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Solubility of Hexaamminenickel(II) Complexes in Aqueous Ammonia Solution and the Thermal Decomposition of Ammine Complexes of Nickel(II)

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The solubility of hexaamminenickel(II) complexes in aqueous ammonia solution (0 to 37 g-free NH_3/100 g-solv.) was investigated at temperatures 0—55 °C. It rapidly decreases with increase in free ammonia concentration but increases with rise in temperature. Hexaamminenickel(II) carbonate, sulfate, and chloride are slightly soluble at ammonia concentration above 30 g-free NH_3/100 g-solv., but nitrate is considerably soluble even at ammonia concentration of 35 g-free NH_3/100 g solv. The thermal decomposition of ammine complexes of nickel(II) was also investigated by means of TG and DTA under a streaming nitrogen gas atmosphere. Ammine complexes of nickel(II) decompose as shown in the following, the reaction orders and activation energies for steps a, b, c, and d being 0.5, 1.5, 1.0, and 0.5, and 16.5, 38.8, 25.3, and 79.4 kcal/mol, respectively.

$$[Ni(NH_3)_6](NO_3)_2 \xrightarrow{a} [Ni(NH_3)_4](NO_3)_2 \xrightarrow{b} [Ni(NH_3)_{2.5}](NO_3)_2 \longrightarrow NiO$$

$$\begin{tikzcd}
{[Ni(NH_3)_6]SO_4\cdot 2H_2O} \arrow[r] & {[Ni(NH_3)_6]SO_4} \arrow[r] & {[Ni(NH_3)_2]SO_4} \arrow[r, "c"] & {[Ni(NH_3)_{0.5}]SO_4} \arrow[r] & {} \\
{[Ni(NH_3)_5]SO_4\cdot H_2O} \arrow[urr] & & & &
\end{tikzcd}$$

$$NiSO_4 \xrightarrow{d} NiO$$

$$[Ni(NH_3)_6]CO_3\cdot 4H_2O \longrightarrow [Ni(NH_3)_4]CO_3\cdot 3H_2O \longrightarrow [Ni(NH_3)]CO_3\cdot H_2O \longrightarrow [Ni(NH_3)]CO_3 \longrightarrow NiCO_3 \longrightarrow NiO$$

X-Ray diffraction data for $[Ni(NH_3)_6]Cl_2\cdot 0.5H_2O$, $[Ni(NH_3)_6](NO_3)_2$, $[Ni(NH_3)_5]SO_4\cdot H_2O$, and $[Ni(NH_3)_2]SO_4$ powder are given.

Various processes have been developed for the extraction of nickel from ores. Recently hydrometallurgical processes have drawn attention, since the recovery of nickel from low grade ores and non-sulfide ores is possible without any pollution problem. They are classified into two processes, leaching by an acid solution and that by an ammoniacal alkaline solution. The latter process has an advantage of little contamination by iron and magnesium. Some commercial operations based on the ammonia leaching process have been established, such as the Sherritt-Gordon process[1)] of leaching sulfide ore, and the Nicaro process[2)] of leaching laterite ore. In both processes, nickel is first leached as ammine complexes of nickel(II), but the subsequent steps differ a great deal. In the Sherritt-Gordon process, nickel metal is recovered by the reduction of hexaamminenickel(II) sulfate solution with compressed hydrogen. In the Nicaro process, nickel(II) oxide is recovered by the thermal decomposition of basic nickel(II) carbonate produced by heating the hexaamminenickel(II) carbonate solution and purging ammonia. In the present study it was found that the solubility of hexaamminenickel(II) complexes decreases rapidly with increase in free ammonia concentration in solution, and that the complexes decompose by releasing ammonia at considerably low temperature. This paper deals with studies of the solubility of hexaamminenickel(II) complexes in aqueous ammonia solution, and the thermal decomposition of solid ammine complexes of nickel(II) for the purpose of recovering highly purified nickel(II) salts or oxide by the thermal decomposition of solid ammine complexes separated by blowing ammonia gas into the leaching solution containing ammine complexes of nickel(II). Ammine complexes of nickel(II) are produced by blowing ammonia gas into aqueous nickel(II) salt solutions.[3—6)] However, nickel has not been found to be completely recovered as hexaamminenikel(II) complex powder by an extreme increase of the free ammonia concentration. No report seems to have appeared on the solubility of hexaamminenikel(II) complexes in aqueous ammonia solution. Although several studies of thermal decomposition of hexaamminenickel(II) chloride,[7—12)] nitrate,[7—9)] and sulfate[7—9)] have been reported, the thermal decomposition processes of hexaamminenickel(II) nitrate and sulfate are not clarified. No investigation of the thermal decomposition of hexaamminenickel(II) carbonate seems to have been carried out.

Part I. Solubility of Hexaamminenickel(II) Complexes in Aqueous Ammonia Solution

Experimental

Chemicals. Basic nickel(II) carbonate ($2NiCO_3\cdot 3Ni(OH)_2\cdot 3H_2O$) of reagent grade was used. All other chemicals were of analytical reagent grade.

