

第 2 章 化学反应速率和化学平衡

第 2 章习题: 1, 2, 3, 4, 5, 6, 7, 9, 10, 12, 15

1.

解: (1) $v = k[c_{NO}]^2[c_{Br_2}]$

(2) 该反应的总级数是 3

(3) 其它条件不变, 如果将容器的体积增加到原来的 2 倍, 则浓度降低为原来的 1/2, 反应速率将为原来的 1/8。

(4) 如果容器体积不变, 而将 NO 的浓度增加到原来的 3 倍, 反应速率将为原来的 9 倍。

2.

解:
$$\ln \frac{v_{T_2}}{v_{T_1}} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) = \frac{53.59 \times 10^3}{8.314} \left(\frac{310 - 300}{310 \times 300} \right) = 0.693$$

$$\therefore \frac{v_{T_2}}{v_{T_1}} = 2$$

温度自 300K 升高到 310K 时反应速率增加到原来的两倍。

3.

解:
$$\ln \frac{k_{T_2}}{k_{T_1}} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) = \frac{101 \times 10^3}{8.314} \left(\frac{400 - 300}{400 \times 300} \right) = 10.123$$

$$\therefore k_{T_2} = 2.492 \times 10^4 \times k_{T_1} = 2.492 \times 10^4 \times 2.80 \times 10^{-5} = 0.698 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$$

4.

解: $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ 的标准平衡常数 $K^\ominus = K_1^\ominus / K_2^\ominus$, 在不同温度下:

T/K	973	1073	1173	1273
K^\ominus	0.618	0.905	1.29	1.66

由计算结果可知, 随着温度 T 的升高, 反应的标准平衡常数 K^\ominus 增大, 故该反应为吸热反应。

5.

解: (1)
$$\text{Fe}_3\text{O}_4 + 4\text{H}_2 = 3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g})$$

$$\Delta_f H_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad -1117.1 \quad 0 \quad 0 \quad -241.84$$

$$S_m^\ominus / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad 146.4 \quad 130.70 \quad 27.1 \quad 188.85$$

$$\begin{aligned} \Delta_r H_m^\ominus &= 4 \Delta_f H_m^\ominus (\text{H}_2\text{O}, \text{g}) - \Delta_f H_m^\ominus (\text{Fe}_3\text{O}_4, \text{s}) \\ &= [4 \times (-241.84) - (-1117.1)] \text{kJ} \cdot \text{mol}^{-1} = 149.74 \text{kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r S_m^\ominus &= 4 S_m^\ominus (\text{H}_2\text{O}, \text{g}) + 3 S_m^\ominus (\text{Fe}, \text{s}) - S_m^\ominus (\text{Fe}_3\text{O}_4, \text{s}) - S_m^\ominus (\text{H}_2, \text{g}) \\ &= [4 \times 188.85 + 3 \times 27.1 - 146.4 - 4 \times 130.70] \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 167.5 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

$$\therefore \ln K^\ominus = -\frac{\Delta_r H_m^\ominus}{RT} + \frac{\Delta_r S_m^\ominus}{R},$$

$$\therefore \ln K^\ominus = -\frac{149740}{8.314 \times 500} + \frac{167.5}{8.314} = -15.87,$$

$$\text{解得: } K^\ominus = 1.28 \times 10^{-7}$$



$$\Delta_f H_m^\ominus / \text{kJ} \cdot \text{mol}^{-1} \quad -110.54 \quad 0 \quad -393.51$$

$$S_m^\ominus / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad 198.01 \quad 205.14 \quad 213.79$$

$$\begin{aligned} \Delta_r H_m^\ominus &= 2 \Delta_f H_m^\ominus (\text{CO}_2, \text{g}) - 2 \Delta_f H_m^\ominus (\text{CO}, \text{g}) \\ &= [2 \times (-393.51) - 2 \times (-110.54)] \text{kJ} \cdot \text{mol}^{-1} = -565.94 \text{kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r S_m^\ominus &= 2 S_m^\ominus (\text{CO}_2, \text{g}) - 2 S_m^\ominus (\text{CO}, \text{g}) - S_m^\ominus (\text{O}_2, \text{g}) \\ &= [2 \times 213.79 - 2 \times 198.01 - 205.14] \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = -173.58 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

$$\therefore \ln K^\ominus = -\frac{\Delta_r H_m^\ominus}{RT} + \frac{\Delta_r S_m^\ominus}{R},$$

$$\therefore \ln K^\ominus = -\frac{-565940}{8.314 \times 500} + \frac{-173.58}{8.314} = 115.26,$$

