

DIFFERENT OXIDATION STATES OF MANGANESE PRODUCED BY THE $Fe(n, p)Mn$ REACTION

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ALPER AND PREEZ¹ noted that Mn^{54} is formed by the $Fe^{54}(n, p)Mn^{54}$ reaction but Frierson and Jones² reported its absence in irradiated iron. Michalowicz and Lederer³ using chromatographic methods of separation also failed to observe any Mn^{54} activity in irradiated iron. While our work was in progress Stafford and Stein⁴ published their results supporting the observations of Alper and Preez. The present investigations confirm the formation of Mn^{54} as a result of (n, p) reaction in Fe^{54} .

Various workers⁵⁻⁹ have observed that the products of (n, p) reactions often exist in different oxidation states. It was therefore decided to study the different oxidation states of Mn^{54} produced from Fe^{54} .

Ferric oxide prepared from carefully purified E. Merck's G.R. quality ferric chloride, was irradiated with fast neutrons at Atomic Energy Research Establishment, Harwell. Spectroscopic analysis of Fe_2O_3 showed that it was of a high degree of purity and that cobalt was completely absent.

To extract any manganese activity in the form of manganous ions, about 0.5 g. of irradiated ferric oxide was treated with a solution of $MnCl_2$ at 100° C. for 6 hours with intermittent stirring. Fe_2O_3 was centrifuged out, the solution filtered through Whatman No. 42 and MnO_2 was precipitated in the filtrate with potassium bromate in 2 N nitric acid solution. The precipitate was centrifuged, washed, dissolved in nitric acid and reprecipitated as above. The cycle of operation was repeated five times. For extracting MnO_4^- ions, ferric oxide was treated with potassium permanganate solution at 100° C. for six hours and after removal of Fe_2O_3 , MnO_2 was precipitated by adding concentrated hydrochloric acid. It was purified as in the previous case. In both cases iron and chromium solutions were added as holdback carriers.

For determination of the total manganese activity 0.5 g. of ferric oxide was dissolved in hydrochloric acid, manganese and chromium were added as carriers, the solution made to 6 N in hydrochloric acid and iron was

extracted with ether. In the aqueous phase manganese was precipitated and purified as described above. The decay curve of the separated fraction shown in Fig. 1 showed that the 320-day activity of Mn^{54} was quite pure.¹⁰