Preparation of Hexaamminenickel(II) Complexes. Hexaamminenickel(II) carbonate was prepared as follows. Ten grams of ammonium carbonate and 19.5 g of basic nickel(II) carbonate were mixed in 100 ml of 16.5 wt% aqueous ammonia solution with a magnetic stirrer for 24 h. After the mixture had been filtered, ammonia gas was blown into the filtrate while being cooled with ice to precipitate hexaamminenickel(II) carbonate. Hexaamminenickel(II) chloride, sulfate, and nitrate were prepared by blowing ammonia gas into saturated aqueous solutions of nickel(II) chloride, sulfate, and nitrate, respectively. These complexes were washed with liquid ammonia and then kept in a

Table 1. Compositions of hexaamminenickel(II) complexes

Compound	Ni(wt%)		NH_3(wt%)	
	Found	Calcd	Found	Calcd
$[Ni(NH_3)_6]CO_3 \cdot 4H_2O$	20.5	20.0	33.5	34.9
$[Ni(NH_3)_6]SO_4 \cdot 2H_2O$	20.0	20.1	34.2	34.8
$[Ni(NH_3)_6](NO_3)_2$	19.4	20.6	36.4	35.8
$[Ni(NH_3)_6]Cl_2 \cdot 0.5H_2O$	23.9	24.4	41.9	42.4

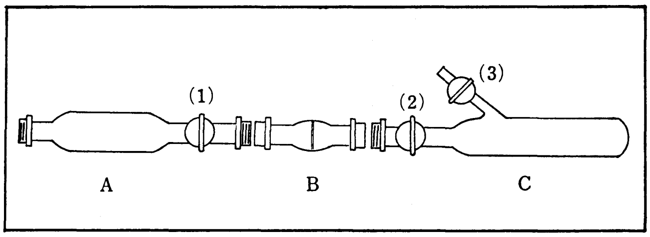

Fig. 1. Apparatus for solubility measurement.
A: Sealed glass tube, B: glass filter, C: sampling tube, 1,2,3: stopcock.

desiccator under ammonia atmosphere. The compositions of these complexes are given in Table 1.

Procedure. The apparatus for measurement of the solubility is shown in Fig. 1. The solubility of hexaamminenickel(II) complexes was determined as follows. Each 25 ml of sealed glass tube(A) was sealed soon after the transfer of 15 ml of aqueous ammonia solution of the desired concentration and excess amount of the sample complex, placed in a thermostat and agitated at 15 r.p.m. for 1 h. The sealed glass tube(A), glass filter(B) and sampling tube(C) were connected with each other. After the pressure of sampling tube(C) was reduced with an aspirator, stopcock(3) was closed, and stopcocks(1) and (2) were opened. A clear supernatant solution was withdrawn.

Analysis. Sampling tube(C) was separated from glass filter(B) and weighed. The sampling solution was acidified with excess standard sulfuric acid solution, diluted to a suitable concentration and subjected to the analysis of nickel(II) and ammonia. The amount of nickel(II) was determined by reacting nickel(II) with excess standard disodium ethylendiaminetetraacetate solution, and back-titrating the excess disodium ethylendiaminetetraacetate with standard zinc(II) chloride solution using Eriochrome Black T for end point detection. The total amount of nickel(II) and ammonia was determined by titrating excess sulfuric acid with standard sodium hydroxide solution using methylred for end point detection. The amount of ammonia was determined by subtracting the amount of nickel(II).

Results and Discussion

The solubility of hexaamminenickel(II) carbonate, chloride, sulfate, and nitrate in aqueous ammonia solution at temperatures 0—55 °C is given in Tables 2, 3, 4, and 5, respectively. The solubility of hexaamminenickel(II) carbonate and of sulfate linearly decreases with increase in free ammonia concentration up to 20 g free NH_3/100 g solvent. The complexes are slightly soluble at the free ammonia concentration above 30 g free NH_3/100 g solvent. The solubility of hexaamminenickel(II) carbonate increases with temperature when the free ammonia concentration is kept constant. The solubility at 55 °C is about twice that at 0 °C. The solubility of hexaamminenickel(II) sulfate

Table 2. Solubility of $[Ni(NH_3)_6]CO_3$ in aqueous ammonia solution

Temp (°C)	Free NH_3 concn (g-free NH_3/100 g-solv.)	Solubility (g/100 g-solv.)	Temp (°C)	Free NH_3 concn (g-free NH_3/100 g-solv.)	Solubility (g/100 g-solv.)
0	3.5	39.85	45	7.4	56.72
	7.3	29.82		9.5	48.56
	10.0	22.12		14.0	34.01
	11.8	16.76		18.8	24.78
	18.6	4.86		21.9	15.55
	20.0	4.14		26.8	6.09
	25.7	1.64		34.1	1.34
	33.2	0.11			
25	6.9	49.50	55	0.2	88.88
	13.7	29.56		4.1	72.86
	17.7	18.27		6.2	64.11
	21.8	8.64		9.6	56.72
	26.3	3.19		12.4	64.11
	28.3	2.03		25.0	12.97
	37.9	0.89		26.9	9.16
	41.0	0.22		33.8	2.03
35	6.4	56.18			
	8.9	49.50			
	9.9	44.26			
	11.9	38.95			
	17.6	22.76			
	19.2	17.05			
	28.6	2.95			
	33.7	1.34			

