

Chemical Effects Accompanying the Decay of Mn51

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TABLE III. Variation of the force constants with the angle in tri-substituted methanes CHX_3 treated as four-particle systems.

	X	F	Cl	Br
A_1	$100(\Delta d_{11}/d_{11})$	2.65	3.18	4.68
	$100(\Delta d_{22}/d_{22})$	4.17	2.73	0.79
	$100(\Delta d_{12}/d_{12})$	-0.62	-0.62	-0.62
(For $\Delta\theta_{\text{XCX}} = +1^\circ$)				
E	$100(\Delta d_{33}/d_{33})$	-0.41	-0.58	-0.68
	$100(\Delta d_{44}/d_{44})$	-2.39	-2.44	-2.46
	$100(\Delta d_{34}/d_{34})$	-0.12	-0.32	-0.47

CONCLUSION

The methods described in this paper are quite general, and the results obtained by their application to simple systems of the type treated may be carried over, generally, to a first approximation. Examination of the results summarized reveals one or two features worthy of

mention. First, in the triatomic molecules (see Table II), the results for the two solutions (a) and (b) are sufficiently similar to justify using the analog of (b) in other systems where it is not possible to obtain an unambiguous solution. Then, in general, it may be noted that the variations in the constants for a given increment in the valence angle involved increase with the masses of the atoms taking part in the vibration whose normal coordinate approximates to the coordinate going with the constant, in the potential energy expression. Regarding the absolute magnitudes of the increments, it may be observed that, in terms of the nomenclature employed here, an error of one percent in a vibration frequency ν_i leads to an error of approximately two percent in the constant d_{ii} . It may also be noted that the conventionally calculated absolute angular displacements for bending vibrations are of the order of 5° to 10° (20° for hydrogen-displacements).

Chemical Effects Accompanying the Decay of Mn^{51}

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An investigation has been made of the chemical forms assumed by Cr^{51} when it is produced by positron decay of Mn^{51} under a variety of conditions. The data have shown that the oxidation state of the parent Mn^{51} plays an important role in determining the oxidation state of daughter Cr^{51} . By variation of experimental conditions some information has been obtained regarding the types of chemical reactions undergone by the Cr^{51} . These reactions have also been shown to play important roles in determining the ultimate chemical form of daughter Cr^{51} .

The complexity of the factors determining the chemical forms of Cr^{51} after Mn^{51} decay has been pointed out, and possible explanations of some of the observed phenomena have been suggested. We believe the results are consistent with the hypothesis that appreciable ionization in the valence shell accompanies the beta-decay process.

Incidentally it has been demonstrated that the manganese isotope of 44-min. half-life (Mn^{51}) decays to the chromium isotope of 26-day half-life (Cr^{51}).

INTRODUCTION

STUDIES of chemical phenomena accompanying nuclear transformations have been carried on, for the most part, with induced nuclear reactions, while studies with spontaneous reactions (decay processes) have received a somewhat smaller amount of attention. In the latter group the most successful and best explained work has been associated with the process of isomeric transition, particularly as accompanied by internal conversion. Only a very small amount of work has been reported in the literature dealing with the chemical consequences of beta-decay.^{1,2} With this

process little is currently understood concerning the relative importance of each of the several factors which might be expected to determine observed chemical phenomena. With positron decay, no work at all has been reported.

Of factors which may influence chemical properties of atoms involved in nuclear processes, one of the more important is the kinetic energy imparted to an atom by a departing particle or photon arising in the nuclear process. Often the recoil energy is of sufficient magnitude to cause severance of chemical bonds holding the atom in a molecule. Thus the atom may be endowed with unusual chemical properties and by virtue of its remaining kinetic energy may be able to initiate chemical reactions which do not ordinarily occur. In beta-decay two particles are emitted, the electron or positron, and the neutrino or antineutrino respectively. In these cases calculations of recoil energies are difficult because for a given radioactive species, the energies

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¹ T. H. Davies, *J. Phys. and Colloid Chem.* **52**, 595 (1948).

² Burgus, Davies, Edwards, Gest, Stanley, Williams, and Coryell, *J. Chim. Phys.* **45**, 165 (1948).

TABLE I. Cr⁵¹ extractions made during decay of Mn⁵¹.

Elapsed time since previous Cr extraction	% of total Cr ⁵¹ in fraction	Theoretical % Cr ⁵¹ in fraction
51 min.	(59.2±1.0)	55.3
45 min.	(21.0±0.5)	22.7
18 hr.	(19.8±0.5)	22.0

TABLE II. Exchange of chromium between Cr(III) and Cr(VI) forms.

Sol. I, pH 1.50		Sol. II, 8.45f HNO ₃		Sol. III, 2.38f NaOH	
Time of ex- change	Percent change	Time of ex- change	Percent change	Time of ex- change	Percent change
18.4 hr.	1.1±0.2	18.2 h.	1.4±0.2	18.2 h.	2.0±0.2
122.0 hr.	2.7±0.2	120.8 h.	2.5±0.2	120.8 h.	3.3±0.2
289.2 hr.	8.6±0.3	289.0 h.	2.2±0.1	289.0 h.	4.7±0.2

of the individual particles are not fixed, but lie between zero and a definite maximum value. In addition the energy distribution may be complicated by the existence of a complex beta-spectrum, and in the case of positron decay electron capture may compete with positron emission. Energy distributions and decay schemes may be experimentally determined, but even with a known energy distribution for a simple beta-spectrum, recoil momentum calculations are difficult because of the present lack of knowledge of electron-neutrino angular correlations.

