

## 竞争型三元配合物生成热的量热测定

### 镍(II)-草酸-甘氨酸三元体系

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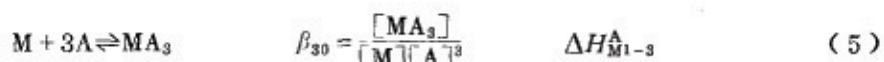
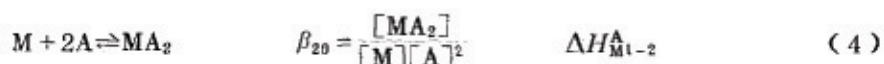
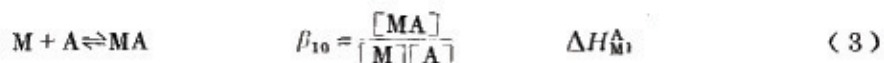
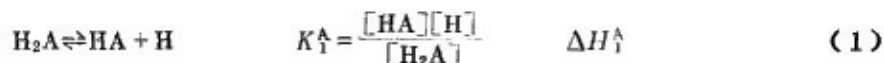
关键词 三元配合物 生成热 量热测定

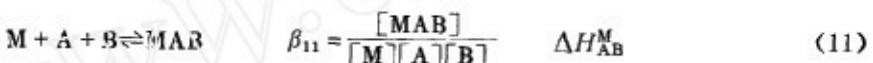
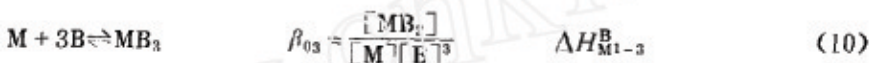
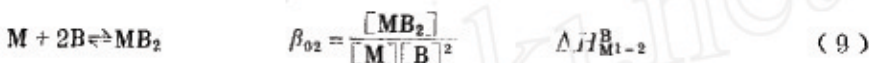
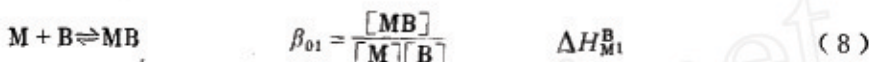
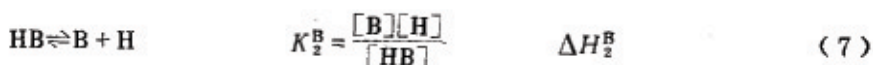
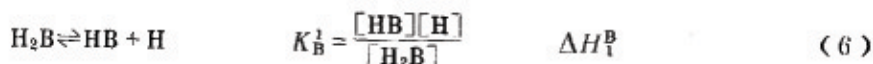
我们曾经报导过铜(II)-草酸-乙二胺三元竞争体系的量热研究<sup>[1]</sup>。由于铜(II)离子的配位数为4,对两个二齿配体(草酸和乙二胺)来说,混配络合物只有一种(MAB),然而对于镍(II)-草酸-甘氨酸的三元体系来说,情况就较复杂,有三种混配络合物(MAB, MA<sub>2</sub>B, MAB<sub>2</sub>)的生成反应必须考虑,所以在热效应计算上就更加复杂,至今尚无文献报道。

本文试图建立一种合理的数据处理方法以计算这样复杂体系的热效应。

## 数学处理和实验

**数学处理** 为了方便,下面以M表示镍(II)离子,A代表草酸根,B代表甘氨酸根。在实验条件下(反应液的pH值接近中性, [A]或[B]≫[M])我们认为无酸(碱)式配合物存在,也无多核配合物生成,并忽略A、B之间的相互作用。这样,当A、B的混合溶液与M的溶液在等温、等离子强度的条件下相混合时,所产生的热效应除加样管中溶液的稀释热外,可归结为如下几个反应热效应的总和:





