076 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta S_{\text{amb}} = \frac{Q}{T} = -87.076 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

(2) 由于 H、G、S 为状态函数，体积始末态相同

$$\therefore \Delta H = 33.35 \text{ kJ} \cdot \text{mol}^{-1}, \quad \Delta G = 0, \quad \Delta S = 87.076 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

在真空箱中汽化， $w=0$

$$\Delta U = \Delta H - \Delta nRT = \Delta H - n_g RT = 33.35 - 3.184 = 30.166 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\therefore Q = \Delta U = 30.166 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S_{amb} = -\frac{Q}{T} = \frac{-30.166 \times 10^3}{383} = -78.76 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta S_{iso} = \Delta S + \Delta S_{amb} = 87.076 - 78.76 = 8.316 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta A = \Delta G - \Delta(PV) = -3.184 \text{ kJ} \cdot \text{mol}^{-1}$$

可用 ΔA 、 ΔS_{iso} 来判断其自发性,

由于恒容, $\Delta A < 0$, 上述过程自发; 由于为隔离体系 $\Delta S_{iso} > 0$, 上述过程自发。

| | | | | |
|-----|-----------|---|--------------------|----------------------------------|
| 3. | A(g) | → | 2B(g) | |
| t=0 | $P_{A,0}$ | | 0 | |
| t=t | P_A | | $2(P_{A,0} - P_A)$ | $P_{总} = P_A + 2(P_{A,0} - P_A)$ |
| t=∞ | 0 | | $2P_{A,0}$ | $2P_{A,0} = P_{∞}$ |

$$\therefore T = 553 \text{ K} \text{ 时, } P_{A,0} = 2.004 \text{ kPa}, t = 454 \text{ s} \text{ 时, } P_A = 2P_{A,0} - P = 4.008 - 2.476 = 1.532 \text{ kPa}$$

$$\ln \frac{P_{A,0}}{P_A} = k_t \Rightarrow k(553 \text{ K}) = \frac{1}{454} \ln \frac{2.004}{1.532} = 5.92 \times 10^{-4} \text{ s}^{-1}$$

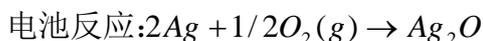
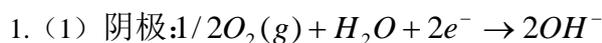
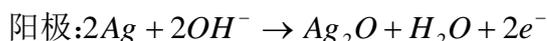
$$\therefore T = 553 \text{ K} \text{ 时的半衰期为 } t_{1/2} = \frac{\ln 2}{k(553 \text{ K})} = 1171.72 \text{ s}$$

$$T = 578 \text{ K} \text{ 时, } P_{A,0} = 1.777 \text{ kPa}, t = 320 \text{ s} \text{ 时, } P_A = 3.554 - 2.838 = 0.716 \text{ kPa}$$

$$\ln \frac{P_{A,0}}{P_A} = kt \Rightarrow k(578 \text{ K}) = \frac{1}{320} \ln \frac{1.777}{0.716} = 2.84 \times 10^{-3} \text{ s}^{-1}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \text{ 代入数据 } \ln \frac{2.84 \times 10^{-3}}{5.92 \times 10^{-4}} = \frac{E_a}{R} \left(\frac{1}{553} - \frac{1}{578} \right) \Rightarrow E_a = 166.680 \text{ kJ} \cdot \text{mol}^{-1}$$

四、选做题



$$(2) E^\theta = \varphi_{\text{O}_2/\text{OH}^-}^\theta - \varphi_{\text{Ag}_2\text{O}/\text{Ag}/\text{OH}^-}^\theta = 0.401 - 0.344 = 0.057 \text{ V}$$

$$\Delta_r G_m^\theta = -zFE^\theta = -2 \times 96485 \times 0.057 = -10.999 \text{ kJ} \cdot \text{mol}^{-1}$$

$$K_p^\theta = \exp\left(-\frac{\Delta_r G_m^\theta}{RT}\right) = 84.55, P_{\text{O}_2} = 0.21 P^\theta$$

$$\therefore J_p = 1/\left\{\frac{P_{\text{O}_2}}{P^\theta}\right\}^{1/2} = \frac{1}{\{0.21\}^{1/2}} = 2.182, J_p < K_p^\theta, \therefore \text{能被 } \text{O}_2 \text{ 氧化}$$