A second factor which may influence the chemical properties of atoms produced by negatron or positron decay is the behavior of the orbital electrons during and after the decay process. Theoretical calculations^{3,4} have been made which predict that electronic excitation and ionization may occur as a result of change in nuclear charge. While it has been impossible to predict accurately the probability of ionization for all shells, the calculations have shown that there is only a rather small probability of ionization in the inner shells. Migdal⁴ has estimated that for negatron decay of an atom of large atomic number Z , the probability of ionization in the K shell is $0.6/Z^2$, in the L shell is $6.8/Z^2$, and in the M shell is $14/Z^2$. For the outermost shells the probability of ionization is much greater and is predicted to be of the order of unity. Numerical calculations for the case of positron decay were not carried out, but Migdal has shown that in rough approximation the probability of ionization in the K shell is the same for negatron or positron decay. Numerical calculations for probabilities of processes leading to various excited states were not carried out.

An additional factor which may play a role in determining chemical properties of atoms resulting from negatron or positron decay is the chemical oxidation state of the parent species. If the parent atoms were in a given oxidation state, and no serious kinetic or elec-

tronic disturbances were to occur, then the daughter of a negatron emitter might be expected to exhibit an oxidation number one higher than that of the parent, while the daughter of a positron emitter might be expected to have an oxidation number one lower.

In addition to the above factors which may directly influence the chemical properties of daughter atoms of negatron or positron emitters, there may also be secondary or indirect factors which can play important roles in determining final chemical forms. A secondary process of great importance in determining final chemical form of a daughter of a negatron or positron emitter, is chemical reaction of daughter atoms with molecules of the surrounding medium. This may occur as a result of one or more of the primary processes of ionization, electronic excitation, or high recoil energy, or as a result of the appearance of the daughter in a non-stable chemical oxidation state. By variation of experimental conditions such as temperatures, composition of solutions, etc., it may be possible for the experimenter to learn something about these chemical reactions which occur.

As a consequence of the primary decay process, the daughter atoms may result at tracer concentrations in a chemical form not ordinarily encountered at macro concentrations. Studies of such phenomena have been meager and little is known about the subject which has been called "tracer solution chemistry." However, such a chemical species could conceivably undergo further reactions which would then determine the final chemical state of the daughter. One of these reactions might be exchange with another chemical form of the element added as a carrier. Thus the bulk of the daughter atoms might ultimately exhibit the chemistry of the added carrier, although not originally formed in the oxidation state of that carrier.

From the preceding considerations it is clear that the final chemical forms in which daughter atoms of negatron or positron emitters are found are determined by one or more of several important and possibly competing factors. The object of the present investigation was to determine the chemical forms assumed by chromium when it is formed by positron decay of manganese. By adjustment of variables such as the oxidation state of the manganese, the temperature, the composition of the medium in which decay occurs, etc., it was hoped to learn something of the nature and importance of two of the factors which may determine the chemical form of the chromium, *viz.* the oxidation state of the parent, and subsequent reactions with other molecules.

EXPERIMENTAL

For determination of the chemical forms of chromium grown from manganese, the manganese isotope of 46 ± 2 min. half-life was employed. It decays by emission of positrons of 2.0-Mev maximum energy and has been

³ E. L. Feinberg, J. Phys. U.S.S.R. 4, 424 (1941).

⁴ A. Migdal, J. Phys. U.S.S.R. 4, 449 (1941).

assigned⁶ mass number 51. The use of this particular isotope was dictated by the requirement that the daughter chromium must also be radioactive to make possible its detection. The chromium isotope to which the mass number 51 has been assigned⁶ decays by electron capture with a half-life of 26.5 days. About 3–5 percent of the transitions⁶ to V^{51} are accompanied by emission of 0.32-Mev⁷ gamma-rays of which less than 0.5 percent are converted.⁶ However the production of Cr^{51} from positron decay of Mn^{51} had not been reported at the time of the present experiments and it was first necessary to demonstrate the parent-daughter relationship of these two nuclides. This genetic relationship was established in an experiment in which a sample of Mn^{51} was prepared, was initially freed of its daughter Cr^{51} , and was allowed to decay. Manganese-chromium separations were then made at measured time intervals and the percentage of Cr^{51} activity found in each chromium daughter fraction was compared with the percentage calculated to arise from decay of a parent of the half-life of Mn^{51} .

To prepare Mn^{51} , a target of metallic chromium plate was bombarded with deuterons in the Washington University cyclotron. The chromium isotope of mass number 50, isotopic abundance 4.49 percent, was transmuted to Mn^{51} by the nuclear reaction $Cr^{50}(d, n)Mn^{51}$. To isolate Mn^{51} from the target, the chromium plate was dissolved in hydrochloric acid, and manganous carrier and appropriate holdback carriers were added. The hydrochloric acid was removed by fuming with

concentrated nitric acid, and manganese dioxide was precipitated from boiling 16f nitric acid solution by addition of potassium chlorate. The precipitated manganese dioxide was centrifuged out, washed once with 0.1f nitric acid, and redissolved in a small quantity of 1f nitric acid by the addition of bisulfite. Chromic and vanadate holdback carriers were added and the precipitation of manganese dioxide was carried out as before. This cycle was repeated a third time. Tests of this procedure with dummy solutions "spiked" with Cr^{51} showed that each manganese dioxide precipitate carried less than 0.5 percent of the chromium present. After three such precipitations of manganese dioxide, the Cr^{51} initially present in the target should have been diminished by a factor of at least 10^6 . Because of the relatively short half-life of Mn^{51} , the removal of other contaminating activities could not be carried out at this point without a prohibitive loss of Mn^{51} through decay. Consequently the removal of these contaminants was deferred until later when they were removed from the individual Cr^{51} daughter fractions.

From the prepared source of Mn^{51} free of Cr^{51} a small aliquot was removed for determination of the Mn^{51} half-life. A value of 44.3 ± 0.5 min. was obtained in a measurement extending over 8 half-lives. The remainder of the Mn^{51} sample was allowed to decay. At measured time intervals manganese-chromium separations were effected with the aid of carriers by precipitation of manganese dioxide in the manner described above. Because it was found necessary to count the weak

TABLE III. Distribution of Cr^{51} grown from $Mn^{51}(II)$.

