

第5章 化学平衡

基本概念

1. (4)

2. =

3. 各反应物的配料比等于反应方程式中各物质的计量系数之比。例如合成氨反应中，氮气和氢气的配料比应为1:3。

4. 平衡原理和平衡移动， $\sum_B \nu_B < 0$ ，惰性气体增加将降低产物的数量，所以定期放空。

5. $K_p = p_{\text{H}_2\text{O}}^{\text{eq}} \cdot p_{\text{CO}_2}^{\text{eq}}$; $K_p = p_{\text{O}_2}^{\text{eq}}$; $K_p = p_{\text{H}_2\text{O}}^{\text{eq}} / p_{\text{H}_2}^{\text{eq}}$; $K_p = (p_{\text{O}_2}^{\text{eq}})^{-1/2}$

6. 11.9Pa

7. 正向

8. $K^\circ(2)/K^\circ(1)$, $\Delta_r G_m^\circ(2) - \Delta_r G_m^\circ(1)$

9. 在 T_1 到 T_2 的范围内， $\Delta_r H_m^\circ$ 为常数或 $\Delta_r C_{p,m}^\circ \approx 0$ 。

10. $\Delta S - \int_A^B \frac{dQ}{T_{\text{环}}} \geq 0$, $\sum_{\alpha=1}^{\pi} \sum_{i=1}^K \mu_i^{(\alpha)} dn_i^{(\alpha)} \leq 0$, $\Delta_r G_m = RT \ln(J/K)$ 。

计算题

1. 解:

CO 在空气中燃烧，开始时 CO、O₂、N₂ 的量分别为 1、1、3.76 mol，平衡时 CO、O₂、CO₂、N₂、 $\sum_B n_B^{\text{eq}}$ 的量分别为(1-x)、(1-0.5x)、x、3.76、(5.76-0.5x) mol。

$$K_p = K^\circ(p^\circ)^{\sum_B \nu_B} = [6.401 \times (100)^{-0.5}] \text{kPa}^{-0.5} = 0.6401 \text{kPa}^{-0.5}$$

$$K_p = K_n \left[\frac{p}{\sum_B n_B^{\text{eq}}} \right]^{\sum_B \nu_B}, \quad \frac{x}{(1-x)(1-0.5x)^{0.5}} \left(\frac{101.325}{5.76-0.5x} \right)^{-0.5} = 0.6401$$

$\therefore x = 0.691$ ，即 CO 的转化率为 69.1%。

CO 在氧气中燃烧，开始时 CO、O₂ 的量分别为 1、1mol，平衡时 CO、O₂、CO₂、 $\sum_B n_B^{\text{eq}}$ 的量分别为(1-x)、(1-0.5x)、x、(2-0.5x) mol，

$$\frac{x}{(1-x)(1-0.5x)^{0.5}} \left(\frac{101.325}{2-0.5x} \right)^{-0.5} = 0.6401,$$

$\therefore x = 0.798$ ，故 CO 的转化率为 79.8%。

惰性气体 N₂ 增加，将降低反应的转化率。

2. 解:

$$\Delta_r C_{p,m}^\ominus = (1 \times 53.97 - 1 \times 19.87 - 2 \times 29.41) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -24.72 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$298\text{K 时}, \Delta_r H^\ominus = [1 \times (-74.81)] \text{ kJ} = -74.81 \text{ kJ}$$

$$\Delta_r S^\ominus = (1 \times 186.264 - 1 \times 5.740 - 2 \times 130.684) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -80.844 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$1000\text{K 时}, \Delta_r H_m^\ominus = [-74.81 + (-24.72) \times (1000 - 298) \times 10^{-3}] \text{ kJ} \cdot \text{mol}^{-1} = -92.16 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_m^\ominus = \left[-80.844 + (-24.72) \ln \frac{1000}{298} \right] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -110.77 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\ominus = [-92.16 - 1000 \times (-110.77) \times 10^{-3}] \text{ kJ} \cdot \text{mol}^{-1} = 18.61 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln K^\ominus = -\frac{\Delta_r G_m^\ominus}{RT} = -\frac{18.61 \times 10^3}{8.3145 \times 1000} = -2.238, \quad K^\ominus = 0.1066,$$

$$K_p = K^\ominus (p^\ominus)^{\sum_B \nu_B} = 0.1066 \times (10^5 \text{ Pa})^{-1} = 1.066 \times 10^{-6} \text{ Pa}^{-1}$$

$$J_p = \frac{py_{\text{CH}_4}}{(py_{\text{H}_2})^2} = \frac{0.10}{101325 \times 0.80^2} \text{ Pa}^{-1} = 1.542 \times 10^{-6} \text{ Pa}^{-1}$$

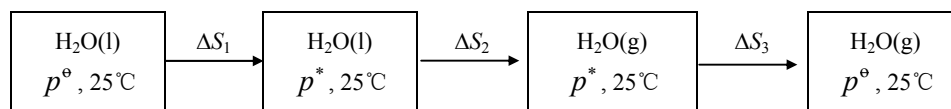
$\therefore J_p > K_p$, \therefore 反应不能正向进行。