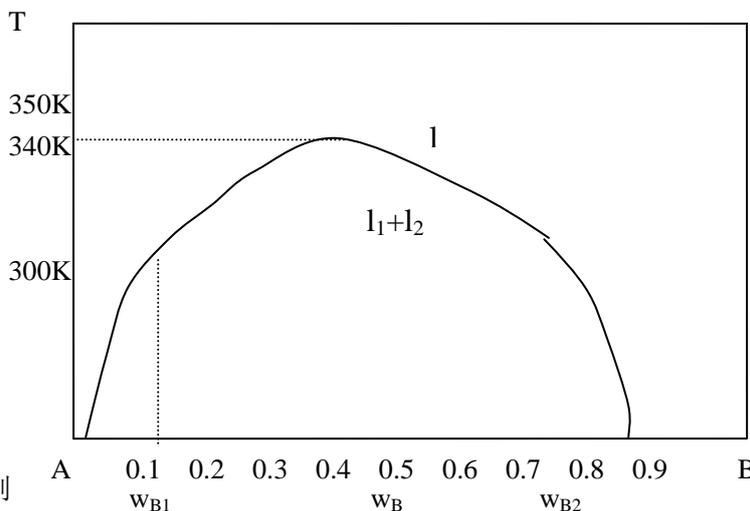


$$\Delta_r H_m^\theta = \Delta_f H_m^\theta(\text{Ag}_2\text{O}) = -31.25 \text{kJ} \cdot \text{mol}^{-1}, \quad \Delta_r G_m^\theta = -10.999 \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m^\theta = \frac{\Delta_r H_m^\theta - \Delta_r G_m^\theta}{T} = \frac{-31.05 + 10.999}{298.15} \times 10^{-3} = -67.25 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\because \Delta_r G_m^\theta(T) = 0 \Rightarrow T = \frac{\Delta_r H_m^\theta}{\Delta_r S_m^\theta} = \frac{-31.05 \times 10^{-3}}{-67.25} = 461.7 \text{K}$$

2.(1)如图所示



(2) 根据杠杆规则

$$\frac{m_1}{m} = \frac{w_{B2} - w_B}{w_{B2} - w_{B1}}$$

$$\text{即 } m_1 = \frac{w_{B2} - w_B}{w_{B2} - w_{B1}} \cdot m = \frac{0.699 - 0.6}{0.699 - 0.0875} \times 320 = 51.8 \text{g}$$

$$m_2 = 320 - 51.8 = 268.2 \text{g}$$

$$w_B = \frac{320 \times 0.6}{320 + 100} = 0.457$$

$$(3) m_{(1)} = \frac{w_{B(2)} - w_B}{w_{B(2)} - w_{B(1)}} \cdot m = \frac{0.699 - 0.457}{0.699 - 0.0875} \times 420 = 166.2 \text{g}$$

$$m_{(2)} = 420 - 166.2 = 253.8 \text{g}$$

北航 2007 年硕士研究生入学考试试题答案参考

一、选择题

1D 2B 3D 4A 5A 6C 7A 8B 9C 10C 11A 12C 13B
14D 15B 16D 17D 18B 19C 20A

二、解答题

1. 这种说法不正确。在刚性容器中 $W=0$, 但 $\Delta(PV)$ 中的 P 是指系统的内力, 而反抗恒外压对外做

功过程 $W = -P\Delta V$ 中的 P 指的是外压，两者不能等同。因此不能认为 $\Delta(PV) = P\Delta V$ ，因而 $\Delta H \neq \Delta V$ 。