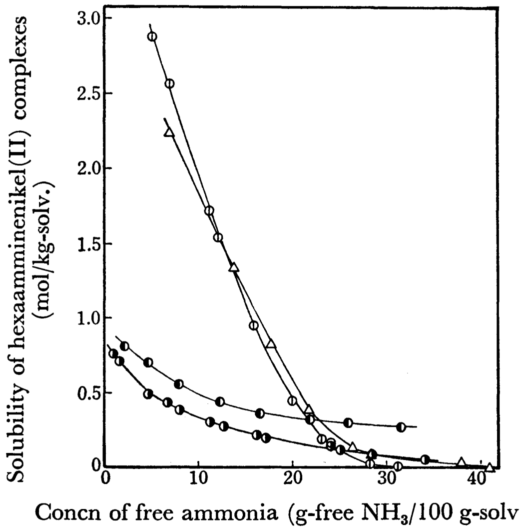

Fig. 2. Solubility of hexaamminenickel(II) complexes in aqueous ammonia solutions at 25 °C.
-Φ-: $[Ni(NH_3)_6]SO_4$, -△-: $[Ni(NH_3)_6]CO_3$, -◐-: $[Ni(NH_3)_6](NO_3)_2$, -◑-: $[Ni(NH_3)_6]Cl_2$.

Table 3. Solubility of $[Ni(NH_3)_6]Cl_2$ in aqueous ammonia solution

Temp (°C)	Free NH$_3$ concn (g-free NH$_3$/100 g-solv.)	Solubility (g/100 g-solv.)	Temp (°C)	Free NH$_3$ concn (g-free NH$_3$/100 g-solv.)	Solubility (g/100 g-solv.)
0	0.7	9.13	45	1.5	23.81
	3.0	7.37		2.7	19.43
	4.5	6.05		4.4	17.12
	6.6	4.30		8.6	12.66
	8.1	3.60		12.9	9.24
	10.9	3.03		15.4	7.41
	14.5	2.62		19.4	5.71
	16.8	2.40		22.6	4.76
	22.3	1.94		25.9	3.85
	33.5	0.54		32.2	2.32
				37.1	1.65
25	1.0	17.63			
	1.7	16.50	55	0.2	31.27
	4.7	11.52		6.0	17.12
	6.8	10.18		10.1	13.73
	8.1	8.93		15.9	9.04
	11.3	7.12		19.3	6.76
	12.7	6.54		30.6	3.06
	16.2	5.34			
	17.1	4.73			
	24.1	3.20			
	25.1	2.88			
	28.5	2.23			
	36.1	1.39			
35	0.7	22.46			
	1.1	21.51			
	3.3	16.40			
	4.5	14.55			
	5.2	13.61			
	5.7	12.84			
	6.6	12.37			
	9.9	9.85			
	14.8	7.12			
	21.6	4.25			
	23.3	4.08			
	32.8	2.03			

Table 4. Solubility of $[Ni(NH_3)_6]SO_4$ in aqueous ammonia solution

Temp (°C)	Free NH$_3$ concn (g-free NH$_3$/100 g-solv.)	Solubility (g/100 g-solv.)	Temp (°C)	Free NH$_3$ concn (g-free NH$_3$/100 g-solv.)	Solubility (g/100 g-solv.)
0	1.9	56.18	35	6.6	77.56
	5.4	36.61		7.5	69.23
	8.7	24.15		9.6	61.71
	11.7	14.64		13.2	45.52
	17.0	3.35		20.8	11.57
	21.3	1.43		25.4	3.92
	22.8	0.96			
	29.6	0.08	45	6.3	75.81
				6.9	73.13
15	3.2	72.00		9.0	63.35
	7.9	49.77		15.0	35.35
	13.5	25.17		15.4	33.72
	20.4	6.34		21.1	12.45
	25.7	2.31		24.7	4.42
	28.5	0.73		26.0	3.51
	33.7	0.28		31.2	0.88
25	5.1	73.67	55	4.8	82.05
	6.9	65.84		10.3	57.98
	11.2	44.22		12.6	32.59
	12.1	39.76		19.9	15.25
	15.9	24.36		24.5	4.45
	20.0	11.48		31.3	0.99
	23.0	5.19			
	24.0	4.37			
	28.2	0.93			
	31.2	0.54			

also increases with temperature up to 35 °C, remaining constant above 35 °C. The solubility of hexaamminenickel(II) chloride and of nitrate also decreases with increase in free ammonia concentration, but increases with rise in temperature. However, the decrements of solubility of these complexes with increase in free ammonia concentration are less than those of carbonate and sulfate. On the other hand, the increments of solubility of the former with temperature are larger than those of the latter; the solubility of hexaamminenickel(II) chloride and of nitrate at 55 °C is about four times as much as that at 0 °C.

Figure 2 shows the solubility of each hexaamminenickel(II) complex in aqueous ammonia solution at 25 °C. It is clear that the solubility of hexaamminenickel(II) carbonate and of chloride at low free ammonia concentration is similar to that of sulfate and nitrate respectively. The solubility of hexaamminenickel(II) carbonate and of sulfate is 3—4 times as much as that of chloride and nitrate at low free ammonia concentration. On the other hand, hexaamminenickel(II) carbonate, sulfate, and chloride are slightly soluble for free ammonia concentration above 30 g free NH$_3$/100 g solvent, nitrate, however, being considerably soluble even for free ammonia concentration of 35 g free NH$_3$/100 g solvent.

