第 1 章　化学反应中的能量关系

第 1 章习题：1、2、3、6 、7、8、9、11、12

1.

解：$\Delta U = Q + W$，　　Q = 6.48 kJ

$W = -p_{外}(V_2 - V_1) = -93.31\times10^3 Pa\times(150-50)\times10^{-3}m^3 = -9.331kJ$

$\Delta U = (6.48-9.331)kJ = -2.851kJ$

∴ 内能的变化为－2.851kJ

2.

解：若以①、②、③分别表示所给的化学方程式，

根据盖斯定律，设计一循环：$\frac{1}{6}[3\times①-②-2\times③]$

可得下列方程：$FeO(s) + CO(g) = Fe(s) + CO_2(g)$

∴ 该反应的 $Q_p = \frac{1}{6}\times[3\times(-27.6)-(-58.6)-2\times38.1]kJ\cdot mol^{-1} = -16.7\ kJ\cdot mol^{-1}$

3.

解：

① $CaO(s) + SO_3(g) + 2H_2O(l) = CaSO_4\cdot2H_2O(s)$

$\Delta_f H_m^\ominus / kJ\cdot mol^{-1}$　　－635.5　　－395.26　　－285.85　　－2021.12

$\Delta_r H_m^\ominus = \Delta_f H_m^\ominus(CaSO_4\cdot2H_2O,s) - \Delta_f H_m^\ominus(CaO,s) - \Delta_f H_m^\ominus(SO_3,g) - 2\Delta_f H_m^\ominus(H_2O,l)$

$= [(-2021.12) - (-635.5) - (-395.26) - 2\times(-285.85)]\ kJ\cdot mol^{-1} = -418.66\ kJ\cdot mol^{-1}$

② $C_6H_6(l) + 7\frac{1}{2}O_2(g) = 6\,CO_2(g) + 3H_2O(l)$

$\Delta_f H_m^\ominus / kJ\cdot mol^{-1}$　　49.04　　0　　－393.51　　－285.85

$\Delta_r H_m^\ominus = 6\Delta_f H_m^\ominus(CO_2,g) + 3\Delta_f H_m^\ominus(H_2O,l) - \Delta_f H_m^\ominus(C_6H_6,l)$

$= [6\times(-393.51) + 3\times(-285.85) - 49.04]\ kJ\cdot mol^{-1} = -3267.65\ kJ\cdot mol^{-1}$

③ $2Al(s) + Fe_2O_3(s) = 2Fe(s) + Al_2O_3(s)$

$\Delta_f H_m^\ominus / kJ\cdot mol^{-1}$　　0　　－822.2　　0　　－1669.79

$\Delta_r H_m^\ominus = \Delta_f H_m^\ominus(Al_2O_3,s) - \Delta_f H_m^\ominus(Fe_2O_3,s)$

$= [(-1669.79) - (-822.2)]\ kJ\cdot mol^{-1} = -847.59\ kJ\cdot mol^{-1}$

6.

解：① 气体分子数增大的反应，熵变增大

② 气体分子数增大的反应，熵变增大

③ 同一物质气态的熵值大于液态，该反应熵变增大

7.

解： ① $SiO_2(s,石英) + 4\ HCl(g) = SiCl_4(g) + 2H_2O(g)$

$\Delta_f G_m^\Theta$ / kJ·mol^{-1} −805.0 −95.27 −569.9 −228.59

$\Delta_r G_{m,298}^\Theta = \Delta_f G_m^\Theta(SiCl_4,g) + 2\times\Delta_f G_m^\Theta(H_2O,g) - \Delta_f G_m^\Theta(SiO_2,石英) - 4\times\Delta_f G_m^\Theta(HCl,g)$

$= [(-569.9)+2\times(-228.59)-(-805.0)-4\times(-95.27)]$ kJ·mol^{-1} = 159.0 kJ·mol^{-1} > 0