2. 由 clapeyron 方程 $\frac{dT}{dP} = \frac{T\Delta V}{\Delta H}$ 可知，熔化过程的 ΔH 总是正值，但 ΔV 因物质而异，多数金属熔化过

程体积增大， $\Delta V > 0$ ，这时物质的凝固点随外压增大而升高，而铋熔化过程体积缩小， $\Delta V < 0$ ，因而熔点随外压增大而下降。

3. 存在。例如理想气体恒容降压过程，此过程温度降低，但 $\Delta S > 0$ 。

4. 空气中水以微小蒸汽颗粒状存在，当遇到干燥纸张时，由于浓差作用，水蒸气扩散在纸张表面，因而颗粒半径增大，曾大到一定程度时， $P_0 > P_r$ ，即水蒸气的蒸汽压大于饱和蒸汽压而凝结在纸张表面，使纸张变温。

5. 说法不对。两公式中 $U_B^0(V)$ 大小意义不同。前者 $U_{x,B}^0$ 为 $x_B=0$ ，即纯 B (v) 且符合亨利定律假象

状态下的 U_B ；后者， $U_{C,B}^0$ 为 $C_B = C^0 = 1 \text{ mol} \cdot \text{dm}^3$ 且符合亨利定律假象状态下的 U_B 。因此不能说由

于 $x_B \neq C_B$ 导致 $U_B(V)$ 不同，事实上，两式 $U_B(V)$ 相同。

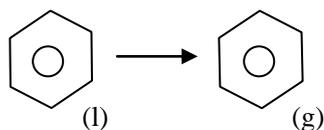
6. 质量作用定律只适用于基元反应，对于基元反应，只有分解为若干个基元反应时，才能对每个基

元反应逐个运用质量作用定律， $V_A = kC_A^{\alpha}C_B^{\beta}$ 。因此非基元反应可有零、一、二、三级及 $\frac{1}{2}$ ， $\frac{3}{2}$ 级反

应塔，而反应级数、分级数必须通过实验测定。例如 $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ 速率方程为

$$d[\text{HCl}]/dt = k[\text{H}_2][\text{Cl}_2]^{\frac{1}{2}}; \quad \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \text{ 速率方程为 } d[\text{HBr}]/dt = \frac{k[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{1+k'[\text{HBr}][\text{Br}_2]}$$

三、1.



$$\Delta S_m^\ominus(25^\circ\text{C}) = \Delta S_{(g)}^\ominus - \Delta S_{(l)}^\ominus = 269.31 - 172.35 = 96.96 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta r S_m^\ominus(80.1^\circ\text{C}) = \Delta r S_m^\ominus(25^\circ\text{C}) + \int_{298.15}^{371.25} \frac{\Delta r C_{p,m}^\ominus}{T} dT = 96.96 + (81.67 - 135.77) \ln \frac{371.25}{298.15}$$

$$= 87.79 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta r H_m(80.1^\circ\text{C}) = T \Delta r S_m = (80.1 + 273.15) \times 87.79 = 31 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta r G_m^\ominus = 0$$

$$2. \Delta_r H_m^\ominus = \Delta_r H_m(80.1^\circ\text{C}) + \int_{271.25}^{298.15} \Delta_r C_{p,m}^\ominus dT = 31 + (81.67 - 135.77)(80.1 - 25)$$

$$= 28 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\ominus = \Delta_r H_m^\ominus - T\Delta_r S_m^\ominus = 28 - 298.15 \times 96.96 \times 10^{-3} = -0.9 \text{ kJ} \cdot \text{mol}^{-1}$$