Part II. Thermal Decomposition of Ammine Complexes of Nickel(II)

Experimental

Preparation of Ammine Complexes of Nickel(II). Ammine complexes of nickel(II) except hexaamminenickel(II) complexes were prepared as follows. Tetraamminenickel(II) carbonate trihydrate: hexaamminenickel(II) carbonate tetrahydrate was left to stand in a desiccator under dilute ammoia atmosphere for at least 24 h. Monoamminenickel(II) carbonate monohydrate: hexaamminenickel(II) carbonate tetrahydrate was heated at 60 °C for 2 h. Pentaammine-

Table 5. Solubility of $[Ni(NH_3)_6](NO_3)_2$ in aqueous ammonia solution

Temp (°C)	Free NH_3 concn (g-free NH_3/100 g-solv.)	Solubility (g/100 g-solv.)	Temp (°C)	Free NH_3 concn (g-free NH_3/100 g-solv.)	Solubility (g/100 g-solv.)
0	0.2	14.48	45	3.1	27.06
	3.9	6.85		9.6	18.76
	4.1	6.52		14.1	14.17
	5.6	5.53		17.2	12.68
	10.4	4.22		23.3	10.93
	15.2	3.72		27.1	9.30
	17.7	3.32		35.0	8.70
	20.0	3.23			
	24.1	3.20	55	3.6	32.12
	27.4	2.88		8.9	22.16
	31.8	2.66		12.9	18.68
				17.6	15.57
25	2.2	18.57		23.1	12.78
	4.7	15.59		29.0	10.89
	7.9	12.42		36.6	10.08
	12.3	10.40			
	16.6	8.62			
	21.9	7.27			
	25.9	6.81			
	31.5	6.03			
35	1.7	24.98			
	9.4	14.77			
	15.8	11.50			
	20.6	9.81			
	24.4	8.86			
	27.3	7.76			
	30.7	7.67			

nickel(II) sulfate monohydrate: hexaamminenickel(II) sulfate dihydrate was washed with ammoniacal ethyl alcohol and ether. Diamminenickel(II) sulfate: hexaamminenickel(II) sulfate dihydrate was heated at 110 °C for 2 h. The compositions of ammine complexes prepared are given in Table 6.

Table 6. Compositions of ammine complexes of nickel(II)

Compound	Ni(wt%)		NH_3(wt%)	
	Found	Calcd	Found	Calcd
$[Ni(NH_3)_4]CO_3 \cdot 3H_2O$	16.2	16.9	30.7	29.4
$[Ni(NH_3)]CO_3 \cdot H_2O$	38.5	38.2	11.4	11.1
$[Ni(NH_3)_5]SO_4 \cdot H_2O$	21.7	21.3	30.3	30.8
$[Ni(NH_3)_2]SO_4$	30.1	31.1	16.6	18.0

Apparatus. A Rigaku Denki Thermoflex high temperature type TG-DTA instrument was used for TG and DTA studies. Samples, 10—20 mg in weight, were pyrolyzed under a streaming nitrogen gas atmosphere. The flow rate of nitrogen gas was 40 ml/min. The heating rate of the furnace was 10 and 20 deg/min. Ignited alumina was used as a reference material in the DTA sample block. X-Ray diffraction patterns were recorded over the range $2\theta = 10$—60° with an X-ray diffractometer, Rigaku Denki Geigerflex, using nickel filtered Cu $K\alpha$ radiation at 30 kV and 15 mA as the X-ray diffraction source, with a 2°/min scanning speed, a 1 s time constant, a 1° divergency slit and 0.2 mm receiving slit.

Results and Discussion

Thermal Decomposition Process. The TG and DTA curves, in nitrogen, for hexaamminenickel(II) sulfate dihydrate and pentaamminenickel(II) sulfate monohydrate are shown in Fig. 3.

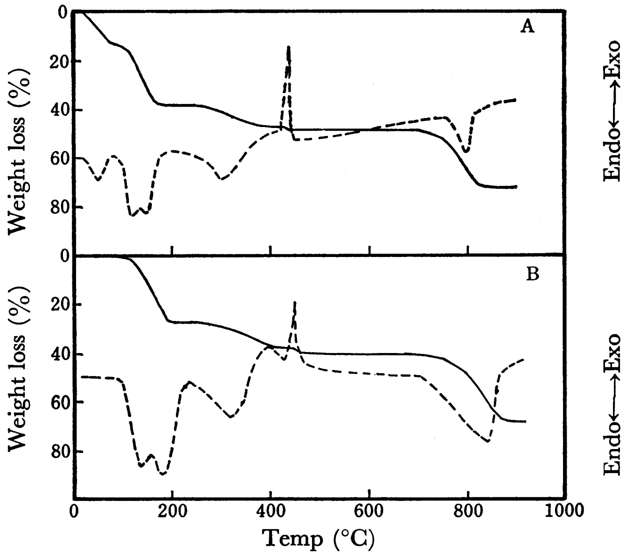

Fig. 3. TG and DTA curves of hexaamminenickel(II) sulfate dihydrate and pentaamminenickel(II) sulfate monohydrate under a nitrogen gas atmosphere. A: $[Ni(NH_3)_6]SO_4 \cdot 2H_2O$, B: $[Ni(NH_3)_5]SO_4 \cdot H_2O$, flow rate of nitrogen gas: 40 ml/min, heating rate of furnace (deg/min)—A: 10, B: 20, amount of sample (mg)—A: 13.4, B: 16.6, —: TG, ---: DTA.

