浙江工业大学 2013 / 2014（2）学年

期终复习卷 2 答案

一、选择题答案

1、a ，2、c ，3、b ，4、b ，5、d，6、d，7、c ，8、a ，9、d ，10、c

11、b ，

12、c，因为不同热力学判据的应用条件如下

$\Delta U_{S,V} \le 0$；　　$\Delta H_{T,p} \le 0$

$\Delta G_{T,p} \le 0$；　　$\Delta S_{隔离} \ge 0$ 故只有 (c) 符合条件。

13、b，14、c，

15、c，体系经历的变化为绝热不可逆变化，所以 $\Delta S_{体} > 0$；环境与体系间没有热交换，压力亦无变化，体积的变化可忽略，所以环境的状态未变，即 $\Delta S_{环} = 0$ （环境的体积变化可忽略是基于下述认识，即一般情况下，总可以认为环境相对于体系是无穷大的）。

16、c，17、a ，18、b，19、d，

20、c 因为 $p=RT/(V_m-b)$

$dU=TdS-pdV$

所以 $\left(\frac{\partial U}{\partial V}\right)_T = T(\partial S/\partial V)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p$

$=RT/(V_m-b)-RT/(V_m-b)=0$

故 $\Delta U=0$

22、d，23、c ，24、a ，25、a ，26、b，

27、b，$K_b = RT_b^2 M_A/\Delta_{vap}H_m$

$dp/dT = \Delta_{vap}H_m/(T_b\Delta_{vap}V_m) \approx \Delta_{vap}H_m/[T_b(RT/p)] = p\Delta_{vap}H_m/(T_bRT_b) = (p/K_b)M_A$

$= (101\ 325\ \text{Pa}/0.5\ \text{K·kg·mol}^{-1})\times(0.018\ \text{kg·mol}^{-1})$

$= 3647.7\ \text{Pa·K}^{-1}$

28、b，29、c ，30、a

31、c ，32、d ，33、c ， 34、b， 35、 c ，36、b， 37、d， 38、b，39、a ， 40、c

二、计算题

1、　解：

$$\Delta_r H_m^\ominus(298K) = \sum \nu_B \Delta_f H_m^\ominus(B, 298\text{K})$$

$$= \Delta_f H_m^\ominus(\text{H}_2\text{O}, g, 298\text{K}) \qquad [4]$$

$$= -241.83\ \text{kJ mol}^{-1}$$

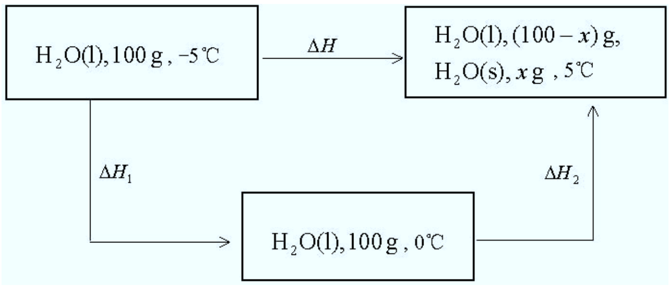
$$\Delta_r H_m^\ominus(800\text{K}) = \Delta_r H_m^\ominus(298K) + \int_{298}^{800}\left[C_{P,m}(\text{H}_2\text{O},g) - C_{P,m}(\text{H}_2) - \frac{1}{2}C_{P,m}(\text{O}_2)\right]dT$$

$$= -241.83 + \int_{298}^{800}\left[33.6 - 28.8 - \frac{1}{2}\times 29.4\right]\times 10^{-3}\,dT$$

$$= -246.81\ \text{kJ mol}^{-1}$$ [6]

2、解：

(1)



恒压且绝热，故

$$\Delta H = Q_p = 0$$ [4]

(2) $$\Delta H_1 = m\int_{T_1}^{T_2} c dT = mc(T_2 - T_1)$$ [2]

$$\Delta H_2 = x(-333.5)\,\text{J}$$ **[2]**

$$\Delta H_1 + \Delta H_2 = \Delta H = 2115 - 333.5x = 0$$ [1]

