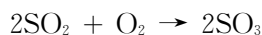


第 1 章 化学反应中的质量关系与能量关系

1.1 化学反应中的质量关系

例题 1.1 利用化学反应计量式作物料衡算

题：某硫酸厂以黄铁矿（ FeS_2 ）为原料生产硫酸（ H_2SO_4 ），其基本反应为：



现需生产 $1 \times 10^4 \text{ t}$ 98% 的硫酸，问需投入含硫 40% 的黄铁矿多少吨？

解：假设需要的黄铁矿质量为 m ，根据反应式，所有 S 元素都转移到了硫酸中，根据 S 元素平衡：

$$\frac{m \times 40\%}{32.07 \text{ g/mol}} = \frac{1 \times 10^4 \text{ t} \times 98\%}{98.09 \text{ g/mol}} \rightarrow \text{解得 } m \approx 8000 \text{ t} \quad \therefore \text{共需黄铜矿约 } 8000 \text{ t}$$

1.2 化学反应中的能量关系

例题 1.2 利用生成焓计算反应焓

题：计算等压反应： $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ 的 $\Delta_r H_m^\ominus$ ，各物质的 $\Delta_f H_m^\ominus$ 如下：

	$\text{NH}_3(\text{g})$	$\text{O}_2(\text{g})$	$\text{NO}(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$\Delta_f H_m^\ominus (\text{kJ} \cdot \text{mol}^{-1})$	-46.11	0	90.25	-241.82

解：由 $\Delta_r H_m^\ominus = \sum_B \nu_B \Delta_f H_{m,B}^\ominus$ ：

$$\begin{aligned}\Delta_r H_m^\ominus &= 4\Delta_f H_m^\ominus(\text{NO}, \text{g}) + 6\Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{g}) - 4\Delta_f H_m^\ominus(\text{NH}_3, \text{g}) - 5\Delta_f H_m^\ominus(\text{O}_2, \text{g}) \\ &= 4 \times 90.25 + 6 \times (-241.82) - 4 \times (-46.11) - 5 \times 0 \\ &= -905.48 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

例题 1.3 生成焓、反应焓与盖斯定律

题：已知以下反应的 $\Delta_r H_m^\ominus$ ，求 $\Delta_f H_m^\ominus(\text{CuO}, \text{s})$

	反应	$\Delta_r H_m^\ominus (\text{kJ} \cdot \text{mol}^{-1})$
①	$2\text{Cu}_2\text{O}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 4\text{CuO}(\text{s})$	-292
②	$\text{CuO}(\text{s}) + \text{Cu}(\text{s}) \rightarrow \text{Cu}_2\text{O}(\text{s})$	-11.3

解：方法一：由生成焓的定义 反应 ③ $\text{O}_2(\text{g}) + 2\text{Cu}(\text{s}) \rightarrow 2\text{CuO}(\text{s})$ $\Delta_r H_m^\ominus(3) = 2\Delta_f H_m^\ominus(\text{CuO}, \text{s})$

由盖斯定律 ③ = ① + 2 × ② $\therefore \Delta_r H_m^\ominus(3) = \Delta_r H_m^\ominus(1) + 2\Delta_r H_m^\ominus(2)$

$$\therefore \Delta_f H_m^\ominus(\text{CuO}, \text{s}) = \frac{\Delta_r H_m^\ominus(1) + 2\Delta_r H_m^\ominus(2)}{2} = \frac{-292 + 2 \times (-11.3)}{2} = -157.3 \text{ kJ} \cdot \text{mol}^{-1}$$

方法二：反应 ① $\Delta_r H_m^\ominus(1) = 4\Delta_f H_m^\ominus(\text{CuO}, \text{s}) - 2\Delta_f H_m^\ominus(\text{Cu}_2\text{O}, \text{s}) - \Delta_f H_m^\ominus(\text{O}_2, \text{g})$

反应 ② $\Delta_r H_m^\ominus(2) = \Delta_f H_m^\ominus(\text{Cu}_2\text{O}, \text{s}) - 2\Delta_f H_m^\ominus(\text{CuO}, \text{s}) - \Delta_f H_m^\ominus(\text{Cu}, \text{s})$

单质生成焓为 0，因此将两式联立即可解出 $\Delta_f H_m^\ominus(\text{CuO}, \text{s})$

第2章 化学反应的方向、速率和限度

例题 2.1 标准摩尔反应熵变的计算

题：计算反应 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ 的 $\Delta_r S_m^\ominus$

解：
$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$$

$$S_m^\ominus / (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \quad 248.22 \quad 205.138 \quad 256.76$$

$$\begin{aligned} \therefore \Delta_r S_m^\ominus &= 2S_m^\ominus(\text{SO}_3) - 2S_m^\ominus(\text{SO}_2) - S_m^\ominus(\text{O}_2) \\ &= 2 \times 256.76 - 2 \times 248.22 - 205.138 = -188.06 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

例题 2.2 标准摩尔反应吉布斯自由能变的计算

题：试判断在 298.15K、标准态下，反应 $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ 能否自发进行？

	$\text{CaCO}_3(\text{s})$	$\text{CaO}(\text{s})$	$\text{CO}_2(\text{g})$
$\Delta_f H_m^\ominus (\text{kJ} \cdot \text{mol}^{-1})$	-1128.79	-604.03	-394.359
$S_m^\ominus (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	92.9	39.75	213.74
$\Delta_f G_m^\ominus (\text{kJ} \cdot \text{mol}^{-1})$	-1206.92	-635.09	-393.509

解：方法一：使用 $\Delta_r G_m^\ominus = \Delta_r H_m^\ominus - T\Delta_r S_m^\ominus$

$$\begin{aligned} \Delta_r H_m^\ominus &= \Delta_f H_m^\ominus(\text{CaO}) + \Delta_f H_m^\ominus(\text{CO}_2) - \Delta_f H_m^\ominus(\text{CaCO}_3) \\ &= (-635.09) + (-393.509) - (-1206.92) \\ &= 178.32 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r S_m^\ominus &= S_m^\ominus(\text{CaO}) + S_m^\ominus(\text{CO}_2) - S_m^\ominus(\text{CaCO}_3) \\ &= (39.75 + 213.74) - 92.9 \\ &= 160.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

$$\Delta_r G_m^\ominus(298.15 \text{ K}) = \Delta_r H_m^\ominus(298.15 \text{ K}) - 298.15 \text{ K} \times \Delta_r S_m^\ominus(298.15 \text{ K})$$

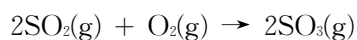
方法二：使用 $\Delta_r G_m^\ominus = \sum \Delta_f G_{m,B}^\ominus$

$$\begin{aligned} \Delta_r G_m^\ominus &= \Delta_f G_m^\ominus(\text{CaO}) + \Delta_f G_m^\ominus(\text{CO}_2) - \Delta_f G_m^\ominus(\text{CaCO}_3) \\ &= (-604.03) + (-394.359) - (-1206.92) \\ &= 130.40 \text{ kJ} \cdot \text{mol}^{-1} > 0 \end{aligned}$$

\therefore 在 298.15K、标准态下，反应不能自发分解

例题 2.3 非标准摩尔反应吉布斯自由能变的计算

题：计算 723K、非标准态下，下列反应的 $\Delta_r G_m$ ，并判断反应自发进行的方向。



$$\text{分压/Pa} \quad 1.0 \times 10^4 \quad 1.0 \times 10^4 \quad 1.0 \times 10^8$$

	$\text{SO}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{SO}_3(\text{g})$
$\Delta_f H_m^\ominus (\text{kJ} \cdot \text{mol}^{-1})$	248.22	205.138	256.76

$S_m^\ominus (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	-296.83	0	-395.72
--	---------	---	---------