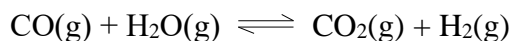
$$\text{解得: } K^\ominus = 1.14 \times 10^{50}$$

6.

$$\text{解: } \Delta_r G_m^\ominus = -RT \ln K^\ominus = (-8.314 \times 3500 \times \ln 8.28) \times 10^{-3} \text{kJ} \cdot \text{mol}^{-1} = -61.51 \text{kJ} \cdot \text{mol}^{-1}$$

7.

解: 设反应开始时 CO 的物质的量为 1mol, H₂O 的物质的量为 x mol



开始时物质的量 /mol 1 x 0 0

变化的物质的量 /mol -0.90 -0.90 0.90 0.90

平衡时物质的量 /mol 0.10 $x-0.90$ 0.90 0.90

平衡时总物质的量 /mol $n_{\text{总}}=0.10+(x-0.90)+0.90+0.90=x+1.0$

平衡分压: $p_{\text{CO}_2}=p_{\text{H}_2}=\frac{0.9}{x+1.0}\times p_{\text{总}}$, $p_{\text{CO}}=\frac{0.1}{x+1.0}\times p_{\text{总}}$, $p_{\text{H}_2\text{O}}=\frac{x-0.9}{x+1.0}\times p_{\text{总}}$

$$K^{\ominus} = \frac{(p_{\text{CO}_2}/p^{\ominus}) \times (p_{\text{H}_2}/p^{\ominus})}{(p_{\text{CO}}/p^{\ominus}) \times (p_{\text{H}_2\text{O}}/p^{\ominus})} = \frac{\left(\frac{0.9}{x+1.0} \times \frac{p_{\text{总}}}{p^{\ominus}}\right)^2}{\left(\frac{0.1}{x+1.0} \times \frac{p_{\text{总}}}{p^{\ominus}}\right) \times \left(\frac{x-0.9}{x+1.0} \times \frac{p_{\text{总}}}{p^{\ominus}}\right)} = \frac{0.9 \times 0.9}{0.10 \times (x-0.9)} = 2.6$$

$\therefore x=4.02 \text{ mol}$, 即 $\text{CO}(\text{g})$ 和 $\text{H}_2\text{O}(\text{g})$ 的摩尔比为 1:4。

9.

解: $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$

开始时物质的量 /mol 1.0 0.667 1.67

变化的物质的量 /mol -0.37 0.185 0.87

平衡时物质的量 /mol 0.63 0.482 2.04

平衡时总物质的量 /mol $0.63 + 0.482 + 2.04 = 3.152$

平衡分压: $p_{\text{NO}} = \frac{n_{\text{NO}}RT}{V} = \frac{0.63 \times 8.314 \times 603}{10 \times 10^{-3}} = 315.84 \text{ kPa}$

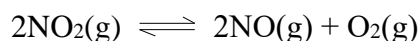
$$p_{\text{Cl}_2} = \frac{n_{\text{Cl}_2}RT}{V} = \frac{0.482 \times 8.314 \times 603}{10 \times 10^{-3}} = 241.64 \text{ kPa}$$

$$p_{\text{NOCl}} = \frac{n_{\text{NOCl}}RT}{V} = \frac{2.04 \times 8.314 \times 603}{10 \times 10^{-3}} = 1022.72 \text{ kPa}$$

$$K^{\ominus} = \frac{(p_{\text{NOCl}}/p^{\ominus})^2}{(p_{\text{NO}}/p^{\ominus}) \times (p_{\text{Cl}_2}/p^{\ominus})} = \frac{\left(\frac{1022.72}{100}\right)^2}{\left(\frac{315.84}{100}\right) \times \left(\frac{241.64}{100}\right)} = 4.34$$

10.