Expt. No.	Mn ⁺⁺ conc. f $\times 10^4$	Cr(III) conc. f $\times 10^3$	Cr(VI) $Cr_2O_7^{--}$ f $\times 10^3$	pH	Distribution of daughter Cr^{51} Cr(III) fraction (%) Cr(VI) fraction (%)		Other experimental conditions
1	1.04	3.84	1.92	4.56	(99.1 \pm 1.9)	(0.9 \pm 0.1)	0.86f acetic acid and 0.86f sodium acetate
2	2.00	7.68	3.84	4.50	(98.8 \pm 2.5)	(1.2 \pm 0.5)	0.86f acetic acid and 0.86f sodium acetate
3	1.85	3.84	1.92	4.65	(98.7 \pm 2.8)	(1.3 \pm 0.4)	0.86f acetic acid and 0.86f sodium acetate
4	1.85	3.84	1.92	2.95	(97.7 \pm 2.1)	(2.3 \pm 0.5)	
5	1.85	3.84	1.92	1.18	(99.7 \pm 1.2)	(0.3 \pm 0.4)	
6	1.00	3.84	1.92	1.13	(98.6 \pm 1.9)	(1.4 \pm 0.8)	Solution cooled to 0°C. during decay.
7	1.04	3.84	1.92	1.40	(98.6 \pm 1.3)	(1.4 \pm 0.9)	
8	1.85	3.84	1.92	0.25	(98.2 \pm 2.0)	(1.8 \pm 0.4)	
9	1.04	3.84	1.92	(8.0f HNO_3)	(97.0 \pm 1.2)	(3.0 \pm 0.2)	
10	1.04	3.84	1.92	~ 2	(94.7 \pm 1.9)	(5.3 \pm 0.3)	Dioxane— H_2O solution mole fraction dioxane = 0.29.
11	1.04	3.84	1.92	~ 2	(89.7 \pm 2.3)	(10.3 \pm 1.3)	Dioxane— H_2O solution mole fraction dioxane = 0.56.
12	1.00	3.84	1.92	~ 2	(88.2 \pm 2.2)	(11.8 \pm 0.9)	Acetone— H_2O solution mole fraction acetone = 0.60.
13	1.85	3.84	1.92	~ 2	(83.4 \pm 1.8)	(16.6 \pm 1.0)	Acetone— H_2O solution mole fraction acetone = 0.60.
14	6.62	24.9	12.45	~ 1	(95.4 \pm 1.5)	(4.6 \pm 0.2)	Frozen in liquid air.
15	6.62	24.9	12.45	~ 1	(95.1 \pm 1.4)	(4.9 \pm 0.1)	Frozen in dry ice-acetone mixture.
16	6.54	24.9	12.45	~ 1	(94.8 \pm 1.5)	(5.2 \pm 0.2)	Frozen in dry ice-acetone mixture during decay and kept frozen for 6 days after decay.
17	Solid $MnCO_3$				(70.2 \pm 1.6)	(29.8 \pm 0.6)	Dissolved in 1.0f HNO_3 containing Cr(III) and Cr(VI) carriers.
18	Solid $MnCO_3$				(71.1 \pm 1.8)	(28.9 \pm 1.4)	Dissolved in 0.1f HNO_3 containing Cr(III) and Cr(VI) carriers.

⁵ J. J. Livingood and G. T. Seaborg, Phys. Rev. **54**, 391 (1938).

⁶ Walke, Thompson, and Holt, Phys. Rev. **57**, 171 (1940).

⁷ L. C. Miller and L. F. Curtiss, Phys. Rev., **70**, 983 (1946).

TABLE IV. Distribution of Cr^{51} grown from $\text{Mn}^{51}\text{O}_4^-$ decay

Expt. No.	MnO_4^- conc. $\times 10^4$	Cr(III) conc. $\times 10^3$	Cr(VI) $\text{Cr}_2\text{O}_7^{2-}$ conc. $\times 10^3$	pH	Distribution of daughter Cr^{51}		Other experimental conditions
					Cr(III) fraction (%)	Cr(VI) fraction (%)	
19	2.50	3.84	1.92	1.17	(48.4 ± 1.9)	(51.6 ± 1.8)	Cooled to 0°C .
20	2.00	3.84	1.92	1.17	(47.0 ± 1.8)	(53.0 ± 1.8)	
21	2.50	3.84	1.92	1.23	(50.1 ± 2.0)	(49.9 ± 1.7)	
22	15.8	3.84	1.92	1.23	(52.5 ± 2.7)	(47.5 ± 1.8)	
23	1.69	3.84	1.92	0.28	(51.2 ± 1.6)	(48.8 ± 1.3)	
24	2.50	1.92	1.92	1.23	(49.9 ± 2.0)	(50.1 ± 1.8)	Solution brought to pH 1 after decay and Cr(III) added.
25	2.00	0	1.92	6.66	(4.6 ± 0.6)	(95.4 ± 2.5)	
26	9.77	3.84	1.92	0.29	(53.0 ± 2.6)	(47.0 ± 1.4)	
27	7.70	14.4	7.20	~ 1	(43.7 ± 0.9)	(56.3 ± 0.8)	
28	6.52	14.4	7.20	~ 1	(42.9 ± 0.8)	(57.1 ± 0.9)	
29	~ 7	14.4	7.20	~ 1	(44.1 ± 0.9)	(55.9 ± 1.2)	Frozen in liquid air. Frozen in dry ice-acetone mixture. Frozen in dry ice-acetone mixture and kept frozen for 6 days after decay.
30	Solid CsMnO_4				(0.4 ± 1.3)	(99.6 ± 2.4)	After decay solid dissolved in cold 1f nitric acid containing Cr(III) and Cr(IV) carriers.

vanadium x-rays (and conversion electrons) accompanying the decay of Cr^{51} , complete removal of all other radioactive species was essential. Each Cr^{51} fraction was therefore subjected to a stringent purification process. The purified chromium samples were finally converted to chromic oxide, and chemical recoveries were determined gravimetrically. The samples were transferred to standard cardboard mounting cards and were covered with cellophane. The Cr^{51} activities were measured under standard geometric conditions using a Geiger counter with a thin mica end-window. No other absorber was interposed between samples and the counter. The average weight of chromic oxide samples mounted for counting was 10.5 mg with a maximum deviation of ± 0.5 mg in individual samples. Each sample was uniformly spread over a circular area of 2.00 cm^2 corresponding to an average thickness of 5.25 mg/cm^2 . The close agreement between duplicate experiments run throughout the present studies indicated that counting errors introduced by differences in sample weight and uniformity were negligibly small.