解: $\Delta_r H_m^\ominus = 2 \Delta_f H_m^\ominus(\text{SO}_3) - [2 \Delta_f H_m^\ominus(\text{SO}_2) + \Delta_f H_m^\ominus(\text{O}_2)]$
 $= [2 \times (-395.72) - 2 \times (-296.830)] = -197.78 \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta_r S_m^\ominus = 2 S_m^\ominus(\text{SO}_3) - [2 S_m^\ominus(\text{SO}_2) + S_m^\ominus(\text{O}_2)]$
 $= 2 \times 256.76 - [2 \times 248.22 + 205.138] = -188.06 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
 $\Delta_r G_m^\ominus(723\text{K}) = \Delta_r H_m^\ominus(723\text{K}) - T \Delta_r S_m^\ominus(723\text{K}) \approx \Delta_r H_m^\ominus(298\text{K}) - T \Delta_r S_m^\ominus(298\text{K})$
 $= [(-197.78 \times 10^3) - 723 \times (-188.06)] = -61813 \text{ J} \cdot \text{mol}^{-1}$
 $RT \ln J = 8.314 \times 723 \ln \frac{[p(\text{SO}_3)/p^\ominus]^2}{[p(\text{SO}_2)/p^\ominus]^2 [p(\text{O}_2)/p^\ominus]}$
 $= 8.314 \times 723 \ln \frac{[1.0 \times 10^8 / 1.0 \times 10^5]^2}{[1.0 \times 10^4 / 1.0 \times 10^5]^2 [1.0 \times 10^4 / 1.0 \times 10^5]} = 124590.5 \text{ J} \cdot \text{mol}^{-1}$
 $\therefore \Delta_r G_m(723\text{K}) = \Delta_r G_m^\ominus(723\text{K}) + RT \ln J = (-61813 + 124590.5) = 62.777 \text{ kJ} \cdot \text{mol}^{-1} > 0$
 \therefore 反应自发向左进行

例题 2.4 实验平衡常数的计算

题: 反应 $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$ 1000K 达平衡时, $c(\text{CO}) = c(\text{H}_2) = 7.6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$
 $c(\text{H}_2\text{O}) = 4.6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, 平衡分压 $p(\text{CO}) = p(\text{H}_2) = 6.3 \times 10^4 \text{ Pa}$, $p(\text{H}_2\text{O}) = 3.8 \times 10^4 \text{ Pa}$
 试计算该反应的 K_c 、 K_p

解: $K_c = \frac{c(\text{CO}) \cdot c(\text{H}_2)}{c(\text{H}_2\text{O})} = \frac{7.6 \times 10^{-3} \times 7.6 \times 10^{-3}}{4.6 \times 10^{-3}} \frac{(\text{mol} \cdot \text{L}^{-1})^2}{\text{mol} \cdot \text{L}^{-1}} = 1.2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$
 $K_p = \frac{p(\text{CO}) \cdot p(\text{H}_2)}{p(\text{H}_2\text{O})} = \frac{6.3 \times 10^4 \times 6.3 \times 10^4}{3.8 \times 10^4} \frac{(\text{Pa})^2}{\text{Pa}} = 1.0 \times 10^5 \text{ Pa}$

例题 2.5 标准平衡常数的计算

题: 计算反应: $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$ 温度为 298.15K 和 1173K 时的标准平衡常数

	C(s)	CO ₂ (g)	CO(g)
$\Delta_f H_m^\ominus (\text{kJ} \cdot \text{mol}^{-1})$	0	-393.509	-110.525
$S_m^\ominus (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	5.740	213.74	197.674
$\Delta_f G_m^\ominus (\text{kJ} \cdot \text{mol}^{-1})$	0	-394.359	-137.168

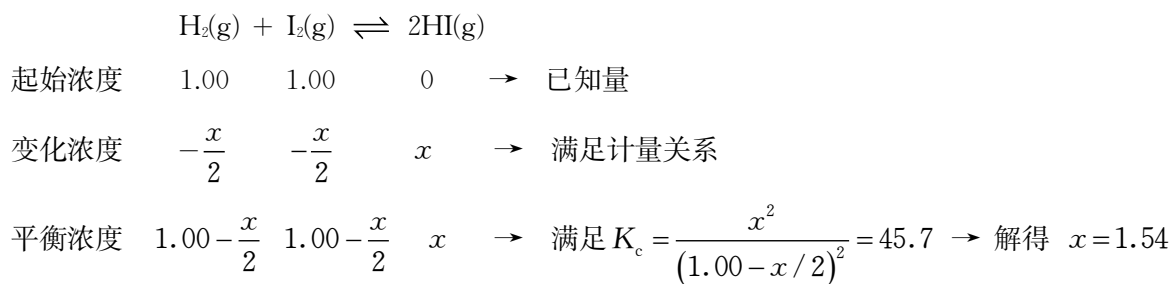
解: $\Delta_r G_m^\ominus(298.15\text{K}) = 2 \Delta_f G_m^\ominus(\text{CO}) - \Delta_f G_m^\ominus(\text{CO}_2)$
 $= [2 \times (-137.168) - (-394.359)] = 120.023 \text{ kJ} \cdot \text{mol}^{-1}$
 $\ln K^\ominus = -\Delta_r G_m^\ominus / RT \rightarrow K^\ominus(298.15\text{K}) = e^{-\frac{\Delta_r G_m^\ominus}{RT}} = e^{-\frac{120.023 \times 10^3}{8.314 \times 298.15}} = 9.5 \times 10^{-22}$
 $\Delta_r H_m^\ominus = [2 \times (-110.525) - (-393.509)] = 172.459 \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta_r S_m^\ominus = [2 \times 197.674 - (5.740 + 213.74)] = 175.87 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
 $\Delta_r G_m^\ominus(1173\text{K}) = \Delta_r H_m^\ominus - T \Delta_r S_m^\ominus = 172.459 \times 10^3 - 1173 \times 175.87 = -33836.51 \text{ J} \cdot \text{mol}^{-1}$
 同理, $K^\ominus(1173\text{K}) = e^{-\frac{\Delta_r G_m^\ominus}{RT}} = e^{-\frac{33836.51}{8.314 \times 1173}} = 32.14$

例题 2.6 平衡转化率的计算 1

题: 763.8K 时, 反应 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ $K_c = 45.7$

- ① 反应开始时 H_2 和 I_2 的浓度均为 $1.00 \text{ mol} \cdot \text{L}^{-1}$, 求平衡时各物质的平衡浓度及 I_2 的平衡转化率。
 ② 假定平衡时要求有 90% I_2 转化为 HI , 问开始时 I_2 和 H_2 应按怎样的浓度比混合?

解: ① 设平衡时 $c(\text{HI}) = x \text{ mol} \cdot \text{L}^{-1}$, 列三段式 (浓度单位均为 $\text{mol} \cdot \text{L}^{-1}$)



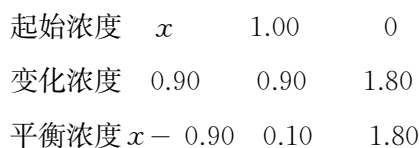
∴ 平衡时 $c(\text{HI}) = 1.57 \text{ mol} \cdot \text{L}^{-1}$, $c(\text{H}_2) = c(\text{I}_2) = 1.00 - 1.57 / 2 = 0.23 \text{ mol} \cdot \text{L}^{-1}$

$$\text{平衡转化率 } \alpha = \frac{1.00 - 0.23}{1.00} \times 100\% = 77\%$$

- ② 不妨设起始的 $c(\text{H}_2) = x \text{ mol} \cdot \text{L}^{-1}$, $c(\text{I}_2) = 1.00 \text{ mol} \cdot \text{L}^{-1}$

∴ I_2 的平衡转化率 90% ∴ $c(\text{I}_2)$ 的变化量为 $1.00 \text{ mol} \cdot \text{L}^{-1} \times 90\% = 0.90 \text{ mol} \cdot \text{L}^{-1}$