Hexaamminenickel(II) sulfate dihydrate appears to decompose in five steps as follows:

$$\text{(I)}\quad [Ni(NH_3)_6]SO_4 \cdot 2H_2O \longrightarrow [Ni(NH_3)_6]SO_4 + 2H_2O$$

$$\text{(II)}\quad [Ni(NH_3)_6]SO_4 \longrightarrow [Ni(NH_3)_2]SO_4 + 4NH_3$$

$$\text{(III)}\quad [Ni(NH_3)_2]SO_4 \longrightarrow [Ni(NH_3)_{0.5}]SO_4 + 1.5NH_3$$

$$\text{(IV)}\quad [Ni(NH_3)_{0.5}]SO_4 \longrightarrow NiSO_4 + 0.5NH_3$$

$$\text{(V)}\quad NiSO_4 \longrightarrow NiO + SO_2 + (1/2)O_2$$

The complex, $[Ni(NH_3)_6]SO_4 \cdot 2H_2O$, begins to decompose at room temperature and loses two moles of water of crystallization per mole of compound to form $[Ni(NH_3)_6]SO_4$ up to 80 °C. The second step, corresponding to the loss of four moles of ammonia per mole of compound, begins immediately after the first step at *ca.* 80 °C, showing a definite break in the TG curve at *ca.* 180 °C. The third step of the decomposition results in the gradual loss of one and half moles of ammonia per mole of compound up to 350 °C. The fourth step of the decomposition begins at *ca.* 350 °C to gradually form $NiSO_4$ up to 450 °C. $NiSO_4$ begins to decompose at *ca.* 650 °C, resulting in the formation of NiO up to 820 °C. Endothermic peaks in the DTA curve at

50, 120—140, 300, 426, and 790 °C seem to correspond to steps I, II, III, IV, and V, respectively. The following studies have been performed on the thermal decomposition process of hexaamminenickel(II) sulfate.

(1) Paris:[8) $[Ni(NH_3)_6]SO_4 \longrightarrow [Ni(NH_3)_2]SO_4 \longrightarrow [Ni(NH_3)]SO_4 \longrightarrow [Ni(NH_3)_{0.5}]SO_4 \longrightarrow NiSO_4$

(2) Ephraim:[9) $[Ni(NH_3)_6]SO_4 \longrightarrow [Ni(NH_3)_4]SO_4 \longrightarrow [Ni(NH_3)_2]SO_4 \longrightarrow [Ni(NH_3)]SO_4 \longrightarrow [Ni(NH_3)_{0.5}]SO_4 \longrightarrow NiSO_4$

(3) Viltange:[10) $[Ni(NH_3)_6]SO_4 \xrightarrow{80-230\,^{\circ}C} [Ni(NH_3)_2]SO_4 \xrightarrow{230-350\,^{\circ}C} [Ni(NH_3)_{0.5}]SO_4 \xrightarrow{350-450\,^{\circ}C} NiSO_4$

(4) George and Wendlandt:[7) $[Ni(NH_3)_6]SO_4 \xrightarrow{100-190\,^{\circ}C} [Ni(NH_3)_2]SO_4 \xrightarrow{190-500\,^{\circ}C} NiSO_4$

Our results agree with the thermal decomposition process given by Viltange,[10) although the temperature we obtained for DTA peaks is lower by 10—20 degrees. A sharp exothermic peak in the DTA curve at 420—440 °C does not seem to have been reported so far.

Pentaamminenickel(II) sulfate monohydrate appears to decompose in four steps. The first step begins at *ca.* 110 °C, showing a definite break in the TG curve at *ca.* 180 °C. The weight loss up to this point corresponds to the loss of three moles of ammonia and one mole of water of crystallization per mole of compound. The thermal decomposition proceeds afterward in a similar manner to that after the third step of hexaamminenickel(II) sulfate dihydrate. The reason why the peaks in DTA curve of pentaamminenickel(II) sulfate monohydrate are situated at higher temperature region than those of hexaamminenickel(II) sulfate dihydrate seems to be due to the fact the heating rate of the furnace in the thermal decomposition of the former is faster than that of the latter.

