

CarrierFree Radioisotopes from Cyclotron Targets. VII. Preparation and Isolation of V48 from Titanium

Herman R. Haymond, Roy D. Maxwell, Warren M. Garrison, and Joseph G. Hamilton

Citation: *The Journal of Chemical Physics* **18**, 756 (1950); doi: 10.1063/1.1747743

View online: <http://dx.doi.org/10.1063/1.1747743>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/18/5?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[CarrierFree Radioisotopes from Cyclotron Targets. XXVI. Preparation and Isolation of W181 from Tantalum](#)

J. Chem. Phys. **20**, 523 (1952); 10.1063/1.1700457

[CarrierFree Radioisotopes from Cyclotron Targets XIV. Preparation and Isolation of Bi204, 206 from Lead](#)

J. Chem. Phys. **19**, 256 (1951); 10.1063/1.1748180

[CarrierFree Radioisotopes from Cyclotron Targets XIII. Preparation and Isolation of Sc 44, 46, 47, 48 from Titanium](#)

J. Chem. Phys. **18**, 1685 (1950); 10.1063/1.1747575

[CarrierFree Radioisotopes from Cyclotron Targets. IX. Preparation and Isolation of Re 183, 184 from Tantalum](#)

J. Chem. Phys. **18**, 995 (1950); 10.1063/1.1747835

[CarrierFree Radioisotopes from Cyclotron Targets V. Preparation and Isolation of Se75 from Arsenic](#)

J. Chem. Phys. **18**, 155 (1950); 10.1063/1.1747447



is performed with respect to the coordinates of one of the molecules, (1), of the set n , Eq. (3) for the cases $k=1$ and $k=2$ is reduced to

$$\psi_1 = -(\rho/kT) \int_V (\partial u(1, 2)/\partial x_1) [F_2(z, (1)(2))/F_1(z, (1))] d(2) \quad (8)$$

and

$$\begin{aligned} \psi_2 = & -(\partial u(1, 2)/\partial x_1) - (\rho/kT) \int_V (\partial u(1, 3)/\partial x_1) \\ & \times \{ [F_3(z, (1)(2)(3))/F_2(z, (1)(2))] \\ & - [F_2(z, (1)(3))/F_1(z, (1))] \} d(3). \quad (9) \end{aligned}$$

Ψ_n 's are average forces so that $\Psi_1 = \psi_1 = 0$ for the gaseous or liquid state. Hence, we obtain, from (8) and (9),

$$\begin{aligned} \{ \partial F_2(z, (1)(2))/\partial x_2 \} + \{ F_2(z, (1)(2))/kT \} (\partial u(1, 2)/\partial x_2) \\ + (\rho/kT) \int_V F_3(z, (1)(2)(3)) (\partial u(1, 3)/\partial x_2) d(3) = 0. \quad (10) \end{aligned}$$

This equation was first derived by Born and Green, and used by Rodriguez³ to study an approximate equation of state. And the Kirkwood approximation used by Kirkwood and Boggs⁴ and by Rodriguez corresponds to the assumption that $\psi_n = 0$ for all values of n except $n=2$. Furthermore, we can prove that the integral equation used by Kirkwood⁵ to determine pair distribution function in liquid [reference 5, Eq. (33)] is also a special case of (3). The above method will be easily extended to multicomponent systems and to the case where G_n^* 's refer to the state at non-zero fugacity.

¹ J. E. Mayer, *J. Chem. Phys.* **15**, 187 (1947).

² M. Born and H. S. Green, *Proc. Roy. Soc. A* **188**, 10 (1946).

³ A. E. Rodriguez, *Proc. Roy. Soc. A* **196**, 73 (1949).

⁴ J. G. Kirkwood and Elizabeth Monroe Boggs, *J. Chem. Phys.* **10**, 394 (1942).