∴ 列三段式: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$



$$\therefore K_c = \frac{1.80^2}{0.10(x - 0.9)} = 45.7 \quad \text{解得} \quad x = 1.6 \quad \therefore \text{比例为 } 1.6 : 1$$

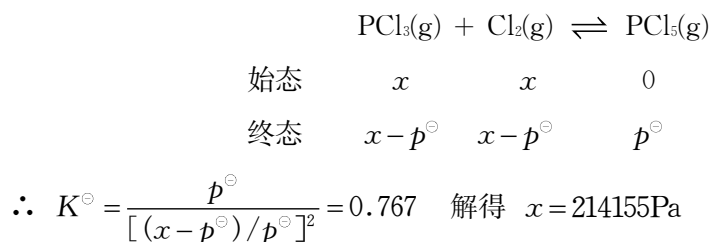
例题 2.7 平衡转化率的计算 2

题: 在 5.00L 容器中装有等物质的量的 $\text{PCl}_3(\text{g})$ 和 $\text{Cl}_2(\text{g})$ 。

523K 时, 反应 $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$ 达平衡时, $p(\text{PCl}_5) = p^\ominus$, $K^\ominus = 0.767$, 求:

- ① 开始装入的 PCl_3 和 Cl_2 的物质的量;
 ② PCl_3 的平衡转化率。

解: ① 设开始时 $p(\text{PCl}_3) = p(\text{Cl}_2) = x \text{ Pa}$, 列三段式 (单位均为 Pa):

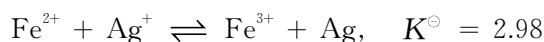


$$\therefore n(\text{PCl}_3) = n(\text{Cl}_2) = \frac{pV}{RT} = \frac{214155\text{Pa} \times 5.00 \times 10^{-3}\text{m}^3}{8.314\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 523\text{K}} = 0.246\text{mol}$$

$$\textcircled{2} \alpha(\text{PCl}_3) = \frac{100000}{214155} \times 100\% = 47.0\%$$

例题 2.8 浓度对平衡的影响

题：含 $0.100 \text{ mol} \cdot \text{L}^{-1} \text{Ag}^+$ 、 $0.100 \text{ mol} \cdot \text{L}^{-1} \text{Fe}^{2+}$ 、 $0.0100 \text{ mol} \cdot \text{L}^{-1} \text{Fe}^{3+}$ 溶液中发生反应：



- ① 判断反应进行的方向；
- ② 计算平衡时 Ag^+ 、 Fe^{2+} 、 Fe^{3+} 的浓度；
- ③ 计算 Ag^+ 的转化率
- ④ 计算 $c(\text{Ag}^+)$ 、 $c(\text{Fe}^{3+})$ 不变， $c(\text{Fe}^{2+}) = 0.300 \text{ mol} \cdot \text{L}^{-1}$ 时 Ag^+ 的转化率。

解：① $J = \frac{0.01/1}{0.1/1 \times 0.1/1} = 1 < 2.98 \quad \therefore$ 反应正向进行

② 三段式： $\text{Fe}^{2+} + \text{Ag}^+ \rightleftharpoons \text{Fe}^{3+} + \text{Ag}$

Start 0.100 0.100 0.0100

Δ $-x$ $-x$ x

Eq. $0.100 - x$ $0.100 - x$ $0.0100 + x$

$$\therefore J = K^\ominus = \frac{0.0100 + x}{(0.100 - x)^2} = 2.98 \quad \text{解得 } x = 0.0130$$

$$\therefore c(\text{Fe}^{3+}) = 0.0100 + 0.0130 = 0.0230 \text{ mol} \cdot \text{L}^{-1}$$

$$c(\text{Fe}^{2+}) = c(\text{Ag}^+) = 0.100 - 0.0130 = 0.0870 \text{ mol} \cdot \text{L}^{-1}$$

$$\textcircled{3} \alpha(\text{Ag}^+) = \frac{0.0130}{0.100} \times 100\% = 13.0\%$$

④ 重新写三段式： $\text{Fe}^{2+} + \text{Ag}^+ \rightleftharpoons \text{Fe}^{3+} + \text{Ag}$

Start 0.300 0.100 0.0100

Δ $-x$ $-x$ x

Eq. $0.300 - x$ $0.100 - x$ $0.0100 + x$

$$\therefore J = K^\ominus = \frac{0.0100 + x}{(0.100 - x)(0.300 - x)} = 2.98 \quad \text{解得 } x = 0.0130 \quad \therefore \alpha = 38.1\%$$

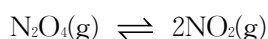
例题 2.9 压力对平衡的影响

题：一密闭容器中含 $1.0 \text{ mol N}_2\text{O}_4$ ，反应： $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ 在 25°C 、 100kPa 下达到平衡时 N_2O_4 的

$\alpha = 50\%$ ，计算：

- ① 反应的 K^\ominus ；
- ② 25°C 、 1000kPa 下达到平衡时 N_2O_4 的 α ， N_2O_4 和 NO_2 的分压。

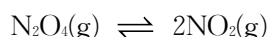
解: ①



起始量/mol	1.0	0	
变化量/mol	$1.0 \times 50\%$	$2.0 \times 50\%$	
平衡量/mol	0.5	1.0	
平衡分压	$\frac{0.5}{1.0+0.5} p_{\text{总}}$	$\frac{1.0}{1.0+0.5} p_{\text{总}}$	(分压 $p_A = \frac{n_A}{n_A + n_B + \dots} p$)

$$K^\ominus = \left(\frac{2 p_{\text{总}}}{3 p^\ominus} \right)^2 / \frac{1 p_{\text{总}}}{3 p^\ominus} = \frac{4 p_{\text{总}}}{3 p^\ominus} = \frac{4 \times 100 \text{ kPa}}{3 \times 100 \text{ kPa}} = 1.33$$

② $\because T$ 不变 $\therefore K^\ominus$ 不变



起始量/mol	1.0	0	
变化量/mol	$1.0 \times \alpha$	$2.0 \times \alpha$	
平衡量/mol	$1.0(1-\alpha)$	$2.0 \times \alpha$! $1.0(1-\alpha) + 2.0 \times \alpha = 1.0(1+\alpha)$
平衡分压	$\frac{1.0(1-\alpha)}{1.0(1+\alpha)} p_{\text{总}}$	$\frac{2.0 \alpha}{1.0(1+\alpha)} p_{\text{总}}$	

$$\therefore K^\ominus = \frac{\left(\frac{2\alpha p_{\text{总}}}{1+\alpha p^\ominus} \right)^2}{\frac{1-\alpha p_{\text{总}}}{1+\alpha p^\ominus}} = 1.33 \quad \text{解得 } \alpha = 18\%$$

$$\therefore p(\text{N}_2\text{O}_4) = \frac{1.0(1-0.18)}{1.0(1+0.18)} \times 1000 \text{ kPa} = 694.9 \text{ kPa}$$

$$p(\text{NO}_2) = \frac{2.0 \times 0.18}{1.0(1+0.18)} \times 1000 \text{ kPa} = 305.1 \text{ kPa}$$

例题 2.10 温度对平衡的影响

题: 反应 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ 在 298.15K 时 $K^\ominus = 6.8 \times 10^{24}$, $\Delta_r H_m^\ominus = -197.78 \text{ kJ} \cdot \text{mol}^{-1}$, 试计算 723K 时的 K^\ominus , 并判断平衡移动方向。

$$\text{解: } \because \ln \frac{K_2^\ominus}{K_1^\ominus} = \frac{\Delta_r H_m^\ominus(298.15\text{K})}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\therefore \ln \frac{K_2^\ominus}{6.8 \times 10^{24}} = \frac{-197.78 \times 10^3}{8.314} \left(\frac{1}{298.15\text{K}} - \frac{1}{723\text{K}} \right) \quad \text{解得 } K^\ominus(723\text{K}) = 2.95 \times 10^4 < 6.8 \times 10^{24}$$

