

第5章 化学热力学

1. 测得2.96g氯化汞在407℃的1L容积的真空系统里完全蒸发达到的压力为60kPa, 求氯化汞蒸气的摩尔质量和化学式。

$$\text{解: } M = \frac{mRT}{PV} = \frac{2.96 \times 8.314 \times (407 + 273)}{60 \times 1} = 278.9$$

$$\therefore \text{HgCl}_2 \text{的式量} = 271.496$$

$$\therefore \text{分子式为: HgCl}_2$$

2. 25℃时将相同压力的5.0L氮气和15L氧气压缩到一个10.0L的真空容器中, 测得总压为150kPa, ①求两种气体的初始压力; ②求混合气体中氮和氧的分压; ③将温度上升到210℃, 容器的总压。

$$\text{解: (1) } \because P_1 V_1 = P_2 V_2 \quad \therefore P_1 = \frac{P_2 V_2}{V_1} = \frac{150 \times 10}{20} = 75 \text{ kPa}$$

$$(2) \quad P_{N_2} = X_{N_2} \cdot P = \frac{5}{20} \times 150 = 37.5 \text{ kPa}$$

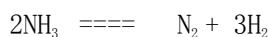
$$P_{O_2} = 150 - 37.5 = 112.5 \text{ kPa}$$

$$(3) \quad \frac{P_1}{T_1} = \frac{P_2}{T_2} \quad P_2 = \frac{150 \times (210 + 273)}{298} = 243 \text{ kPa}$$

3. 25℃, 1.47MPa 下把氨气通入容积为 1.00L 刚性密闭容器中, 在 350℃ 下用催化剂使部分氨分解为氮气和氢气, 测得总压为 5MPa, 求氨的解离度和各组分的摩尔分数和分压。

$$\text{解: } n_1 = \frac{P_1 V}{RT_1} = \frac{1.47 \times 10^3 \times 1}{8.314 \times 298} = 0.593 \text{ mol}$$

$$n_2 = \frac{P_2 V}{RT_2} = \frac{5 \times 10^3 \times 1}{8.314 \times (350 + 273)} = 0.965 \text{ mol}$$



$$n_{\text{平}} \quad 0.593 - 2x \quad x \quad 3x$$

$$0.593 - 2x + x + 4x = 0.965 \quad x = 0.186 \text{ mol}$$

$$\alpha = \frac{2 \times 0.186}{0.593} \times 100\% = 62.7\%$$

$$X_{\text{NH}_3} = \frac{0.593 - 2 \times 0.186}{0.965} = 0.229$$

$$P_{\text{NH}_3} = 0.229 \times 5 = 1.14 \text{ MPa}$$

$$X_{\text{H}_2} = \frac{0.186}{0.965} = 0.193$$

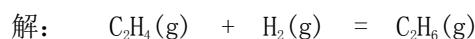
$$P_{\text{N}_2} = 0.193 \times 5 = 0.965 \text{ MPa}$$

$$X_{\text{N}_2} = 1 - 0.229 - 0.193 = 0.578$$

$$P_{\text{H}_2} = 5 \times 0.578 = 2.89 \text{ MPa}$$

4. 某乙烯和足量的氢气的混合气体的总压为6930Pa, 在铂催化剂下发生如下反应: $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) = \text{C}_2\text{H}_6(\text{g})$, 反应结束时温度降至原温度后测得总压为4530Pa。求原混合气体中乙烯

的摩尔分数。



$$P_{\text{始}} \quad X \quad \quad Y \quad \quad 0$$

$$P_{\text{终}} \quad 0 \quad \quad Y-X \quad \quad X$$

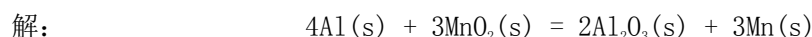
$$P_{\text{始}} = X+Y = 6930\text{Pa} \quad P_{\text{终}} = Y-X+X = 4530\text{Pa}$$

$$\therefore X_{\text{乙烯}} = \frac{X}{X+Y} = \frac{6930-4530}{6930} = 0.346$$

5. 反应 $\text{CaC}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) = \text{Ca}(\text{OH})_2(\text{s}) + \text{C}_2\text{H}_2(\text{g})$ 在 298K 下的标准摩尔热力学能变化量为 $-128.0\text{kJ}\cdot\text{mol}^{-1}$, 求该反应的标准摩尔焓变。

$$\begin{aligned} \text{解: } \Delta H^\circ &= \Delta U^\circ + P\Delta V = \Delta U^\circ + RT\sum \nu_B(\text{g}) \\ &= 128.0 + 8.314 \times 10^{-3} \times 298 \times 1 \\ &= -125.5 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

