2004 年研究生物理化学考试试题答案

一．填空：1.1717J , 1239J, > 2. a　3.△H+10S　4.所做的功 5.等温等压 6.降低，增大 7.0，$n_A RT\ln x_A + n_B RT\ln x_B$ 8.3 9.2,0 10.> 11. 恒沸混合物 12. Kp=P. Kx 13. 1.47×10^{13} 14.1, $C_A = C_{A0}e^{-kt}$ 15. 中间物 16. ξ 17.所传导总电量中 18.低于 19.196.7kJ/mol 20. 4.95×10^{-10}, 7.424×10^{-6}

二．解：$V_1 = \dfrac{RT}{P_1} = 12.24dm^3$

代入$P = 10132.5V + b$　202650=10132.5+b

解得 b=78628

P_2=10132.5×24.48 +78628=326672　$T_2 = \dfrac{P_2V_2}{RT} = 961.8K$

$$\Delta U = C_v(T_2 - T_1) = \frac{3}{2}R(961.8 - 298) = 8276J$$

$$W = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} [10132.5V + b]dV = 3239J$$

$$Q = \Delta U + W = 11520J$$

三．解：100℃下，容器中水蒸气的压力最大只能为 101325Pa

发生相变的水量为：

$$n(H_2O,g) = \frac{P^0V}{RT} = \frac{101325\times61.236\times10^{-3}}{8.314\times373} = 2.0mol$$

状态函数的变化值通过设计始终态相同的可逆相变过程求算。

$$\Delta H = n(H_2O,g)\Delta_{vap}H_m = 2mol\times40670J/mol = 81340J$$

$$\Delta U = \Delta H - \Delta(pV) = \Delta H - nRT = 81340J - 2\times8.314\times373J = 75135J$$

$$\Delta S = \frac{\Delta H}{T} = \frac{81340J}{373K} = 218.0J/K$$

$$\Delta G = 0$$

$$\Delta F = \Delta U - T\Delta S = -\Delta(pV) = -nRT = -2\times 8.314\times 373 = -6205J$$

$$Q\ W = 0 \qquad Q = \Delta U = 75135J$$

四.解：设计下列过程：

$$Ag_2CO_3(S,383K) \xrightarrow{\Delta_r G_m^{\theta} = ?} Ag_2O(S,383K) + CO_2(g,383K)$$

$$\downarrow \qquad\qquad\qquad\qquad\qquad\qquad \uparrow$$

$$Ag_2CO_3(S,298K) \rightarrow Ag_2O(S,298K) + CO_2(g,298K)$$

通过 298K 时的 $\Delta_r H_m^{\theta}$ 和 $\Delta_r S_m^{\theta}$ 求 383K 时的 $\Delta_r H_m^{\theta}$ 和 $\Delta_r S_m^{\theta}$

$\Delta_r H_m^{\theta}(298K) = -30585 - 393510 + 501660 = 77565J/mol$

$\Delta_r S_m^{\theta}(298K) = 121.8 + 213.8 - 167.4 = 168.2J/K.mol$

$\Delta C_p = 65.7 + 37.6 - 109.6 = -6.3J/K.mol$

$$\Delta_r H_m^{\theta}(383K) = \Delta_r H_m^{\theta}(298K) + \int_{298}^{383} \Delta C_p dT$$

$$= 77565 - 6.3(383.15 - 298.15) = 77029.5J/mol$$

$$\Delta_r S_m^{\theta}(383K) = \Delta_r S_m^{\theta}(298K) + \int_{298}^{383} \Delta C_p \frac{dT}{T} = 168.2 - 6.3\times \ln\frac{383}{298} = 166.62J/K$$

$$\Delta_r G_m^{\theta}(383K) = \Delta_r H_m^{\theta} - T\Delta_r S_m^{\theta} = 77029.5 - 383\times 166.62 = 13189J/mol$$

$$Q\ \Delta_r G_m^{\theta} = -RT\ln K_p^{\theta}$$

$$\therefore \ln K_p^{\theta} = -\frac{\Delta_r G_m^{\theta}}{RT} = -\frac{13189}{8.314\times 383} = -4.14$$

