[CONTRIBUTION FROM THE METALLURGY DIVISION OF THE OAK RIDGE NATIONAL LABORATORY]

Alkali Metal–Nickel Oxides of the Type $MNiO_2$

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This article describes the preparation and properties of two compounds of trivalent nickel which have not previously been isolated. The compounds sodium nickelate(III), $NaNiO_2$, and lithium nickelate(III), $LiNiO_2$, were prepared by bubbling oxygen through sodium hydroxide and lithium hydroxide, respectively, contained in nickel tubes at about 800°. The crystals obtained upon removing the top section of the cooled melt were washed with absolute ethyl alcohol to remove the hydroxide. The sodium compound was also prepared by heating a one to three mixture of sodium peroxide and sodium hydroxide in a nickel tube and treating as described above. Lithium nickelate(III) is rhombohedral with the cesium dichloroiodide, $CsCl_2I$, structure. The unit cell dimensions, referred to hexagonal axes, are a = 2.88 Å., c = 14.2 Å. The hexagonal cell contains three formula weights and the calculated density is 4.78 g./cc. (measured 4.81 g./cc.). Two crystal modifications were found for sodium nickelate(III) with a transformation temperature of about 220°. The low temperature crystal form is a monoclinic distortion of the lithium nickelate(III) structure. The unit cell dimensions are a = 5.33 Å., b = 2.86 Å., c = 5.59 Å., β = 110° 30′. There are two formula weights per unit cell and the calculated density is 4.74 g./cc. (measured 4.72 g./cc.). The high temperature crystal form is isomorphous with lithium nickelate(III). The unit cell dimensions, referred to hexagonal axes, are a = 2.96 Å., c = 15.77 Å. The reactions of sodium nickelate(III) and lithium nickelate(III) with alkaline solutions, with water, and with various acids were investigated and the results reported here.

Introduction

The higher oxidation states of metals have been the subject of much recent work and discussion.[1] Tri- and tetrapositive nickel hold a place of primary importance in this work. This paper reports the preparation, properties and crystal structure of two alkali metal–nickel oxides in which the nickel is formally tripositive. This nickel will be designated as Ni^{III}, although it may be a mixture of Ni^{II} and Ni^{IV}.

Hofmann and Hiendlmaier[2] reported obtaining potassium nickelate(III), $KNiO_2$, by fusion of potassium superoxide on a nickel plate. Glemser and Einerhand[3] inferred the existence of sodium nickelate(III) and potassium nickelate(III) as intermediates in preparing γ-nickelic oxyhydroxide hydrate, γ-$NiOOH \cdot xH_2O$, but did not separate or study either. Lander and Wooten[4,5] obtained a product ($BaNiO_3$) from fusing barium peroxide in nickel in which the formal valence of nickel was four. They also obtained a product of variable composition around $Ba_2Ni_2O_5$. They made crystal structure analyses and measured resistivities and magnetic susceptibilities of the two products to determine the bond types.

Verwey, Haaijman, Romeijn and van Oosterhout[6] prepared a series of lithium–nickel oxides containing Ni^{III} in which the lithium content varied up to a composition which may be written as $Li_{0.2}Ni_{1.8}O_2$. For these solid solutions they report the X-ray diffraction pattern to be similar to that of nickelous oxide with a small contraction of the lattice with increasing amounts of lithium. These authors point out the importance of substances of this type to the study of ionic semiconductors and their possible application as "thermistors."

Tichenor[7] has postulated the formation of higher valent nickel in the nickel oxide of Edison storage batteries by the replacement of divalent nickel ions with monovalent lithium ions, which would explain the higher conductivity observed with lithium salt additives.

Experimental Procedures

Materials and Apparatus.—All reaction tubes were of grade "A" 99.4% nickel plus cobalt, containing 0.1% copper, 0.15% iron, 0.25% manganese, 0.05% silicon. The outer tube dimensions were 2.5 cm. by 30 cm., one mm. wall thickness. The inner tubes were 1.2 cm. by 45 cm., 0.9 mm. wall. Some thicker walled tubes were used for the lithium nickelate(III) preparations. The tube dimensions were 2.2 cm. by 35 cm., 2 mm. wall thickness.

