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. 某理想气体对恒定外压(93.1kPa)膨胀，其体积从 50L 变化至 150L，同时吸收 6.48kJ 的热量，试计算内能的变化。

解：$\Delta U = Q + W$，　　Q = 6.48 kJ

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

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

∴ 内能的变化为－2.851kJ

2. 已知下列热化学方程式：

$Fe_2O_3(s) + 3CO(g) = 2Fe(s) + 3CO_2(g)$，　$Q_p = -27.6\text{kJ}\bullet\text{mol}^{-1}$

$Fe_2O_3(s) + CO(g) = 2Fe_3O_4(s) + CO_2(g)$，　$Q_p = -58.6\text{kJ}\bullet\text{mol}^{-1}$

$Fe_3O_4(s) + CO(g) = 3FeO(s) + CO_2(g)$，　$Q_p = 38.1\text{kJ}\bullet\text{mol}^{-1}$

不用查表，计算下列反应的 Q_p：$FeO(s) + CO(g) = Fe(s) + CO_2(g)$

(提示：根据盖斯定律，利用已知反应方程式，设计一循环，消去 Fe_2O_3 和 Fe_3O_4，而得到所需反应方程式。)

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：$\frac{1}{6}$[3×①－②－2×③]

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

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

3. 试用书末附录 1 提供的标准摩尔生成焓 $\Delta_f H_m^\Theta$ 数据，计算下列反应的 $\Delta_r H_m^\Theta$。

① $CaO(s) + SO_3(g) + 2H_2O(l) = CaSO_4\bullet2H_2O(s)$

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

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

解：①

	$CaO(s)$ +	$SO_3(g)$ +	$2H_2O(l)$ =	$CaSO_4\bullet2H_2O(s)$
$\Delta_f H_m^\Theta$ / kJ·mol^{-1}	－635.5	－395.26	－285.85	－2021.12

$\Delta_r H_m^\Theta = \Delta_f H_m^\Theta(CaSO_4\bullet2H_2O,s) - \Delta_f H_m^\Theta(CaO,s) - \Delta_f H_m^\Theta(SO_3,g) - 2\Delta_f H_m^\Theta(H_2O,l)$

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

②

	$C_6H_6(l)$ +	$7\frac{1}{2}O_2(g)$ =	$6\,CO_2(g)$ +	$3H_2O(l)$
$\Delta_f H_m^\Theta$ / kJ·mol^{-1}	49.04	0	－393.51	－285.85

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

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

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

	$2Al(s)$	$Fe_2O_3(s)$	$2Fe(s)$	$Al_2O_3(s)$
$\Delta_f H_m^\Theta / kJ\cdot mol^{-1}$	0	-822.2	0	-1669.79

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

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

6. 判断下列反应或过程中熵变的数值是正值还是负值。

① $2C(g) + O_2(g) = 2CO(g)$

② $2NO_2(g) = 2NO(g) + O_2(g)$

③ $Br_2(l) = Br_2(g)$

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. 利用书末附录 1 所提供的 $\Delta_f G_m^\Theta$ 数据计算下列反应的 $\Delta_r G_m^\Theta$，判断这些反应能否自发进行。

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

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

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

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

	SiO_2(s,石英)	$HCl(g)$	$SiCl_4(g)$	$H_2O(g)$
$\Delta_f G_m^\Theta / kJ\cdot mol^{-1}$	-805.0	-95.27	-569.9	-228.59

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

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

∴ 各物质在标准状态下，反应不能正向进行。

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

	$CO(g)$	$H_2O(g)$	$CO_2(g)$	$H_2(g)$
$\Delta_f G_m^\Theta / kJ\cdot mol^{-1}$	-137.30	-228.59	-394.38	0

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

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

∴ 各物质在标准状态下，反应可以正向进行。

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

	$Fe_2O_3(s)$	$3CO(g)$	$2Fe(s)$	$3CO_2(g)$
$\Delta_f G_m^\Theta / kJ\cdot mol^{-1}$	-741.0	-137.30	0	-394.38

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

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

∴ 各物质在标准状态下，反应可以正向进行。

8. 利用书末附录 1 所提供的 $\Delta_f H_m^\ominus$ 和 $S_m^\ominus$ 数据，计算下列反应在 298K 时的 $\Delta_r G_m^\ominus$。

① $N_2(g) + 3H_2(g) = 2NH_3(g)$
② $2HgO(s) = 2Hg(l) + O_2(g)$
③ $CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l)$

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

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

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

$= -32.83\ kJ\cdot mol^{-1}$

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

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

$\Delta_r G_m^\ominus = \Delta_r H_m^\ominus - T\ \Delta_r S_m^\ominus = (181.42-298\times 0.216)\ kJ\cdot mol^{-1} = 117.05\ kJ\cdot mol^{-1}$

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

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

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

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

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

9. 用二氧化锰制取金属锰可采取下列两种方法：

① $MnO_2(s) + 2H_2(g) = Mn(s) + 2H_2O(g)$
② $MnO_2(s) + 2C(s) = Mn(s) + 2CO(g)$

上述两个反应在 25℃、100kPa 下能否自发进行？如果希望反应温度尽可能低一些，试通过计算，说明采用何种方法比较好？

解：①

	$MnO_2(s)$	+ $2H_2(g)$	= $Mn(s)$	+ $2H_2O(g)$
$\Delta_f H_m^\ominus / kJ\cdot mol^{-1}$	−520.9	0	0	−241.84
$S_m^\ominus / J\cdot mol^{-1}\cdot K^{-1}$	53.1	130.70	31.76	188.85
$\Delta_f G_m^\ominus / kJ\cdot mol^{-1}$	−466.1	0	0	−228.59