即 $$x = \frac{2115}{333.5} = 6.34$$

故析出 6.34 g 冰。 **[1]**

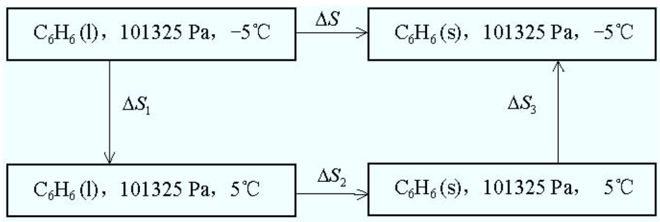
3、解：理想热机可逆循环，因此工作物质(体系) A 及热源 R 的总熵变为零。

即$\Delta S_{总} = \Delta S_{体} + \Delta S_A + Q_1/T_1 = 0$

因为$\Delta S_{体} = 0$

故$\Delta S_A + Q_1/T_1 = 0$，从而 $Q_1 = -T_1\Delta S_A$

4、解：



$$Q = \Delta H = \left\{-9916 + (122.6 - 126.8) \times \left[(-5) - 5\right]\right\}\text{J} = -9874\text{J}$$ [1]

$$\Delta U = Q + W \approx Q = -9874\text{J}$$ **[1]**

$$\Delta S_1 = C_{p,m(s)} \ln\frac{T_1}{T_2} = \left(126.8\times\ln\frac{5+273.15}{-5+273.15}\right)\mathrm{J\cdot K^{-1}} = 4.643\mathrm{J\cdot K^{-1}}$$ [1]

$$\Delta S_2 = \frac{\Delta H_2}{T_2} = \left(\frac{-9916}{5+273.15}\right)\mathrm{J.K^{-1}} = -35.65\mathrm{J.K^{-1}}$$ [1]

$$\Delta S_3 = C_{p,m(l)} \ln\frac{T_1}{T_2} = \left(126.6\times\ln\frac{5+273.15}{-5+273.15}\right)\mathrm{J.K^{-1}} = -4.489\mathrm{J.K^{-1}}$$ [1]

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -35.50\mathrm{J.K^{-1}}$$ [1]

$$\Delta A = \Delta U - T\Delta S = \left[-9874-(-5+273.15)\times(-35.50)\right]\mathrm{J} = -355\mathrm{J}$$ [1]

$$\Delta G = \Delta H - T\Delta S = -355\mathrm{J}$$ [1]

5、解：

Q=0 [1]

ΔS=0 [1]

$\Delta S_{隔离}$=0 [1]

T_2=297.0 K [2]

W= ΔU= $nC_{v,m}(T_2-T_1)$=−4.126 kJ [2]

ΔH=$nC_{p,m}(T_2-T_1)$=−5.776 kJ [1]

ΔA=ΔU−$S\Delta T$=33.89 kJ [1]

ΔG=ΔH−$S\Delta T$=32.24 kJ [1]

6、解：因为 $dU = TdS - pdV$

所以 $$(\frac{\partial U}{\partial V})_T = T(\frac{\partial p}{\partial T})_V - p = T\left\{\partial\left[RT/(V_m-\mathrm{b})\right]/\partial T\right\} - RT/(V_m-\mathrm{b}) = 0$$

故 $\Delta U_m = 0$ [2]

$$\Delta H_m = \Delta U_m - \Delta(pV_m) = p_2V_{m,2} - p_1V_{m,1} = \mathrm{b}(p_2-p_1) = 3.948\mathrm{kJ\cdot mol^{-1}}$$ [2]

$$\Delta G_m = \int_{p_1}^{p_2} Vdp = \int_{p_1}^{p_2}(RT/p+\mathrm{b})dp = RT\ln(p_2/p_1) + \mathrm{b}(p_2-p_1)$$

$$= 32.66\mathrm{kJ\cdot mol^{-1}}$$ [2]