C.P. sodium hydroxide and sodium peroxide were used. For the lithium nickelate(III) preparations, lithium hydroxide was obtained by heating C.P. lithium hydroxide monohydrate at 200° for two days. Commercial cylinder oxygen was used.

Heating was done in a tube furnace. Temperatures were measured by a chromel–alumel thermocouple wired to the tube.

Preparation of $NaNiO_2$. First Method.—Sixty grams of sodium hydroxide was melted in a nickel tube preheated to 500°. A smaller nickel tube, constricted at one end, was placed so that the constricted end lay in the melt. Oxygen was forced through the inner tube and bubbled into the melt at about 3 cc./second. Preparations were made by heating from two to four days at temperatures from 650 to 850°. The only effect of increasing temperature which was noted was an increase in the rate of formation of sodium nickelate(III). After heating, the tubes were quenched from the reaction temperature by immersing first in oil and then in water. During cooling the sodium hydroxide contracted considerably leaving a large cluster of sodium nickelate(III) crystals on both inner and outer tubes covered only by a thin film of hydroxide at what had been the liquid–gas interface. This cluster of crystals was removed and washed with absolute alcohol until a pH paper test indicated absence of hydroxide.

For the X-ray determinations special preparations were made which were allowed to cool in a helium filled dry-box. For determination of the low temperature modification, a single crystal on the order of 0.2 to 0.3 mm. was selected with the aid of a binocular microscope inside the dry-box but with its eye-pieces mounted outside the view glass. The crystal was placed inside a 0.5-mm. glass capillary and held stationary by a bit of wax which also served to seal off the capillary's open end. The X-ray patterns of a crystal prepared in this manner showed no change in a period in excess of a month. These precautions were found to be necessary, since otherwise the sodium nickelate(III) reacted with moisture and carbon dioxide in air during the several hours required for the taking of an X-ray photograph. For determination of the high temperature modification some sodium nickelate(III) was crushed to a powder in the dry-box and loaded into a glass capillary as described above except that the capillary was sealed by fusing the glass at the open end.

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(1) W. Klemm, *Angew. Chem.*, **63**, 396 (1951).

(2) K. A. Hofmann and H. Hiendlmaier, *Ber.*, **39**, 3184 (1906).

(3) O. Glemser and J. Einerhand, *Z. anorg. Chem.*, **261**, 26, 43 (1950).

(4) J. J. Lander and L. A. Wooten, THIS JOURNAL, **73**, 2452 (1951).

(5) J. J. Lander, *Acta Cryst.*, **4**, 148 (1951).

(6) E. J. Verwey, P. W. Haaijman, F. C. Romeijn and G. W. van Oosterhout, *Philips Research Repts.*, **5**, 173 (1950).

(7) R. L. Tichenor, *Ind. Eng. Chem.*, **44**, 973 (1952).

Second Method.—Sixty grams of sodium hydroxide was mixed with 20 g. of sodium peroxide and added to a nickel tube at 650° and heated for seven days. The tube was quenched and treated as described above. The crystals had a different habit and were larger, but gave the same X-ray and chemical analysis as those produced by the first method.

Preparation of $LiNiO_2$.—Fifty grams of lithium hydroxide was melted in a nickel tube and a smaller tube inserted through which oxygen was bubbled as before. The tube was heated at 800° for 24 hours then quenched as before. The total contents were removed and washed with alcohol. Metallic particles were removed by a magnet, and the finely divided gray product was dried in a vacuum desiccator. This method yielded the product of highest oxidizing power. The structure was determined from a powder spectrometer trace of a sample from this preparation.

Results of the analyses of other preparations indicate that by heating the reaction tube at 850° and passing oxygen over or through the melt, products of about 75% of the theoretical oxidizing power could be obtained. Preparations at lower temperature (600–750°) were always more deficient in oxidizing power. The X-ray patterns of preparations deficient in oxidizing power were frequently identical with that of the first preparation, although some showed NiO lines in addition.

