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Thermal Exchange between Vanadyl and Pervanadyl Ions[1]

BY H. A. TEWES, J. B. RAMSEY AND C. S. GARNER

The only published work on exchange reactions of vanadium compounds is that of Sue and Yuasa[2] who reported that vanadium(IV) and vanadium(V) ions undergo relatively slow exchange with solid vanadium 8-hydroxyquinoline and solid vanadium cupferronate.

This investigation was undertaken in order to determine whether vanadium(IV) ion undergoes thermal exchange with vanadium(V) ion in 0.6 *f* and 0.9 *f* perchloric acid, and in 7 *f* hydrochloric acid, and to study the kinetics of such an exchange reaction provided the proper conditions could be found.

Experimental

Radiovanadium Tracer.—Sixteen-day V^{48} was prepared by the $Ti^{48}(p,n)$ reaction in the U.C.L.A. 37-inch frequency modulated cyclotron.[3] The vanadium activity was separated by dissolution of the bombarded metal in concentrated hydrochloric acid, addition of pervanadyl carrier, oxidation with hot dilute nitric acid, and precipitation of the titanium as the hydrated dioxide from a solution sufficiently basic to keep the vanadium in solution. The vanadium was further purified by precipitating it from the acidified filtrate as the cupferronate. The washed vanadium cupferronate was ignited in air to vanadium(V) oxide at 450°. Radioactive vanadium(V) perchlorate solution was prepared by dissolving the active oxide in C. P. sodium hydroxide solution and acidifying with C. P. perchloric acid. Reduction of a portion of the radiovanadium(V) solution with sulfur dioxide, followed by removal of the excess reducing agent by the passage of air through the heated solution, gave a radioactive vanadium(IV) perchlorate solution. The half-life and radiation characteristics[4] of the purified vanadium fractions were those of the expected 16-day V^{48} since shorter-lived radioisotopes of vanadium decayed out prior to measurement and use of the V^{48}.

Vanadium(IV) and Vanadium(V) Stock Solutions.—Pure vanadium(V) oxide was prepared by heating recrystallized ammonium metavanadate to 450°. The oxide was placed in contact with a dilute solution of redistilled perchloric acid, the vanadium(V) was electrolytically reduced to vanadium(III), then sufficient oxide was added to react completely with the vanadium(III), giving a solution containing vanadium only in the +4 oxidation state. Standardization of this solution was effected by oxidation of the vanadium present in an aliquot to vanadium(V) which was determined by the iodometric method of Ramsey.[5] A trace of chloride was present in this solution, apparently from the reduction of perchlorate ion, either electrolytically or by the vanadium(III).

A stock vanadate solution was prepared by dissolving a portion of the pure vanadium(V) oxide in a solution of C. P. sodium hydroxide. This solution was standardized iodometrically.

Sodium Hexacyanoferrate(III).—A solution of C. P. potassium hexacyanoferrate(III) was metathesized with an excess of sodium perchlorate, the potassium perchlorate formed being filtered out. The resulting solution was found to be free of hexacyanoferrate(II).

Other Reagents.—All perchloric acid used was redistilled C. P. grade. All other reagents were C. P. quality.

Measurement of Radioactivity.—The 0.72-Mev. positrons and 0.98- and 1.33-Mev. gamma radiation (plus annihilation gammas) associated with the decay of V^{48} were counted. In early experiments the solid vanadium compounds precipitated in the separations were mounted, dried, and counted with a Geiger–Mueller counter, but it was difficult to get consistent results. Subsequently, all precipitates were dissolved, made up to a 10.0-ml. volume and 8.0-ml. aliquots taken for radioassay with a dipping counter and scale-of-64 or scale-of-128; constant geometry was maintained. Corrections were made for decay and changes in counting efficiency (by use of standard V^{48} aliquots) and for background (~12 c./m.).

Procedure.—The exchange mixtures were synthesized volumetrically from the stock solutions, the radiovanadium being initially present as vanadium(IV) in one-half of the experiments of a given type and as vanadium(V) in the other half. Exchange was allowed to proceed for one minute in each case before addition of the separating agent. Three distinct methods were used for the separation of vanadium(IV) and vanadium(V).