The percentages of the total Cr^{51} daughter activity associated with each sample, corrected for chemical losses, are shown in Table I. The percentage of total daughter activity calculated to be present in a given fraction, assuming growth from a 44-min. parent, is also shown. Comparison of observed and calculated percentages confirms the parent-daughter relationship of these two nuclides, although the amount of Cr^{51} in the first sample is seen to be too large by several percent. (This discrepancy may have been due to incomplete removal of Mn^{51} from the Cr^{51} fraction or to growth of Cr^{51} during the ~ 2 min. required for the precipitation, washing, and centrifugation of the manganese dioxide.) The errors shown in Table I are those attributable only to standard deviations in counting.

The radioactivity in each daughter fraction was identified as Cr^{51} by following the x-ray (and conversion electron) decay curve. Also the gamma-ray decay curve of the first Cr^{51} extract was followed through 1.0 g/cm^2

of aluminum. Half-lives of 24.5 to 26 days were observed for all samples, in agreement with published values. Absorption curves were obtained consistent with a decay scheme involving vanadium K x-rays and 0.3-Mev gamma-rays.

Exchange of Chromium between Cr(III) and Cr(VI)

The chemically stable oxidation states of chromium and therefore the states in which chromium daughter might ultimately be found, are those with formal oxidation numbers +2, +3, and +6. In order to determine the relative amounts of daughter Cr^{51} appearing in each state, chemical separations with the aid of carriers were employed. Because of the ready oxidation of Cr(II) by Cr(VI) in aqueous solutions, and because exchange might be expected to occur between Cr(II) and Cr(III) , investigation of Cr^{51} appearing as Cr(II) was not undertaken. Decay-product Cr^{51} was therefore separated into only two fractions, the first containing Cr^{51} formed directly in, or entered by exchange, the Cr(VI) state, and the second containing Cr^{51} formed directly in, exchanged with, or oxidized or reduced to the Cr(III) state. Obviously it was necessary to establish that no rapid exchange occurs between the Cr(III) and Cr(VI) forms.

Investigation of the exchange between Cr(III) and Cr(VI) was carried out with Cr^{51} tracer obtained from the U. S. Atomic Energy Commission. The tracer, carefully purified, was converted to chromic nitrate solution and "diluted" with additional inactive chromic nitrate before use in the exchange experiments. Exchange was studied at room temperature in three different solutions, one strongly acidic, the second at measured pH 1.50, and the third strongly basic. In all solutions equivalent amounts of Cr(III) and Cr(VI) carriers were present. The final concentration of Cr(III) was in each case 0.0358f; final concentrations of other reagents are shown in Table II. In brief, the experiments consisted of addition of equivalent amounts of Cr^{51} nitrate and inactive $\text{Cr}_2\text{O}_7^{2-}$ to the solution in which

exchange was to be studied. At chosen time intervals, given in Table II, aliquots of the mixtures were withdrawn and the pH of each adjusted to 2.0. The Cr(VI) was then separated from Cr(III) by precipitation as lead chromate. The Cr(VI) fractions were converted to chromic oxide, and the specific activities of the samples were determined by measurements of the 0.32-Mev gamma-rays through an aluminum absorber of 1000 mg/cm².

Data of the Cr(III)-Cr(VI) exchange experiments are presented in Table II. Errors shown are those calculated to result from standard deviations in counting. A somewhat larger error due to co-precipitation of Cr(III) with the lead chromate, estimated at about 0.5 percent is not included. The results show that no rapid exchange occurs under the conditions of the experiments. These results are consistent with those reported by Muxart *et al.*,⁸ who found essentially no exchange beginning either with active Cr(VI) or Cr(III). Because the concentrations of Cr(III) and Cr(VI) carriers employed in Cr⁵¹ daughter experiments were usually a factor of ten smaller than the concentrations used in the above exchange experiments, only very small errors should have resulted due to exchange between the two forms.

Oxidation States Assumed by Cr⁵¹ Grown from Mn⁵¹(II)

To determine Cr⁵¹ distribution between Cr(III) and Cr(VI) fractions when grown from decay of Mn⁵¹ present as divalent manganese, the following general procedure was employed. The Mn⁵¹ samples were produced by deuteron irradiation of chromium targets and were isolated from the irradiated targets by the procedure already described. The irradiation of 1.5 hours at a beam current of about 120 microamperes gave enough Mn⁵¹ for division into six to eight samples each producing sufficient Cr⁵¹ for convenient measurement. After isolation of the Mn⁵¹ in 10 mg of carrier manganese dioxide as previously described, the final manganese dioxide precipitate was dissolved in 3-4 ml of 1f nitric acid by addition of a few milligrams of solid sodium bisulfite. The resulting Mn(II) solution was then boiled to remove excess sulfite and was diluted with water. This solution, filtered through a fine sintered glass filter to remove dust particles, served as a stock solution. Aliquots were withdrawn, added to previously prepared solutions, and the Mn⁵¹(II) allowed to decay under various conditions.