四、1. 半衰期与压力成正比可判断为二级反应

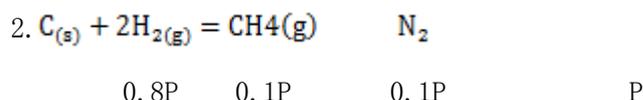
$$2. C_{A,0,1} = \frac{P_1}{RT_1} = \frac{156.787 \times 10^3}{8.314 \times 967} = 19.5 \text{ mol} \cdot \text{L}^{-1} \quad C_{A,0,2} = \frac{P_2}{RT_2} = \frac{47.996 \times 10^3}{8.314 \times 1030} = 5.6 \text{ mol} \cdot \text{L}^{-1}$$

$$k_1 = \frac{1}{kC_{A,0}} = 1.35 \times 10^{-4} \text{ mol}^{-1} \cdot \text{L} \cdot \text{S}^{-1} \quad k_2 = \frac{1}{kC_{A,0}} = 8.42 \times 10^{-4} \text{ mol}^{-1} \cdot \text{L} \cdot \text{S}^{-1}$$

$$\ln \frac{k_3}{k_2} = \frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_3} \right) \rightarrow k_3 = 7.74 \times 10^{-4} \text{ mol}^{-1} \cdot \text{L} \cdot \text{S}^{-1}$$

$$\frac{1}{C_A} - \frac{1}{C_{A,0}} = kt \quad \text{即} \quad \frac{3}{12.19} = 7.74 \times 10^{-4} t \rightarrow t \approx 318 \text{ s}$$

$$五、1. \Delta_r G_m^\ominus = \Delta_f G_{\text{CH}_4}^\ominus = 19.39 \text{ kJ} \cdot \text{mol}^{-1} \quad \rightarrow K^\ominus = e^{-\frac{\Delta_r G_m^\ominus}{RT}} = e^{-\frac{19397}{8.314 \times 1000}} = 0.1$$



$$J^\ominus = \frac{0.1P}{P^\ominus} \bigg/ \left(\frac{0.8P}{P^\ominus} \right)^2 = \frac{0.1P^\ominus}{0.8P} \quad \text{令} J^\ominus = K^\ominus$$

去 P, $P^\ominus = 0.8^2 P \rightarrow P = 160 \text{ kPa}$, 即 P = 160 kPa 时达到平衡

P < 160 kPa 时反应逆向进行, P > 160 kPa 时反应正向进行

要形成甲烷需加 160 kPa 以上压力

3. 不能。K[⊖]只是温度的函数。

$$六、1. (1) \text{阳极: } \frac{1}{2}\text{H}_2(p^\ominus) \rightarrow \text{H}^+ + \text{e}^- \quad \text{阴极: } \text{AuI}_{(s)} + \text{e}^- \rightarrow \text{Au}_{(s)} + \text{I}_{(a)}^-$$



$$(2) E_1 = E^\ominus - 0.05916 \lg a[\text{H}^+]a[\text{I}^-] = E^\ominus - 0.05916 \lg r_{\pm} b_{\pm}^2$$

$$E_2 = E^\ominus - 0.05916 \lg r_{\pm}^2 b_{\pm}^2 \quad \text{即 } 0.56 = 0.05916 [\lg 9 r_{\pm}^2 - \lg 10^{-9}] \rightarrow r_{\pm}^2 = 3.25$$

$$(3) E_{(\text{AuI} \backslash \text{Au})}^\ominus = E_1 + 0.05916 \lg r_{\pm}^2 b_{\pm}^2 = 0.97 + 0.05916 \lg 10^{-9} = 0.5 \text{ v}$$



$$E^\ominus = E_{(\text{AuI} \backslash \text{Au})}^\ominus - E_{(\text{Au}^+ \backslash \text{Au})}^\ominus = 0.5 - 1.68 = -1.18 \text{ v}$$

$$E = E^\ominus - 0.05916 \lg k_{\text{sp}} = 0 \rightarrow 1.18 = -0.05916 \lg k_{\text{sp}} \rightarrow k_{\text{sp}} = 1.13 \times 10^{-20}$$

北航 2008 年硕士研究生入学考试试题答案参考

一. 填空题

1. 0 在温度恒定时，理想气体的熵与压强无关 2. > <

3. 增加 减少(?) 4. $\frac{dQ_r}{T}$ $K \ln V$

5. $\frac{[C_{\text{B,H}_2\text{O}}/C^\ominus]^2}{C_{\text{B,苯}}/C^\ominus}$ 6. >0 =0