\therefore 平衡向左移动

第3章 酸碱反应和沉淀反应

例题 3.1 一元弱酸弱碱溶液 pH 的计算

题: 计算 $0.100 \text{ mol} \cdot \text{L}^{-1}$ 氨水溶液中的 $c(\text{OH}^-)$ 、pH 和氨水的解离度, 已知 $K_b^\ominus(\text{NH}_3 \cdot \text{H}_2\text{O}) = 1.8 \times 10^{-5}$

解: 设 $c(\text{OH}^-) = x \text{ mol} \cdot \text{L}^{-1}$: $\text{NH}_3 \cdot \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

平衡浓度/ $\text{mol} \cdot \text{L}^{-1}$ $0.100 - x$ x x

$$\therefore K_b^\ominus = \frac{x^2}{0.100 - x} = 1.8 \times 10^{-5}$$

$\therefore (c/c^\ominus)/K_b^\ominus(\text{NH}_3 \cdot \text{H}_2\text{O}) = 0.100/(1.8 \times 10^{-5}) > 500 \quad \therefore$ 水的解离可忽略

$\therefore 0.100 - x \approx 0.100$ 解得 $x = c(\text{OH}^-) = 1.34 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$

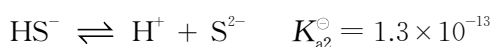
$\therefore c(\text{H}^+) = K_w^\ominus / c(\text{OH}^-) = 10^{-14} / 1.34 \times 10^{-3} = 7.5 \times 10^{-12} \text{ mol} \cdot \text{L}^{-1}$

$\therefore \text{pH} = -\lg(7.5 \times 10^{-12}) = 11.12$

$\alpha = c(\text{OH}^-) / c = 1.34 \times 10^{-3} / 0.100 \times 100\% = 1.34\%$

例题 3.2 多元弱酸的分步解离计算

题: 已知常温常压下 H_2S 的溶解度为 $0.10 \text{ mol} \cdot \text{L}^{-1}$, 计算 H_2S 饱和溶液中 $c(\text{H}^+)$ 、 $c(\text{S}^{2-})$ 和 H_2S 的解离度



解: 列三段式 (此处只写出平衡浓度)



平衡浓度/ $(\text{mol} \cdot \text{L}^{-1})$ $0.10 - x$ x x

$$\therefore K_{a1}^\ominus = \frac{[c(\text{H}^+)/c^\ominus][c(\text{HS}^-)/c^\ominus]}{[c(\text{H}_2\text{S})/c^\ominus]} = \frac{x^2}{0.10 - x} = 1.1 \times 10^{-7}$$

同理, 忽略水的解离且 $0.10 - x \approx 0.10$, 解得 $x = c(\text{H}^+) = 1.1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$

对于第二步解离 $\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-}$

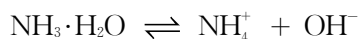
由于 $K_{a2}^\ominus \ll K_{a1}^\ominus$, 可认为第二步解离很微弱, $c(\text{H}^+) \approx c(\text{HS}^-)$

$$\therefore K_{a2}^\ominus = \frac{[c(\text{H}^+)/c^\ominus][c(\text{S}^{2-})/c^\ominus]}{[c(\text{HS}^-)/c^\ominus]} \approx c(\text{S}^{2-})/c^\ominus = 1.3 \times 10^{-13} \quad \text{解得 } c(\text{S}^{2-}) = 1.3 \times 10^{-13} \text{ mol} \cdot \text{L}^{-1}$$

例题 3.3 同离子效应

题: 在 $0.10 \text{ mol} \cdot \text{L}^{-1} \text{NH}_3 \cdot \text{H}_2\text{O}$ 溶液中, 加入固体 NH_4Cl , 使其浓度为 $0.10 \text{ mol} \cdot \text{L}^{-1}$, 计算溶液中 $c(\text{OH}^-)$ 、 $\text{NH}_3 \cdot \text{H}_2\text{O}$ 的解离度

解: 设 $c(\text{OH}^-) = x \text{ mol} \cdot \text{L}^{-1}$, 列三段式 (此处只写出平衡浓度)



平衡浓度/ $\text{mol} \cdot \text{L}^{-1}$ $0.10 - x$ $0.10 + x$ x

$$\text{则 } K_b^\ominus = \frac{x(0.10+x)}{0.10-x} = 1.8 \times 10^{-5}$$

$$\because (c/c^\ominus)/K_b^\ominus(\text{NH}_3 \cdot \text{H}_2\text{O}) = 0.100/(1.8 \times 10^{-5}) > 500$$

$$\therefore 0.10-x \approx 0.10 \quad \text{且} \quad 0.10+x \approx 0.10$$

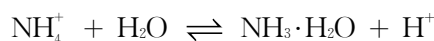
$$\therefore \frac{x(0.10+x)}{0.10-x} \approx x = 1.8 \times 10^{-5} \quad \text{即} \quad c(\text{OH}^-) = 1.8 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$\therefore \alpha(\text{NH}_3 \cdot \text{H}_2\text{O}) = \frac{1.8 \times 10^{-5}}{0.10} \times 100\% = 1.8 \times 10^{-2}\% \quad (\text{请与例题 3.1 的结果相比})$$

例题 3.4 盐溶液 pH 值的近似计算

题: 计算 $0.10 \text{ mol} \cdot \text{L}^{-1}$ NH_4Cl 溶液的 pH 和水解度

解: 设溶液中 $c(\text{H}^+) = x \text{ mol} \cdot \text{L}^{-1}$



$$\begin{array}{ccccccc} \text{平衡浓度}/(\text{mol} \cdot \text{L}^{-1}) & & 0.10 - x & & x & & x \end{array}$$

$$\therefore K_h^\ominus = \frac{x^2}{0.10-x} = \frac{K_w^\ominus}{K_b^\ominus(\text{NH}_3 \cdot \text{H}_2\text{O})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$\because 0.10 - x \approx 0.10 \quad \text{解得} \quad x = 7.5 \times 10^{-6} \quad \text{即} \quad c(\text{H}^+) = 7.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

$$\therefore \text{pH} = -\lg(7.5 \times 10^{-6}) = 5.12$$

$$h(\text{NH}_4\text{Cl}) = \frac{7.5 \times 10^{-6}}{0.10} \times 100\% = 7.5 \times 10^{-3}\%$$

例题 3.5 溶解度与溶度积的相互换算

题: 已知 298.15K 时 $K_{\text{sp}}^\ominus(\text{BaSO}_4) = 1.08 \times 10^{-10}$, 计算 298.15K 时的 $s(\text{BaSO}_4)$

解: $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$

$$\begin{array}{ccccccc} \text{平衡浓度}/(\text{mol} \cdot \text{L}^{-1}) & & x & & x & & \end{array}$$

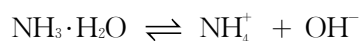
$$\therefore K_{\text{sp}}^\ominus(\text{BaSO}_4) = [c(\text{Ba}^{2+})/c^\ominus][c(\text{SO}_4^{2-})/c^\ominus] = x^2 = 1.08 \times 10^{-10} \quad \text{解得} \quad x = 1.04 \times 10^{-5}$$

$$\text{即} \quad s(\text{BaSO}_4) = 1.04 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

例题 3.6 溶度积判断 I

题: 在 10mL $0.10 \text{ mol} \cdot \text{L}^{-1}$ MgSO_4 溶液中加入 10mL $0.10 \text{ mol} \cdot \text{L}^{-1}$ $\text{NH}_3 \cdot \text{H}_2\text{O}$, 问有无 $\text{Mg}(\text{OH})_2$ 沉淀生成? 已知 $K_{\text{sp}}^\ominus[\text{Mg}(\text{OH})_2] = 5.61 \times 10^{-12}$