⁵ J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

Ferrous-Ferric Electron Transfer Reaction in Perchloric Acid Solution

HENRY A. KIERSTEAD*

Institute for Nuclear Studies, University of Chicago, Chicago, Illinois
March 16, 1950

THE electron transfer exchange reaction between ferrous and ferric ions in 3 molar perchloric acid solution has been investigated by Van Alten and Rice¹ and Linnenbom and Wahl,² both using the diffusion separation technique devised by the former authors. Van Alten and Rice obtained separation factors of about 2 in favor of ferric ion and observed a half-time 18.5 ± 2.5 days for the exchange reaction. Linnenbom and Wahl, on the other hand, obtained separation factors of 1.2 to 1.6 in favor of ferrous ion and observed complete exchange within the experimental time of 1 to 2 hours. Some preliminary experiments by the present author, using the same separation technique, provide confirmation for the long half-life observed by Van Alten and Rice and for the observation of Linnenbom and Wahl that ferrous ion diffuses more rapidly than ferric ion. Data on these experiments are collected in Table I.

Fe^{59} activity, in the form of spectroscopically pure iron powder, was supplied by the Oak Ridge National Laboratory on allocation from the Isotopes Division, U. S. AEC. The iron powder was

TABLE I.

c_2 moles $\cdot \text{l}^{-1}$	c_3 moles $\cdot \text{l}^{-1}$	S	t days	α , %	$t_{1/2}$ days
0.952×10^{-2}	1.011×10^{-2}	3.301	0.058	1.2 ± 0.5	—
1.071×10^{-2}	1.050×10^{-2}	2.805	6.024	10.0 ± 0.6	39 ± 2
1.044×10^{-2}	1.059×10^{-2}	3.983	80.14	2.8 ± 0.5	166 ± 12

$S = c_2^0 c_3 / c_2 c_3^0$, where c_2 and c_3 are the concentrations of ferrous and ferric ions, respectively, before separation, and c_2^0 and c_3^0 are the concentrations after separation. t is the time allowed for exchange; α is the percent of exchange; and $t_{1/2}$ is the half-life for exchange, calculated from t and α .

dissolved in 3.0M perchloric acid, oxidized with excess 3 percent hydrogen peroxide, boiled to destroy the peroxide, and diluted with sufficient water and concentrated perchloric acid ("Baker's Analyzed") to make a solution 0.15M in ferric perchlorate and 3.0M in perchloric acid. Aliquots of this stock solution were mixed with solutions of ferrous perchlorate prepared in the same manner from inactive iron powder, omitting the hydrogen peroxide oxidation. The mixed solution was stored in a glass-stoppered volumetric flask for various lengths of time. The ferrous and ferric ions were then partially separated by diffusion through a sintered glass disk. Separation factors were measured by analysis for ferrous and ferric ion both before and after the diffusion separation. Ferric ion was determined by measuring the absorption by the perchlorate solution of ultraviolet light at 2400Å, using a Beckmann ultraviolet spectrophotometer. 3.0M perchloric acid was used in the blank cell. A correction was made for the small absorption due to ferrous ion. Total iron was determined by the same method, after oxidizing with 3 percent hydrogen peroxide and boiling to destroy excess peroxide. Ferrous ion was obtained by difference. Samples of the solution taken before and after separation were prepared for counting by deposition as metallic iron on copper electrodes by the method of Ross and Chapin.³

Calculation of the percent exchange was made by the same method as that used by Van Alten and Rice.¹

Lack of agreement between Van Alten and Rice,¹ Linnenbom and Wahl,² and the present author, and our failure to observe the same half-life in different experiments, may be explained by catalysis by traces of impurities in the reagents. In this connection we should like to point out that the only materials we have used in preparation of our reagents are pure metallic iron, "Baker's Analyzed" perchloric acid, hydrogen peroxide, and distilled water.

Numerous attempts by the present author to separate ferrous and ferric ions by chemical methods have all resulted in complete exchange.

We gratefully acknowledge the assistance and interest of Professor W. F. Libby, Dr. G. Zimmerman, and Dr. T. J. Neubert.

* Present address: Metcalf Research Laboratory, Brown University, Providence, Rhode Island.

¹ Van Alten and Rice, *J. Am. Chem. Soc.* **70**, 883 (1948).

² Linnenbom and Wahl, *J. Am. Chem. Soc.* **71**, 2589 (1949).

³ J. F. Ross and M. A. Chapin, *Rev. Sci. Instr.* **13**, 77 (1942).