Analysis for Oxidizing Power.—The analysis for oxidizing power of the sodium nickelate(III) products was made by dissolving the sodium nickelate(III) in a hydrochloric acid–potassium iodide mixture under an inert gas and titrating with thiosulfate the iodine released. Blank runs titrated from 0.00 to 0.05 cc. of 0.1 *N* sodium thiosulfate.

The lithium compound presented the difficulty of not dissolving readily in the dilution of acid of ordinary iodometric titrations; also the blanks sharply rose in oxidation titer and decreased in reproducibility as the acid concentration was raised. Therefore, a more elaborate method had to be used. A satisfactory procedure for the analysis of the lithium nickelate(III) was the following. About 0.3 g. of the lithium compound was added to a two-necked reaction flask containing a stirring magnet and 3 g. of potassium iodide.

A vacuum pump with liquid nitrogen trap and a helium tank with a hot copper purifier were connected to one neck of the flask through a separatory funnel. An oil-filled gas trap was connected to the other neck. The reaction flask was evacuated and flushed with helium several times, then it was filled with helium, and the stopcock of the separatory funnel closed. Fifty cc. of distilled 6 *N* hydrochloric acid was added to the funnel, and the dissolved gases pumped off. The 50 cc. of hydrochloric acid was then forced into the reaction flask by helium pressure. The mixture was stirred for two hours, then 200 cc. of 1.0 *N* sodium hydroxide was degassed the same way and added. Finally the solution was titrated with thiosulfate. Blanks then titrated 0.01 to 0.03 cc. of 0.1 *N* sodium thiosulfate.

Results

Analysis of Products.—The sodium nickelate(III) products contained by analysis 20.8 ± 0.6% sodium, 51.2 ± 0.4% nickel, from less than 0.001 up to 0.11% cobalt and had an oxidizing power, calculated as Ni^{III}/Ni, of 1.000 ± 0.004. The theoretical compound, $NaNiO_2$, has 20.23% sodium, 51.62% nickel and $Ni^{III}/Ni = 1.000$. No manganese was detected in the sodium nickelate(III) product.

The results of the analyses of the lithium nickelate(III) products for lithium, nickel, manganese, cobalt and oxidizing power are shown in Table I.

The manganese in the lithium compound was found as the permanganate; therefore, in calculating the Ni^{III} present, five equivalents per mole of manganese found were subtracted from the value obtained in the oxidizing power determination. The cobalt found by analysis was counted as tripositive, and the data were corrected in the same manner.

Table I

Analyses of $LiNiO_2$ Preparations

Temp. of prep., °C.	Li, %	Ni, %	Co, %	Mn, %	Oxidizing power in meq./g.	Ni^{III}/Ni
800	8.48	54.9	0.11	0.11	9.05	0.95
750	6.0	61.6	.14	.18	8.01	.74
800	4.0	66.0	.41[a]	.20	5.65	.48
850	10.15[b]	54.2	.14	.16	7.22	.77
850	7.89[b]	56.4	.028	.15	6.53	.67
$LiNiO_2$	7.11	60.11	.00	.00	10.24	1.000

[a] Made in an impure nickel crucible, thus the high Co content. [b] No alcohol washing; Li_2O present by X-ray analysis.

Lithium monoxide was found in the lithium nickelate(III) before washing with alcohol, which may account for the high lithium content of the products before washing.

Properties of $NaNiO_2$.—The sodium nickelate(III) was obtained as lustrous black intergrowing platelets with a pycnometrically measured density of 4.72 g./cc. The temperature of the crystal structure transformation was determined to be (220 ± 10°) with the use of a differential thermal analysis apparatus[8] modified for operation in a purified argon atmosphere. The temperature difference *vs.* temperature curve showed only one peak between room temperature and 600°. The peak corresponded to a process which was endothermic on heating.