解: $c(\text{Mg}^{2+}) = c_0(\text{NH}_3 \cdot \text{H}_2\text{O}) = 0.10 / 2 = 0.050 \text{ mol} \cdot \text{L}^{-1}$



$$\begin{array}{ccccccc} \text{平衡浓度}/(\text{mol} \cdot \text{L}^{-1}) & & 0.050 - x & & x & & x \end{array}$$

$$\therefore K_b^\ominus = \frac{x^2}{0.050-x} = 1.8 \times 10^{-5}; \quad 0.050 - x \approx 0.050 \rightarrow x = 9.5 \times 10^{-4}$$

$$\therefore c(\text{OH}^-) = 9.5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

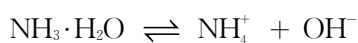
$$\therefore J = \frac{c(\text{Mg}^{2+})}{c^\ominus} \cdot \left[\frac{c(\text{OH}^-)}{c^\ominus} \right]^2 = 0.050 \times (9.5 \times 10^{-4})^2 = 4.5 \times 10^{-8} > K_{\text{sp}}^\ominus \therefore \text{有 } \text{Mg}(\text{OH})_2 \text{ 沉淀生成}$$

例题 3.7 溶度积判断 II

题: 在 10 mL $0.10 \text{ mol} \cdot \text{L}^{-1}$ MgSO_4 溶液中加入 10 mL $0.10 \text{ mol} \cdot \text{L}^{-1}$ $\text{NH}_3 \cdot \text{H}_2\text{O}$, 若使 $\text{Mg}(\text{OH})_2$ 沉淀溶解, 最少要加入多少克 NH_4Cl ?

解: 使沉淀溶解的条件: $c(\text{Mg}^{2+}) \cdot [c(\text{OH}^-)]^2 < K_{\text{sp}}^\ominus [\text{Mg}(\text{OH})_2] \times (c^\ominus)^3$

$$\therefore c(\text{OH}^-) < \sqrt{\frac{K_{\text{sp}}^\ominus [\text{Mg}(\text{OH})_2] (c^\ominus)^3}{c(\text{Mg}^{2+})}} = \sqrt{\frac{5.61 \times 10^{-12}}{5.0 \times 10^{-2}}} = 1.1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$



$$\text{平衡浓度}/(\text{mol} \cdot \text{L}^{-1}) \quad 0.050 - 1.1 \times 10^{-5} \quad y \quad 1.1 \times 10^{-5}$$

$$\therefore K_{\text{b}}^\ominus = \frac{1.1 \times 10^{-5} y}{0.050 - 1.1 \times 10^{-5}} = 1.8 \times 10^{-5} \rightarrow y = 8.2 \times 10^{-2} \quad \text{即} \quad c(\text{NH}_4^+) = 8.2 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$\therefore c(\text{NH}_4\text{Cl}) > (8.2 \times 10^{-2} - 1.1 \times 10^{-5}) \text{ mol} \cdot \text{L}^{-1} \approx 0.082 \text{ mol} \cdot \text{L}^{-1}$$

最少要加入 NH_4Cl $(0.082 \times 0.020 \times 53.5) = 0.087 \text{ g}$

例题 3.8 沉淀的同离子效应

题: 计算 BaSO_4 在 $0.10 \text{ mol} \cdot \text{L}^{-1}$ Na_2SO_4 溶液中的溶解度。

解: $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$

$$\text{平衡浓度}/(\text{mol} \cdot \text{L}^{-1}) \quad x \quad x + 0.10 \quad \text{近似认为 } x + 0.10 \approx 0.10$$

$$K_{\text{sp}}^\ominus (\text{BaSO}_4) = x(x + 0.10) = 1.08 \times 10^{-10} \quad s = x = 1.1 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$$

例题 3.9 pH 对沉淀的影响

题: 为除去 $1.0 \text{ mol} \cdot \text{L}^{-1}$ ZnSO_4 溶液中的 Fe^{3+} , 溶液的 pH 值应控制在什么范围?

$$\text{已知: } K_{\text{sp}}^\ominus [\text{Fe}(\text{OH})_3] = 2.79 \times 10^{-39}, \quad K_{\text{sp}}^\ominus [\text{Zn}(\text{OH})_2] = 3 \times 10^{-17}$$

$$\text{解: } \text{Fe}(\text{OH})_3 \text{ 沉淀完全时 } c(\text{OH}^-) = \sqrt[3]{\frac{2.79 \times 10^{-39}}{1.0}} = 6.53 \times 10^{-12} \text{ mol} \cdot \text{L}^{-1} \rightarrow \text{pH} = 2.81$$

$$\text{Zn}(\text{OH})_2 \text{ 开始沉淀时 } c(\text{OH}^-) = \sqrt[3]{\frac{3 \times 10^{-17}}{1.0}} = 5 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1} \rightarrow \text{pH} = 5.7$$

\therefore pH 应控制为: $2.81 < \text{pH} < 5.7$

例题 3.10 先后沉淀 I

题: 在含浓度均为 $0.010 \text{ mol} \cdot \text{L}^{-1}$, I^- 、 Cl^- 溶液中滴加 AgNO_3 溶液是否能达到分离目的?

$$\text{已知: } K_{\text{sp}}^\ominus (\text{AgCl}) = 1.77 \times 10^{-10}, \quad K_{\text{sp}}^\ominus (\text{AgI}) = 8.52 \times 10^{-17}$$

解: \because 两者同类型, $K_{\text{sp}}^{\ominus}(\text{AgCl}) > K_{\text{sp}}^{\ominus}(\text{AgI}) \therefore \text{AgI}$ 先沉淀

$$\cdot \text{AgCl 开始沉淀时 } c(\text{Ag}^+) > \frac{K_{\text{sp}}^{\ominus}(\text{AgCl}) \times (c^{\ominus})^2}{c(\text{Cl}^-)} = \frac{1.77 \times 10^{-10}}{0.010} = 1.77 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$

$$\cdot \text{此时 } c(\text{I}^-) > \frac{K_{\text{sp}}^{\ominus}(\text{AgI}) \times (c^{\ominus})^2}{c(\text{Ag}^+)} = \frac{8.52 \times 10^{-17}}{1.77 \times 10^{-8}} = 4.81 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1} < 1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

即 AgCl 开始沉淀时 AgI 已沉淀完全, 因此可以达到分离目的

例题 3.11 先后沉淀 II

题: 在含 $0.20 \text{ mol} \cdot \text{L}^{-1} \text{Ni}^{2+}$ 、 $0.30 \text{ mol} \cdot \text{L}^{-1} \text{Fe}^{3+}$ 溶液中加入 NaOH 溶液使其分离, 计算溶液的 pH 控制范围

$$\text{已知: } K_{\text{sp}}^{\ominus}[\text{Fe}(\text{OH})_3] = 2.79 \times 10^{-39}, K_{\text{sp}}^{\ominus}[\text{Ni}(\text{OH})_2] = 5.48 \times 10^{-16}$$

$$\text{解: Fe}(\text{OH})_3 \text{ 开始沉淀时 } c(\text{OH}^-) = \sqrt[3]{\frac{2.79 \times 10^{-39}}{0.30}} = 2.10 \times 10^{-13} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{Ni}(\text{OH})_2 \text{ 开始沉淀时 } c(\text{OH}^-) = \sqrt{\frac{5.48 \times 10^{-16}}{0.20}} = 5.23 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1} \rightarrow \text{pH} = 6.72$$

