

## 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。

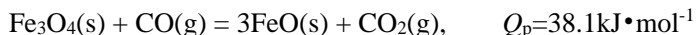
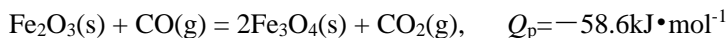
解： $\Delta U = Q + W$ ， $Q = 6.48 \text{ kJ}$

$$W = -p_{\text{外}}(V_2 - V_1) = -93.1 \times 10^3 \text{ Pa} \times (150 - 50) \times 10^{-3} \text{ m}^3 = -9.331 \text{ kJ}$$

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

$\therefore$  内能的变化为  $-2.851 \text{ kJ}$

2. 已知下列热化学方程式：



不用查表，计算下列反应的  $Q_p$ ： $\text{FeO}(\text{s}) + \text{CO}(\text{g}) = \text{Fe}(\text{s}) + \text{CO}_2(\text{g})$

(提示：根据盖斯定律，利用已知反应方程式，设计一循环，消去  $\text{Fe}_2\text{O}_3$  和  $\text{Fe}_3\text{O}_4$ ，而得到所需反应方程式。)

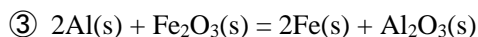
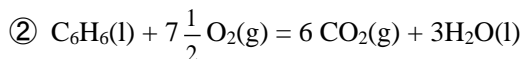
解：若以①、②、③分别表示所给的化学方程式，

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

可得下列方程： $\text{FeO}(\text{s}) + \text{CO}(\text{g}) = \text{Fe}(\text{s}) + \text{CO}_2(\text{g})$

$$\therefore \text{该反应的 } Q_p = \frac{1}{6} \times [3 \times (-27.6) - (-58.6) - 2 \times 38.1] \text{ kJ} \cdot \text{mol}^{-1} = -16.7 \text{ kJ} \cdot \text{mol}^{-1}$$

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

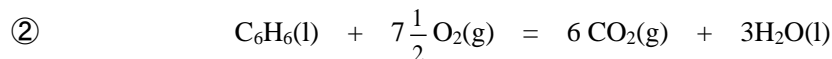


解：①  $\text{CaO}(\text{s}) + \text{SO}_3(\text{g}) + 2\text{H}_2\text{O}(\text{l}) = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$

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

$$\Delta_r H_m^\ominus = \Delta_f H_m^\ominus(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}, \text{s}) - \Delta_f H_m^\ominus(\text{CaO}, \text{s}) - \Delta_f H_m^\ominus(\text{SO}_3, \text{g}) - 2\Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{l})$$

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



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

$$\Delta_r H_m^\ominus = 6\Delta_f H_m^\ominus(\text{CO}_2, \text{g}) + 3\Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_f H_m^\ominus(\text{C}_6\text{H}_6, \text{l})$$

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

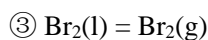
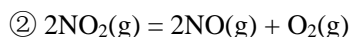
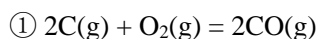


$$\Delta_f H_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad 0 \quad -822.2 \quad 0 \quad -1669.79$$

$$\Delta_r H_m^\ominus = \Delta_f H_m^\ominus (\text{Al}_2\text{O}_3, \text{s}) - \Delta_f H_m^\ominus (\text{Fe}_2\text{O}_3, \text{s})$$

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

6. 判断下列反应或过程中熵变的数值是正值还是负值。

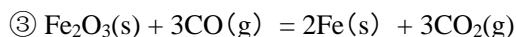
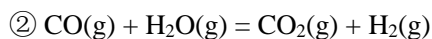
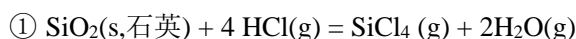


解: ① 气体分子数增大的反应, 熵变增大

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  $\Delta_f G_m^\ominus$  数据计算下列反应的  $\Delta_r G_m^\ominus$ , 判断这些反应能否自发进行。



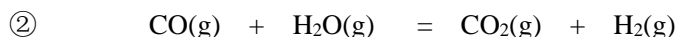
解: ①  $\text{SiO}_2(\text{s, 石英}) + 4\text{HCl(g)} = \text{SiCl}_4(\text{g}) + 2\text{H}_2\text{O(g)}$

$$\Delta_f G_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad -805.0 \quad -95.27 \quad -569.9 \quad -228.59$$

$$\Delta_r G_m^\ominus = \Delta_f G_m^\ominus (\text{SiCl}_4, \text{g}) + 2 \times \Delta_f G_m^\ominus (\text{H}_2\text{O, g}) - \Delta_f G_m^\ominus (\text{SiO}_2, \text{石英}) - 4 \times \Delta_f G_m^\ominus (\text{HCl, g})$$