解: 设反应开始时 NO_2 的物质的量为 1mol, 则:



开始时物质的量 /mol 1 0 0

变化的物质的量 /mol -0.56 0.56 0.28

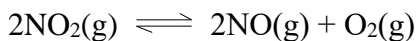
平衡时物质的量 /mol 0.44 0.56 0.28

平衡时总物质的量 /mol $0.44+0.56+0.28=1.28$

平衡分压: $p_{\text{NO}_2} = \frac{0.44}{1.28} \times 100 \text{ kPa}$, $p_{\text{NO}} = \frac{0.56}{1.28} \times 100 \text{ kPa}$, $p_{\text{O}_2} = \frac{0.28}{1.28} \times 100 \text{ kPa}$

$$\therefore K^{\ominus} = \frac{(p_{\text{NO}} / p^{\ominus})^2 \times (p_{\text{O}_2} / p^{\ominus})}{(p_{\text{NO}_2} / p^{\ominus})^2} = \frac{(\frac{0.56}{1.28})^2 \times (\frac{0.28}{1.28})}{(\frac{0.44}{1.28})^2} = 0.354$$

设若要使 NO₂ 转化率增加到 80%，平衡时的压力为 p ，反应开始时 NO₂ 的物质的量为 1mol 则：



开始时物质的量 /mol	1	0	0
变化的物质的量 /mol	-0.80	0.80	0.40
平衡时物质的量 /mol	0.20	0.80	0.40
平衡时总物质的量 /mol	0.20+0.80+0.40=1.40		

$$\text{平衡分压: } p_{\text{NO}_2} = \frac{0.20}{1.40} \times p, \quad p_{\text{NO}} = \frac{0.80}{1.40} \times p, \quad p_{\text{O}_2} = \frac{0.40}{1.40} \times p$$

$$\therefore K^{\ominus} = \frac{(p_{\text{NO}} / p^{\ominus})^2 \times (p_{\text{O}_2} / p^{\ominus})}{(p_{\text{NO}_2} / p^{\ominus})^2} = \frac{(\frac{0.80}{1.40})^2 \times (\frac{0.40}{1.40})}{(\frac{0.20}{1.40})^2} \times \frac{p}{p^{\ominus}} = 0.354$$

$$\therefore p = 7.74 \text{ kPa} \quad (7.85 \text{ kPa}, K^{\ominus} = 0.359)$$

12.

解：	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
开始时物质的量 /mol	0.04		0		0.20
变化的物质的量 /mol	-0.04×0.51		0.04×0.51		0.04×0.51
平衡时物质的量 /mol	0.0196		0.0204		0.2204
平衡时总物质的量 /mol	0.0196+0.0204+0.2204=0.2604 mol				
平衡分压：					

$$p_{\text{PCl}_5} = \frac{0.0196}{0.2604} \times 200 \text{ kPa},$$

$$p_{\text{PCl}_3} = \frac{0.0204}{0.2604} \times 200 \text{ kPa},$$

$$p_{\text{Cl}_2} = \frac{0.2204}{0.2604} \times 200 \text{ kPa}$$

$$K^{\ominus} = \frac{(p_{\text{PCl}_3} / p^{\ominus}) \times (p_{\text{Cl}_2} / p^{\ominus})}{(p_{\text{PCl}_5} / p^{\ominus})} = \frac{(\frac{0.0204}{0.2604}) \times (\frac{0.2204}{0.2604})}{(\frac{0.0196}{0.2604})} \times \frac{200}{100} = 1.76$$

15.

$$\text{解: } \because \ln \frac{K_2^\ominus}{K_1^\ominus} = \frac{\Delta_r H_m^\ominus}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) = \frac{-92.20 \times 10^3}{8.314} \left(\frac{573 - 473}{573 \times 473} \right) = -4.09$$

$$\therefore K_2^\ominus = e^{-4.09} \times 0.44 = 7.35 \times 10^{-3}$$