6. 已知 $\text{Al}_2\text{O}_3(\text{s})$ 和 $\text{MnO}_2(\text{s})$ 的标准摩尔生成焓为 $-1676\text{kJ}\cdot\text{mol}^{-1}$ 和 $-521\text{kJ}\cdot\text{mol}^{-1}$, 计算 1g 铝与足量 $\text{MnO}_2(\text{s})$ 反应产生的热量。

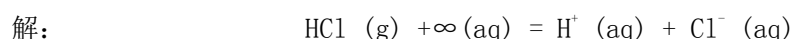


$$\Delta_f H_m^\circ / \text{kJ}\cdot\text{mol}^{-1} \quad 0 \quad -521 \quad -1676 \quad 0$$

$$\Delta_r H_m^\circ = 2 \times (-1676) - 3 \times (-521) = -1789\text{kJ}\cdot\text{mol}^{-1}$$

$$\therefore Q = \frac{1}{4 \times 27} \cdot (-1789) = -16.56\text{kJ}$$

7. 已知 $\text{Cl}^-(\text{aq})$ 的标准摩尔生成焓为 $-167.5\text{kJ}\cdot\text{mol}^{-1}$, 计算 1mol $\text{HCl}(\text{g})$ 溶于足量水中释放出多少热?



$$\Delta_f H_m^\circ / \text{kJ}\cdot\text{mol}^{-1} \quad -92.307 \quad 0 \quad -167.5$$

$$\Delta_r H_m^\circ = (-167.5) - (-92.307) = -75.2\text{kJ}\cdot\text{mol}^{-1}$$

8. 已知 N_2 、 NO 和 O_2 的解离焓分别为 $941.7\text{kJ}\cdot\text{mol}^{-1}$ 、 $631.8\text{kJ}\cdot\text{mol}^{-1}$ 和 $493.7\text{kJ}\cdot\text{mol}^{-1}$, 仅利用这些数据判断 NO 在常温常压下能否自发分解。

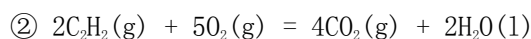
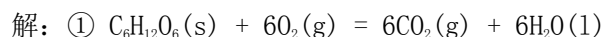


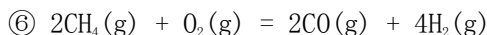
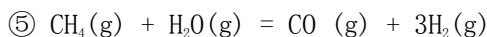
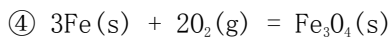
$$\Delta_r H_m^\circ = 2 \times 631.8 - 941.7 - 493.7 = -171.8\text{kJ}\cdot\text{mol}^{-1}$$

$\therefore$ 反应前后气体分子数相同, ΔS° 变化不大。

$\therefore$ 反应的 ΔG° 主要取决于 ΔH° , 故 $\Delta G^\circ < 0$, 反应自发。

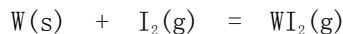
9. 下列反应是熵增还是熵减反应? ①葡萄糖燃烧; ②乙炔燃烧; ③碳酸氢钠分解; ④铁丝燃烧; ⑤甲烷与水蒸气反应生成水煤气; ⑥甲烷与氧气反应生成合成气。





$$\textcircled{1}、\textcircled{3}、\textcircled{5}、\textcircled{6} \quad \Delta S > 0 \quad \textcircled{2}、\textcircled{4} \quad \Delta S < 0$$

10. 碘钨灯灯内发生如下可逆反应:



$$\Delta_f G_m^\circ / \text{kJ} \cdot \text{mol}^{-1} \quad 0 \quad 19.327 \quad -8.37$$

$$S_m^\circ / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad 33.5 \quad 260.69 \quad 251$$

① 求623K时, 上式反应的 $\Delta_r G_m^\circ$

② 估算 $\text{WI}_2(\text{g})$ 在钨丝上分解所需的最低温度。

$$\text{解: ①} \quad \Delta_r G_{298}^\circ = -8.37 - 19.327 = -27.697 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_{298}^\circ = 251 - 33.5 - 260.69 = -43.19 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta_r H_{298}^\circ = \Delta_r G_{298}^\circ + 298 \Delta_r S_{298}^\circ$$