7. $\mu_A(\alpha) = \mu_A(\beta)$ $\mu_B(\alpha) = \mu_B(\beta)$ 8. $V_B = V_{m,B}^*$ $G_B = G_{m,B}^* + RT \ln \dots$

9. 食盐 > 醋 > 糖 (?) 10. (?) 增加 $\Delta_1^g H_m(T_2) - \Delta_1^g H_m(T_1) = \int_{T_1}^{T_2} \Delta_1^g C_{p,m} dT$

11. 萃取临界条件容易进行 无毒、无公害（超纲） 12. 2.1

13. 3 2 14. (?) $\frac{\alpha_{\pm}}{\sqrt[4]{27b}}$

15. $\text{Pt} | \text{H}_2(\text{P}) | \text{HI}(\text{a}) | \text{AuI}(\text{s}) | \text{Au}(\text{s})$ 16. Q = 0

17. 升温 加压 18. $P^* e^{\frac{2\gamma M}{RT\rho}}$

19. $\frac{k_1 k_2 C_{\text{O}_3}^2}{k_{-1} C_{\text{O}_2}}$ (?) 20. $\frac{2k_1 k_2 C_{\text{O}_3}^2 C_M}{k_2 C_{\text{O}_3} + k_{-1} C_{\text{O}_2} C_M}$

二. 简答题

$k^\theta(T)$ 也是温度的函数, 由VantHoff方程得 $\frac{d \ln k^\theta}{dT} = \frac{\Delta_r H_m^\theta}{RT^2}$

1. 答: 不能。因为可以看出 k^θ 与温度的关系与 $\Delta_r H_m^\theta$ 有关。当 $\Delta_r H_m^\theta < 0$ 时,

即反应放热时, 有 T 升高, k^θ 下降, $\Delta_r G_m^\theta$ 升高

2. 答: (?) 不对。隔离系统包括反应系统和相应的环境系统, 即 $\Delta S_{\text{iso}} = \Delta S_{\text{sys}} + \Delta S_{\text{amb}}$ 不能仅仅由反应系统的熵变来决定。(熵增加原理适用于绝热, 孤立系统的简单物理变化过程, 故不适用于化学变化, 结论不正确)

3. 答: 由 $p_B = k_B a_B = k_B \gamma_B x_B$ 则绘制 $p_B \leftrightarrow x_B$ 曲线, 由于在稀溶液中 $\gamma_B \approx 0$, 因此在低浓度区域的斜率即为 k_B

4. 电池电动势受浓度影响 $E = E^\theta - \frac{RT}{ZF} \ln J$, 标准电动势不受浓度影响, 电池温度系数受浓度影响

5. 产生过饱和溶液的原因是在同样温度下小颗粒晶体的溶解度大于普通晶体的溶解度, 及 $\mu_{\text{颗粒}} > \mu_{\text{普通}} = \mu_{\text{饱和溶液}}$, 因此由于小颗粒的化学势大于饱和溶液的化学势, 因此不能够析出。

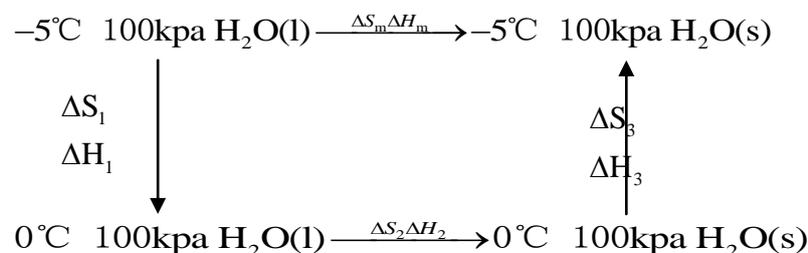
三计算题

1. 解

$$(1) W = -P\Delta V = -2.23 \text{ KJ} \quad \Delta U = 0 \quad Q = -W = 2.23 \text{ KJ} \quad \Delta S = \frac{Q}{T} = 7.48 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$$

$$(2) Q = 0, \Delta U = W = -1.59 \text{ KJ}, \Delta S = 10.44 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$$