(1) **Precipitation of Vanadium(IV) as the Hexacyanoferrate(III).**—Eight experiments were run. In half (method 1a) the vanadyl hexacyanoferrate(III) was precipitated from a solution prepared by the addition of 7.0 ml. of 0.5 *f* sodium hexacyanoferrate(III) to 3.0 ml. of the exchange mixture. After addition of the precipitating agent, twenty minutes were required for the formation of a solid which could be centrifuged. The remaining four precipitations were carried out (method 1b) from solutions prepared by adding 0.2-ml. portions of 0.5 *f* sodium hexacyanoferrate(III) to 4.8-ml. portions of the exchange mixture. Under these altered conditions five minutes were required for the formation of a satisfactory precipitate.[6] All precipitates were centrifuged out, washed once with a 0.35 *f* solution of sodium hexacyanoferrate(III), and then dissolved with fuming sulfuric and perchloric acids. The resulting solutions were made up to 10.0-ml. volumes, and 8-ml. aliquots taken for radioassay and vanadium determination.

(2) **Precipitation of Vanadium(IV) as a Complex Fluoride.**—Six experiments were run. To 3.3 ml. of the exchange mixture was added 0.4 ml. of 28.5 *f* hydrofluoric acid and 3.3 ml. of 5 *f* ammonium fluoride. Five minutes were required for the formation of the sodium vanadyl fluoride precipitate.[7] These precipitates were washed once with hydrofluoric acid–ammonium fluoride solution and were then dissolved with fuming sulfuric and perchloric acids. These solutions were diluted to 10.0-ml. volumes.

(3) **Ether Extraction of Vanadium(V) as a Complex Chloride.**—Six experiments were run, using a separation procedure suggested by the work of Lingane and Meites.[8] About 20% of the vanadium(V) in the exchange mixtures

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[1] From a thesis by H. A. Tewes presented to the Graduate Faculty of the University of California, Los Angeles, in partial fulfillment of the requirements for the M.S. degree, January, 1950.

[2] P. Sue and T. Yuasa, *J. chim. phys.*, **41**, 160 (1944).

[3] We wish to acknowledge the coöperation of Professor J. R. Richardson and the cyclotron crew in arranging the bombardments. A target containing V^{48} was supplied from the Berkeley 60-inch cyclotron for our early experiments through the courtesy of Professors Seaborg and Hamilton.

[4] See V^{48} bibliography in paper of G. T. Seaborg and I. Perlman, *Revs. Modern Phys.*, **20**, 593 (1948).

[5] J. B. Ramsey, THIS JOURNAL, **49**, 438 (1927).

[6] Chemical analyses of this precipitate gave the value 3/2 for the atomic ratio of vanadium to iron. The empirical formula $(VO)_3[Fe(CN)_6]_2 \cdot xH_2O$ may be assigned on this basis. A compound of this composition apparently has not been reported heretofore.

[7] Chemical analyses of this precipitate gave a composition corresponding to the formula $(Na,NH_4)_3VOF_5 \cdot 2H_2O$. This compound is apparently similar to the complex fluoride $3NH_4F \cdot VOF_2$ reported by E. Petersen, *J. prakt. Chem.*, [ii] **40**, 194 (1889).

[8] J. J. Lingane and L. Meites, THIS JOURNAL, **68**, 2443 (1946).

TABLE I

THERMAL EXCHANGE OF LABELED VANADIUM(V*) BETWEEN VANADYL AND PERVANADYL IONS

Room temperature; exchange time 1 min.

Sepn. method[a]	Exchange mixture, *f*			V* initially as	Specific activity, c./m./eq. V.[b]		% Exch.[c]
	$V(OH)_4ClO_4$	$VO(ClO_4)_2$	$HClO_4$		Sep. frac.	Std. aliq.	
1a	0.0162	0.0163	0.92	V(V)	775	1538	101
	.0160	.0165	.92	V(IV)	772	1489	98
1b	.0099	.0102	.29	V(V)	787	1538	102
	.0098	.0103	.29	V(IV)	772	1489	98
2	.0157	.0148	.61	V(V)	409	816	100
	.0155	.0150	.61	V(IV)	429	824	95
3	.0101	.0098	.05, 7.1 HCl	V(V)	651	1194	93
	.0100	.0099	.05, 7.1 HCl	V(IV)	598	1157	103

[a] 1a = Hexacyanoferrate(III) precipitation of V(IV) from solution 0.35 *f* in $Na_3Fe(CN)_6$; 1b same as 1a, except precipitation from solution 0.02 *f* in $Na_3Fe(CN)_6$; 2 = fluoride precipitation of V(IV) from solution 2.1 *f* in both HF and NH_4F; 3 = ether extraction of V(V). [b] Counting rates ranged between 500 and 1500 c./m; statistical counting error, taken as the square root of the sum of the squares of the standard deviations of sample and of background, was 1–2%. [c] Mean deviation is 1%, except in last case where it is 3.5%.

was extracted[9] with 1.5 volumes of peroxide-free diethyl ether saturated with 7 *f* hydrochloric acid. The extraction required approximately three minutes. The vanadium was subsequently re-extracted into an aqueous solution which was then made up to a 10.0-ml. volume.