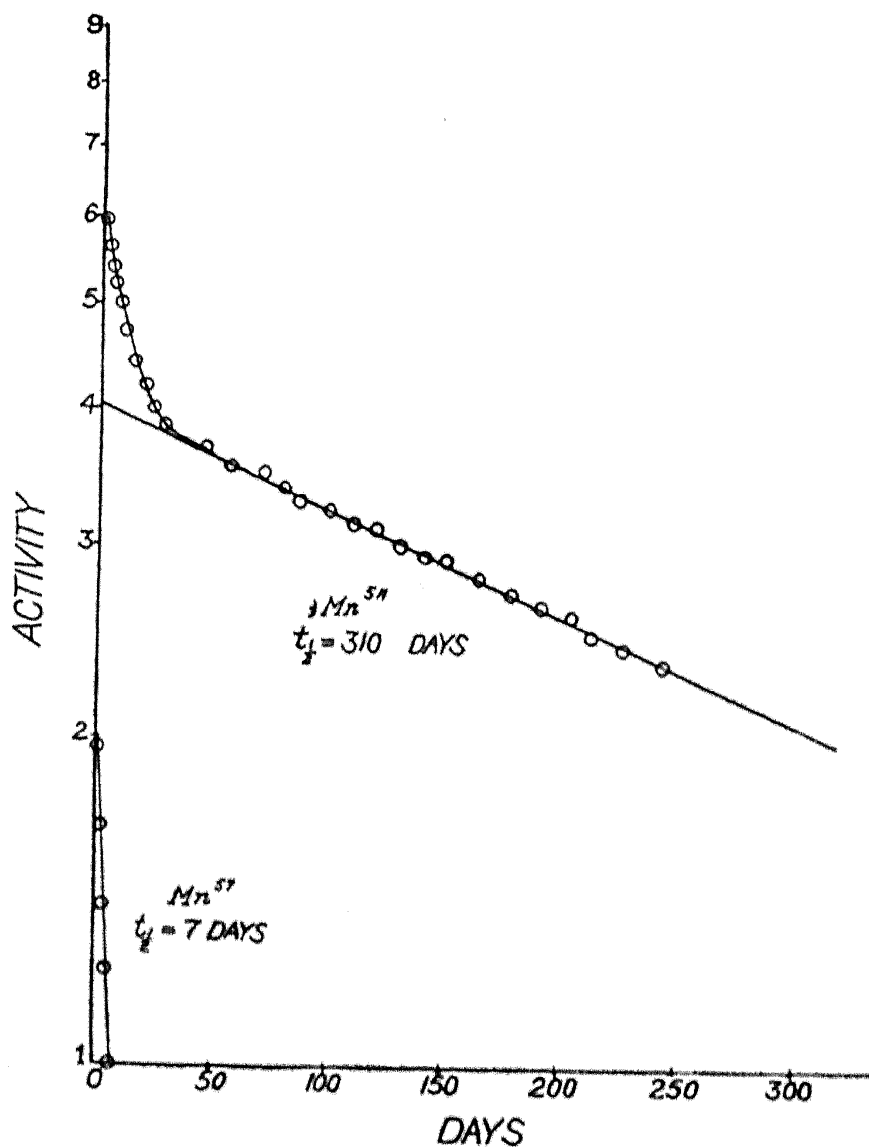


FIG. 1, Decay Curve of Manganese Fraction

To further confirm the formation of Mn^{54} , some of this active MnO_2 was dissolved in hydrochloric acid, some Co^{60} and Fe^{59} added and a drop of the resulting mixture chromatographed according to the methods described by Michalowicz and Lederer³ and Burstall *et al.*¹¹ Unequivocal proof of the presence of Mn^{54} was obtained by this method.

Isotopic exchange of MnO_2 with $MnCl_2$ and $KMnO_4$ solutions was studied by Polissar¹² at ordinary temperatures and by the authors at 100° C.

No exchange whatsoever was observed. In the extraction of manganese activity with MnCl_2 and KMnO_4 , weighed amount of irradiated ferric oxide was treated with successive amounts of the respective solutions till the extract showed no activity. Several determinations gave the following mean results:

Extraction with KMnO_4 at pH 9	..	274 ± 30 cpm.
Extraction with MnCl_2 at pH 5	..	327 ± 30 cpm.
Total Manganese	$13,350 \pm 100$ cpm.

Whereas all Mn^{++} was completely extracted out with MnCl_2 is about 3 extractions, MnO_4^- required about 6 extractions with KMnO_4 . In the case of potassium permanganate, it was noticed that the separable activity at pH 2.5 was greater than that at pH 12.

DISCUSSION

The results obtained in the present investigations leaves no doubt that Mn^{54} is formed as a result of the (n, p) reaction in Fe^{54} thus confirming the recent observations of Stafford and Stein.⁴ Further it is found that some manganese is present in manganous and permanganate states but principally it is present as manganese dioxide.

In the (n, p) reaction the nuclear charge is reduced by one unit and hence iron in the trivalent state in such a reaction, one would essentially obtain manganese in bivalent state if no additional ionization occurs in an atom undergoing such a transformation. The formation of higher oxidation states as obtained in our experiments can be due to several complex and competing factors which are hardly understood for the present as pointed out by Burgus and Kennedy.¹³ Some of them are as follows:—

- (1) Passage of proton through the electronic shells.
- (2) Production of daughter atom in an excited state which decays by γ -emission which may in turn be internally converted.
- (3) Dissipation of recoil energy imparted to daughter nuclei (of the order of 100 KeV in this case).
- (4) Secondary reactions of the recoil fragments with neighbouring molecules.

Michalowicz and Lederer³ did not find manganese in irradiated iron perhaps because the amount of manganese in the solution chromatographed was very small. Since in the present work Mn^{54} was concentrated in the MnO_2 fraction used for chromatography, a clear zone of manganese was obtained.

SUMMARY

Formation of Mn^{54} by (n, p) reaction in Fe^{54} has been confirmed. It has been found that Mn^{54} thus formed occurs in the several oxidation states.

REFERENCES

1. Alper, T. and du Preez, L. .. *Nature*, 1950, **165**, 689.
2. Frierson, W. J. and Jones, W. .. *Anal. Chem.*, 1951, **23**, 1447.
3. Michalowicz, A. and Lederer, M. .. *J. de Phys. et le. Radium*, 1952, **13**, 669.
4. Stafford, G. H. and Stein, L. H. .. *Nature*, 1953, **172**, 1103.
5. Aten, A. Jr. .. *Phys. Rev.*, 1947, **71**, 641.
6. Edward, R. R. *et al.* .. *J. Amer. Chem. Soc.*, 1948, **70**, 1670.
7. Kamen, M. D. .. *Phys. Rev.*, 1941, **60**, 537.
8. Ruben, S. and Kamen, M. D. .. *Ibid.*, 1941, **59**, 349.
9. Yankwich, P. E., Rollefson, G. K. .. *J. Chem. Phys.*, 1946, **14**, 131.
and Norris, T. H.
10. Livingwood, J. J. and Seaborg, G. T. .. *Phys. Rev.*, 1938, **54**, 391.
11. Burstall, F. H. *et al.* .. *J. Chem. Soc.*, 1950, 516.
12. Polissar, M. J. .. *J. Amer. Chem. Soc.*, 1936, **58**, 1372.
13. Burgus, W. H. and Kennedy, J. W. .. *J. Chem. Phys.*, 1950, **18**, 97.