∴ 各物质在标准状态下，反应不能正向进行。

② $CO(g) + H_2O(g) = CO_2(g) + H_2(g)$

$\Delta_f G_m^\Theta$ / kJ·mol^{-1} −137.30 −228.59 −394.38 0

$\Delta_r G_{m,298}^\Theta = \Delta_f G_m^\Theta(CO_2,g) - \Delta_f G_m^\Theta(CO,g) - \Delta_f G_m^\Theta(H_2O,g)$

$= [(-394.38)-(-137.30)-(-228.59)]$ kJ·mol^{-1} = −28.49 kJ·mol^{-1} < 0

∴ 各物质在标准状态下，反应可以正向进行。

③ $Fe_2O_3(s) + 3CO(g) = 2Fe(s) + 3CO_2(g)$

$\Delta_f G_m^\Theta$ / kJ·mol^{-1} −741.0 −137.30 0 −394.38

$\Delta_r G_{m,298}^\Theta = 3\times\Delta_f G_m^\Theta(CO_2,g) - \Delta_f G_m^\Theta(Fe_2O_3,s) - 3\times\Delta_f G_m^\Theta(CO,g)$

$= [3\times(-394.4)-(-741.0)-3\times(-137.30)]$ kJ·mol^{-1} = −30.24 kJ·mol^{-1} < 0

∴ 各物质在标准状态下，反应可以正向进行。

8.

解：① $\Delta_r H_m^\Theta = 2\times\Delta_f H_m^\Theta(NH_3,g) = [2\times(-45.96)]$ kJ·mol^{-1} = −91.92 kJ·mol^{-1}

$\Delta_r S_m^\Theta = (2\times192.70-3\times130.70-191.60)$ J·K^{-1}·mol^{-1} = −198.30 J·K^{-1}·mol^{-1}

$\Delta_r G_m^\Theta = \Delta_r H_m^\Theta - T\ \Delta_r S_m^\Theta = [-91.92-298\times(-198.30)\times10^{-3}]$ kJ·mol^{-1}

= −32.83 kJ·mol^{-1}

② $\Delta_r H_m^\Theta = -2\Delta_f H_m^\Theta(HgO,s) = -2\times(-90.71)$ kJ·mol^{-1} = 181.42 kJ·mol^{-1}

$\Delta_r S_m^\Theta = [(205.14 + 2\times77.4-2\times72.0)\times10^{-3}]$ kJ·mol^{-1}· K^{-1} = 0.216 kJ·mol^{-1}· K^{-1}

$\Delta_r G_m^\Theta = \Delta_r H_m^\Theta - T\ \Delta_r S_m^\Theta = (181.42-298\times0.216)$ kJ·mol^{-1} = 117.05 kJ·mol^{-1}

③ $\Delta_r H_m^\Theta = 2\Delta_f H_m^\Theta(H_2O,l) + \Delta_f H_m^\Theta(CO_2,g) - \Delta_f H_m^\Theta(CH_4,g)$

$= [2\times(-285.85)+(-393.51)-(-74.85)]\ \text{kJ·mol}^{-1} = -890.36\ \text{kJ·mol}^{-1}$

$\Delta_r S_m^\Theta = [2\times 69.96+213.79-2\times205.14-186.38]\times10^{-3}\ \text{kJ·mol}^{-1}\cdot\text{K}^{-1}$

$= -0.243\ \text{kJ·mol}^{-1}\cdot\text{K}^{-1}$

$\Delta_r G_m^\Theta = \Delta_r H_m^\Theta - T\times\Delta_r S_m^\Theta = [-890.36-298\times(-0.243)]\ \text{kJ·mol}^{-1} = -817.95\ \text{kJ·mol}^{-1}$

9.