$$K_p^{\theta} = 0.0159$$

Ag_2CO_3 分解反应的 K_p^{θ} 为：

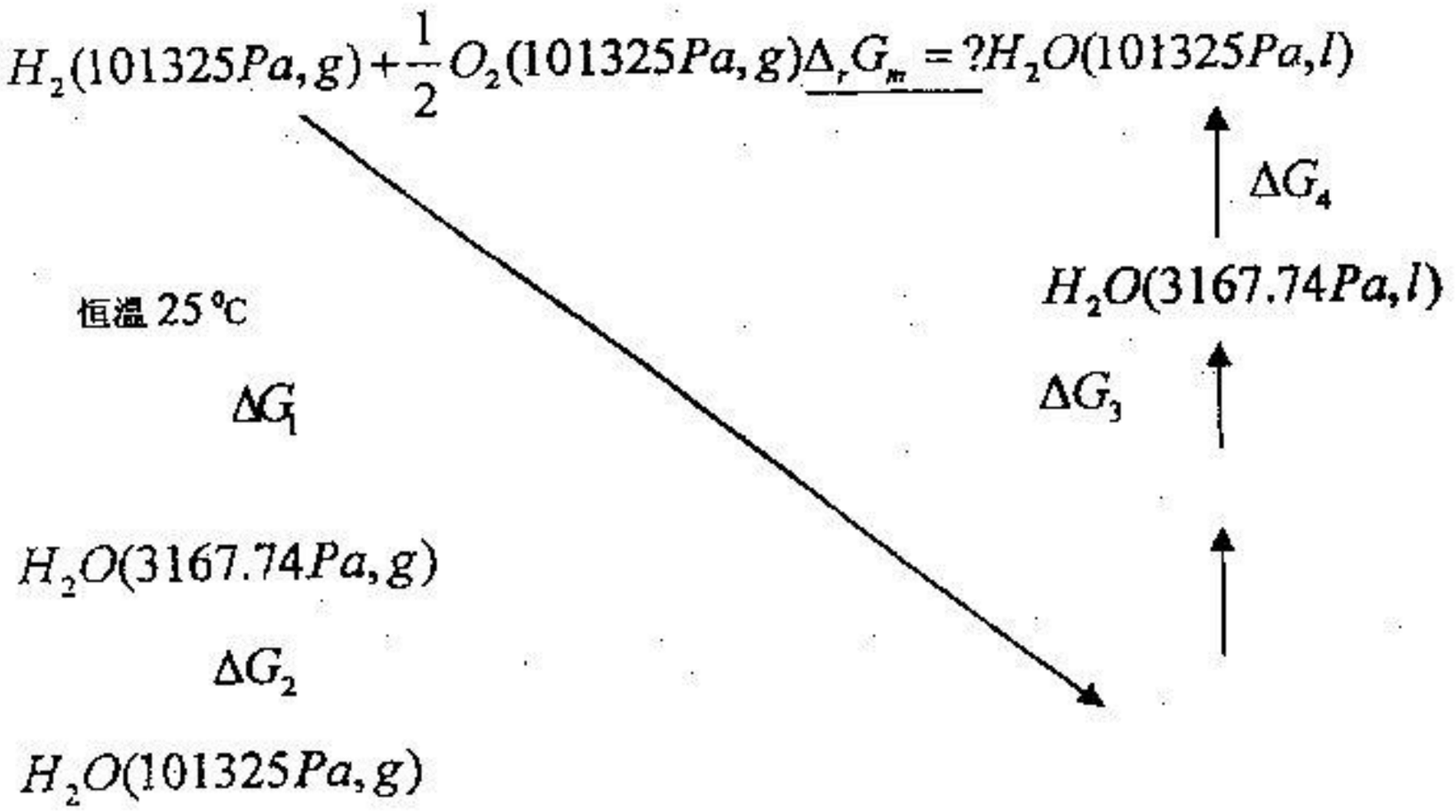
$$K_p^{\theta}=\frac{P_{CO_2}}{P^{\theta}}=0.0159 \qquad \therefore P_{CO_2}=0.0159P^{\theta}=1.61\times10^3\,Pa$$

当空气中的 CO_2 分压大与 1.61×10^3Pa 时，Ag_2CO_3 才不致分解。

五.解：电池反应为：

$$H_2(101325Pa,g)+\frac{1}{2}O_2(101325Pa,g)\rightarrow H_2O(101325Pa,l)$$

先设计过程计算反应的 Δ_rG_m，再通过 $\Delta_rG_m=-ZEF$ 求算电池的电动势



$$\Delta G_1=\Delta_fG_m^{\theta}(H_2O,g,25^{\circ}C)=-228570J/mol$$

$$\Delta G_2=\int VdP=\int_{101325}^{3167.74}\frac{RT}{P}dP=RT\ln\frac{3167.74}{101325}=8.314\times298\times\ln\frac{3167.74}{101325}$$

$$=-8557.26J/mol$$

$$\Delta G_3=0$$

$$\Delta G_4 = \int_{3167.74}^{101325} V_m(l)dP = 18.053\times10^{-6} m^3 mol^{-1}(101325-3167.74)Pa$$

$$= 1.748 J/mol$$

$$\Delta_r G_m = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 = --237126 J/mol$$

$$E = \frac{\Delta_r G_m}{ZF} = \frac{-237126 J/mol}{2\times96500 C/mol} = 1.229 V$$

六. 解：从 k 的量纲可以看出此反应为二级反应

1.