$$\Delta A_m = -\int_{V_1}^{V_2} pdV = -\int_{V_{m,1}}^{V_{m,2}}\left[RT/(V_m-\mathrm{b})\right]d(V_m-\mathrm{b})$$

$$= -RT\ln\left[(V_{m,2}-\mathrm{b})/(V_{m,1}-\mathrm{b})\right] = RT\ln(p_2/p_1) = 28.72\mathrm{kJ.mol^{-1}}$$ [2]

$$\Delta S_m = (\Delta H_m - \Delta G_m)/T = -57.42\mathrm{J.K^{-1}\cdot mol^{-1}}$$ [2]

7、解：燃烧反应 $C_6H_{12}O_6(s) + 6O_2(g) = 6CO_2(g) + 6H_2O(l)$ [2]

$\Delta_c H_m^{\ominus} = -2.808\ \mathrm{MJ \cdot mol^{-1}}$ [2]

$\Delta_c S_m^{\ominus} = 6\Delta S_m^{\ominus}(\mathrm{CO_2}) + 6\Delta S_m^{\ominus}(\mathrm{H_2O}) - 6\Delta S_m^{\ominus}(\mathrm{O_2}) - \Delta S_m^{\ominus}(\mathrm{C_6H_{12}O_6})$

$= 182.4\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ [2]

$\Delta_c G_m^{\ominus} = \Delta_c H_m^{\ominus} - T\Delta_c S_m^{\ominus} = -2.862\ \mathrm{MJ \cdot mol^{-1}}$ [2]

$\Delta_c G_m^{\ominus} = W_r^{'}$ 即为恒温恒压下所能作的最大功。 [2]

8、解：(1) $\Delta_r H_m^{\ominus} = \Delta_C H_m^{\ominus}(\text{金刚石}) - \Delta_C H_m^{\ominus}(\text{石墨}) = 1.88\ \mathrm{kJ \cdot mol^{-1}}$ [2]

$\Delta_r S_m^{\ominus} = S_m^{\ominus}(\text{金刚石}) - S_m^{\ominus}(\text{石墨}) = -3.263\ \mathrm{J \cdot K^{-1} mol^{-1}}$ [2]

$\Delta_r G_m^{\ominus} = \Delta_r H_m^{\ominus} - T\Delta_r S_m^{\ominus} = 5.143\mathrm{kJ \cdot mol^{-1}}$ [2]

(2) $\left(\partial \Delta G^{\ominus} / \partial p\right)_r = \Delta V$

$\Delta_r G_m^{\ominus}(p_2) = \Delta_r G_m^{\ominus}(p_1) + \Delta V \int_{p_1}^{p_2} \mathrm{d}p$

若要 $\Delta_r G_m^{\ominus}(p_2) \leqslant 0$，$p_2 \geqslant 1.51 \times 10^9\ \mathrm{Pa}$ [4]

10、解: $x(\mathrm{Pb}) = \dfrac{0.055/207}{0.055/207 + 0.945/197} = 0.052487$ [2]

$\Delta_{fus} H_m = RT_f T_f^* x(\mathrm{Pb}) / \Delta T_f$

$= 8.314 \times 1335.5 \times 1272.5 \times 0.05248 / (1335.5 - 1272.5)$

$= 11770\mathrm{J \cdot mol^{-1}}$ [3]

11、解：$\pi = -\dfrac{RT}{V_\mathrm{m}(\text{水})} \ln x_{\text{水}}$

对于真实溶液，上式中的 x 要用活度 a

$$\pi = -\frac{RT}{V_\mathrm{m}(\text{水})} \ln a_{\text{水}} = -\frac{RT}{V_\mathrm{m}(\text{水})} \ln \frac{p_{\text{水}}}{p_{\text{水}}^*} = 5.578 \times 10^6\ \mathrm{Pa}$$

12、解：

(1) $\Delta T_A = K_A m_B$ [2]