解： ①

$$MnO_2(s) + 2H_2(g) = Mn(s) + 2H_2O(g)$$

$\Delta_f H_m^\Theta$ / kJ·mol^{-1}	−520.9	0	0	−241.84
S_m^Θ / J·mol^{-1}·K^{-1}	53.1	130.70	31.76	188.85
$\Delta_f G_m^\Theta$ / kJ·mol^{-1}	−466.1	0	0	−228.59

$\Delta_r H_{m,1}^\Theta = 2\times\Delta_f H_m^\Theta(H_2O, g) + \Delta_f H_m^\Theta(Mn,s) - \Delta_f H_m^\Theta(MnO_2,s) - 2\times\Delta_f H_m^\Theta(H_2,g)$

$= [2\times(-241.84) - (-520.9)]\ \text{kJ·mol}^{-1} = 37.22\ \text{kJ·mol}^{-1}$

$\Delta_r S_{m,1}^\Theta = 2\times S_m^\Theta(H_2O, g) + S_m^\Theta(Mn,s) - S_m^\Theta(MnO_2,s) - 2\times S_m^\Theta(H_2,g)$

$= [2\times188.85+31.76-53.1-2\times130.70]\ \text{J·mol}^{-1}\cdot\text{K}^{-1} = 94.96\ \text{J·mol}^{-1}\cdot\text{K}^{-1}$

$\Delta_r G_{m,1}^\Theta = \Delta_r H_{m,1}^\Theta - T\ \Delta_r S_{m,1}^\Theta = (37.22-298\times 94.96\times10^{-3})\ \text{kJ·mol}^{-1} = 8.92\ \text{kJ·mol}^{-1} > 0$

或者 $\Delta_r G_{m,1}^\Theta = 2\times\Delta_f G_m^\Theta(H_2O, g) + \Delta_f G_m^\Theta(Mn,s) - \Delta_f G_m^\Theta(MnO_2,s) - 2\Delta_f G_m^\Theta(H_2,g)$

$= [2\times(-228.59) - (-466.1)]\ \text{kJ·mol}^{-1} = 8.92\ \text{kJ·mol}^{-1} > 0$

②

$$MnO_2(s) + 2C(s) = Mn(s) + 2CO(g)$$

$\Delta_f H_m^\Theta$ / kJ·mol^{-1}	−520.9	0	0	−110.54
S_m^Θ / J·mol^{-1}·K^{-1}	53.1	5.69	31.76	198.01
$\Delta_f G_m^\Theta$ / kJ·mol^{-1}	−466.1	0	0	−137.30

$\Delta_r H_{m,2}^\Theta = 2\times\Delta_f H_m^\Theta(CO, g) + \Delta_f H_m^\Theta(Mn,s) - \Delta_f H_m^\Theta(MnO_2,s) - 2\times\Delta_f H_m^\Theta(C,g)$

$= [2\times(-110.54) - (-520.9)]\ \text{kJ·mol}^{-1} = 299.82\ \text{kJ·mol}^{-1}$

$\Delta_r S_{m,2}^\Theta = 2\times S_m^\Theta(CO, g) + S_m^\Theta(Mn,s) - S_m^\Theta(MnO_2,s) - 2\times S_m^\Theta(C,g)$

$=[2\times198.01+31.76-53.1-2\times5.69]\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}=363.3\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$

$\Delta_r G^\ominus_{m,2}=\Delta_r H^\ominus_{m,2}-T\ \Delta_r S^\ominus_{m,2}=(299.82-298\times363.3\times10^{-3})\ \mathrm{kJ\cdot mol^{-1}}=191.56\ \mathrm{kJ\cdot mol^{-1}}>0$

或者 $\Delta_r G^\ominus_{m,2}=2\times\Delta_f G^\ominus_m(\mathrm{CO,g})+\Delta_f G^\ominus_m(\mathrm{Mn,s})-\Delta_f G^\ominus_m(\mathrm{MnO_2,s})-2\Delta_f G^\ominus_m(\mathrm{C,g})$

$=[2\times(-137.30)-(-466.1)]\ \mathrm{kJ\cdot mol^{-1}}=191.5\ \mathrm{kJ\cdot mol^{-1}}>0$

∴ 以上两反应在 25℃和 100kPa 下均不能正向进行。

要使反应能够正向进行，则必须 $\Delta_r H^\ominus_m-T\ \Delta_r S^\ominus_m<0$，即 $T>\dfrac{\Delta_r H^\ominus_m}{\Delta_r S^\ominus_m}$

∴ $T_1>\dfrac{37.22}{94.96\times10^{-3}}\ \mathrm{K}=391.95\ \mathrm{K}$

$T_2>\dfrac{299.82}{363.3\times10^{-3}}\ \mathrm{K}=825.3\ \mathrm{K}$

故从温度考虑，第一种方法较好。

11.