X-Ray evidence shows that the sodium nickelate(III) crystals take up moisture and carbon dioxide from the air to form sodium carbonate monohydrate on the crystal surfaces. In the presence of 6 *N* sulfuric acid, perchloric acid or nitric acid the crystals slowly dissolve with the evolution of oxygen. In all cases hydrogen peroxide accelerates the solution. Hydrochloric acid rapidly dissolves the compound with the evolution of chlorine.

Dilute acid suspensions of the compound rapidly oxidize manganous ions to manganese dioxide and permanganate, and oxidize iodide to iodine which is further oxidized to iodate.

The action of water on sodium nickelate(III) was studied. The results of X-ray and chemical analyses of water-washed products show that γ-nickelic oxyhydroxide hydrate, $\gamma\text{-NiOOH}\cdot x H_2O$, and nickelous hydroxide, $Ni(OH)_2$, are formed; and that by cautious hydrolysis in a cold, alkaline solution, the amount of nickelous hydroxide formed can be lessened greatly. An intermediate phase between sodium nickelate(III) and γ-nickelic oxyhydroxide hydrate was indicated by some patterns of sodium nickelate(III) exposed only a few minutes to water, but this intermediate was not isolated.

The leaching of sodium atoms out of the crystals as obtained (not ground) was slow. Even after two weeks of washing a sample of sodium nickelate(III) with water, the sodium content was still 1.0%.

Properties of $LiNiO_2$.—The lithium nickelate(III) was obtained as a gray-black powder with a pycnometrically measured density of 4.81 g./cc. Microscopic examination of some of the products

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(8) *Cf.*, W. J. Smothers, Y. Chiang and A. Wilson, "Bibliography of Differential Thermal Analysis," University of Arkansas Institute of Science and Technology, Fayetteville, Ark., 1951.

revealed, along with the powder, some lustrous black crystals which appeared to be octahedra.

The cold dilute acids sulfuric, perchloric and nitric dissolve it very slowly. Hydrochloric acid dissolves it more rapidly with the evolution of chlorine.

Studies of reaction of lithium nickelate(III) with water and 1 *N* lithium hydroxide indicate that lithium nickelate(III) remains unchanged in cold water and slowly decomposes to nickelous oxide in hot water, without the formation of any observed intermediate compounds. The rate of decomposition is even slower in cold lithium hydroxide solution.

Crystal Structure Determinations. The Crystal Structure of $LiNiO_2$.—The sample was packed into a flat specimen holder, and a spectrometer trace was taken. The pattern was successfully indexed by assuming the structure to be rhombohedral of the cesium dichloroiodide, $CsCl_2I$, type. The cell dimensions, referred to hexagonal axes, are $a = 2.878$ Å., $c = 14.19$ Å. The hexagonal cell contains three formula weights, and the calculated density is 4.78 g./cc. The measured density is 4.81 g./cc. The atoms lie in the following positions of space group $D_{3d}^5 - R\bar{3}m$

$(000,\ ^1/_3\,^2/_3\,^1/_3,\ ^2/_3\,^1/_3\,^2/_3)\ +$
Ni $3a$: 000
Li $3b$: $00^1/_2$
O $6c$: $00z,\ 00\bar{z}$

An oxygen parameter of $z = 0.25$ gave good agreement between observed and calculated intensities, as shown in Table II. Also compared in this table are values of observed and calculated $\sin^2\theta$. The indices listed refer to the hexagonal cell.