由反应终了溶液的 pH 值、金属离子总浓度 ( $T_M$ )、酸总浓度 ( $T_H$ ) 和任一配体的总浓度 ( $T_A$  或  $T_B$ )，按质量平衡原理，可以建立如下三个方程式：

$$T_H + [\text{OH}] - [\text{H}] = [\text{A}] (2[\text{H}]^2 / (K^1 K^2) + [\text{H}] / K^2) + [\text{B}] (2[\text{H}]^2 / (K^3 K^4) + [\text{H}] / K^4) \quad (15)$$

$$T_M = \beta_{30}[\text{M}][\text{A}]^3 + \beta_{20}[\text{M}][\text{A}]^2 + \beta_{10}[\text{M}][\text{A}] + \beta_{03}[\text{M}][\text{B}]^3 + \beta_{02}[\text{M}][\text{B}]^2 + \beta_{01}[\text{M}][\text{B}] + \beta_{11}[\text{M}][\text{A}][\text{B}] + \beta_{21}[\text{M}][\text{A}]^2[\text{B}] + \beta_{12}[\text{M}][\text{A}][\text{B}]^2 + [\text{M}] \quad (16)$$

$$T_A = 3\beta_{30}[\text{M}][\text{A}]^3 + 2\beta_{20}[\text{M}][\text{A}]^2 + \beta_{10}[\text{M}][\text{A}] + \beta_{11}[\text{M}][\text{A}][\text{B}] + \beta_{12}[\text{M}][\text{A}][\text{B}]^2 + 2\beta_{21}[\text{M}][\text{A}]^2[\text{B}] + [\text{H}]^2[\text{A}] / (K^1 K^2) + [\text{H}][\text{A}] / K^2 + [\text{A}] \quad (17)$$

由 (15) — (17) 三式，采用消元法，可以得到一个只含配体 A 浓度的四次方程：

$$OY[\text{A}]^4 + (OZ + T_M X - T_A Y)[\text{A}]^3 + (T_M W + OU - T_A Z)[\text{A}]^2 + (T_M V + OS - T_A U)[\text{A}] - T_A S = 0 \quad (18)$$

(18) 式中：O, Y, Z, X, W, U, V 和 S 都是 [H]、 $T_H$ 、[OH] 以及 (1) — (13) 中各平衡常数的函数<sup>[2]</sup>，用中值法利用自编程序在 Apple II e 计算机上求 (18) 式的解得配体 A 的游离浓度 [A]，并随之可以求出反应终了其它各物种的浓度。利用已知的 (1) — (10) 及 (14) 反应的摩尔焓变，可以计算出这些反应的热贡献。设  $Q_{校正}$  为经扣除这些反应热贡献后的总的热效应，可以建立一个只涉及 (11) — (13) 反应热的能量平衡方程：

$$Q_{校正} = [\text{MAB}]\Delta H_{AB}^M + [\text{MA}_2\text{B}]\Delta H_{A_2B}^M + [\text{MAB}_2]\Delta H_{AB_2}^M \quad (19)$$

如此，原则上作三组不同摩尔比的平行量热数据便可以求出这三种混配络合物的生成热。

**实验** 草酸钾为分析纯 (B. D. H 生产，上海化学试剂公司分装)，甘氨酸为生化试剂

(北京化工厂生产), 硝酸镍(A.R.天津试剂三厂生产), 硝酸钾(A.R.天津试剂三厂生产), 使用前未经进一步处理。反应液均用二次蒸馏水配制, 镍(II)离子浓度用EDTA标定, 两种配体的总浓度按重量法配制计算得到。用标准酸、碱来调节混合液中的氢离子总浓度, 使用PHS-2型酸度计测定反应前后溶液的pH值。用改进的RD-1型热导式自动量热计( $K = (3.66 \pm 0.06) \times 10^{-3} \text{ J} \cdot \text{mm}^{-2}$ )作量热测定, 实验方法同前文<sup>[1]</sup>

## 结果与讨论

(1)~(13)式的平衡常数及(1)~(10)的焓变值分别列于表1和表2。表3列出了我们的实验数据和最终的结果。从表3所列的三个混配型络合物的生成热来看, 两个饱和三元配合物( $\text{MA}_2\text{B}$ 和 $\text{MAB}_2$ )的生成热与二元配合物的生成热相比较, 键能的加和性得到了证明。在前文<sup>[6]</sup>的实验结果中也发现了这种现象。而且在这种三元配合物中不存在 $\sigma-\pi$ 反馈键。但对于不饱和的MAB来说, 键能的加和性相差较大。(约 $5\text{kJ} \cdot \text{mol}^{-1}$ )这种趋势在Ni(II)-草酸-乙二胺竞争三元体系中有相似的表现<sup>[2]</sup>。

表1 Ni(II)与草酸根, 甘氨酸分别生成二元和共同生成三元配合物的表现生成常数

Table 1 The apparent formation constants of Ni(II)-Oxalate, -Glycine two binary and Ni(II)-Oxalate-Glycine ternary systems at  $25.0 \pm 0.1^\circ\text{C}$ ,  $I = 0.1 \text{ mol} \cdot \text{dm}^{-3} (\text{KNO}_3)$