Carrier-Free Radioisotopes from Cyclotron Targets. VII. Preparation and Isolation of V^{48} from Titanium*

HERMAN R. HAYMOND, ROY D. MAXWELL,† WARREN M. GARRISON,
AND JOSEPH G. HAMILTON

*Crocker Laboratory and Divisions of Medical Physics, Experimental
Medicine, and Radiology; Radiation Laboratory; University
of California, Berkeley, California*

March 3, 1950

V^{48} can be prepared¹ by the reactions $\text{Ti}^{47}(d, n)\text{V}^{48}$ and $\text{Ti}^{48}(d, 2n)\text{V}^{48}$. The present paper reports a chemical procedure used in isolating carrier-free V^{48} from a titanium target which had been bombarded with 19-Mev deuterons in the 60-inch cyclotron at Crocker Laboratory. The carrier-free V^{48} was separated from the target element and from milligram amounts of calcium and scandium which were added as holdback carriers for the radioisotopes² produced concurrently by the reactions: $\text{Ti}^{48}(d, \alpha p)\text{Ca}^{48}$, $\text{Ti}^{48}(d, 2p)\text{Sc}^{48}$.

The Ti target (C.P. metal powder supported on a copper target plate with 0.25 mil Ta foil) was bombarded for 200 $\mu\text{a}\cdot\text{hr.}$ at a maximum beam intensity of 20 $\mu\text{a.}$ After aging for 24 hours, the Ti powder (approximately 1 g) was dissolved in a minimum volume of 36N H_2SO_4 and the solution was evaporated to dryness. 5.0 g of Na_2CO_3 and 0.1 g of NaNO_3 were added and the mixture was fused at 500°C for 30 minutes. The sub-micro amount of V^{48} ,

presumably as vanadate, was extracted from the insoluble titanium oxide by repeated washings with cold water. To remove any Ca and Sc activities which may have been extracted with the V^{48} , the solution was acidified with HCl, 10 mg of Ca and Sc were added and precipitated from 1M Na_2CO_3 . The supernatant containing the V^{48} was neutralized with 12N HCl and evaporated to dryness. The V activity was separated from most of the NaCl by extraction with approximately 5 ml of 12N HCl. The HCl solution containing the activity and milligram amounts of NaCl was evaporated to dryness and diluted with water to give an isotonic saline solution of carrier-free V^{48} which was used in biological tracer studies.

The V^{48} was identified by the assigned³ 16-day half-life and by the 0.7-Mev positron and 1.33-Mev gamma-ray which have been reported.¹ Chemical separations with added Ca, Sc, Ti, and V carriers further identified the activity as V^{48} .

We are grateful to the staff of the 60-inch cyclotron for bombardments and to Professor G. T. Seaborg for his interest and helpful suggestions.

* This document is based on work performed under the auspices of the AEC.

† Lieutenant Colonel, U. S. Army, now stationed at Walter Reed Hospital, Washington, D. C.

¹ H. Walke, *Phys. Rev.* **52**, 777 (1937).

² G. T. Seaborg and I. Perlman, *Rev. Mod. Phys.* **20**, 585 (1948).

³ W. C. Peacock and M. Deutsch, *Phys. Rev.* **69**, 306 (1946).

X-Ray Patterns of Soaps

A. J. STOSICK

Department of Chemistry, University of Southern California,
Los Angeles, California

February 27, 1950

THE x-ray diffraction patterns of solid soaps have been examined by many investigators using either single crystals or samples which have been described as powders. The single crystal patterns are not different in kind from those of other organic substances except for the fact that one of the unit cell axes is very long compared to the other two axes. Probably the most important difference is the appearance of a series of "long spacings" in the small angle region. These diffraction maxima can be called the (001) reflections if we label the long crystal axis a_3 . The length of the long axis is related to the thickness of the micellar layer. This micellar layer consists of a central layer of metal ions, not necessarily in a single plane, and of two fatty acid ion layers with the acid ions extending outward on both sides from the metal ion layer. The hydrocarbon end groups form the outer surface of the micellar layer. The values obtained for the long spacing indicate that the chains are tipped rather than perpendicular to the median plane. Such micellar layers presumably form in solution, probably starting as ion pairs or triplets, and the solids consist of a stacking of such micellar layers. The forces leading to the coalescence of such layers are the weak van der Waals forces between hydrocarbon chain ends.