设反应正向进行时混合气体的压力为 p , 则

$$K_p = \frac{py_{\text{CH}_4}}{(py_{\text{H}_2})^2} = \frac{y_{\text{CH}_4}}{py_{\text{H}_2}^2}$$

$$\therefore p = \frac{y_{\text{CH}_4}}{K_p y_{\text{H}_2}^2} = \frac{0.10}{1.066 \times 10^{-6} \times 0.80^2} \text{ Pa} = 146.6 \text{ kPa}$$

3. 解:



$$\Delta S_1 \approx 0$$

$$\Delta S_2 = \frac{\Delta H_m}{T} = \frac{[-241.818 - (-285.830)] \times 10^3}{25 + 273.15} \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 147.62 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta S_3 = R \ln \frac{p^*}{p^\ominus} = \left(8.3145 \ln \frac{3.167 \times 10^3}{10^5} \right) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -28.70 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1},$$

$$\Delta S = 118.92 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$S_{\text{m(H}_2\text{O,g)}}^\ominus = S_{\text{m(H}_2\text{O,l)}}^\ominus + \Delta S = (69.91 + 118.92) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 188.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

4. 解:

$$\ln K^\ominus = \int \frac{\Delta_r H_m^\ominus}{RT^2} dT = \frac{1}{R} \int \left\{ \left[\frac{122675 + 38.28(T/K) - 53.35 \times 10^{-3}(T/K)^2}{T^2} \right] \text{J} \cdot \text{mol}^{-1} \right\} dT$$

$$= \frac{1}{8.3145} \left[-\frac{122675}{T/K} + 38.28 \ln(T/K) - 53.35 \times 10^{-3}(T/K) \right] + C$$

$$\lg K^\ominus = -\frac{6407}{T/K} + 4.604 \lg(T/K) - 2.786 \times 10^{-3}(T/K) + C'$$

$$298.15\text{K 时}, \lg K^\ominus = -\frac{\Delta_r G_m^\ominus}{RT \ln 10} = -\frac{29623}{8.3145 \times 298.15 \ln 10} = -5.190$$

得 $C' = 5.737$

$$\therefore \lg K^\ominus = -\frac{6407}{T/K} + 4.604 \lg(T/K) - 2.786 \times 10^{-3}(T/K) + 5.737$$

$$K^\ominus = \left(\frac{p/2}{p^\ominus} \right)^2 = \frac{1}{4} \left(\frac{p}{p^\ominus} \right)^2, \quad \lg K^\ominus = 2 \lg \left(\frac{p}{p^\ominus} \right) - \lg 4$$

$$\therefore \lg \left(\frac{p}{p^\ominus} \right) = \frac{1}{2} (\lg K^\ominus + \lg 4) = -\frac{3204}{T/K} + 2.302 \lg(T/K) - 1.393 \times 10^{-3}(T/K) + 3.170$$

$$T = 343\text{K}, \quad \lg \left(\frac{p}{p^\ominus} \right) = -0.813, \quad p = 15.4 \text{ kPa}$$

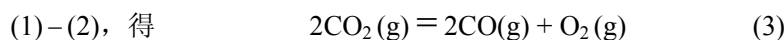
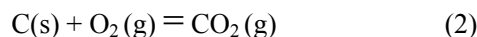
5. 解:

$$\text{反应 } \text{CO}_2(\text{g}) + \text{C}(\text{s}) = 2\text{CO}(\text{g}), \quad K^\ominus = \frac{(py_{\text{CO}}/p^\ominus)^2}{py_{\text{CO}_2}/p^\ominus} = \frac{p}{p^\ominus} \cdot \frac{y_{\text{CO}}^2}{y_{\text{CO}_2}}$$

$$1073\text{K 时}, K^\ominus(T_1) = \frac{260.41}{10^5 \times 10^{-3}} \times \frac{(1-0.2645)^2}{0.2645} = 5.326$$

$$1173\text{K 时}, K^\ominus(T_2) = \frac{233.05}{10^5 \times 10^{-3}} \times \frac{(1-0.0692)^2}{0.0692} = 29.18$$

$$\Delta_r H_m^\ominus = \frac{RT_2 T_1}{T_2 - T_1} \ln \frac{K^\ominus(T_2)}{K^\ominus(T_1)} = \left(\frac{8.3145 \times 1173 \times 1073}{1173 - 1073} \ln \frac{29.18}{5.326} \right) \text{J} \cdot \text{mol}^{-1} = 178.0 \text{ kJ} \cdot \text{mol}^{-1}$$



故对于反应 (3),

$$\Delta_r H_m^\ominus(T_2) = [178.0 - (-393.5)] \text{kJ} \cdot \text{mol}^{-1} = 571.5 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r G_m^\ominus(T_2) = -RT_2 \ln K^\ominus(T_2) = -[8.3145 \times 1173 \ln(1.27 \times 10^{-16})] \text{ J} \cdot \text{mol}^{-1} = 357.0 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned}\Delta_r S_m^\ominus(T_2) &= \frac{\Delta_r H_m^\ominus(T_2) - \Delta_r G_m^\ominus(T_2)}{T_2} = \frac{(571.5 - 357.0) \times 10^3}{1173} \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= 182.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$