TABLE II

OBSERVED AND CALCULATED INTENSITIES AND $\sin^2\theta$ FOR $LiNiO_2$

	I		$\sin^2\theta$	
hkl	Obsd.	Calcd.	Obsd.	Calcd.
003	160	170	0.0266	0.0265
011	66	84	.0986	.0986
006	16	10	.1062	.1062
102	23	29	.1073	.1074
014	151	135	.1428	.1428
105	25	34	.1693	.1694
009		6		.2389
017	28	19	.2401	.2401
108	42	38	.2843	.2844
110	41	38	.2868	.2868
113	21	24	.3132	.3134
201	9	8	.3855	.3854
01, 10		5		.3906
116	15	9	.3926	.3930
022		3		.3942
00, 12	7	6	.4249	.4248
204	17	18	.4292	.4296
10, 11	12	6	.4529	.4525
025		6		.4561
119	12	11	.5262	.5258
207		5		.5269
028	12	13	.5706	.5712
01, 13		5		.5941

The oxygen ions in this structure are very nearly perfectly cubic close packed. If the packing were perfect, c/a would be $2\sqrt{6}$ or 4.90; observed c/a is 4.93. The small nickel and lithium cations lie in alternate layers in the octahedral interstices of the oxygen array. Each cation has six oxygen neighbors, and each anion has three lithium neighbors and three nickel neighbors.

The Low Temperature Crystal Structure of $NaNiO_2$.—A series of precession photographs was taken of a single crystal mounted in a capillary as described above. Zirconium filtered Mo Kα radiation was used. These photographs showed sodium nickelate(III) to be monoclinic C-centered with $a = 5.33$ Å., $b = 2.86$ Å., $c = 5.59$ Å. and $\beta = 110°\ 30'$. No extinctions characteristic of a glide plane were observed. If there are two formula weights per unit cell the calculated density is 4.74 g./cc. as compared with the measured value of 4.72 g./cc.

A comparison with $NaFeO_2$, sodium ferrate(III), proved useful. This salt is rhombohedral,[9] $A = 5.59$ Å., $\alpha = 31°\ 20'$, with the cesium dichloroiodide structure. A coördinate transformation from the rhombohedral cell defined by the vectors A_1, A_2, A_3 to a monoclinic C-centered cell defined by vectors a, b, c may be made according to the relations

$$\begin{aligned} a &= A_1 + A_2 - 2A_3 \\ b &= A_1 - A_2 \\ c &= A_3 \end{aligned}$$

The monoclinic cell dimensions are $a = 5.23$ Å., $b = 2.02$ Å., $c = 5.59$ Å., $\beta = 108°\ 9'$. There are two formula weights per unit cell. The space group may be chosen to be $C_{2h}^3 - C2/m$, and the atomic positions are

$(000,\ ^1/_2\,^1/_2\,0)\ +$
2Fe in a: 000
2Na in d: $0\,^1/_2\,^1/_2$
4 0 in i: $x0z,\ \bar{x}0\bar{z},\ x = 0.278,\ z = 0.834$

The similarity between the sodium ferrate(III) lattice constants for the monoclinic coördinate system and those of sodium nickelate(III) is striking. Intensity measurements showed the analogy to go further.

If the two nickel atoms are at the origin and at $(^1/_2\,^1/_2\,0)$, and if the twofold axis is assumed to exist, the $h0l$ projection of the electron density is centro-symmetrical; and the signs of all the structure factors for this zone are positive. Structure factors measured by visual comparison with an intensity scale were obtained from the $h0l$ precession photograph and used to construct the electron density map shown in Fig. 1. The atomic array obviously corresponds to the monoclinic description of sodium ferrate(III). Oxygen parameters measured from this map are $x = 0.278$, $z = 0.795$. Table III is a comparison of observed and calculated structure factors for the $h0l$ zone for the oxygen parameters given above. The calculated values do not include a temperature correction.

To test the possibility that the atoms do not all lie in planes at $y = 0$ and $y = {}^1/_2$, as could be the case if the space group were C2 instead of C2/m, structure factors were measured from an $hk0$ precession photograph and compared with values calculated by assuming the existence of the mirror

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[9] S. Goldsztaub, *Bull. soc. franc. minéral.*, **58**, 6 (1935).