	$NO_2(g)$	→	$NO(g)$	$+1/2O_2$ (g)
t=o	26664Pa		0	0
t=t	26664Pa-P		P	1/2P

P（总） = 26664Pa + 1/2P =31997Pa　　P=10666Pa

$$\ln k_c = -58957/4.576 = -\frac{58957}{4.576\times673} + 18.424 = -0.72$$

k_C = 0.487 $(mol.dm^3)^{-1}.S^{-1}$　　$k_P = k_c/RT$

$$t = \frac{1}{k_p}\cdot\frac{P}{P_0(P_0-P)} = \frac{RT}{K_c}\cdot\frac{P}{P_0(P_0-P)}$$

$$= \frac{8.314(J.K^{-1}.mol^{-1})\times673K\times10666Pa}{0.487\times10^{-3}(m^3.mol^{-1}.S^{-1})\times26664Pa(26664Pa-10666Pa)} = 287S$$

2. 根据 $\ln k = \ln A - \frac{Ea}{RT}$ 与已知公式对照得：**lnA = 18.424**

$A = 1.0\times10^8 (mol.dm\text{-}^3)^{-1}.s^{-1}$

Ea/R = 58957/4.576 = 12884 K　　Ea = 107.1 kJ/mol

七. 解：1.

	A	+	2B	→	2C	+	D
t=0	0.01		0.02		0		0
t=t	0.01-z		0.02-2z		2z		z

$r=-d[A]/dt=dz/dt=k[A]^x[B]^y=k[0.01-z]^x[0.02-2z]^y=2^y.k[0.01-z]^{x+y}$

B 的初始浓度[B]=0.02mol.dm^{-3}时，$t_{1/2}$=90h

B 的初始浓度[B]=0.01mol.dm^{-3}时，$t_{1/2}$=217-90=127h

$$x+y=1+\frac{\lg\frac{90}{127}}{\lg\frac{0.01}{0.02}}=1.497\approx 1.5$$

2. $r_{0.1}=k[A_0]_1^x[B_0]_1^y=k[0.01]^x[0.02]^{1.5-x}$

$r_{0.2}=k[A_0]_2^x[B_0]_2^y=k[0.02]^x[0.02]^{1.5-x}$

两式相除得：$\frac{r_{0.1}}{r_{0.2}}=(\frac{0.01}{0.02})^x=\frac{1}{1.4}$　　$x\lg(\frac{0.01}{0.02})=\lg\frac{1}{1.4}$

解出　x=0.5　y=1

八. 解：1. $r=\frac{d[p]}{dt}=k_2\theta_A P_B$　　而 $\theta_A=\frac{a_A P_A}{1+a_A P_A}$（其中 $a_A=k_1/k_{-1}$）

$$\therefore r=\frac{k_2 a_A P_A P_B}{1+a_A P_A}$$

2. 若 A 为强吸附，则 a_AP_A 1，$r=k_2P_B$，

对 A 是零级反应，对 B 是一级反应　　表观活化能 $Ea=E_2$

若 A 为弱吸附，则 a_AP_A 1，$r=k_2a_AP_AP_B$，

对 A 是一级反应，对 B 是一级反应　　表观活化能 $Ea=E_2-Q_{吸附}$

九. 解：1. $q=g_0e^{-\varepsilon_0/kT}+g_1e^{-10\varepsilon_0/kT}+g_2e^{-100\varepsilon_0/kT}$

2.

$$N_0 / N = g_0 e^{-a/kT} /(g_0 e^{-a/kT} + g_1 e^{-10a/kT} + g_2 e^{-100a/kT})$$

$$N_1 / N = g_1 e^{-10a/kT} /(g_0 e^{-a/kT} + g_1 e^{-10a/kT} + g_2 e^{-100a/kT})$$

$$N_2 / N = g_2 e^{-100a/kT} /(g_0 e^{-a/kT} + g_1 e^{-10a/kT} + g_2 e^{-100a/kT})$$

3. $$S = Lk \ln \frac{g_0 e^{-a/kT}}{L!} + LkT(\frac{\partial \ln g_0 e^{-a/kT}}{\partial T})_{V,L}$$