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

$\therefore$  各物质在标准状态下, 反应不能正向进行。



$$\Delta_f G_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad -137.30 \quad -228.59 \quad -394.38 \quad 0$$

$$\Delta_r G_m^\ominus = \Delta_f G_m^\ominus (\text{CO}_2, \text{g}) - \Delta_f G_m^\ominus (\text{CO, g}) - \Delta_f G_m^\ominus (\text{H}_2\text{O, g})$$

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

$\therefore$  各物质在标准状态下, 反应可以正向进行。



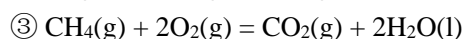
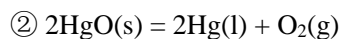
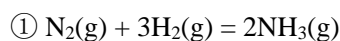
$$\Delta_f G_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad -741.0 \quad -137.30 \quad 0 \quad -394.38$$

$$\Delta_r G_m^\ominus = 3 \times \Delta_f G_m^\ominus (\text{CO}_2, \text{g}) - \Delta_f G_m^\ominus (\text{Fe}_2\text{O}_3, \text{s}) - 3 \times \Delta_f G_m^\ominus (\text{CO, g})$$

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

∴ 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  $\Delta_r G_m^\ominus$ 。



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

$$\Delta_r S_m^\ominus = (2 \times 192.70 - 3 \times 130.70 - 191.60) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -198.30 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\ominus = \Delta_r H_m^\ominus - T \Delta_r S_m^\ominus = [-91.92 - 298 \times (-198.30) \times 10^{-3}] \text{ kJ} \cdot \text{mol}^{-1}$$

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

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

$$\Delta_r S_m^\ominus = [(205.14 + 2 \times 77.4 - 2 \times 72.0) \times 10^{-3}] \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 0.216 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

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

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

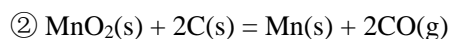
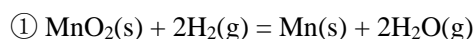
$$= [2 \times (-285.85) + (-393.51) - (-74.85)] \text{ kJ} \cdot \text{mol}^{-1} = -890.36 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m^\ominus = [2 \times 69.96 + 213.79 - 2 \times 205.14 - 186.38] \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

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

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

9. 用二氧化锰制取金属锰可采取下列两种方法：



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

$$\Delta_f H_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad -520.9 \quad 0 \quad 0 \quad -241.84$$

$$S_m^\ominus / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad 53.1 \quad 130.70 \quad 31.76 \quad 188.85$$

$$\Delta_f G_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad -466.1 \quad 0 \quad 0 \quad -228.59$$

$$\Delta_r H_{m1}^\ominus = 2 \times \Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{g}) + \Delta_f H_m^\ominus(\text{Mn}, \text{s}) - \Delta_f H_m^\ominus(\text{MnO}_2, \text{s}) - 2 \times \Delta_f H_m^\ominus(\text{H}_2, \text{g})$$

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

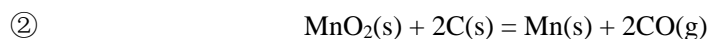
$$\Delta_r S_{m1}^\ominus = 2 \times S_m^\ominus(\text{H}_2\text{O}, \text{g}) + S_m^\ominus(\text{Mn}, \text{s}) - S_m^\ominus(\text{MnO}_2, \text{s}) - 2 \times S_m^\ominus(\text{H}_2, \text{g})$$

$$= [2 \times 188.85 + 31.76 - 53.1 - 2 \times 130.70] \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 94.96 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta_r G_{m1}^\ominus = \Delta_r H_{m1}^\ominus - T \Delta_r S_{m1}^\ominus = (37.22 - 298 \times 94.96 \times 10^{-3}) \text{ kJ} \cdot \text{mol}^{-1} = 8.92 \text{ kJ} \cdot \text{mol}^{-1} > 0$$

或者  $\Delta_r G_{m1}^\ominus = 2 \times \Delta_f G_m^\ominus(\text{H}_2\text{O}, \text{g}) + \Delta_f G_m^\ominus(\text{Mn}, \text{s}) - \Delta_f G_m^\ominus(\text{MnO}_2, \text{s}) - 2 \Delta_f G_m^\ominus(\text{H}_2, \text{g})$

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



$$\Delta_f H_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad -520.9 \quad 0 \quad 0 \quad -110.54$$

$$S_m^\ominus / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad 53.1 \quad 5.69 \quad 31.76 \quad 198.01$$

$$\Delta_f G_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad -466.1 \quad 0 \quad 0 \quad -137.30$$

$$\Delta_r H_{m2}^\ominus = 2 \times \Delta_f H_m^\ominus(\text{CO}, \text{g}) + \Delta_f H_m^\ominus(\text{Mn}, \text{s}) - \Delta_f H_m^\ominus(\text{MnO}_2, \text{s}) - 2 \times \Delta_f H_m^\ominus(\text{C}, \text{g})$$