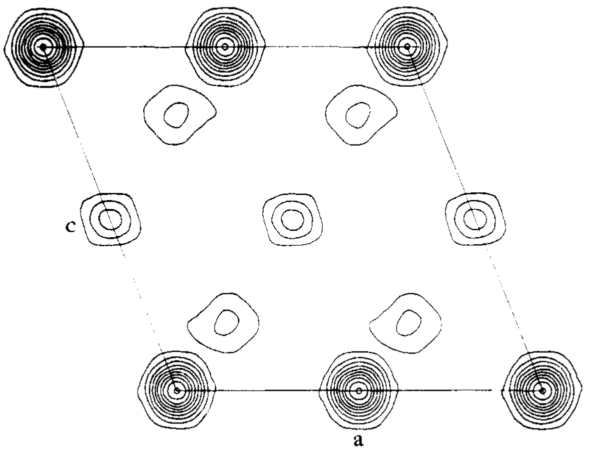

Fig. 1.—Fourier projection of $NaNiO_2$ on (010).

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THE *h0l* ZONE OF THE LOW TEMPERATURE MODIFICATION OF $NaNiO_2$

h0l	F Obsd.	F Calcd.	*h0l*	F Obsd.	F Calcd.
200	207	185	$20\bar{3}$	159	145
400	228	241	$40\bar{3}$	101	86
600	120	127	$60\bar{3}$	68	71
001	232	203	004	213	230
201	76	56	204	182	166
401	143	129	404	100	127
601	34	44	$20\bar{4}$	169	169
$20\bar{1}$	167	136	$40\bar{4}$	210	227
$40\bar{1}$	91	72	$60\bar{4}$	96	109
$60\bar{1}$	107	105	005	144	131
002	191	197	205	49	42
202	244	274	$20\bar{5}$	47	46
402	153	156	$40\bar{5}$	110	104
602	133	124	$60\bar{5}$	47	64
$20\bar{2}$	360	378	006	158	156
$40\bar{2}$	156	150	206	112	116
$60\bar{2}$	167	188	$20\bar{6}$	150	166
003	53	47	$40\bar{6}$	132	130
203	157	145	$60\bar{6}$	158	157
403	0	39	$20\bar{7}$	120	110
			$40\bar{7}$	33	44

plane. This comparison is shown in Table IV. Since the agreement is within the accuracy of our measurements, the space group was taken to be C2/m. The atomic positions are 2 Ni in *a*, 2 Na in *d*, and 4 O in *i*, $x = 0.278$, and $z = 0.795$. The coördination number for nickel, sodium and oxygen is six. Nickel has four oxygen neighbors at 1.95 Å. and two at 2.17 Å. The sum of the ionic radii is about 2.0 Å. Four of the oxygen neighbors of sodium have sodium–oxygen distances of 2.29 Å., and two have distances of 2.34 Å. The radius sum in this case is 2.35 Å. Each oxygen ion is coördinated to two nickel ions at 1.95 Å., one nickel ion at 2.17 Å., two sodium ions at 2.29 Å., and one sodium ion at 2.34 Å.

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THE *hk*0 ZONE OF THE LOW TEMPERATURE MODIFICATION OF $NaNiO_2$ AS MEASURED FROM A PRECESSION PHOTOGRAPH

*hk*0	F Obsd.	F Calcd.	*hk*0	F Obsd.	F Calcd.
200	198	185	020	271	291
400	245	241	220	141	148
600	127	127	420	173	201
110	122	106	620	93	109
310	151	133	130	88	75
510	54	50	330	101	97

The High Temperature Crystal Structure of $NaNiO_2$.—The glass capillary which contained sodium nickelate(III) powder was placed in a high temperature X-ray camera[10] and three Debye–Scherrer photographs were taken. The first photograph, made before heating, showed only lines of the monoclinic structure already described. The second photograph, taken at a specimen temperature somewhat in excess of 400°, showed a different structure which will be described below. The sharp lines in this high temperature photograph showed that the specimen temperature had been held satisfactorily constant during the exposure. The third photograph was taken after the specimen had cooled to room temperature and showed only lines of the room temperature phase.