Figure 4 shows the results of the thermal decomposition of hexaamminenickel(II) nitrate and carbonate tetrahydrate and tetraamminenickel(II) carbonate trihydrate. Tetraamminenickel(II) carbonate trihydrate and monoamminenickel(II) carbonate monohydrate (Table 6) are formed by the isothermal decomposition of hexaamminenickel(II) carbonate tetrahydrate at room temperature under a dilute ammonia atmosphere and at 60 °C in the air, respectively. Hexaamminenickel(II) carbonate tetrahydrate appears to decompose in five steps as follows:

(I) $[Ni(NH_3)_6]CO_3 \cdot 4H_2O \longrightarrow [Ni(NH_3)_4]CO_3 \cdot 3H_2O + 2NH_3 + H_2O$

(II) $[Ni(NH_3)_4]CO_3 \cdot 3H_2O \longrightarrow [Ni(NH_3)]CO_3 \cdot H_2O + 3NH_3 + 2H_2O$

(III) $[Ni(NH_3)]CO_3 \cdot H_2O \longrightarrow [Ni(NH_3)]CO_3 + H_2O$

(IV) $[Ni(NH_3)]CO_3 \longrightarrow NiCO_3 + NH_3$

(V) $NiCO_3 \longrightarrow NiO + CO_2 + (1/2)O_2$

Although no clear distinction is found between the first step and the second step from the TG curve, the complex, $[Ni(NH_3)_6]CO_3 \cdot 4H_2O$, seems to decompose *via* the complex, $[Ni(NH_3)_4]CO_3 \cdot 3H_2O$, because two endothermic peaks are found in the DTA curve at a temperature between 25 and 140 °C, and because $[Ni(NH_3)_4]CO_3 \cdot 3H_2O$ is produced from $[Ni(NH_3)_6]CO_3 \cdot 4H_2O$ at room temperature under a dilute ammonia atmosphere and is comparatively stable. Namely, $[Ni(NH_3)_6]CO_3 \cdot 4H_2O$ begins to decompose at room temperature and becomes $[Ni(NH_3)]CO_3 \cdot H_2O$ up to 140 °C *via* $[Ni(NH_3)_4]CO_3 \cdot 3H_2O$. The third step, corresponding to the loss of remaining water of crystallization, begins immediately after the second step at 140 °C to form $[Ni(NH_3)]CO_3$ up to 220 °C. The fourth step of the decomposition results in the gradual loss of remaining ammonia with the formation of $NiCO_3$ up to 300 °C. The fifth decomposition step begins at *ca.* 300 °C and results in abrupt weight loss with the formation of NiO up to 400 °C. The endothermic peaks in DTA curve at 95, 105, 153, and 345 °C seem to correspond to steps I, II, III, and IV, respectively.

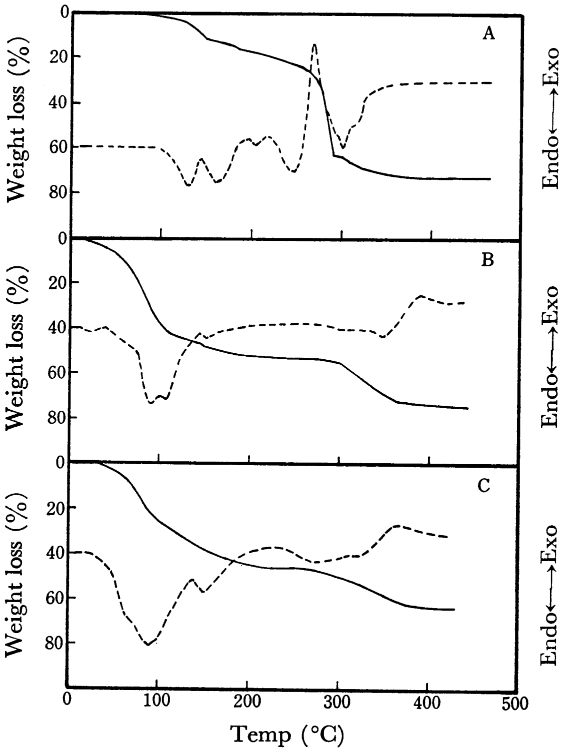

Fig. 4. TG and DTA curves of hexaamminenickel(II) nitrate and carbonate tetrahydrate and tetraamminenickel(II) carbonate trihydrate under a nitrogen gas atmosphere.
A: $[Ni(NH_3)_6](NO_3)_2$, B: $[Ni(NH_3)_6]CO_3 \cdot 4H_2O$, C: $[Ni(NH_3)_4]CO_3 \cdot 3H_2O$, flow rate of nitrogen gas: 40 ml/min, heating rate of furnace (deg/min)—A, B: 10, C: 20, amount of sample (mg)—A: 13.6, B: 16.6, C: 15.6, —: TG, ---: DTA.

The decomposition of tetraamminenickel(II) carbonate trihydrate seems to proceed in four steps. The first step of the decomposition begins at *ca.* 40 °C, showing a definite break in the TG curve at *ca.* 140 °C. The weight loss up to this point corresponds to the loss of three moles of ammonia and two moles of water of crystallization per mole of compound. The next steps are similar to the processes after the third step of hexaamminenickel(II) carbonate tetrahydrate.