The final composition of each solution, after addition of an aliquot of Mn⁵¹(II) stock solution, is shown in Table III. In preparing all solutions water distilled from alkaline permanganate solution was used. In some early experiments nitrogen was bubbled through the solutions to remove dissolved oxygen, but this pre-

caution was abandoned after it was shown to make no difference in the distribution of daughter chromium. (As the solutions were all quite acidic, this result might have been expected.) In all solutions, 10.0 mg of Cr(III) and 10.0 mg of Cr(VI) carriers were present during decay of the parent Mn⁵¹.

After decay of Mn⁵¹, Cr(III) and Cr(VI) fractions were separated for determination of their Cr⁵¹ content. The separations were made by precipitation of lead chromate from the solutions adjusted to a pH of 2.3-2.4. Each of the chromium fractions was carefully purified of contaminating activities and was finally mounted as chromic oxide for counting. As in the experiment demonstrating the parent-daughter relationship, it was necessary for sensitivity to count the V⁵¹ x-rays and thin samples were therefore required.

To check on the recovery of Cr⁵¹ in the Cr(III) and Cr(VI) fractions, an aliquot of Mn⁵¹ stock solution after decay was analyzed for total Cr⁵¹ content. It was found that from about 97 to 102 percent of Cr⁵¹ was always recovered in the two fractions.

In addition to decay of Mn(II) ions in solution, experiments were carried out in which Mn(II) was incorporated into solid manganous carbonate before decay. To prepare microcrystalline manganous carbonate into which Mn⁵¹ was incorporated, an aliquot of Mn⁵¹(II) stock solution was mixed with a few milligrams of Mn(II) carrier. The mixture was diluted about tenfold with 95 percent alcohol and then manganous carbonate was precipitated by addition of a small amount of aqueous sodium carbonate solution. The precipitate was centrifuged out and washed once with alcohol and then with ether. Titration experiments showed that only about 2 percent of the manganese was oxidized by air to higher valence forms.

To separate Cr⁵¹ which had grown in solid manganous carbonate, the solid was dissolved in nitric acid solution containing 10 mg each of Cr(III) and Cr(IV) carriers. In one experiment the nitric acid concentration was 0.1f and in another was 1.0f. After solution, Cr(III)-Cr(VI) separations were carried out in the standard manner.

Table III shows the distribution of Cr⁵¹ between Cr(III) and Cr(VI) fractions when the Cr⁵¹ arises from decay of Mn⁵¹(II) under various conditions. In the second, third, and fourth columns of Table III are shown the concentrations of Mn(II), Cr(III), and Cr(VI) carriers present in solutions during decay. When solutions were frozen before decay, these columns give concentrations before freezing. In the fifth column are shown the pH values of solutions, as measured with a Beckman pH meter where two decimal places are given. In the sixth and seventh columns are shown the distributions of daughter Cr⁵¹ between the Cr(III) and Cr(VI) fractions. Errors shown are those attributed only to standard deviations in counting; they do not include co-precipitation errors or errors due to weighing.

⁸ Muxart, Daudel, Daudel, and Haissinsky, *Nature* **159**, 538 (1947).

The eighth column shows other important experimental conditions.

Oxidation States of Cr^{51} Grown from $\text{Mn}^{51}(\text{VII})$

To learn whether the chemical oxidation state of parent Mn^{51} plays an important role in determining the oxidation state of daughter Cr^{51} , experiments were run in which Mn^{51} was prepared in the form of permanganate, allowed to decay, and then Cr^{51} distributions determined and compared with the distributions previously observed when the Cr^{51} had grown from $\text{Mn}(\text{II})$ under similar conditions.

In order to prepare Mn^{51} as permanganate the irradiation and isolation procedures of the preceding experiments were followed. After isolation, the final manganese dioxide precipitate was dissolved in 10 ml of 4.0*f* nitric acid by addition of a few milligrams of solid sodium bisulfite. To this solution about 1 g of solid sodium bismuthate was added to oxidize the manganous ions to permanganate. The suspension was thoroughly stirred and was allowed to stand at room temperature for about one minute. The excess sodium bismuthate was filtered off on a fine sintered glass filter funnel, and was washed free of permanganate with several ml of 0.1*f* nitric acid. The washings were collected with the filtrate. The clear permanganate solution was diluted to about 20 ml and bismuth was precipitated as the hydroxide by addition of 4*f* sodium hydroxide solution until the solution was slightly basic to litmus; the bismuth precipitate was centrifuged out. In the removal of bismuth at this point, some loss of permanganate could not be avoided. Tests showed that the bismuth hydroxide carried chromium and thus eliminated Cr^{51} grown during the bismuthate oxidation.

The permanganate solution remaining after removal of the bismuth hydroxide was made slightly acidic with nitric acid and again quickly passed through a fine sintered glass filter to remove a small amount of manganese dioxide. The filtered permanganate solution served as a stock solution. Aliquots were withdrawn, added to previously prepared solutions, and allowed to decay to Cr^{51} under various conditions simulating the conditions of previous experiments with $\text{Mn}^{51}(\text{II})$. Analysis of inactive stock solution prepared in this manner showed that greater than 99.4 percent of the manganese present was in the form of permanganate.

The final composition of each solution after addition of an aliquot of active permanganate stock solution is shown in Table IV. Procedures followed in the preparation of these solutions and separation of the daughter Cr^{51} into $\text{Cr}(\text{III})$ and $\text{Cr}(\text{VI})$ fractions were those used in the preceding experiments with growth from $\text{Mn}(\text{II})$. Purification, mounting, and counting procedures were likewise those of the previous experiments. In all cases of decay in solution 10.0 mg of $\text{Cr}(\text{III})$ and 10.0 mg of $\text{Cr}(\text{VI})$ carriers were present. Unless otherwise

indicated in Table IV solutions were kept at room temperature and in the dark.