Table V shows observed and calculated values of

TABLE V

OBSERVED AND CALCULATED $\sin^2\theta$ AND OBSERVED INTENSITIES FOR THE TWO CRYSTAL MODIFICATIONS OF $NaNiO_2$ AS MEASURED FROM DEBYE–SCHERRER PHOTOGRAPHS

S = strong, M = moderate, W = weak.

Low temperature				High temperature			
hkl	$\sin^2\theta$ Calcd.	$\sin^2\theta$ Obsd.	Obs. *I*	*hkl*	$\sin^2\theta$ Calcd.	$\sin^2\theta$ Obsd.	Obs. *I*
001	0.0217	0.0215	S	003	0.0215	0.0216	S−
$20\bar{1}$	.0855	.0864	M+	006	.0860	.0870	M
002	.0870			011	.0928	.0940	M−
200	.0958	.0969	M	102	.1000	.1013	M+
110	.0972			014	.1287	.1302	S
$11\bar{1}$	.1029	.1042	M+	105	.1502	.1518	tr
$20\bar{2}$	.1188	.1192	S	009	.1936		
111	.1349	.1350	S+	017	.2076	.2094	M
201	.1495			108	.2434	.2446	M+
$11\bar{2}$	.1521	.1537	W−	110	.2714	.2724	M+
$20\bar{3}$	.1955	.1964	W+	113	.2929	.2934	M−
003	.1957			10, 10	.3294	.3298	M
112	.2161	.2168	M	00, 12	.3442	.3441	W+
$11\bar{3}$	.2448	.2456	S	116	.3574	.3574	M
202	.2468			201	.3642		
$31\bar{1}$	.2625	.2628	S−	022	.3714	.3716	W
$31\bar{2}$	.2797	.2795	W	10, 11	.3796	.3798	W
310	.2887	.2885	W+	204	.4000	.4005	M
020	.2928	.2936	M	025	.4216		
021	.3145	.3159	M−	119	.4649		
$20\bar{4}$	.3156			207	.4789	.4782	W−
$31\bar{3}$	.3404	.3407	M+	01, 13	.4944		
113	.3408			028	.5148	.5136	M−
$40\bar{1}$	.3409			00, 15	.5378		
$40\bar{2}$	.3422			10, 14	.5589	.5577	W+
004	.3478	.3485	M−	20, 10	.6008	.5998	W
311	.3585	.3582	M−				
$22\bar{1}$	.3783						
022	.3798	.3807	M+				
$11\bar{4}$	.3810						
400	.3832						
$40\bar{3}$	.3869						
203	.3875	.3885	M−				
220	.3886						
$22\bar{2}$	.4116	.4118	M+				
221	.4423						
$31\bar{4}$	.4446						
401	.4689	.4672	W−				

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(10) An article describing this camera, designed by J. R. Johnson, is soon to be submitted for publication.

$\sin^2 \theta$ and observed intensities for the room temperature and high temperature photographs. The high temperature picture was indexed on the basis of a rhombohedral centered hexagonal unit cell, a = 2.96 Å., c = 15.77 Å. It is isomorphous with lithium nickelate(III) (a = 2.878 Å., c = 14.19 Å.) and with sodium ferrate(III) (a = 3.01 Å., c = 15.93 Å.). One extra line of weak intensity was observed on the high temperature picture. It corresponds with the strongest line (hkl = 111) of the room temperature monoclinic form.

Acknowledgment.—The authors are indebted to Dr. J. R. Johnson who took the Debye–Scherrer photographs of sodium nickelate(III), to Mr. S. D. Fulkerson who did the differential thermal analysis, and to Mr. J. H. Edgerton and co-workers who performed some of the chemical analyses.