The more common type of diffraction diagram, referred to as a powder diagram, is notorious for its apparent variability. These patterns for a given sample sometimes change with time, they change if the sample is heated and then restored to its original temperature, and they depend on the method of preparing the soap. These diagrams show a series of (001) long spacings at small angles and a broad diffraction band, with no resolved *sharp* lines, in the region $2\theta \approx 20^\circ$ (using copper x-rays). This broad band frequently shows broad sub-structure suggesting that it is the superposition of two or more broad peaks. Sometimes it is resolved into two or more broad peaks. Only very rarely are there additional broad peaks at larger scattering angles. Frequently there is a series of small narrow maxima extending out to $2\theta \approx 40^\circ$.

It is possible to account for these diagrams in terms of a disordered structure in which the micellar layers are superimposed with stacking disorder, together with some physically reasonable assumptions concerning disorder within a micellar layer. The

proposal that stacking disorder is present is certainly reasonable since the forces which would lead to an orderly arrangement are only the weak van der Waals forces of hydrocarbon chain ends. The central ion layers cannot exert strong interactions from one micellar layer to another.

The consequences of this proposal are that the (001) spectra are unaffected by the stacking disorder and are no different in sharpness or intensity from those given by a well-ordered layer sequence. An examination of published data and of unpublished data, very kindly provided by Professor R. D. Vold of this laboratory, shows that almost without exception all of the regular series of spacings past $2\theta \approx 20^\circ$ can be identified as high orders of the (001) series. Previously these were called "side spacings."

On the other hand, when h and k are not both zero, then random stacking disorder causes the index 1 to become meaningless. The resulting (hkl) reflections become broad (hk) diffraction maxima of the two-dimensional lattice of the micellar layer. The present case differs from that discussed by Warren¹ for carbon black in that here the layers are many atoms thick. Elementary considerations concerning the Fourier transform from crystal space to reciprocal space shows that the (hk) maxima for thick distributions are narrower in scattering angle range than for thin layers. This is observed to be true for soaps as compared to carbon black, whose layers are presumed to be one atom thick.

Within a micellar layer the fatty acid ions must approximate a hexagonal array. This requires that there can be only three different (hk) pairs (and their negatives) which give diffraction maxima near $2\theta \approx 20^\circ$. These are the (10), (01), and ($\bar{1}\bar{1}$) maxima. The (11) maximum should occur at a value of $\sin\theta$ which is $\sqrt{3}$ times that of (10), and that for (20) should have a value of $\sin\theta$ twice that for (10). If the net is not exactly hexagonal the (10), (01), and ($\bar{1}\bar{1}$) maxima occur at different but nearly equal angles, and the 20° peak may resolve.

If we assume that in a micellar layer the fatty acid ions are randomly oriented about their long axes, it can readily be shown that the only strong (hk) maxima should be (10), (01), and ($\bar{1}\bar{1}$), i.e., those at $2\theta \approx 20^\circ$.

These considerations permit a consistent and physically reasonable unification of the discordant observations. It is apparent that the great list of different diffraction patterns, which have been identified with different polymorphic forms, merely represent different conditions of ordering, and that probably only the single crystal specimens represent phases in the thermodynamic sense. A more complete report is in preparation.

¹ B. E. Warren, *Phys. Rev.* **59**, 693 (1941).

The Exchange of Water between Aqueous Chromic Ion and Solvent*

JOHN P. HUNT† AND HENRY TAUBE

George Herbert Jones Laboratory, University of Chicago, Chicago, Illinois
March 10, 1950

A PROBLEM of interest in the chemistry of aqueous solutions is that of determining the formulas of the species which result upon the interaction of cations and water. With cations of one extreme type, including probably those of low charge and large radius, the complexes may be very labile, and the configuration even in the first sphere of coordination may be so indefinite, that it would be impossible to assign definite formulas to them. For other cations, of appropriate properties, it can be expected that a definite configuration with respect to water in the first sphere of coordination is maintained, and for these, in principle at least, meaningful formulas can be assigned to the complex consisting of the cation and directly bound water.

An indirect method which has been used to establish the coordination number of a cation for water in aqueous solution is to determine the maximum coordination number with respect to other ligands, the assumption being made that the coordination