Hexaamminenickel(II) nitrate seems to decompose in three steps as follows:

$$\text{(I)}\ [\mathrm{Ni(NH_3)_6}](\mathrm{NO_3})_2 \longrightarrow [\mathrm{Ni(NH_3)_4}](\mathrm{NO_3})_2 + 2\mathrm{NH_3}$$

$$\text{(II)}\ [\mathrm{Ni(NH_3)_4}](\mathrm{NO_3})_2 \longrightarrow [\mathrm{Ni(NH_3)_{2.5}}](\mathrm{NO_3})_2 + 1.5\mathrm{NH_3}$$

$$\text{(III)}\ [\mathrm{Ni(NH_3)_{2.5}}](\mathrm{NO_3})_2 \longrightarrow \mathrm{NiO}$$

The complex $[\mathrm{Ni(NH_3)_6}](\mathrm{NO_3})_2$ begins to decompose at *ca.* 80 °C, showing a definite break in the curve at *ca.* 145 °C. The weight loss up to this point corresponds to the loss of two moles of ammonia per mole of compound. The second step begins immediately after the first step, losing one and half moles of ammonia per mole of compound up to 200 °C. The third step of the decomposition results in the abrupt weight loss with the formation of NiO at *ca.* 380 °C. Endothermic peaks at 140 and 160 °C, and exothermic peak at 250 °C seem to correspond to steps I, II, and III, respectively. George and Wendlandt[7] indicated that the ratio of evolved ammonia to nickel up to 180 °C is 2.76: 1. However, the ratio of that up to 200 °C has been found to be 3.5: 1 in the present study. Since the third step of the decomposition does not seem to be a single elementary reaction and is difficult to analyze, the detailed mechanism of the reaction has not been clarified. George and Wendlandt[7] observed that only nitrogen, water and oxygen are present in the decomposition gases above 260 °C by mass spectrographic analysis, and considered that the reaction between nitrate and ammonia should proceed. This conclusion has been confirmed on the basis of the appearance of the large exothermic peak at 250 °C.

Kinetics. The methods of Freeman-Carroll[13] and Coats-Redfern[14] were used to study the kinetics. The methods can be used only when the reaction is a single elementary reaction. Thus the kinetics was studied only for the first and second steps of hexaamminenickel(II) nitrate decomposition, and the third and the fifth steps of hexaamminenickel(II) sulfate dihydrate decomposition. The formula of the Freeman-Carroll method can be written as

$$\Delta \log (\mathrm{d}W/\mathrm{d}t)/\Delta \log W_\mathrm{r} = x - E\Delta(1/T)/2.303RT(\Delta \log W_\mathrm{r}), \qquad (1)$$

where $\mathrm{d}W/\mathrm{d}t$ is the weight change in mg·per minute, x the order of the reaction, T the absolute temperature and $W_\mathrm{r} = W - W_\mathrm{c}$, where W is the weight (mg) at time T, and W_c the weight (mg) of the sample at the end of the reaction. E is the energy of activation. If the plot of the ratio $\Delta \log (\mathrm{d}w/\mathrm{d}t)/\Delta \log W_\mathrm{r}$ values *vs.* $\Delta(1/T)/\log W_\mathrm{r}$ lie on a straight line, the activation energy and the reaction order will be given by its slope and intercept, respectively. This is illustrated in Figs. 5 and 6 for the decomposition of hexaamminenickel(II) nitrate and sulfate dihydrate, respectively.

The formula of the Coats-Redfern method can be written as

$$\left.\begin{array}{l} x \neq 1: \log\{1 - (1 - \alpha)^{1-x}/(1 - x)T^2\} \\ x = 1: \log\{- \log(1 - \alpha)/2.303T^2\} \end{array}\right\},$$
$$= \log(AR/\phi E)(1-2RT/E) - E/2.303RT, \qquad (2)$$

where α is the fraction of reaction, ϕ the heating rate of furnace and A the frequency factor. Graphic repre-

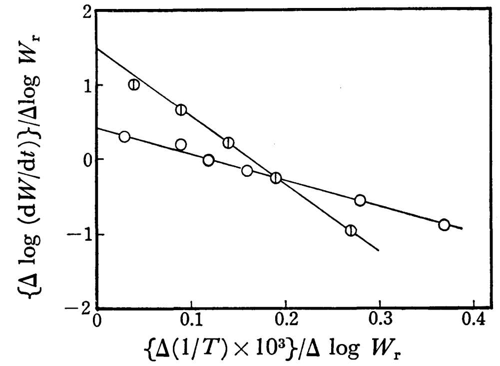

Fig. 5. Freeman-Carroll straight line for the I and II steps of hexaamminenickel(II) nitrate decomposition. -○-: Step I, -⦶-: Step II.

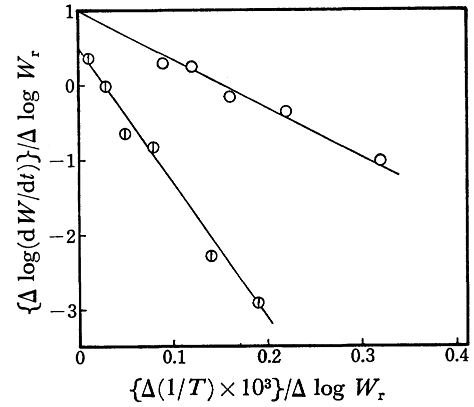

Fig. 6. Freeman-Carroll straight line for the III and V steps of hexaamminenickel(II) sulfate dihydrate decomposition.
-○-: Step III, -⦶-: Step V.