System	Equilibrium Constants							
	$\log K_1$	$\log K_2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_{11}$	$\log \beta_{21}$	$\log \beta_{12}$
H <sup>+</sup> -Oxa	-1.04	-3.81 <sup>[2]</sup>						
H <sup>+</sup> -Gly	-2.36	-9.56 <sup>[2]</sup>						
Ni(II)-Oxa			3.86	6.92	9.15 <sup>[1]</sup>			
Ni(II)-Gly			5.78	10.58	14.00 <sup>[2]</sup>			
Ni(II)-Oxa-Gly						9.97	11.50	12.25 <sup>[2]</sup>

Oxa-Oxalate, Gly-Glycine

表2 Ni(II)-草酸根, Ni(II)-甘氨酸二元配合物的表现生成热及二配体的质子化热

Table 2 The apparent heats of formation of two binary systems (Ni(II)-Oxa and Ni(II)-Gly) and the heats of protonation of ligands (Oxa and Gly) at  $25.0 \pm 0.2^\circ\text{C}$ ,  $I = 0.1 \text{ mol} \cdot \text{dm}^{-3} (\text{KNO}_3)$

System	Enthalpy Changes/ $\text{kJ} \cdot \text{mol}^{-1}$				
	$\Delta H_1$	$\Delta H_2$	$\Delta H_{M1}$	$\Delta H_{M2}$	$\Delta H_{M3}$
H <sup>+</sup> -Oxa	5.81	2.59 <sup>[2]</sup>			
H <sup>+</sup> -Gly	$-47.7 \pm .2$	$-3.81 \pm .10$ <sup>[2]</sup>			
Ni(II)-Oxa			$-2.94 \pm .31$	$-6.00 \pm 1.22$	$-9.56 \pm 1.94$ <sup>[2]</sup>
Ni(II)-Gly			-18.83	-38.07	$-61.50$ <sup>[2]</sup>

表3 Ni(II)-草酸根-甘氨酸三元配合物的量热测定

Table 3 The measurements of the heats of formation of ternary system (Ni(II)-Oxalate-Glycine) at  $25.0 \pm 0.2^\circ\text{C}$ ,  $I = 0.1 \text{ mol} \cdot \text{dm}^{-3} (\text{KNO}_3)$ 

$T_i / \text{mol} \cdot \text{dm}^{-3}$				$\text{pH}_i$	$\text{pH}_f$	$\frac{Q_m}{J}$	$\frac{\Delta H_{AB}^M}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta H_{A_2B}^M}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta H_{AB_2}^M}{\text{kJ} \cdot \text{mol}^{-1}}$
$T_M \times 10^3$	$T_H \times 10^3$	$T_A \times 10^3$	$T_E \times 10^3$						
4.501	6.347	1.611	6.347	6.68	5.89	$-0.788 \pm 0.020$	$-14.3 \pm 2.0$		
4.501	6.016	0.9419	9.663	9.43	7.47	$-2.13 \pm 0.02$		$-27.0 \pm 2.0$	
4.501	9.057	1.058	12.70	9.28	7.55	$-2.46 \pm 0.02$			$-40.2 \pm 2.0$

## 参考文献

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## CALORIMETRIC DETERMINATION OF THE HEAT OF FORMATION OF COMPETITIVE TERNARY COMPLEX COMPOUNDS

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## ABSTRACT

By utilizing the formation constants of Ni(II)-Glycine binary complex compounds and the corresponding heats of formation from literature as well as the formation constants of Ni(II)-Oxalate binary complex compounds and the corresponding heats of formation incorporating with the formation constants of Ni(II)-Oxalate-Glycine competitive ternary complex compounds determined in our laboratory, the heats of formation of Ni(II)-Oxalate-Glycine competitive ternary complex compounds have been determined at  $25^\circ\text{C}$ ,  $I = 0.1 \text{ mol} \cdot \text{dm}^{-3} (\text{KNO}_3)$  in aqueous solution by means of RD-1 model automatic conduction calorimeter. The results obtained are:

$$\Delta H_{AB}^M = -14.3 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_{A_2B}^M = -27.0 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_{AB_2}^M = -40.2 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$$

**Keywords:** Ternary complex compounds, Heats of formation, Calorimetric determination