Because it is thermodynamically possible for permanganate to be reduced by both chromium and water under the conditions of some of the experiments in which both permanganate and chromic carriers were present in solution, tests were made to determine how rapidly the reduction occurs. Dummy solutions were made up in which concentrations of nitric acid, chromic, dichromate, and permanganate carriers were approximately equal to the concentrations of these constituents in some of the actual decay experiments of Table IV. The rate of reduction of permanganate in these solutions (stored in the dark at room temperature) was then followed spectrophotometrically. The results showed that the rate of reduction of permanganate was very slow compared to the rate of decay of Mn^{51} so that in the permanganate decay experiments only about 2 percent of the total Mn^{51} decay occurred with the parent in reduced forms.

In addition to experiments in which permanganate was allowed to decay in solution, an experiment was carried out in which Mn^{51} was incorporated into solid cesium permanganate and then allowed to decay. After complete decay, the solid cesium permanganate was dissolved in a cold solution 1*f* in nitric acid containing 10.0 mg each of $\text{Cr}(\text{III})$ and $\text{Cr}(\text{VI})$ carriers. Separation of fractions was then made in the standard manner. To prepare solid cesium permanganate, a few milligrams of potassium permanganate carrier were added to an aliquot of active permanganate stock solution, the solution was quickly cooled to 0°C, and a large excess of saturated cesium nitrate solution was added. The mixture was allowed to stand in an ice bath for about one minute, and the solid cesium permanganate crystals were removed by centrifugation, and washed once with a few milliliters of cold acetone containing a small quantity of permanganate. The precipitate was re-centrifuged, and the acetone removed by decantation and evacuation. This left dry crystals of cesium permanganate, contaminated with a little cesium nitrate.

Table IV shows the distribution of Cr^{51} between $\text{Cr}(\text{III})$ and $\text{Cr}(\text{VI})$ fractions when the Cr^{51} arises from decay of permanganate under various conditions. In the second, third, and fourth columns of Table IV are shown the concentrations of permanganate, $\text{Cr}(\text{III})$ and $\text{Cr}(\text{VI})$ carriers present in solutions during decay. When solutions were frozen before decay, these columns give concentrations before freezing. In the fifth column, pH values of the various solutions are shown as before. In the sixth and seventh columns are shown the distribution of Cr^{51} between the $\text{Cr}(\text{III})$ and $\text{Cr}(\text{VI})$ fractions. As in the experiments with decay of $\text{Mn}(\text{II})$, Cr^{51} analyses of other aliquots of parent manganese solutions showed that the sum of activities in the two fractions totaled from 97 percent to 102 percent of the Cr^{51} . Errors shown are those attributed to standard deviations in counting. Errors arising from co-precipita-

tion of Cr(III) with lead chromate (estimated at about 0.5 percent) and errors resulting from reduction of permanganate are not included. The last column of Table IV gives other important experimental conditions.

Oxidation States of Cr^{51} Grown from Mn^{51} (IV)

In addition to the experiments with parent Mn^{51} in states with formal oxidation numbers II and VII, an experiment was also carried out with the Mn^{51} in the IV state as manganese dioxide. Because of the insolubility of manganese dioxide, experiments in solution were impossible. Further, if experiments were conducted in which Cr^{51} grew from Mn^{51} incorporated into manganese dioxide, complete separation of Cr^{51} daughter into Cr(III) and Cr(VI) fractions would necessitate solution of the manganese dioxide and addition of chromium carriers. Because procedures available for putting manganese dioxide into aqueous solution require changing the oxidation state of the manganese, risk of also changing the oxidation state of the chromium daughter would be involved. The procedure actually followed was to prepare a sample of solid active manganese dioxide, and to suspend it in a solution containing Cr(III) and Cr(VI) carriers, with the expectation that some of the recoil Cr^{51} daughter atoms might be ejected from the surface of the manganese dioxide and thus escape into solution.

The solution chosen for suspension of manganese dioxide consisted of 10 mg each of Cr(III) and Cr(VI) carriers in 50 ml of 1.030f nitric acid cooled to 0°C in an ice bath. Under these conditions the rate of reduction of the solid manganese dioxide by Cr(III) carrier in solution was found to be negligibly slow. A 10-mg sample of active manganese dioxide was prepared in the usual way. The fresh precipitate was then stirred in the solution described until all the Mn^{51} had decayed. The manganese dioxide was then removed by centrifugation, and examined for Cr^{51} content, and the liquid phase was divided into Cr(III) and Cr(VI) fractions in the standard manner. Of the total Cr^{51} produced from decay of Mn^{51} , (61.0 ± 0.6) percent remained trapped in the solid phase. Of Cr^{51} which made its way into solution (43.8 ± 0.6) percent was included in the Cr(III) fraction, and (56.2 ± 0.7) percent was in the Cr(VI) fraction. The errors are those due to standard deviation in counting.

DISCUSSION

Discussion of Experimental Observations

Referring first to Table III, experiments 1 through 9, in which Cr^{51} was produced by decay of Mn^{51} in the form of manganous ion in aqueous solution, we see that in each experiment almost all of the Cr^{51} appeared in a form which followed the chemistry of Cr(III) carrier. Comparison of experiment 6 with experiment 5 shows that there was no determinable difference in Cr^{51} distribution between 0°C and room temperature.

Reference is now made to experiments 17 and 18 of Table III. In these experiments the parent Mn^{51} was again in the form of Mn(II) but was incorporated into solid dry manganous carbonate and allowed to decay. The data show that unlike the cases of aqueous solutions where nearly all of the Cr^{51} appeared in reduced forms, about 30 percent now appeared in the form of Cr(VI) or a form exchangeable with it.

Because it was suspected that the observed absence of highly oxidized Cr^{51} in aqueous solution (experiments 1 through 9) was due in part to chemical reduction by water, experiments 10 through 16 were designed to reduce this effect of the water. In experiments 10 through 13, organic reagents were added to the aqueous solutions to reduce the mole fraction of water. While it was expected that these compounds, acetone and dioxane, could also act as reducing agents, the results show that they were effective to some degree in decreasing the chemical reduction effect of water.