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies on Aging and Coprecipitation. XLIV. Aging of Silver Bromide in the Colloidal State[1]

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Upon aging of freshly prepared colloidal supensions of silver bromide a marked decrease of the specific surface is found as measured by adsorption of wool violet and by electron microscopy. This decrease is a result of Ostwald ripening. After about one day at room temperature, no further change occurs by Ostwald ripening and a metastable period is attained when the concentration of ions in solution is below the rapid flocculation value. This may be followed by a period of slow flocculation. Effects of temperature, dialysis and potassium nitrate in various concentrations on Ostwald ripening and slow coagulation have been investigated. Cyanide and an excess of bromide promote Ostwald ripening. The rate of exchange between freshly prepared silver bromide particles in colloidal suspension and radioactive bromide in solution is extremely great, homogeneous distribution being attained within a few seconds. With a well-aged dialyzed colloid the rapid exchange is limited to a distance of 50 to 80 Å. beyond the surface of the particles. This very rapid exchange is attributed to Schottky defects which cause, even at room temperature and at 0°, a high silver and bromide mobility. Adsorbed wool violet limits the exchange to the surface layer only; adsorbed dye also prevents Ostwald ripening.

The aging of silver bromide in the flocculated state, either in contact with a solvent or as a dry powder has been studied by Kolthoff and O'Brien[2] who concluded that silver bromide is subject to thermal aging, which they attribute to the relatively high thermal mobility (even at room temperature) of the silver and bromide ions held at the surface of the precipitate. In measurements of the electrical conductivity of pellets of silver bromide, Shapiro and Kolthoff[3] substantiated this high mobility of the surface ions of silver bromide. No exact picture could be given of the nature of the thermal mobility. It was thought that the thermal mobility caused a cementing together and then a complete fusion of the primary particles in a floc of silver bromide.

In order to learn more of the nature of the thermal mobility of silver and bromide ions in silver bromide, it was decided to first study the aging of silver bromide in the colloidal state in which no fusion of particles can occur. In a subsequent paper the aging of silver bromide flocs prepared from colloidal solutions of varying age will be described. It will be shown there that the aging of flocculated silver bromide is entirely thermal in nature, not only in the dry state, but also in dilute aqueous bromide solution.

As long as the particles are in the colloidal state the main type of aging to be anticipated is so-called Ostwald ripening, *i.e.*, small particles with a larger solubility go into solution and larger particles grow at the cost of the small ones. As is shown in the present paper the Ostwald ripening is found to be surprisingly rapid and gives rise to a very considerable decrease of the number of particles upon aging of the colloidal solution. This could be followed by measurements of the specific surface by means of wool violet[4] and by taking electron micrographs. Further insight into the thermal mobility of silver and bromide ions in colloidal particles of silver bromide was obtained by measuring the rate of exchange between inactive particles and radioactive bromide dissolved in the medium. In freshly prepared colloids complete homogeneous exchange between solid and liquid was observed within a few seconds. When sols were dialyzed and permitted to age no complete exchange between all the bromide in the particles and that in solution was found, but the very rapid exchange was several times greater than would correspond to surface exchange only.

Experimental

Preparation and Aging of Colloidal Silver Bromide Suspensions. Stock Solutions.—0.1000 M silver nitrate solutions were prepared from Mallinckrodt A.R. silver nitrate which had been powdered and dried at 150°.

0.03214 M and 0.1000 M potassium bromide solutions were made from potassium bromide prepared by thermal decomposition of Mallinckrodt A.R. potassium bromate.

Method I. Non-dialyzed Colloid.—Forty-five-ml. samples of colloid were prepared by adding with a pipet having a drainage time of 13 seconds, 10 ml. of 0.1000 M silver nitrate to 35 ml. of 0.03214 M potassium bromide contained in a 100-ml. bottle. All of the non-dialyzed samples of colloid were prepared in this manner with the exception of a few where the effect of the concentration of potassium nitrate or the concentration of excess bromide was to be studied. In general the colloidal suspensions were 0.0222 M in solid

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[2] (a) I. M. Kolthoff and A. S. O'Brien, THIS JOURNAL, **61**, 3414 (1939); (b) *J. Chem. Phys.*, **7**, 401 (1939).

[3] I. Shapiro and I. M. Kolthoff, *J. Phys. Colloid Chem.*, **52**, 1319 (1948).

[4] I. M. Kolthoff and A. S. O'Brien, THIS JOURNAL, **61**, 3409 (1939).