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

$$\Delta_r S_{m2}^\ominus = 2 \times S_m^\ominus(\text{CO}, \text{g}) + S_m^\ominus(\text{Mn}, \text{s}) - S_m^\ominus(\text{MnO}_2, \text{s}) - 2 \times S_m^\ominus(\text{C}, \text{g})$$

$$= [2 \times 198.01 + 31.76 - 53.1 - 2 \times 5.69] \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 363.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta_r G_{m2}^\ominus = \Delta_r H_{m2}^\ominus - T \Delta_r S_{m2}^\ominus = (299.82 - 298 \times 363.3 \times 10^{-3}) \text{ kJ} \cdot \text{mol}^{-1} = 191.56 \text{ kJ} \cdot \text{mol}^{-1} > 0$$

或者  $\Delta_r G_{m2}^\ominus = 2 \times \Delta_f G_m^\ominus(\text{CO}, \text{g}) + \Delta_f G_m^\ominus(\text{Mn}, \text{s}) - \Delta_f G_m^\ominus(\text{MnO}_2, \text{s}) - 2 \Delta_f G_m^\ominus(\text{C}, \text{g})$

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

∴ 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  $\Delta_r H_m^\ominus - T \Delta_r S_m^\ominus < 0$ ，即  $T > \frac{\Delta_r H_m^\ominus}{\Delta_r S_m^\ominus}$

$$\therefore T_1 > \frac{37.22}{94.96 \times 10^{-3}} \text{ K} = 391.95 \text{ K}$$

$$T_2 > \frac{299.82}{363.3 \times 10^{-3}} \text{ K} = 825.3 \text{ K}$$

故从温度考虑，第一种方法较好。

11. 25℃、100kPa 下， $\text{CaSO}_4(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{SO}_3(\text{g})$ ，已知： $\Delta_r H_m^\ominus = 401.92 \text{ kJ} \cdot \text{mol}^{-1}$ ，

$\Delta_r S_m^\ominus = 189.13 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ，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  $\Delta_r G_m^\ominus = \Delta_r H_m^\ominus - T \times \Delta_r S_m^\ominus = [401.92 - 298 \times 189.13 \times 10^{-3}] \text{ kJ} \cdot \text{mol}^{-1}$

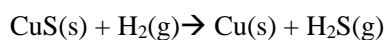
$= 345.56 \text{ kJ} \cdot \text{mol}^{-1} > 0$   $\therefore$  该反应在 25℃、100kPa 下不能自发进行。

②  $\because \Delta_r H_m^\ominus > 0$ ， $\Delta_r S_m^\ominus > 0$ ，若使上述反应正向进行，即  $\Delta_r G_m^\ominus = \Delta_r H_m^\ominus - T \times \Delta_r S_m^\ominus < 0$   
 $\therefore$  升高温度对反应有利。

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

$$\therefore T > \frac{\Delta_r H_m^\ominus}{\Delta_r S_m^\ominus} = \frac{401.92}{189.13 \times 10^{-3}} \text{ K} = 2125 \text{ K}$$

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



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

解：①  $\text{CuS}(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{Cu}(\text{s}) + \text{H}_2\text{S}(\text{g})$

$$\Delta_f H_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad -48.5 \quad 0 \quad 0 \quad -20.17$$

$$\Delta_f G_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad -48.9 \quad 0 \quad 0 \quad -33.05$$

$$S_m^\ominus / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad 66.5 \quad 130.70 \quad 33.30 \quad 205.88$$

$$\Delta_r H_m^\ominus = \Delta_f H_m^\ominus (\text{H}_2\text{S}, \text{g}) + \Delta_f H_m^\ominus (\text{Cu}, \text{s}) - \Delta_f H_m^\ominus (\text{CuS}, \text{s}) - \Delta_f H_m^\ominus (\text{H}_2, \text{g})$$

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

$$\Delta_r G_m^\ominus = \Delta_f G_m^\ominus (\text{H}_2\text{S}, \text{g}) + \Delta_f G_m^\ominus (\text{Cu}, \text{s}) - \Delta_f G_m^\ominus (\text{CuS}, \text{s}) - \Delta_f G_m^\ominus (\text{H}_2, \text{g})$$

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

②  $\Delta_r S_m^\ominus = S_m^\ominus (\text{H}_2\text{S}, \text{g}) + S_m^\ominus (\text{Cu}, \text{s}) - S_m^\ominus (\text{CuS}, \text{s}) - S_m^\ominus (\text{H}_2, \text{g})$

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

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

$$\begin{aligned} 1000 \text{ K 时 } \Delta_r G_m^\ominus(1000\text{K}) &= \Delta_r H_m^\ominus(298) - T \Delta_r S_m^\ominus \\ &= [28.33 - 1000 \times 41.98 \times 10^{-3}] \text{kJ} \cdot \text{mol}^{-1} = -13.65 \text{kJ} \cdot \text{mol}^{-1} \end{aligned}$$