

36.8 g., 1.6 moles of sodium) in refluxing benzene. No apparent reaction occurred until the mixture had been refluxed for 30 minutes; an exothermic reaction then started and some of the benzene boiled out of the top of the condenser and the product in the flask set up to a solid mass. This product was recrystallized from benzene yielding 109 g. (47%) of bis-(cyclopentadienyl)-zirconium dichloride, m.p. 241–243°.

Anal. Calcd. for $C_{10}H_{10}ZrCl_2$: C, 41.09; H, 3.45; Cl, 24.26; Zr, 31.21. Found: C, 41.10; H, 3.81; Cl, 24.30; Zr, 31.15.

Attempts to Prepare Carbonyls of Zirconium.—Zirconium tetrachloride in tetrahydrofuran was treated with four equivalents of cyclopentadienyl sodium at room temperature and the resulting product heated with carbon monoxide or carbon monoxide–hydrogen to 150° at 280 atm. for 8 hr. The product showed no characteristic metal carbonyl infrared bands and did not evolve carbon monoxide on treatment with iodine. Also, reaction of bis-(cyclopentadienyl)-zirconium dichloride with butyl lithium followed by reaction with carbon monoxide–hydrogen at 150° and 280 atm. gave no product identifiable as a zirconium carbonyl.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CONNECTICUT, STORRS, CONNECTICUT]

Replacement of Potassium Ions in Solid Potassium Hexatitanate by Sodium Ions from a Chloride Flux

BY ARTHUR L. PLUMLEY AND WILLIAM C. ORR

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Samples of fibrous potassium hexatitanate, $K_2Ti_6O_{13}$, were heated in a flux containing various mixtures of radiosodium chloride, sodium chloride and potassium chloride to study the replacement of potassium ions by sodium ions and to attempt the preparation of sodium hexatitanate having the same fibrous character as the potassium compound. An equilibrium constant of unity is indicated for the system $Na_{melt} + K_{solid} \rightleftharpoons Na_{solid} + K_{melt}$. The exchange studies using $Na^{22}Cl$ in the melt and X-ray studies indicate preparation of sodium hexatitanate. Preliminary microscopic examination of the compound reveals that it too is fibrous in nature.

Introduction

Potassium hexatitanate, $K_2Ti_6O_{13}$, recently has been prepared¹ in the form of slender, fibrous crystals. This physical form and its high melting point (1370°) suggested its use as a solid phase in studies of the distribution of ions between solids and molten salts. When a sample was heated in a low-melting $NaCl$ – $NaNO_3$ flux containing sodium-22 as a tracer, the radioactivity acquired by the solid indicated an appreciable replacement of potassium by sodium. Carried out quantitatively, a series of such experiments could be expected to show whether or not the process was reversible, whether equilibrium was attained and whether complete exchange of one cation by the other was possible.

Experimental

Replacement experiments were conducted by holding solid fibrous potassium hexatitanate at 900°, covered by a flux of sodium and potassium chloride, for a period of 8 hr. About 20 mg. of titanate and 2 g. of the chlorides, in various proportions, were used in each run. The temperature was selected to be above the melting point of the flux but considerably below that of the hexatitanate. Sodium chloride of known specific activity was used as the source of sodium-22 tracer in preparing the flux mixture.

The procedure consisted in weighing the required materials into a platinum crucible and heating them in a thermostatically controlled oven. (The use of porcelain crucibles was found to be unsatisfactory, as excessive amounts of the tracer were absorbed in the glaze.) After cooling, the halides were leached from the fused mass with water and the titanate, now containing labeled sodium, was collected on sintered glass, washed and dried for 1 hr. at 110°. Samples of the titanate were weighed and mounted for counting by collection on paper filters supported in perforated plastic planchets.² Samples of about 10 mg. were mounted, as this was a sufficient quantity of the rather fluffy titanate to cover the planchet uniformly and to give an adequate counting rate. Counting standards were prepared by evaporating aliquots

of a standard solution of the tracer sodium chloride on similar, unperforated planchets. After a scintillation counter of the well type became available, certain samples were transferred to glass vials, reweighed and counted again. Appropriate counting standards were prepared by evaporation of the standard solution in similar glass vials. The data that are used in the calculation of an equilibrium constant were obtained with this more efficient counting system.

In order to obtain samples for X-ray study, replacement reactions were repeated without the presence of tracer in the flux mixtures. Powder diffraction patterns of the products were made with a Debye-Scherrer camera using $CuK\alpha$ radiation. For diffraction patterns of the hexatitanate samples before and after complete replacement of the potassium by sodium, a General Electric recording diffractometer, Model XRD-5, was used.