$\therefore \text{Fe}^{3+}$ 先沉淀

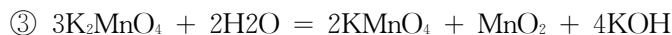
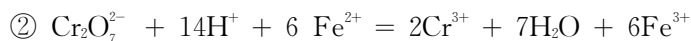
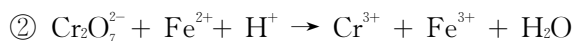
$$\text{Fe}(\text{OH})_3 \text{ 沉淀完全时 } c(\text{OH}^-) = \sqrt[3]{\frac{2.79 \times 10^{-39}}{10^{-5}}} = 6.53 \times 10^{-12} \text{ mol} \cdot \text{L}^{-1} \rightarrow \text{pH} = 2.81$$

\therefore 为使离子分离, pH 应控制在 2.81 ~ 6.72 之间

第 4 章 氧化还原反应与应用电化学

例题 4.1 氧化还原方程式的配平

题: 配平下列方程式:



例题 4.2 氧化剂强弱判断

题: 试比较 KMnO_4 、 Cl_2 、 FeCl_3 在酸性介质中的氧化能力

电对	$\text{MnO}_4^- / \text{Mn}^{2+}$	$\text{Cl}_2 / \text{Cl}^-$	$\text{Fe}^{3+} / \text{Fe}^{2+}$
E^{\ominus} / V	1.51	1.3583	0.771

解: 氧化能力: $\text{KMnO}_4 > \text{Cl}_2 > \text{FeCl}_3$

例题 4.3 还原剂强弱判断

题：试比较 KMnO_4 、 Cl_2 、 FeCl_3 在酸性介质中的氧化能力

电对	$\text{Zn}^{2+} / \text{Zn}$	$\text{S} / \text{H}_2\text{S}$	$\text{Sn}^{4+} / \text{Sn}^{2+}$
E^\ominus / V	-0.763	0.144	0.154

解：还原能力： $\text{Zn} > \text{H}_2\text{S} > \text{SnCl}_2$

例题 4.4 用电极电势计算解离常数

题：已知 $E^\ominus(\text{HCN}/\text{H}_2) = -0.545\text{V}$ ，计算 $K_a^\ominus(\text{HCN})$

解：将 HCN/H_2 和 H^+/H_2 两电对组成原电池

$$(+)\ 2\text{HCN} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{CN}^- \quad E_+ = E^\ominus(\text{HCN}/\text{H}_2) + \frac{0.0592}{2} \lg \frac{[\text{c}(\text{HCN})/c^\ominus]^2}{[p(\text{H}_2)/p^\ominus][\text{c}(\text{CN}^-)/c^\ominus]^2}$$

$$(-)\ \text{H}_2 - 2\text{e}^- \rightarrow 2\text{H}^+ \quad E_- = E^\ominus(\text{H}^+/\text{H}_2) + \frac{0.0592}{2} \lg \frac{[\text{c}(\text{H}^+)/c^\ominus]^2}{[p(\text{H}_2)/p^\ominus]}$$

反应达平衡时：

$$\textcircled{1} \quad E = E_+ - E_- = 0$$

$$\therefore E^\ominus(\text{HCN}/\text{H}_2) + \frac{0.0592}{2} \lg \frac{[\text{c}(\text{HCN})/c^\ominus]^2}{[p(\text{H}_2)/p^\ominus][\text{c}(\text{CN}^-)/c^\ominus]^2} = E^\ominus(\text{H}^+/\text{H}_2) + \frac{0.0592}{2} \lg \frac{[\text{c}(\text{H}^+)/c^\ominus]^2}{[p(\text{H}_2)/p^\ominus]}$$

$$\because E^\ominus(\text{H}^+/\text{H}_2) = 0$$

$$\therefore E^\ominus(\text{HCN}/\text{H}_2) + \frac{0.0592}{2} \lg \frac{[\text{c}(\text{HCN})/c^\ominus]^2}{[\text{c}(\text{H}^+)/c^\ominus]^2[\text{c}(\text{CN}^-)/c^\ominus]^2} = 0$$

$$\textcircled{2} \quad K_a^\ominus(\text{HCN}) = \frac{[\text{c}(\text{HCN})/c^\ominus]}{[\text{c}(\text{H}^+)/c^\ominus][\text{c}(\text{CN}^-)/c^\ominus]}$$

$$\therefore E^\ominus(\text{HCN}/\text{H}_2) + \frac{0.0592}{2} \lg [K_a^\ominus(\text{HCN})]^2 = 0 \rightarrow \lg [K_a^\ominus(\text{HCN})] = -\frac{E^\ominus(\text{HCN}/\text{H}_2)}{0.0592}$$

$$\text{代入 } E^\ominus(\text{HCN}/\text{H}_2) = -0.545\text{V}, \text{ 解得 } K_a^\ominus(\text{HCN}) = 6.2 \times 10^6$$

例题 4.5 用电极电势计算溶度积

题：已知 $E^\ominus(\text{PbSO}_4/\text{Pb}) = -0.356\text{V}$ ， $E^\ominus(\text{Pb}^{2+}/\text{Pb}) = -0.126\text{V}$ ，计算 $K_{\text{sp}}^\ominus(\text{PbSO}_4)$

解：将 PbSO_4/Pb 和 Pb^{2+}/Pb 两电对组成原电池

$$(+)\ \text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-} \quad E_+ = E^\ominus(\text{PbSO}_4/\text{Pb}) + \frac{0.0592}{2} \lg \frac{1}{\text{c}(\text{SO}_4^{2-})/c^\ominus}$$

$$(-)\ \text{Pb} - 2\text{e}^- \rightarrow \text{Pb}^{2+} \quad E_- = E^\ominus(\text{Pb}^{2+}/\text{Pb}) + \frac{0.0592}{2} \lg [\text{c}(\text{Pb}^{2+})/c^\ominus]$$

$$\text{平衡时，电池电动势 } E = E_+ - E_- = 0 \quad \text{且} \quad K_{\text{sp}}^\ominus(\text{BaSO}_4) = [\text{c}(\text{SO}_4^{2-})/c^\ominus][\text{c}(\text{Pb}^{2+})/c^\ominus]$$

$$\text{则 } E^\ominus(\text{PbSO}_4/\text{Pb}) + \frac{0.0592}{2} \lg \frac{1}{\text{c}(\text{SO}_4^{2-})/c^\ominus} = E^\ominus(\text{Pb}^{2+}/\text{Pb}) + \frac{0.0592}{2} \lg [\text{c}(\text{Pb}^{2+})/c^\ominus]$$

$$E^{\ominus}(\text{PbSO}_4 / \text{Pb}) - E^{\ominus}(\text{Pb}^{2+} / \text{Pb}) = \frac{0.0592}{2} \lg [c(\text{SO}_4^{2-}) / c^{\ominus}] [c(\text{Pb}^{2+}) / c^{\ominus}]$$

$$E^{\ominus}(\text{PbSO}_4 / \text{Pb}) - E^{\ominus}(\text{Pb}^{2+} / \text{Pb}) = \frac{0.0592}{2} \lg [K_{\text{sp}}^{\ominus}(\text{PbSO}_4)]$$

代入数据, 解得 $K_{\text{sp}}^{\ominus}(\text{PbSO}_4) = 1.6 \times 10^{-8}$

例题 4.6 氧化还原反应方向判断 I

题: 试判断反应 $\text{Pb}^{2+} + \text{Sn} \rightleftharpoons \text{Pb} + \text{Sn}^{2+}$ 在标准态时反应自发进行的方向

电对	Pb^{2+}/Pb	Sn^{2+}/Sn
E^{\ominus} / V	-0.126	-0.136

解: $\because E^{\ominus} = E^{\ominus}(\text{Pb}^{2+} / \text{Pb}) - E^{\ominus}(\text{Sn}^{2+} / \text{Sn}) = 0.010 \text{V} > 0 \quad \therefore$ 反应正向进行