0.62 K = 1.86 K·kg·mol^{-1}×(6×10^{-4} kg/M_B)/0.012 kg

M_B= 0.150 kg·mol^{-1} [2]

(2) N(H) = Mr(b) W_B/Ar(H) = (0.150×0.093)/1.008 = 13.8

同理得 N(N) = 2；N(C) = 9 [3]

尼古丁分子式为 $C_9H_{14}N_2$ [1]

13、解：$a_A = \frac{p_A}{p_A^*} = 0.43, \qquad \gamma_A = \frac{a_A}{x_A} = \frac{0.433}{0.497} = 0.871$

14、解：

解：设计下列三步变化过程。

$$冰(-10℃) \xrightarrow[\Delta H_1,\ \Delta S_1]{1} 冰(0℃) \xrightarrow[\Delta H_2,\ \Delta S_2]{2} 水(0℃) \xrightarrow[\Delta H_3,\ \Delta S_3]{3} 水(-10℃)$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = [37.6\times10 + 6020 - 75.3\times10]\ \mathrm{J} = 5643\ \mathrm{J} \qquad [3]$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = [37.6\ln\frac{273.15}{263.15} + \frac{6020}{273.15} + 75.13\ln\frac{263.15}{273.15}]\ \mathrm{J\ K^{-1}} \qquad [3]$$

$$= 20.64\ \mathrm{J\ K^{-1}}$$

$$\Delta G = \Delta H - T\Delta S = [5643 - 263.15\times20.64]\ \mathrm{J\ mol^{-1}} = 210\ \mathrm{J\ mol^{-1}} \qquad [2]$$

(2) 101325Pa 下，－10℃的冰变化同样压力下，－10℃的水的过程，可以设计下列步骤来实现

$$冰（-10℃,101325Pa) \xrightarrow{\Delta G_1\approx0} 冰（-10℃，p_s^*) \xrightarrow{\Delta G_2\approx0} H_2O(g, -10℃, p_s^*)$$
$$\xrightarrow{\Delta G_3} H_2O(g, -10℃, p_l^*) \xrightarrow{\Delta G_4\approx0} H_2O(l, -10℃, p_l^*) \xrightarrow{\Delta G_5\approx0} H_2O(l, -10℃, 101325Pa)$$

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 + \Delta G_5 \approx \Delta G_3 = nRT\ln\frac{P_l^*}{P_S^*} = 210\ \mathrm{J\ mol^{-1}} \qquad [5]$$

$$\therefore \quad p_l^* / p_s^* = 1.10 \qquad [2]$$

15、解：

(1) $p_A = p_A^* \cdot x_A$

$$x_{H_2O} = p_A / p_A^* = 1600/1700 = 0.941$$

$$x_{蔗糖} = 1 - x_{H_2O} = 0.059 \qquad [5]$$

(2) $\mu_{H_2O} = \mu^*{}_{H_2O} + RT\ln x_{H_2O}$

$$\Delta\mu = \mu^*_{H_2O} - \mu_{H_2O} = -RT\ln x_{H_2O}$$

$$= -8.314\times(15+273.15)\ln 0.941\ \ \mathrm{J\cdot mol^{-1}}$$

$$= 145.7\ \ \mathrm{J\cdot mol^{-1}}$$ [5]

16、解：H_2 (g, $p^{\ominus}$)+1/2O_2 (g, $p^{\ominus}$) $\longrightarrow$ H_2O(g, $p^{\ominus}$)- - - - (1)

$\Delta_r G_m^{\ominus}$,1=-228.59kJ • mol^{-1};

H_2 (g, $p^{\ominus}$)+1/2O_2 (g, $p^{\ominus}$) $\longrightarrow$ H_2O(l, $p^{\ominus}$) - - - - - (2)

$\Delta_r G_m^{\ominus}$,2=-237.19kJ • mol^{-1}

(1)-(2)得　H_2O(l, $p^{\ominus}$) $\longrightarrow$ H_2O(g, $p^{\ominus}$)