The fibrous potassium hexatitanate used in this work was supplied by E. I. du Pont de Nemours & Co., Wilmington, Delaware.³

The tracer sodium chloride was prepared by evaporating a sodium chloride solution to which had been added sodium-22, obtained in HCl solution from Nuclear Science and Engineering Corp., Pittsburgh. The solid was fused, then ground and stored in a screw-capped vial.

Reagent grade sodium and potassium chlorides were fused, ground in a mortar and stored under vacuum prior to use.

Results and Discussion

Prior to conducting an equilibrium study, determination of the conditions for equilibrium necessitated some early experiments of an exploratory nature. The first of these experiments, using a low melting (300°) flux of $NaNO_3$ – $NaCl$ in a 20:1 ratio, indicated that up to 70% replacement of potassium by sodium could be achieved after 1 hr. Use of a pure sodium chloride flux (m.p. 801°) resulted in approximately 85% replacement for the same period of time. Reaction time was increased until it was found that nearly complete replacement could be achieved within 4 to 5 hr. As a result of these observations, a heating period of 8 hr. was judged to be ample for attainment of complete replacement. The data for these experiments are shown in Table I.

(1) K. L. Berry, V. D. Aftandilian, W. W. Gilbert, E. P. H. Meibohm and H. S. Young, *J. Inorg. Nuclear Chem.*, **14**, 231 (1960).

(2) T. E. Burgess, J. Looby and W. C. Orr, *J. Chem. Educ.*, to be published.

(3) Courtesy of R. M. Joyce, Asst. Laboratory Director, Central Research Department.

TABLE I
DETERMINATION OF COMPLETE REPLACEMENT OF K BY Na

Time, hr.	Temp., °C.	Original mixture			Hexatitanate recovered		% replacement	
		K ₂ Ti ₆ O ₁₃ , mg.	NaCl, mg.	Sp. activity, c/m/meq. Na	Weight, mg.	Activity, c/m	Obsd.	Theor.
1	800	29.2	990.0	4980	25.2	199	86.2	99.6
3	800	30.8	1002.1	3930	25.7	172	92.1	99.6
4	800	29.6	1025.3	8540	25.7	358	88.9	98.9
4	800	31.2	510.6	8420	26.4	391	95.3	99.6
8	900	19.9	2041.0	3200	17.5	103	99.0	99.8

TABLE II
DETERMINATION OF EQUILIBRIUM CONSTANT
Mixtures heated for 8 hr. at 900°

Original mixture			At equilibrium					[Na _s]/[K _s]	[Na _L]/[K _L]	K _{eq}
K ₂ Ti ₆ O ₁₃ , mg.	KCl, mg.	NaCl, mg.	Sp. activity, c/m/meq. Na × 10 ⁻⁴	Weight, mg.	Activity, c/m	% replacement obsd.	% replacement theor.			
8.5	1006.4	9.6	289	0.6	84	1.3	1.29	0.0140	0.0122	1.15 ± 0.23 ^a
20.2	2256.1	268.5	20.43	18.9	1254	9.8	13.1	.122	.149	0.82 ± 0.03
20.1	1902.2	520.5	11.38	14.2	1462	24.4	25.8	.343	.348	0.99 ± 0.05
21.7	1287.4	1021.7	5.98	15.3	1782	52.2	50.2	1.19	1.01	1.18 ± 0.08
8.3	509.9	526.1	7.09	0.6	69	45.0	56.4	0.825	1.31	0.63 ± 0.23 ^a
19.8	640.2	1524.9	3.88	13.5	1407	72.6	75.0	2.80	3.01	0.93 ± 0.13
19.9	324.3	1774.7	3.99	12.2	1644	91.2	87.2	11.0	6.87	1.60 ± 0.93 ^b

Weighted mean 0.95 ± 0.03

^a The magnitude of uncertainty results from the small weight of hexatitanate sample recovered. ^b The magnitude of error here results from the uncertainty involved in calculation of [K_L] which is found as a small difference between large amounts

Per cent. replacement is calculated as

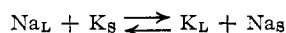
$$\% \text{ replacement} = \frac{\text{mg. Na}_2\text{Ti}_6\text{O}_{13}}{\text{mg. sample recovered}} \times 100$$

$$\text{mg. Na}_2\text{Ti}_6\text{O}_{13} = \frac{(\text{observed } c/m) \times (\text{meq. wt. Na}_2\text{Ti}_6\text{O}_{13})}{c/m/\text{meq. total sodium orig. in flux}}$$

A sample of sodium hexatitanate containing tracer sodium was heated in a flux containing a high percentage of potassium chloride. A count of the sample recovered from this run indicated that the replacement of potassium by sodium in potassium hexatitanate is a reversible reaction.