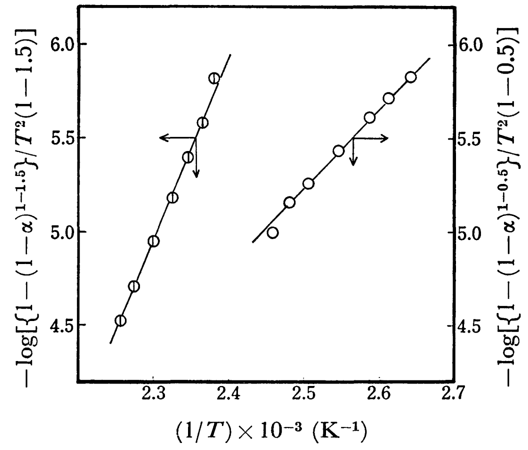

Fig. 7. Coats-Redfern straight line for the I and II steps of hexaamminenickel(II) nitrate decomposition. -○-: Step I, -⦶-: Step II, x— -○-: 0.5, -⦶-: 1.5.

TABLE 7. REACTION ORDERS AND ACTIVITION ENERGIES OF THE THERMAL DECOMPOSITION OF NICKEL(II) AMMINE COMPLEXES

Nickel(II) ammine complexes	Decomposition step	E_1	E_2	E_{av}	x_1	x_2	x_{av}
$[Ni(NH_3)_6](NO_3)_2$	I	16.2	16.8	16.5	0.4	0.5	0.5
	II	38.2	39.4	38.8	1.5	1.5	1.5
$[Ni(NH_3)_6]SO_4\cdot 2H_2O$	III	27.9	22.6	25.3	1.0	1.0	1.0
	V	80.6	78.2	79.4	0.5	0.5	0.5

E_1, x_1: determined by the Freemann-Carroll method, E_2, x_2: determined by the Coats-Redfern method, E_1, E_2: activation energy (kcal/mol), x_1, x_2: reaction order.

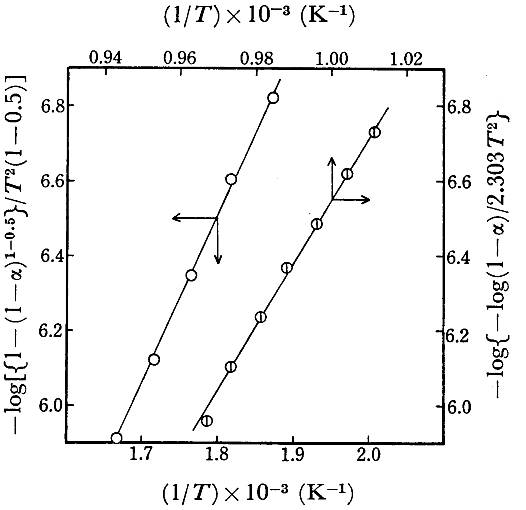

Fig. 8. Coats-Redfern straight line for the III and V steps of hexaamminenickel(II) sulfate dihydrate decomposition.
-○-: Step III, -⦶-: Step V.

sentation of the $\log\{1-(1-\alpha)^{1-x}/(1-x)\,T^2\}$ or $\log\{-\log(1-\alpha)/2.303T^2\}$ values as a function of $1/T$ gives a straight line of slope $-E/2.303R$ for the correct value of x. This is illustrated in Figs. 7 and 8 for the decomposition of hexaamminenickel(II) nitrate and sulfate dihydrate, respectively. The results are given in Table 7.

X-Ray Diffraction Data for Nickel(II) Ammine Complexes Powders. X-Ray diffraction data of four kinds of nickel(II) ammine complexes powders are given in Table 8. Hexaamminenickel(II) carbonate tetrahydrate and sulfate dihydrate decompose so rapidly in the air even at room temperature that their X-ray diffraction data have not been investigated.

TABLE 8. X-RAY DIFFRACTION DATA OF NICKEL(II) AMMINE COMPLEXES POWDERS

d(Å)	I/I_1	d(Å)	I/I_1
$[Ni(NH_3)_6]Cl_2\cdot 0.5H_2O$		$[Ni(NH_3)_6](NO_3)_2$	
5.83	100	6.28	100
3.56	30	3.85	31
3.04	8	3.29	9
2.91	23	3.14	8
2.52	16	2.72	7
2.06	9	2.43	3
1.94	6	2.09	4
1.78	6	1.92	3
1.70	6		
1.59	6		
$[Ni(NH_3)_5]SO_4\cdot H_2O$		$[Ni(NH_3)_2]SO_4$	
6.07	53	5.57	100
5.61	77	4.93	50
5.34	32	3.60	25
5.19	45	3.24	38
4.42	100	2.59	31
4.19	69	1.93	21
4.02	57	1.77	20
3.47	30		
3.15	24		
3.00	30		

This study is a part of studies on *Gasification of Coals Treated with Non-aqueous Solvents* being carried out by Coal Gasification Research Group (representative, Prof. Y. Tamai) in the Chemical Research Institute of Non-aqueous Solutions, Tohoku University. The object of the study is the recovery of nickel used as a catalyst in the coal gasification process.

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