Vanadium was iodometrically determined in all separated fractions after oxidation to vanadium(V).

Results and Discussion

Table I summarizes the results. The extent of exchange was calculated in the usual manner from the specific activities of vanadium in the original and separated solutions.

Complete and substantially instantaneous exchange between vanadyl and pervanadyl ions was observed in every case. Inasmuch as kinetic measurements could not be made, the possibility of rapid exchange arising during the chemical separations cannot be ruled out. The fact that three different separation procedures gave identical results might be taken as circumstantial evidence against such induced exchange. In this connection the work of Coryell and Yost[10] on the measurement of the oxidation–reduction potential of the vanadyl–pervanadyl couple in hydrochloric acid solutions has shown that equilibrium with a platinum electrode was attained slowly with hydrochloric acid concentrations in excess of 0.25 *f*. Iron(III) chloride was found to act as a catalyst. Hexacyanoferrate(III) may play the same catalytic role in the exchange studied by the hexacyanoferrate(III) separation method. The slow approach to equilibrium in the absence of a catalyst may indicate that exchange between these vanadium species should be slow.

To check the possibility of formation of some kind of a stable complex between vanadyl and pervanadyl ions, which might account for the apparent rapid exchange, a spectrophotometric study was made of a mixture of vanadyl and pervanadyl ions in a solution comparable to one of the exchange studies (method 1a). Reference to Fig. 1 indicates that there is only a small difference between the absorption spectrum of the mixture and that of the additive spectrum[11] of the separate components, so that a stable

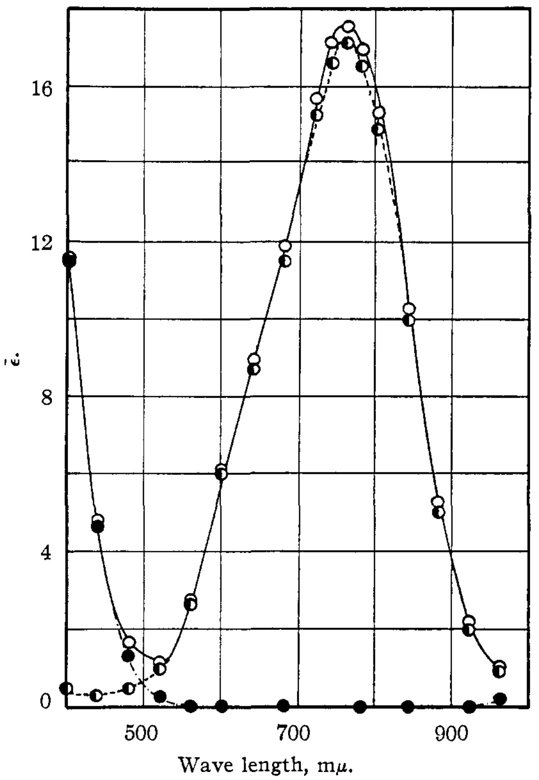

Fig. 1.—Comparison of absorption spectrum of vanadyl–pervanadyl mixture with spectra of separate vanadium components at room temperature: ○, 0.0167 *f* $V(OH)_4ClO_4$, 0.0163 *f* $VO(ClO_4)_2$, 0.92 *f* $HClO_4$, 0.067 *f* $NaClO_4$, μ = 2.1; ●, 0.0167 *f* $V(OH)_4ClO_4$, 0.92 *f* $HClO_4$, 0.09 *f* $NaClO_4$, μ = 2.1; ◐, 0.0163 *f* $VO(ClO_4)_2$, 0.89 *f* $HClO_4$, 0.08 *f* $NaClO_4$, μ = 2.0.

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[9] Experiments using radiovanadium tracer disclosed that only about 0.2% of the vanadium(IV) was extracted under identical conditions.

[10] C. D. Coryell and D. M. Yost, THIS JOURNAL, **55**, 1909 (1933).

[11] The spectrum of vanadium(IV) under the experimental conditions agrees well with that reported for the vanadyl ion, VO^{++}, by S. Furman and C. Garner, *ibid.*, **72**, 1785 (1950).

complex seems not to form under the experimental conditions.