例题 4.7 氧化还原反应方向判断 II

题: 试判断反应 $\text{Pb}^{2+} + \text{Sn} \rightleftharpoons \text{Pb} + \text{Sn}^{2+}$ 在 $\frac{c(\text{Pb}^{2+})}{c(\text{Sn}^{2+})} = \frac{0.0010}{1.0}$ 时反应自发进行的方向

解: \because 此时 $E(\text{Pb}^{2+} / \text{Pb}) = E^{\ominus}(\text{Pb}^{2+} / \text{Pb}) + \frac{0.0592}{2} \lg [c(\text{Pb}^{2+}) / c^{\ominus}]$

$$E(\text{Sn}^{2+} / \text{Sn}) = E^{\ominus}(\text{Sn}^{2+} / \text{Sn}) + \frac{0.0592}{2} \lg [c(\text{Sn}^{2+}) / c^{\ominus}]$$

$$\therefore E = E(\text{Pb}^{2+} / \text{Pb}) - E(\text{Sn}^{2+} / \text{Sn})$$

$$= E^{\ominus}(\text{Pb}^{2+} / \text{Pb}) + \frac{0.0592}{2} \lg [c(\text{Pb}^{2+}) / c^{\ominus}] - E^{\ominus}(\text{Sn}^{2+} / \text{Sn}) - \frac{0.0592}{2} \lg [c(\text{Sn}^{2+}) / c^{\ominus}]$$

$$= E^{\ominus}(\text{Pb}^{2+} / \text{Pb}) - E^{\ominus}(\text{Sn}^{2+} / \text{Sn}) + \frac{0.0592}{2} \lg \left[\frac{c(\text{Pb}^{2+})}{c(\text{Sn}^{2+})} / c^{\ominus} \right]$$

$$= -0.079 < 0 \quad \text{反应自发向左进行}$$

例题 4.8 氧化还原反应平衡

题: 已知反应 $\text{Pb}^{2+} + \text{Sn} \rightleftharpoons \text{Pb} + \text{Sn}^{2+}$, 反应开始时 $c(\text{Pb}^{2+}) = 2.0 \text{ mol} \cdot \text{L}^{-1}$, 计算反应达平衡时 Pb^{2+} 和 Sn^{2+} 的浓度

解: $\because E^{\ominus} = E^{\ominus}(\text{Pb}^{2+} / \text{Pb}) - E^{\ominus}(\text{Sn}^{2+} / \text{Sn}) = 0.010 \text{V}$

$$\therefore \lg K^{\ominus} = \frac{zE^{\ominus}}{0.0592} = \frac{2 \times 0.010}{0.0592} = 0.34 \quad \therefore K^{\ominus} = 2.2$$

设 $c(\text{Sn}^{2+}) = x \text{ mol} \cdot \text{L}^{-1}$: $\text{Pb}^{2+} + \text{Sn} \rightleftharpoons \text{Pb} + \text{Sn}^{2+}$

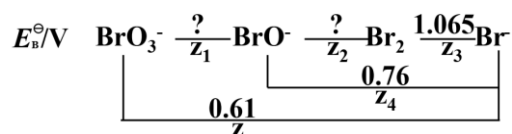
Equilibrium $2.0 - x$ x

$$\therefore K^{\ominus} = \frac{c(\text{Sn}^{2+}) / c^{\ominus}}{c(\text{Pb}^{2+}) / c^{\ominus}} = \frac{x}{2.0 - x} = 2.2 \quad \text{解得 } x = 1.4 \text{ mol} \cdot \text{L}^{-1}$$

$$\therefore c(\text{Sn}^{2+}) = 1.4 \text{ mol} \cdot \text{L}^{-1} \quad c(\text{Pb}^{2+}) = 0.6 \text{ mol} \cdot \text{L}^{-1}$$

例题 4.9 元素电势图

题：完成电势图



解：记电势 E_i 对应的转移电子数为 z_i

$$\text{由电势图可得} \quad zE^\ominus = z_1E_1^\ominus + z_4E_4^\ominus \rightarrow 6 \times 0.61 = 4E_1^\ominus + 2 \times 0.76 \rightarrow E_1^\ominus = 0.54\text{V}$$

$$z_4E_4^\ominus = z_2E_2^\ominus + z_3E_3^\ominus \rightarrow 2 \times 0.76 = E_2^\ominus + 1.065 \rightarrow E_2^\ominus = 0.46\text{V}$$

第 8 章 配合物的结构与性质

例题 8.1 配合物溶液离子浓度计算 I

题： $c([\text{Cu}(\text{NH}_3)_4]^{2+}) = 1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $c(\text{NH}_3) = 1.0 \text{ mol} \cdot \text{L}^{-1}$, 计算溶液中的 $c(\text{Cu}^{2+})$

已知 $K_f^\ominus = 2.09 \times 10^{13}$

$$\text{解：} K_f^\ominus = \frac{c([\text{Cu}(\text{NH}_3)_4]^{2+})/c^\ominus}{[c(\text{Cu}^{2+})/c^\ominus][c(\text{NH}_3)/c^\ominus]^4} = 2.09 \times 10^{13}, \text{ 代入, 解得 } c(\text{Cu}^{2+}) = 4.8 \times 10^{-17}$$

例题 8.2 配合物溶液离子浓度计算 II

题：将 10.0mL $0.20 \text{ mol} \cdot \text{L}^{-1} \text{ AgNO}_3$ 溶液与 10.0mL $1.00 \text{ mol} \cdot \text{L}^{-1} \text{ NH}_3 \cdot \text{H}_2\text{O}$ 混合, 计算溶液中 $c(\text{Ag}^+)$

已知 $[\text{Ag}(\text{NH}_3)_2]^+$ 的 $K_f^\ominus = 1.12 \times 10^7$

解：列三段式 $\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$

Start 0.10 0.50 0

Change 0.10 - x 2(0.10 - x) 0.10 - x

Equilibrium x 0.30 + 2x 0.10 - x

$$K_f^\ominus = \frac{c([\text{Ag}(\text{NH}_3)_2]^+)/c^\ominus}{[c(\text{Ag}^+)/c^\ominus][c(\text{NH}_3)/c^\ominus]^2} = \frac{0.10 - x}{x(0.30 + 2x)^2} = 1.12 \times 10^7 \quad \text{解得 } x = 9.9 \times 10^{-8}$$

$$\therefore c(\text{Ag}^+) = 9.9 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$

例题 8.3 配离子与沉淀之间的转化 I

题：在 1 升 [例 8.1] 溶液中加入 0.0010 mol NaOH。问有无 $\text{Cu}(\text{OH})_2$ 沉淀生成？

解： $c(\text{OH}^-) = 0.0010 \text{ mol} \cdot \text{L}^{-1}$, $c(\text{Cu}^{2+}) = 4.8 \times 10^{-17} \text{ mol} \cdot \text{L}^{-1}$ $K_{\text{sp}}^\ominus = 2.2 \times 10^{-20}$

$$J = 4.8 \times 10^{-17} \times 0.0010^2 = 4.8 \times 10^{-23} < K_{\text{sp}}^\ominus \quad \therefore \text{无沉淀生成}$$

例题 8.4 配离子与沉淀之间的转化 II

题：在 1 升 [例 8.1] 溶液中, 加入 Na_2S , 使 $c(\text{S}^{2-}) = 0.0010 \text{ mol} \cdot \text{L}^{-1}$ 。问有无 CuS 沉淀生成？

解: $c(\text{S}^{2-}) = 0.0010 \text{ mol} \cdot \text{L}^{-1}$, $c(\text{Cu}^{2+}) = 4.8 \times 10^{-17} \text{ mol} \cdot \text{L}^{-1}$ $K_{\text{sp}}^{\ominus} = 6.3 \times 10^{-36}$

$$J = 4.8 \times 10^{-17} \times 0.0010 = 4.8 \times 10^{-20} > K_{\text{sp}}^{\ominus} \therefore \text{有沉淀生成}$$

例题 8.5 配离子之间的转化

题: 向 $[\text{Ag}(\text{NH}_3)_2]^+$ 溶液中加入 KCN, 通过计算判断 $[\text{Ag}(\text{NH}_3)_2]^+$ 能否转化为 $[\text{Ag}(\text{CN})_2]^-$?