Experiments 19 through 24 inclusive, and experiment 26, show that in aqueous solution about one-half of the Cr^{51} grown from permanganate appeared in reduced forms, and one-half appeared in oxidized forms. Comparison of experiments 19 and 20 shows that there is no effect on distribution when the temperature of the solution is lowered from room temperature to 0°C. If permanganate were responsible for the oxidation of Cr^{51} to the Cr(VI) state, a dependence of Cr^{51} distribution on permanganate concentration should be observable. There is no significant dependence on permanganate concentration.

In the single experiment in which Mn^{51} was incorporated into manganese dioxide and the dioxide suspended in a nitric acid solution of carriers of Cr(III) and Cr(VI), it was found that of the Cr^{51} recoils that escaped into solution, about 56 percent were in the oxidized form and 44 percent in the reduced form. Again it is seen that an increase in oxidation number was involved.

Possible Explanations of Observed Phenomena

Because the phenomena observed in the present experiments clearly result from a number of complex and competing factors, some of which are not understood at the present time, it is difficult to explain all of the experimental results. However certain ideas do present themselves and these will be discussed in the following paragraphs. It should be pointed out, however, that the suggestions offered may not be the correct ones, and alternative explanations are certainly possible.

One of the more interesting experiments is that in which Mn^{51} (II) was incorporated into solid manganous carbonate and allowed to decay to Cr^{51} . After decay the solid was dissolved in an acidic solution and the Cr^{51} was separated with the aid of carriers into Cr(III) and Cr(VI) fractions. Approximately 30 percent of the

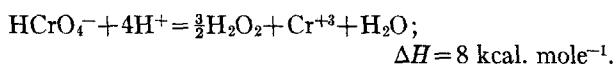
total Cr^{51} was separated as Cr(VI) or a form rapidly exchangeable with this state. The appearance of Cr^{51} in a considerably higher oxidation state than its parent is in agreement with the hypothesis that ionization accompanies the decay.

If no electronic loss were to occur, the decay reaction could be written: $\text{Mn}^{++} \rightarrow \text{Cr}^+ + \beta^+$. How a singly charged chromium ion would behave in the crystal lattice of manganous carbonate cannot be stated. However, if it were possible for the Cr^{51} ion to lose its recoil energy and still remain singly, or become doubly or triply charged, dissolution of the solid in an acidic solution of Cr(VI) carrier would likely result in formation of $\text{Cr}^{51}\text{(III)}$. On the other hand should considerable ionization accompany decay, a more highly charged Cr^{51} ion could be produced. If this ion were to lose its recoil energy in the solid without losing its charge, then upon solution of the solid, hydration of the ion to some stable form might occur. An equation for an over-all hydration reaction could be written $\text{Cr}^{+6} + 4\text{H}_2\text{O} = \text{HCrO}_4^- + 7\text{H}^+$. Reactions of this type have been proposed by Libby.⁹ It should be pointed out that ionization to Cr^{+6} may not be necessary. Although stable chromium compounds of oxidation numbers IV and V are unknown in macro quantities, their existence on a tracer scale might be possible. If such ions existed, they might be transformed to Cr(VI) through rapid exchange with chromate carrier, in a manner analogous to the exchange of manganate and permanganate. It might also be possible that chromium in one of these forms could be oxidized to Cr(VI) by some other mechanism. This seems less likely because the bulk of the experiments indicate that aqueous solutions act as reducing agents rather than oxidizing agents for the Cr^{51} . Of course it is possible that such unknown species might simply have co-precipitated with lead chromate. Regardless of what mechanisms may be in operation to stabilize the Cr^{51} in solution, its appearance in a form higher than Cr(III) implies that considerable ionization must occur, leaving Cr^{51} trapped in the crystal lattice with formal charge of at least IV.

In the experiments in which $\text{Mn}^{51}\text{(II)}$ ions were allowed to decay in aqueous solutions, the question arises as to why almost all of the Cr^{51} daughter was found in lower oxidation forms. In view of the assumption that considerable ionization occurs, it might be expected that the higher charged Cr^{51} ions would be stabilized in solution through the same mechanisms operating for ions introduced into solution by dissolving solid manganous carbonate. However there is at least one very significant difference between these two kinds of experiments. In the solid manganous carbonate experiment, the Cr^{51} ions had lost their recoil energy before being introduced into solution. In the experiments where decay occurred in solution, such was not the case. This suggests that the recoil energy of the Cr^{51} ions is responsible for their reduction in aqueous

solutions. Such reduction reactions, occurring as a result of high recoil energy, have been observed in a large number of cases where the momentum was supplied by gamma-emission following neutron capture.⁹

The question of how much energy a highly charged Cr^{51} ion must have in order to undergo chemical reduction is difficult to answer. For the sake of an estimate it might be assumed that a reaction such as the following is involved: $\text{Cr}^{+6} + 3\text{H}_2\text{O} = \text{Cr}^{+3} + \frac{3}{2}\text{H}_2\text{O}_2 + 3\text{H}^+$, and a rough idea of the energy required might be obtained from available thermochemical data¹⁰ for ΔH . If an equation for hydration of Cr^{+6} and its subsequent dissociation to HCrO_4^- is subtracted from the above equation, a third equation is obtained for which ΔH is known:



Because ΔH for the hydration of Cr^{+6} is likely to be a large negative quantity, ΔH for the first reaction must have a value much smaller than 8 kcal. mole⁻¹. This would correspond to <0.35 ev per ion. Should the energy from recoil considerably exceed this approximate value then it may be assumed that the reduction might occur. As the experiments indicate, reduction is the common result.