2. 解: 设计过程如下:



$$\begin{aligned}
 \Delta H_m &= \Delta H_1 + \Delta H_2 + \Delta H_3 = \int_{268.15}^{273.15} C_{p,m}(\text{H}_2\text{O}, \text{l}) dT + (-\Delta_{\text{fus}} H_m(\text{H}_2\text{O})) + \int_{273.15}^{268.15} C_{p,m}(\text{H}_2\text{O}, \text{s}) dT \\
 &= -5820.5 \text{ J} \cdot \text{mol}^{-1}
 \end{aligned}$$

$$\Delta S_m = \Delta S_1 + \Delta S_2 + \Delta S_3 = nC_{p,m}(\text{H}_2\text{O}, \text{l}) \ln \frac{T_2}{T_1} + \frac{-\Delta_{\text{fus}} H_m(\text{H}_2\text{O})}{268.15} + nC_{p,m}(\text{H}_2\text{O}, \text{s}) \ln \frac{T_1}{T_2} = -21.3 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta G_m = \Delta H_m - T\Delta S_m = -108.91 \text{ J} \cdot \text{mol}^{-1}$$

3. 解

$$(1) \Delta G = \Delta H - T\Delta S, \text{ 当 } T \text{ 足够大时, } \Delta G < 0, \left(\frac{\partial \Delta G}{\partial T}\right)_P = -\frac{\Delta H}{T^2} \Rightarrow \frac{d \ln k^\theta}{dT} = \frac{\Delta H}{T^2} > 0 \Rightarrow T \uparrow, K^\theta \uparrow, a \uparrow$$

$$(2) k^\theta = \frac{a^2}{1-a^2} P/P^\theta \Rightarrow P \uparrow, a \downarrow, P=9.37 \text{ kPa}$$

4. 解

$$(1): k = \frac{1}{t} \ln \frac{1}{1-a} = 0.0193 \text{ min}^{-1}$$

$$(2): -\frac{dc}{dt} \Big|_{t=0} = 5.79 \times 10^{-3} \text{ mol l}^{-1} \text{ min}^{-1}, -\frac{dc}{dt} \Big|_{t=0} = 3.94 \times 10^{-3} \text{ mol l}^{-1} \text{ min}^{-1}$$

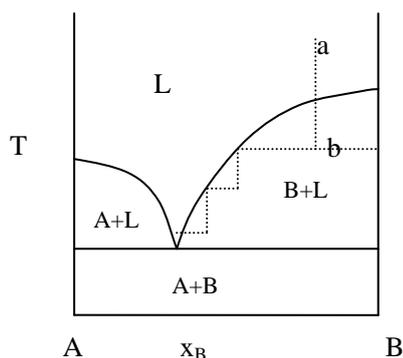
$$(3): \text{水解率 } a=0.538, t_{a=0.60}=47.48 \text{ min}$$

$$(4): 207.7 \text{ L}$$

四 选做题

1. 解:

图形如下: 要提纯, 设组成为 a 的液相, 降温至 b , 分离液相与纯 B , 液相继续降温再分离纯 B , 如图中虚线所示。各相区的自由度分别为: $L:F=2$ $A+L:F=1$ $B+L:F=1$ $A+B:F=1$



2 解:

$$(1) \text{Pb-Hg}(a_{\text{Pb}}=0.0150) | \text{Pb}(\text{NO}_3)_2(a_{\text{Pb}^{2+}}) | \text{Pb-Hg}(a_{\text{Pb}}=0.000500)$$

$$\text{Pb-Hg}(a_{\text{Pb}}=0.0150) = \text{Pb-Hg}(a_{\text{Pb}}=0.000500)$$

$$(2) E=0.044 \text{ V}, \left(\frac{\partial E}{\partial T}\right)_P = 1.47 \times 10^{-4} \text{ V/K}$$