A series of experiments using fluxes containing various mixtures of sodium and potassium chlorides was undertaken to study the effect of added potassium ions in the flux on the extent of replacement and to establish a value for the equilibrium constant for the reaction.

The exchange of sodium and potassium between the liquid and the solid phases may be represented by the equation



and the corresponding equilibrium constant may be written

$$K_{eq} = \frac{[\text{K}_L][\text{Na}_S]}{[\text{Na}_L][\text{K}_S]}$$

Assuming that activity coefficients, as well as volume factors, will cancel, one may replace the bracketed quantities by the number of milliequivalents of potassium or sodium in the indicated phase at equilibrium. A value for the equilibrium constant may thus be found for each different flux mixture. These results are presented in Table II.

In calculating the ratios and the values of K_{eq} given in the last three columns of the table, the number of milliequivalents of sodium in the solid phase, [Na_s], is found from the observed activity and weight of the hexatitanate recovered and the

TABLE III
X-RAY POWDER PATTERN DATA
(After 8 hr. at 900°)

Indices hkl	K ₂ Ti ₆ O ₁₃			Na ₂ Ti ₆ O ₁₃		
	calcd. d, Å.	obsd.	Rel. int. ^a	calcd. d, Å.	obsd.	Rel. int. ^a
001	9.00	..		9.10	8.52	v.v.w.
200	7.69	7.74	s.	7.46	7.42	v.s.
201	6.40	6.42	m.s.	6.29	6.28	s.
102	4.48	4.50	v.v.w.	4.555	4.51	v.v.w.
102	4.14	4.18	m.s.	4.17	4.17	m.s.
400	3.84	..		3.73	3.73	w.
401	3.77	..		3.67		
110	3.69	3.67	m.	3.68	3.65	m.
402	3.20	3.20	v.v.w.	3.145	3.14	v.v.w.
103	3.04			3.07	3.07	v.v.w.
310	3.05	3.03	m.	3.02	3.02	s.
311	2.98			2.96		
203	2.97	2.97	s.	2.98	2.97	m.
012	2.90	2.91	v.v.w.	2.92	2.93	m.
303	2.80	2.79	w.	2.795	2.77	v.w.
410	2.70	2.70	m.	2.66		
203	2.65	2.66	v.v.w.	2.67	2.68	m.s.
312	2.65			2.64		
403	2.59	2.57	w.	2.56	2.57	v.w.
404	2.10	2.10	m.s.	2.10	2.08	m.
204	2.07	2.08	m.	2.08		
313	2.04	2.04	v.v.w.	2.04	2.04	m.
214	1.95	1.98	v.v.w.	1.955	1.96	v.v.w.
020	1.90	1.90	m.s.	1.903	1.87	v.w.

^a v. = very; s. = strong; w. = weak; m. = medium. Calculations based on the lattice parameters of Berry, *et al.* K₂Ti₆O₁₃: a₀ = 15.60; b₀ = 3.80; c₀ = 9.13; β = 99.6°; Na₂Ti₆O₁₃: a₀ = 15.13; b₀ = 3.80; c₀ = 9.21; β = 99.2°.

known specific activity of sodium in the mixture. The other three bracketed quantities are found by difference from the original amounts under the assumption that the exchange proceeds according to the equation given above.

The equilibrium constant is found to be approximately unity for the range of concentrations used.

Examination of the powder patterns of the alleged sodium hexatitanate revealed a decrease in "d" spacings compared with the potassium compound, which is in approximate agreement with that expected upon replacement of potassium atoms by the smaller sodium atoms in the same structure.

A comparison of interplanar spacings determined from powder patterns of the original $K_2Ti_6O_{13}$ and $Na_2Ti_6O_{13}$ obtained by replacement with those calculated from the lattice parameters of Berry, *et al.*,¹ is shown in Table III. It is to be noted that agreement is quite satisfactory.

Microscopic examination reveals identical fi-

brous character for both potassium and sodium hexatitanate.