It may be shown that E_r , the kinetic energy imparted to the Cr^{51} by a positron of energy E_β and an antineutrino of energy E_ν , is given by the equation

$$E_r = 10.5[E_\beta^2 + 1.02E_\beta + E_\nu^2 + 2E_\nu(E_\beta^2 + 1.02E_\beta)^{1/2} \cos \theta]$$

when E_β and E_ν are in millions of electron volts and θ is the angle between directions of emission of positron and antineutrino. The positrons have energies between zero and a maximum energy of 2.0 Mev. The positron spectrum of Mn^{51} has not been determined, but a spectrum may be calculated from the Fermi theory of beta-decay. Then calculation of the recoil energy distribution could be carried out if information about the angular correlation of positrons and antineutrinos were available. Experimental determinations of the correlation for beta-particles and neutrinos have been made, but the results are said by the authors to be somewhat inconclusive.¹¹⁻¹⁵

We have calculated recoil spectra of Cr^{51} atoms for several different values of the angle θ . The mass of the neutrino was taken as zero. The distributions are strongly dependent on the value of θ . For the case of parallel directions of positron-antineutrino emission ($\theta=0^\circ$), all recoils have energies above 43 ev. For

¹⁰ F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936), pp. 20 and 95.

¹¹ J. C. Jacobsen, and O. Kofoed-Hansen, *Kgl. Danske Vid. Sels. Math.-Fys. Medd.* 23, No. 12, 1-34 (1945).

¹² Christy, Cohen, Fowler, Lauritsen, and Lauritsen, *Phys. Rev.* 72, 698 (1947).

¹³ C. W. Sherwin, *Phys. Rev.* 73, 216 (1948).

¹⁴ C. W. Sherwin, *Phys. Rev.* 73, 1173 (1948).

¹⁵ Allen, Paneth, and Morrish, *Phys. Rev.* 75, 570 (1949).

⁹ W. F. Libby, *J. Am. Chem. Soc.* 62, 1930 (1940).

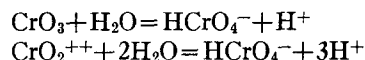
$\theta=180^\circ$ a large share of the recoils have energies over 5 ev, and for $\theta=135^\circ$ (the most probable angle in one theory) all recoils have energies above 8.9 ev. For any case the maximum recoil energy is 63.5 ev. For any of the distributions it seems likely that a large fraction of recoil Cr^{+6} ions would be able to oxidize water readily.

When a comparison is made of the decay of $Mn^{51}(II)$ ions in solution with the decay of permanganate ions in solution, an apparent anomaly is encountered. In the former case all Cr^{51} daughters were reduced, while in the later only about one-half were reduced. If no molecular disruption were to occur, an equation for the decay reaction of permanganate might be written, $MnO_4^- = CrO_4^{+6} + \beta^+$, and in that case all the daughter atoms would initially have the oxidation number VI. As it has been assumed that highly oxidized Cr^{51} ions are produced by the ionization accompanying decay of $Mn^{51}(II)$, the question arises as to why all of these were usually completely reduced whereas only a part of the $Cr^{51}(VI)$ ions from permanganate decay were reduced. To answer this question is difficult but a possible explanation may be as follows. In the case of $Mn(II)$ decay it was assumed that highly charged chromium ions were produced. These ions in almost all cases were assumed to have sufficient kinetic energy to undergo chemical reduction reactions with water. In the case of decay of permanganate, momentum may be conserved not by Cr^{51} alone, but by motion of the whole chromate ion. The suggestion that a large fraction of recoil energy may appear as translational energy for a whole molecule (or ion) with a small fraction as "internal" energy, has been made by Suess.¹⁶ As the mass of chromate is greater than the mass of a bare chromium ion by a factor of 2.24, the recoil kinetic energy of chromate could be at most 0.44 that of the bare Cr^{51} ion. This could partially account for the observation that

¹⁶ H. Suess, *Zeits. f. physik. Chemie* **B45**, 312 (1939).

some of the Cr^{51} grown from permanganate is not chemically reduced. A further consideration involves the assumption that bare highly charged Cr^{51} ions result from $Mn(II)$ decay whereas $Cr(VI)$ resulting from permanganate decay is initially bonded to some oxygen atoms. A non-oxygenated $Cr(VI)$ ion would probably be a much better oxidizing agent than one bound to oxygen atoms.

The preceding argument takes little account of the effect of the ionization on the stability of chromate. Cooper¹⁷ has calculated that the acquisition of positive charge by a bromine atom in bromate can result in formation of excited vibrational states in the ion. In the bromine case the positive charge was assumed to be built up by Auger processes following internal conversion. In the present experiments if ionization of Cr^{51} in chromate were to occur, a similar effect might be expected. As a result one or more oxygen ions might be split out of the chromate ion leaving fragments such as CrO_3 , CrO_2^{+2} , etc. The rupture of chromium-oxygen bonds could also occur in cases with high initial recoil energy. If such fragments were produced by either process they could undergo two competing types of reactions.⁹ The first is hydration to stable acid chromate ion by over-all reactions such as:



The second-type reaction is chemical reduction to $Cr(III)$ as has already been mentioned.

Of course if singly charged or neutral oxygen is split out of the chromate ion this could account for reduction in such cases. From all of the considerations it is evident that the factors which can determine chemical forms are quite complex and the tentative descriptions offered are probably over simplified.

¹⁷ E. P. Cooper, *Phys. Rev.* **61**, 1 (1942).

The Magnetic Susceptibility of Potassium Ferrate*

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A method of preparation of potassium ferrate of 97 percent purity is described. Although the product contained an inseparable ferromagnetic impurity, the susceptibility of the ferrate was determined by extrapolation to infinite field strength of data obtained by the Gouy method. The observed effective magnetic moment of the ferrate ion agrees approximately with that expected for hexavalent iron.

INTRODUCTION

THE difficulty of preparing pure salts of hexavalent iron has resulted in a scarcity of reliable physical data regarding its compounds. No magnetic data are

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available with the exception of qualitative measurements made on solutions containing ferrate.¹ A method for preparing potassium ferrate has been developed in this laboratory, resulting in a product of sufficient purity to make possible the determination of the magnetic susceptibility of the ferrate ion. This investigation

¹ O. Liebknecht and A. P. Wills, *Ann. d. Physik.* (4) **1**, 380 (1900).