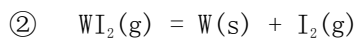
$$= -27.697 + 298 \times 10^{-3} \times (-43.19)$$

$$= -40.568 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_{623}^\circ \approx \Delta_r H_{298}^\circ - 623 \Delta_r S_{298}^\circ$$

$$= -40.568 - 623 \times (-43.19) \times 10^{-3}$$

$$= -13.66 \text{ kJ} \cdot \text{mol}^{-1}$$



$$\Delta_r H_{298}^\circ = 40.568 \text{ kJ} \cdot \text{mol}^{-1} \quad \Delta_r S_{298}^\circ = 43.19 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$T = \frac{40.568 \times 1000}{43.19} = 939.3 \text{ K}$$

11. 用凸透镜聚集太阳光加热分解倒置在液汞上的装满液汞试管内的氧化汞, 使其分解。估算: 使氧气的压力达到标态压力和1kPa所需的最低温度, 并估计为使氧气压力达1kPa, 试管的长度至少为多长?



$$\Delta_f H_m^\circ / \text{kJ} \cdot \text{mol}^{-1} \quad -90.46 \quad 0 \quad 0$$

$$S_m^\circ / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad 71.1 \quad 76.02 \quad 205.138$$

$$\Delta_r H_{298}^\circ = 90.46 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_{298}^\circ = \frac{1}{2} \times 205.138 + 76.02 - 71.1 = 107.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

① 标态下的分解温度

$$T = \frac{90460}{107.5} = 841.5 \text{ K}$$

② 1kPa下的分解温度

$$T = \frac{90460}{107.5 - 8.314 \ln\left(\frac{1}{100}\right)^{1/2}} = 714.3 \text{ K}$$

试管的长度应大于760mm。

12. 石灰窑的碳酸钙需加热到多少度才能分解? 若在一个用真空泵不断抽真空的系统内, 系统内的气体压力保持10Pa, 加热到多少度才能分解?

解: $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

$$\Delta_f H_m^\circ / \text{kJ} \cdot \text{mol}^{-1} \quad -1206.92 \quad -635.09 \quad -393.509$$

$$S_m^\circ / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad 92.9 \quad 39.75 \quad 213.74$$

$$\Delta_r H_{298}^\circ = (-393.509) + (-635.09) - (-1206.92) = 178.321 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_{298}^\circ = 213.74 + 39.75 - 92.9 = 160.59 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

①标态下的分解温度

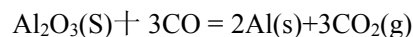
$$T = \frac{178321}{160.59} = 1110.4 \text{ K}$$

②10Pa下的分解温度

$$T = \frac{\Delta H^\theta}{\Delta S^\theta - R \ln J} = \frac{178321}{160.59 - 8.314 \ln\left(\frac{0.010}{100}\right)} = 751.9 \text{ K}$$

13. 试用热力学原理说明用一氧化碳还原三氧化二铝是否可行?

解: 一氧化碳还原氧化铝的反应方程式为:



$$298\text{K}: \Delta_r G^\theta = 2\Delta_f G^\theta(\text{Al}, \text{s}) + 3\Delta_f G^\theta(\text{CO}_2, \text{g}) - \Delta_f G^\theta(\text{Al}_2\text{O}_3, \text{s}) - 3\Delta_f G^\theta(\text{CO}, \text{g})$$

$$= 0 + 3 \times (-394) - (-1582) - 3 \times (-137) = 811 \text{ kJ} \cdot \text{mol}^{-1}$$

反应在常温下不能自发进行。

$$298\text{K}: \Delta_r H^\theta = 2\Delta_f H^\theta(\text{Al}, \text{s}) + 3\Delta_f H^\theta(\text{CO}_2, \text{g}) - \Delta_f H^\theta(\text{Al}_2\text{O}_3, \text{s}) - 3\Delta_f H^\theta(\text{CO}, \text{g})$$

$$= 0 + 3 \times (-393) - (-1676) - 3 \times (-110)$$

$$= 827 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S^\theta = 2S^\theta(\text{Al}, \text{s}) + 3S^\theta(\text{CO}_2, \text{g}) - S^\theta(\text{Al}_2\text{O}_3, \text{s}) - 3S^\theta(\text{CO}, \text{g})$$

$$= 2 \times 28.3 + 3 \times 214 - 50.9 - 3 \times 198$$

$$= 53.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

由于 $\Delta_r S^\theta > 0$, 温度升高时 $\Delta_r G^\theta$ 减小, 故反应在高温下可自发进行。自发进行的温度是

$$T \geq \frac{\Delta_r H^\theta}{\Delta_r S^\theta} = \frac{827 \times 10^3}{53.7} = 15400 \text{ K}$$

反应自发进行的温度高于 15400K, 理论上可行, 但目前实际上很难达到这样高的温度。