解：① $\Delta_r G^\theta_m=\Delta_r H^\theta_m-T\times\Delta_r S^\theta_m=[401.92-298\times189.13\times10^{-3}]\ \mathrm{kJ\cdot mol^{-1}}$

$=345.56\ \mathrm{kJ\cdot mol^{-1}}>0$ ∴ 该反应在 25℃、100kPa 下不能自发进行。

② ∵ $\Delta_r H^\theta_m>0$, $\Delta_r S^\theta_m>0$，若使上述反应正向进行，即 $\Delta_r G^\theta_m=\Delta_r H^\theta_m-T\times\Delta_r S^\theta_m<0$

∴ 升高温度对反应有利。

③ 若使上述反应正向进行，则 $\Delta_r G^\theta_m<0$，即 $\Delta_r H^\theta_m-T\times\Delta_r S^\theta_m<0$

∴ $T>\dfrac{\Delta_r H^\theta_m}{\Delta_r S^\theta_m}=\dfrac{401.92}{189.13\times10^{-3}}\ \mathrm{K}=2125\ \mathrm{K}$

12.

解：①

	$CuS(s)+H_2(g)$	→	$Cu(s)+H_2S(g)$
$\Delta_f H^\ominus_m$ / kJ·mol	−48.5	0	0	−20.17
$\Delta_f G^\ominus_m$ / kJ·mol^{-1}	−48.9	0	0	−33.05
$S^\ominus_m$ / J·mol^{-1}·K^{-1}	66.5	130.70	33.30	205.88

$\Delta_r H^\ominus_m=\Delta_f H^\ominus_m(\mathrm{H_2S,g})+\Delta_f H^\ominus_m(\mathrm{Cu,s})-\Delta_f H^\ominus_m(\mathrm{CuS,s})-\Delta_f H^\ominus_m(\mathrm{H_2,g})$

$=[(-20.17)-(-48.5)]\ \mathrm{kJ\cdot mol^{-1}}=28.33\ \mathrm{kJ\cdot mol^{-1}}$

$$\Delta_r G_m^\Theta = \Delta_f G_m^\Theta(H_2S,g) + \Delta_f G_m^\Theta(Cu,s) - \Delta_f G_m^\Theta(CuS,s) - \Delta_f G_m^\Theta(H_2,g)$$

$$= [(-33.05)-(-48.9)]\ kJ\cdot mol^{-1} = 15.85\ kJ\cdot mol^{-1}$$

② $\Delta_r S_m^\Theta = S_m^\Theta(H_2S,g) + S_m^\Theta(Cu,s) - S_m^\Theta(CuS,s) - S_m^\Theta(H_2,g)$

$$= [205.88+33.30-66.5-130.70]J\cdot mol^{-1}\cdot K^{-1} = 41.98\ J\cdot mol^{-1}\cdot K^{-1}$$

或者 $\Delta_r S_m^\Theta(298K) = \dfrac{\Delta_r H_m^\Theta - \Delta_r G_m^\Theta}{298} = \dfrac{(28.33-15.85)\times 10^3}{298} = 41.88\ J\cdot mol^{-1}\cdot K^{-1}$

1000 K 时 $\Delta_r G_m^\Theta(1000K) = \Delta_r H_m^\Theta(298) - T\Delta_r S_m^\Theta$

$$= [28.33-1000\times 41.98\times 10^{-3}]\ kJ\cdot mol^{-1} = -13.65\ kJ\cdot mol^{-1}$$