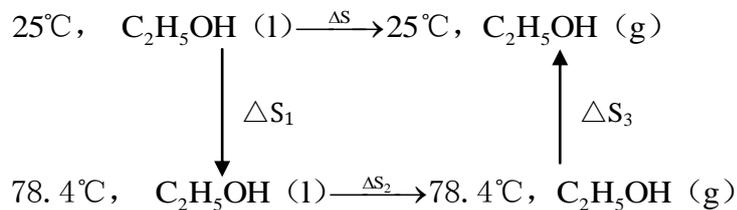
$$(3) W = \Delta G = -8.5 \times 10^3 \text{ J} \quad Q = ZFT \left(\frac{\partial E}{\partial T}\right)_P = 8.45 \times 10^3 \text{ J}$$

北航 2009 年硕士研究生入学考试试题答案参考

一. 选择题

1.D 2.B 3.A 4.C 5.C 6.B 7.B 8.A 9.C 10.B 11.B 12.D 13.C 14.A 15.A 16.B
17.D

二. 解: 设计可逆过



78.4°C下

$$\Delta_f H_m(\text{C}_2\text{H}_5\text{OH}(\text{l})) = \Delta_f H_m^\theta + C_{p,m} \Delta T = -277.69 + 111.46 \times (78.4 - 25.0) / 1000 \text{ kJ} \cdot \text{mol}^{-1} = -271.74 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H_m(\text{C}_2\text{H}_5\text{OH}(\text{g})) = \Delta_f H_m^\theta + C_{p,m} \Delta T = -235.10 + 65.44 \times (78.4 - 25.0) / 1000 \text{ kJ} \cdot \text{mol}^{-1} = -231.61 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\text{则 } 78.4^{\circ}\text{C} \text{ 下 } \Delta_{\text{vap}} H_m = \sum \nu_B \Delta_f H_m^\theta = -231.61 + 271.74 \text{ kJ} \cdot \text{mol}^{-1} = 40.13 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S_2 = \frac{\Delta_{\text{vap}} H_m}{T} = \frac{40130}{351.4} \text{ Jk}^{-1} \text{mol}^{-1} = 114.20 \text{ Jk}^{-1} \text{mol}^{-1}$$

$$\Delta S_1 = \int_{298}^{351.4} \frac{C_{p,m} dT}{T} = 111.46 \times \ln \frac{351.4}{298} \text{ Jk}^{-1} \text{mol}^{-1} = 18.37 \text{ Jk}^{-1} \text{mol}^{-1}$$

$$\Delta S_3 = \int_{351.4}^{298} \frac{C_{p,m} dT}{T} = 65.44 \times \ln \frac{298}{351.4} \text{ Jk}^{-1} \text{mol}^{-1} = -10.79 \text{ Jk}^{-1} \text{mol}^{-1}$$

$$25^{\circ}\text{C} \text{ 时 } \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 121.78 \text{ Jk}^{-1} \text{mol}^{-1}$$

三解:

$$\Delta G_m^\theta = \Delta H_m^\theta - T \Delta S_m^\theta = 56.91 - 400 \times 174.4 / 1000 \text{ kJ} \cdot \text{mol}^{-1} = -12.85 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G_m^\theta = -RT \ln K^\theta \Rightarrow K^\theta = e^{-\frac{\Delta G_m^\theta}{RT}} = 47.65$$

| | | | |
|------|----------------------------------|---|--------------------------|
| | $\text{N}_2\text{O}_4(\text{g})$ | = | $2\text{NO}_2(\text{g})$ |
| 初始 | 1 | | 0 |
| 平衡 | 1-a | | 2a |
| 摩尔分数 | $\frac{1-a}{1+a}$ | | $\frac{2a}{1+a}$ |