The principal vanadium species present in the exchange mixtures appear to be the pervanadyl ion,[12] generally formulated as $V(OH)_4^+$, and the vanadyl ion,[13,14] written as VO^{++}. The potential measurements of Carpenter[12] and of Coryell and Yost[10] suggest that formation of chloride complexes (as might form in the ether extraction separation method) does not take place in hydrochloric acid solutions up to 2 *f*, although such complexes could exist at higher chloride ion concentrations.

Rona[15] has found rapid, but measurable, exchange of uranium between uranium(IV) oxychloride, $UOCl_2$, and uranyl chloride, UO_2Cl_2, in aqueous solutions, which system bears a formal resemblance to that reported in this paper.

Summary

Exchange of radiovanadium between vanadyl and pervanadyl ions in 0.6 and 0.9 *f* perchloric acid and in 7 *f* hydrochloric acid has been found to be complete at room temperature in exchange times of one minute. Although identical results were obtained with three different chemical separation methods, the possibility of an induced exchange cannot be ruled out.

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[12] J. E. Carpenter, This Journal, **56**, 1847 (1934).

[13] H. T. S. Britton, *J. Chem. Soc.*, 1842 (1934).

[14] H. T. S. Britton and G. Welford, *ibid.*, 758 (1940).

[15] E. Rona, Abstracts, 113th Meeting of the A. C. S., Chicago, Illinois, April, 1948.

[Contribution No. 18 from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines]

2,3-Dithiabutane: Low Temperature Heat Capacity, Heat of Fusion, Heat of Vaporization, Vapor Pressure, Entropy and Thermodynamic Functions[1,2]

By D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie and H. M. Huffman

The organic sulfur compounds are divided into a number of structural classes, and it is of interest to study the thermodynamic properties of members of each class to determine the effect of structure on these properties. The simplest member of the alkyl disulfide class, 2,3-dithiabutane (dimethyl disulfide), was selected for the initial study of that class. In this paper are presented: (a) the results of low temperature thermal studies and vapor pressure measurements which yield a value of the entropy of 2,3-dithiabutane in the vapor state, and (b) thermodynamic functions of 2,3-dithiabutane calculated from spectroscopic and molecular structure data.

The Material.—The 2,3-dithiabutane was an API–BM "Sample of Organic Sulfur Compounds" prepared and purified by API Project 48A at the Laramie Station of the Bureau of Mines.

In the course of the low temperature investigations, a calorimetric study was made of the melting point against the fraction melted. From these data the impurity was calculated to be 0.03 ± 0.01 mole per cent. The results of this study are given in Table I.

In the ebulliometric vapor pressure studies, the boiling and condensation temperatures of the sample were found to differ by only 0.001° at the normal boiling point. The material is therefore in group V on Swietoslawski's scale of degree of purity[3] (difference in boiling and condensation temperatures 0.000–0.005°).

Table I

2,3-Dithiabutane Melting Point Summary, 0°C. = 273.16°K., $N_2/F = 0.0311\,\Delta T$

% Melted	*T*, °K. Obsd.	*T*, °K. Calcd.
10.5	188.368	188.343
26.1	.404	.401
50.7	.420	.420
70.8	.426	.426
90.9	.429	.429
100		.430
Pure		.440
Triple point	188.44°K.	
Impurity	0.031 ± 0.010 mole%	

The Apparatus.—The low-temperature measurements were made in an apparatus similar to that described by Ruehrwein and Huffman.[4] Very briefly, the method was as follows: about 0.57 mole of the material under investigation was contained in a sealed platinum calorimeter, which was mounted in the adiabatic calorimetric system. A measured amount of electrical energy was supplied to the calorimeter, and at all times the temperature of the environment was maintained at that of the calorimeter to prevent heat interchange. The initial and final temperatures of the calorimeter were measured by means of a platinum resistance thermometer. The electrical measurements required for the determination of the resistance of the thermometer and the elec-

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[1] This investigation was performed at the Petroleum Experiment Station of the Bureau of Mines jointly by The Thermodynamics Laboratory and the American Petroleum Institute Research Project 48A on The Production, Isolation, and Purification of Sulfur Compounds and Measurement of Their Properties.

[2] Article not copyrighted.

[3] Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corp., New York, N. Y., 1945.

[4] Ruehrwein and Huffman, This Journal, **65**, 1620 (1943).