$\Delta_r G_m^{\ominus}$ $=\Delta_r G_m^{\ominus}$,1- $\Delta_r G_m^{\ominus}$,2=8.6 kJ • mol^{-1} [5 分]

$K^{\ominus}$ =exp(- $\Delta_r G_m^{\ominus}$ /RT) =0.03108=p(H_2 O)/ $p^{\ominus}$ [2 分]

p(H_2O) =0.03108×101325 =3149 Pa [2 分]

17、解：2Ag(s) + (1/2) O_2(g) = Ag_2O(s)

$\Delta_r G_m^{\ominus}$ (298 K) = -10.84 kJ·mol^{-1}

$\Delta_r H_m^{\ominus}$ (298 K) = -30.59 kJ·mol^{-1}

$\Delta C_{p,m}$= -2.55 J·K^{-1}·mol^{-1}

$\Delta_r H_m^{\ominus}(T) = \Delta_r H_m^{\ominus}(298\ \mathrm{K}) + \int_{T_1}^{T_2}\Delta C_{p,m}\,\mathrm{d}T$

$= -29830\ \mathrm{J\cdot mol^{-1}} - 2.55T\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ [4 分]

$(\Delta G_2/T_2) - (\Delta G_1/T_1) = -\int_{T_1}^{T_2}(\Delta_r H/T^2)\mathrm{d}T$

得　$\Delta G_2 = \Delta_r G_m^{\ominus}(823\ \mathrm{K}) = 20.48\ \mathrm{kJ\cdot mol^{-1}}$ [3 分]

$\Delta_r G_m^{\ominus}(823\ \mathrm{K}) = -RT\ln K_p^{\ominus} = -RT\ln[1/(p_{O_2}/p^{\ominus})^{1/2}]$

$p_{O_2} = 4.03\times10^7$ Pa [2 分]

现体系压力为 10^5 Pa，反应中不能生成 Ag_2O。 [1 分]

18、解：(1) 依据 $\Theta_v = h\nu/k = hc\tilde{\nu}/k = \dfrac{6.626\times10^{-34}\times3\times10^8\times\tilde{\nu}}{1.38\times10^{-23}} = 0.0144\tilde{\nu}$ [1]

求得各简正振动的特征温度为：

1944 K， 3447 K， 967 K， 967 K. [2]

(2) CO_2分子以基态为能量零点的振动配分函数为：

$$q_v = \prod_i [1-\exp(-\Theta_{v,i}/T)]^{-1} \quad [1]$$

$$=[1-\exp(-1944/300)]^{-1}\times[1-\exp(-3447/300)]^{-1}$$

$$\times[1-\exp(-967/300)]^{2}$$

$$=1.0015\times1.0000\times1.0415=1.043 \quad [1]$$

19、解： $\Theta_v = h\nu/k = hc\tilde{\nu}/k$

$$=(6.626\times10^{-34}\times3\times10^{8}\times440530/1.38\times10^{-23})\mathrm{K}$$

$$=6345.6\ \mathrm{K} \quad [1]$$

$$q_v=1/[1-\exp(-6345.6/3000)]=1.14 \quad [2]$$

$$S_v=R\{(\Theta_v/T)/[\exp(\Theta_v/T)-1]-\ln[1-\exp(-\Theta_v/T)]\}$$

$$=8.314\times\{\frac{6345.6/3000}{\exp(6345.6/3000)-1}-\ln[1-\exp(-6345.6/3000)]\}\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$$

$$=8.314\times(0.290+0.129)\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$$

$$=3.48\mathrm{J\cdot mol^{-1}\cdot K^{-1}} \quad [2]$$

20、解：根据 Boltzmann 熵定理：$S=k\ln\Omega$ 有： [1]

$$\Delta S=k\ln\Omega_{终}/\Omega_{始} \quad [2]$$

根据热力学有 $\Delta S=Lk\ln(2V/V)=k\ln2^{L}$ [1]

故 $\Omega_{终}/\Omega_{始}=2^{L}$ [1]