设 a 为平衡转化率,

$$\text{N}_2\text{O}_4 \text{ 分压 } P_{\text{N}_2\text{O}_4} = \frac{1-a}{1+a} \times 0.8P^\theta \quad \text{NO}_2 \text{ 分压 } P_{\text{NO}_2} = \frac{2a}{1+a} \times 0.8P^\theta$$

$$K^\theta = \frac{(P_{\text{NO}_2} / P^\theta)^2}{P_{\text{N}_2\text{O}_4} / P^\theta} = \frac{3.2a^2}{1-a^2} \Rightarrow a = \sqrt{\frac{K^\theta}{K^\theta + 3.2}} = 0.968$$

四. 解:

根据 K 的单位 \Rightarrow 反应为一级反应, 有 $-\frac{dc}{dt} = kc \Rightarrow \ln \frac{c_0}{c} = kt$

$$\text{由 } t_{1/2} = \frac{\ln 2}{k} \Rightarrow 36.0^\circ\text{C 时 } k_1 = \frac{\ln 2}{t_{1/2}} = 0.122\text{h}^{-1}$$

$$\text{由 } k = Ae^{-\frac{E_a}{RT}} \Rightarrow \frac{k_1}{k_2} = e^{-\frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})} \Rightarrow E_a = \frac{R \ln \frac{k_1}{k_2}}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{8.314 \times \ln \frac{0.122}{0.173}}{\frac{1}{343} - \frac{1}{303}} \text{kJ} \cdot \text{mol}^{-1} = 7.54 \text{kJ} \cdot \text{mol}^{-1}$$

$$\text{反应物衰减 } 7/8 \text{ 时 } c = \frac{1}{8}c_0 \text{ 则有 } t_{7/8} = \frac{1}{k} \ln \frac{c_0}{\frac{1}{8}c_0} = \frac{1}{0.173} \ln 8\text{h} = 12.02\text{h}$$

五.解: (1)

负极: $\text{H}_2 = 2\text{H}^+ + 2\text{e}$

正极: $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e} = 2\text{OH}^-$

电池: $\text{H}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = 2\text{H}^+ + 2\text{OH}^- \dots\dots(1)$

(2)

$\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O} \dots\dots(2)$ 此反应的 $\Delta G_m^\theta = -237.13 \text{kJ} \cdot \text{mol}^{-1}$

$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \dots\dots(3)$ 此反应的 $\Delta G_m^\theta = -RT \ln k_w^\theta = 79.87 \text{kJ} \cdot \text{mol}^{-1}$

$$\text{由方程 } (1) = (2) + 2 \times (3) \Rightarrow \Delta G_{m,1}^\theta = \Delta G_{m,2}^\theta + 2 \times \Delta G_{m,3}^\theta = -237.13 + 2 \times 79.87 \text{kJ} \cdot \text{mol}^{-1} \\ = -77.40 \text{kJ} \cdot \text{mol}^{-1}$$

(3)

$$\Delta G_m^\theta = -zFE^\theta \Rightarrow E^\theta = -\frac{\Delta G_m^\theta}{zF} = -\frac{-77400}{2 \times 96485} \text{V} = 0.401 \text{V}$$

$$E^\theta = \varphi_+^\theta - \varphi_-^\theta \text{ 而 } \varphi^\theta(\text{H}^+ / \text{H}_2) = 0 \Rightarrow \varphi^\theta(\text{H}_2\text{O}, \text{OH}^- / \text{O}_2(\text{g}) | \text{Pt}) = E^\theta = 0.401 \text{V}$$

$$\text{电池电动势 } E = \varphi_+ - \varphi_- = \varphi_+^\theta - \varphi_-^\theta + \frac{0.05916}{z} \lg \frac{P_{\text{H}_2} / P^\theta}{a^2(\text{H}^+)} = 0.401 + \frac{0.05916}{2} \lg \frac{1}{0.0798^2} \text{V} = 0.466 \text{V}$$