解: 预期反应为: $[\text{Ag}(\text{NH}_3)_2]^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2]^- + 2\text{NH}_3$

$$K^{\ominus} = \frac{c\{[\text{Ag}(\text{CN})_2]^{-}\} [c(\text{NH}_3)]^2}{c\{[\text{Ag}(\text{NH}_3)_2]^{+}\} [c(\text{CN}^{-})]^2} \left[\times \frac{c(\text{Ag}^{+})/c^{\ominus}}{c(\text{Ag}^{+})/c^{\ominus}} \right] = \frac{c\{[\text{Ag}(\text{CN})_2]^{-}\}}{c(\text{Ag}^{+}) [c(\text{CN}^{-})]^2} \times \frac{c(\text{Ag}^{+}) [c(\text{NH}_3)]^2}{c\{[\text{Ag}(\text{NH}_3)_2]^{+}\}}$$

$$= \frac{K_{\text{f}}^{\ominus}\{[\text{Ag}(\text{CN})_2]^{-}\}}{K_{\text{f}}^{\ominus}\{[\text{Ag}(\text{NH}_3)_2]^{+}\}} = \frac{1.26 \times 10^{21}}{1.12 \times 10^7} = 1.13 \times 10^{14}$$

$\therefore [\text{Ag}(\text{NH}_3)_2]^+$ 能转化为 $[\text{Ag}(\text{CN})_2]^-$, 并转化完全

例题 8.6 配离子的电极电势 I

题: 已知 $E^{\ominus}(\text{Au}^{+}/\text{Au}) = 1.83\text{V}$, $K_{\text{f}}^{\ominus}([\text{Au}(\text{CN})_2]^{-}) = 1.99 \times 10^{38}$, 计算 $E^{\ominus}([\text{Au}(\text{CN})_2]^{-}/\text{Au})$

解: 对于配位平衡: $\text{Au}^{+} + 2\text{CN}^{-} \rightleftharpoons [\text{Au}(\text{CN})_2]^{-}$ $K_{\text{f}}^{\ominus} = \frac{c\{[\text{Au}(\text{CN})_2]^{-}\}/c^{\ominus}}{[c(\text{Au}^{+})/c^{\ominus}][c(\text{CN}^{-})/c^{\ominus}]^2}$

将两个电极组成原电池: $(-) \text{Au} + 2\text{CN}^{-} - e^{-} \rightleftharpoons [\text{Au}(\text{CN})_2]^{-}$

$(+) \text{Au}^{+} + e^{-} \rightleftharpoons \text{Au}$

$$\text{则 } E = E^{\ominus}(\text{Au}^{+}/\text{Au}) + \frac{0.0592}{1} \lg [c(\text{Au}^{+})] - E^{\ominus}([\text{Au}(\text{CN})_2]^{-}/\text{Au}) - \frac{0.0592}{1} \lg \frac{c\{[\text{Au}(\text{CN})_2]^{-}\}}{[c(\text{CN}^{-})]^2}$$

$$= E^{\ominus}(\text{Au}^{+}/\text{Au}) - E^{\ominus}([\text{Au}(\text{CN})_2]^{-}/\text{Au}) - 0.0592 \lg \frac{c\{[\text{Au}(\text{CN})_2]^{-}\}}{[c(\text{CN}^{-})]^2 c(\text{Au}^{+})}$$

平衡时 $0 = E^{\ominus}(\text{Au}^{+}/\text{Au}) - E^{\ominus}([\text{Au}(\text{CN})_2]^{-}/\text{Au}) - 0.0592 \lg K_{\text{f}}^{\ominus}$

代入数据, 解得 $E^{\ominus}([\text{Au}(\text{CN})_2]^{-}/\text{Au}) = -0.44\text{V}$

例题 8.6 配离子的电极电势 II

题: 已知 $E^{\ominus}(\text{Co}^{3+}/\text{Co}^{2+}) = 1.92\text{V}$, $K_{\text{f}}^{\ominus}([\text{Co}(\text{NH}_3)_6]^{3+}) = 1.58 \times 10^{35}$, $K_{\text{f}}^{\ominus}([\text{Co}(\text{NH}_3)_6]^{2+}) = 1.29 \times 10^5$, 计算 $E^{\ominus}([\text{Co}(\text{NH}_3)_6]^{3+}/[\text{Co}(\text{NH}_3)_6]^{2+})$

解: 设计原电池, 使得电池反应为 $[\text{Co}(\text{NH}_3)_6]^{3+} + \text{Co}^{2+} \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{2+} + \text{Co}^{3+}$

\therefore 电极反应: $(-) \text{Co}^{2+} - e^{-} \rightleftharpoons \text{Co}^{3+}$ $E_{-} = E^{\ominus} + 0.0592 \lg \frac{c(\text{Co}^{3+})}{c(\text{Co}^{2+})}$

$(+) [\text{Co}(\text{NH}_3)_6]^{3+} + e^{-} \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{2+}$ $E_{+} = E^{\ominus} + 0.0592 \lg \frac{c\{[\text{Co}(\text{NH}_3)_6]^{3+}\}}{c\{[\text{Co}(\text{NH}_3)_6]^{2+}\}}$

$$\therefore E = E^{\ominus}([\text{Co}(\text{NH}_3)_6]^{3+}/[\text{Co}(\text{NH}_3)_6]^{2+}) - E^{\ominus}(\text{Co}^{3+}/\text{Co}^{2+}) + 0.0592 \lg \frac{c\{[\text{Co}(\text{NH}_3)_6]^{3+}\} c(\text{Co}^{2+})}{c\{[\text{Co}(\text{NH}_3)_6]^{2+}\} c(\text{Co}^{3+})}$$

$$\text{平衡时} \quad \frac{c\{\text{Co}(\text{NH}_3)_6\}^{3+} \cdot c(\text{Co}^{2+})}{c\{\text{Co}(\text{NH}_3)_6\}^{2+} \cdot c(\text{Co}^{3+})} = \frac{c\{\text{Co}(\text{NH}_3)_6\}^{3+}}{c(\text{Co}^{3+}) [c(\text{NH}_3)]^6} \cdot \frac{c(\text{Co}^{2+}) [c(\text{NH}_3)]^6}{c\{\text{Co}(\text{NH}_3)_6\}^{2+}} = \frac{K_f^\ominus\{\text{Co}(\text{NH}_3)_6\}^{3+}}{K_f^\ominus\{\text{Co}(\text{NH}_3)_6\}^{2+}}$$

$$\therefore E^\ominus\{\text{Co}(\text{NH}_3)_6\}^{3+} / \{\text{Co}(\text{NH}_3)_6\}^{2+} - E^\ominus(\text{Co}^{3+} / \text{Co}^{2+}) + 0.0592 \lg \frac{K_f^\ominus\{\text{Co}(\text{NH}_3)_6\}^{3+}}{K_f^\ominus\{\text{Co}(\text{NH}_3)_6\}^{2+}} = 0$$

代入数据，解得 $E^\ominus\{\text{Co}(\text{NH}_3)_6\}^{3+} / \{\text{Co}(\text{NH}_3)_6\}^{2+} = 0.14\text{V}$

作者：化学工程与工艺 2019 级 SAVIA

整理自俞豪杰老师课件

P.S. 考试的计算题不会比这些题难