$\Delta_r H^{\ominus}_{m,1} = 2\times \Delta_f H^{\ominus}_m(H_2O, g) + \ \Delta_f H^{\ominus}_m(Mn,s)\ - \Delta_f H^{\ominus}_m(MnO_2,s)\ - 2\times \Delta_f H^{\ominus}_m(H_2,g)$

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

$\Delta_r S^{\ominus}_{m,1} = 2\times S^{\ominus}_m(H_2O, g) + \ S^{\ominus}_m(Mn,s)\ - S^{\ominus}_m(MnO_2,s)\ - 2\times S^{\ominus}_m(H_2,g)$

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

$\Delta_r G^{\ominus}_{m,1} = \Delta_r H^{\ominus}_{m,1} - T\ \ \Delta_r S^{\ominus}_{m,1} = (37.22-298\times 94.96\times10^{-3})kJ\cdot mol^{-1}\ = 8.92\ kJ\cdot mol^{-1} > 0$

或者 $\Delta_r G^{\ominus}_{m,1} = 2\times \Delta_f G^{\ominus}_m(H_2O, g) + \ \Delta_f G^{\ominus}_m(Mn,s)\ - \Delta_f G^{\ominus}_m(MnO_2,s)\ - 2\,\Delta_f G^{\ominus}_m(H_2,g)$

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

②	$MnO_2(s)$ +	$2C(s)$ =	$Mn(s)$ +	$2CO(g)$
$\Delta_f H^{\ominus}_m$ / $kJ\cdot mol^{-1}$	−520.9	0	0	−110.54
$S^{\ominus}_m$ / $J\cdot mol^{-1}\cdot K^{-1}$	53.1	5.69	31.76	198.01
$\Delta_f G^{\ominus}_m$ / $kJ\cdot mol^{-1}$	−466.1	0	0	−137.30

$\Delta_r H^{\ominus}_{m,2}\ = 2\times \Delta_f H^{\ominus}_m(CO, g) + \ \Delta_f H^{\ominus}_m(Mn,s)\ - \Delta_f H^{\ominus}_m(MnO_2,s)\ - 2\times \Delta_f H^{\ominus}_m(C,g)$

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

$\Delta_r S^{\ominus}_{m,2} = 2\times S^{\ominus}_m(CO, g) + \ S^{\ominus}_m(Mn,s)\ - S^{\ominus}_m(MnO_2,s)\ - 2\times S^{\ominus}_m(C,g)$

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

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

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

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

∴ 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 $T > \dfrac{\Delta_r H^{\ominus}_m}{\Delta_r S^{\ominus}_m}$

$$\therefore\quad T_1 > \frac{37.22}{94.96\times10^{-3}}\ K = 391.95\ K$$

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

故从温度考虑，第一种方法较好。

11. 25℃、100kPa 下，$CaSO_4(s) \rightarrow CaO(s) + SO_3(g)$，已知：$\Delta_r H_m^\Theta$=401.92kJ•mol^{-1}，

$\Delta_r S_m^\Theta$=189.13J •mol^{-1} • K^{-1}，问：

① 上述反应能否自发进行？

② 对上述反应，是升高温度有利，还是降低温度有利？

③ 若使上述反应正向进行，其所需的最低温度是多少？

解：① $\Delta_r G_m^\Theta = \Delta_r H_m^\Theta - T\times\Delta_r S_m^\Theta = [401.92-298\times189.13\times10^{-3}]\ kJ\cdot mol^{-1}$

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

② ∵ $\Delta_r H_m^\Theta > 0$，$\Delta_r S_m^\Theta > 0$，若使上述反应正向进行，即 $\Delta_r G_m^\Theta = \Delta_r H_m^\Theta - T\times\Delta_r S_m^\Theta < 0$

∴ 升高温度对反应有利。

③ 若使上述反应正向进行，则 $\Delta_r G_m^\Theta < 0$，即 $\Delta_r H_m^\Theta - T\times\Delta_r S_m^\Theta < 0$

$$\therefore\ T > \frac{\Delta_r H_m^\Theta}{\Delta_r S_m^\Theta} = \frac{401.92}{189.13\times10^{-3}}\ K = 2125\ K$$

12. ① 利用附录 1 所提供的数据，计算下列反应在 298K 时的 $\Delta_r H_m^\Theta$ 和 $\Delta_r G_m^\Theta$。

$CuS(s) + H_2(g) \rightarrow Cu(s) + H_2S(g)$

② 求该反应在 1000K 时的 $\Delta_r G_m^\Theta$。

解：①

	$CuS(s)$	$+ H_2(g)$	$\rightarrow Cu(s)$	$+ H_2S(g)$
$\Delta_f H_m^\Theta$ / kJ·mol	−48.5	0	0	−20.17
$\Delta_f G_m^\Theta$ / kJ·mol^{-1}	−48.9	0	0	−33.05
S_m^Θ / J·mol^{-1}·K^{-1}	66.5	130.70	33.30	205.88

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

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

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

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

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

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

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

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

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