This evidence, together with the observations described in the tracer replacement experiments, indicates that fibrous sodium hexatitanate has been prepared by the exchange of ions in a flux.

Acknowledgments.—The foregoing investigation forms part of a program of research on distribution of ions between melts and solid phases using radioactive tracers which is supported by contract AT(30-1)-1154 with the Atomic Energy Commission. The authors wish to thank Dr. Roland Ward for his continued interest and suggestions throughout the course of this investigation.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, AMHERST COLLEGE, AMHERST, MASSACHUSETTS, AND BRISTOL UNIVERSITY, BRISTOL, ENGLAND]

Components of Charge and Potential in the Inner Region of the Electrical Double Layer: Aqueous Potassium Chloride Solutions in Contact with Mercury at 25°

BY DAVID C. GRAHAME^{1a} AND ROGER PARSONS

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Following similar work with potassium iodide solutions,^{1b} the differential capacity of the interface between mercury and aqueous potassium chloride solutions of seventeen different concentrations between 0.01 and 4 *M* has been measured at 25°. The components of the charge in the solution have been computed and analyzed into contributions from the diffuse layer and from the inner layer. The potential drop across the inner region due to the ionic double layer has been computed from the experimental measurements. Using these results, the inner layer capacity has been analyzed into a capacity at constant amount of specific adsorption and one at constant charge on the mercury. The former is similar to that for the potassium iodide system and hence to the total inner layer capacity for potassium fluoride solutions. The latter is considerably larger than that for the potassium iodide system indicating that the inner Helmholtz layer is probably thicker for the chloride ion than for the iodide ion. Somewhat less laborious methods have been developed for calculating the relative thicknesses of inner and outer Helmholtz layers and the potential at an anion site in the inner Helmholtz plane, although it is clear that the value of these results is limited by the simplicity of the model assumed for the inner layer.

Introduction

A recent analysis² of the structure of the inner region of the double layer at the mercury-aqueous solution interface has been applied to experimental results for the mercury-aqueous potassium iodide interface.^{1b} The experimental results were in satisfactory agreement with the theory and in fact led to a somewhat simpler model of the inner layer than might have been expected *a priori*. Nevertheless certain anomalies were apparent and were expressed in terms of a non-uniform dielectric constant in the inner region. The measurements reported here were undertaken to extend and confirm this analysis.

Experimental Details and Methods of Calculation

The experimental measurement of the capacity of the mercury electrode in contact with aqueous solutions of potassium chloride at 25° followed the methods described previously.^{1b,3,4} Twice recrystallized reagent grade salt was dissolved in conductivity water to make solutions of seventeen concentrations.

The calculation of the surface excess of cations and anions in the double layer was carried out precisely as described for the potassium iodide system.^{1b} Values of the potential of the electrocapillary maximum were taken from previous work.^{5a,5b}

(1) (a) Late professor at Amherst College. (b) D. C. Grahame, *THIS JOURNAL*, **80**, 4201 (1958).

(2) D. C. Grahame, *Z. Elektrochem.*, **62**, 264 (1958).

(3) D. C. Grahame, *THIS JOURNAL*, **71**, 2975 (1949).

(4) D. C. Grahame, *Z. Elektrochem.*, **59**, 740 (1955).

(5) (a) D. C. Grahame, E. M. Coffin and J. I. Cummings, Techn. Rep. No. 2 to the Office of Naval Research March 9, 1950; (b) J. R.

Results

For direct comparison with the results for the potassium iodide system, the present results are plotted in two ways. In Fig. 1, n_i is plotted against $\log a_{\pm}$ for a given value of q . The corresponding plot for KI gave straight lines whenever n_i was greater than about 6 $\mu\text{coul. cm.}^{-2}$. These results on the other hand show marked curvature at all values of q irrespective of the value of n_i , though there is some suggestion that each curve approaches linearity at the higher concentrations. Further, it is worth noting that the slope of this approximately linear region is about twice that of the straight lines obtained for KI. If n_i , the surface concentration of specifically adsorbed ions, is plotted against q , the charge density on the mercury surface, for each solution, the plot is very similar to that for KI and, as previously noted, the slope of the approximately linear section is nearly the same for KI and for KCl. The main difference noticeable is that the curves for the more dilute solutions are more crowded together for KCl than they are for KI. In Fig. 2, the potential across the inner region, ψ^u , is plotted against n_i for a given value of q . Like the data for KI, these suggest that the relation between ψ^u and n_i is approximately linear. However, for KCl quite large deviations from linearity are apparent with

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