

TABLE I  
HEAT CAPACITY OF 373.42 G. ( $1/2$  MOLE) OF  
 $Gd_2(SO_4)_3 \cdot 8H_2O$

Value of calorie taken equals 4.185 absolute joules

$T_{AV.}$ , °K.	$\Delta T$	$C_P^{1/2}$ mole in cal./deg.	$T_{AV.}$ , °K.	$\Delta T$	$C_P^{1/2}$ mole in cal./deg.
16.06	3.675	1.301	105.82	6.026	31.21
20.21	3.189	2.208	107.52	4.290	31.53
24.81	5.070	3.577	111.72	5.567	32.68
29.65	4.142	5.213	116.20	5.732	33.98
34.02	4.255	6.747	124.20	4.749	35.90
38.86	4.500	8.713	130.08	7.600	37.50
43.41	4.432	10.19	138.65	7.636	39.23
47.98	4.598	11.91	146.55	7.550	41.56
52.54	4.314	13.76	154.55	7.803	43.37
56.98	4.501	15.43	163.03	7.970	45.21
61.94	5.703	17.23	171.26	8.095	47.15
67.01	4.238	19.10	180.12	8.821	48.97
67.65	5.346	19.36	189.13	8.204	51.02
71.32	4.210	20.54	197.81	8.557	52.93
73.01	5.132	21.07	207.46	7.924	55.33
75.58	4.187	21.93	217.09	8.236	56.81
78.42	5.446	22.92	227.17	7.743	58.64
80.21	4.976	23.46	236.06	8.005	60.27
83.64	4.910	24.53	244.77	8.105	61.96
85.14	4.506	24.94	254.45	7.691	63.30
88.67	4.900	26.23	263.22	7.328	64.77
89.68	4.547	26.45	272.13	8.381	66.44
94.01	5.581	27.60	281.58	8.024	67.87
95.48	4.531	28.01	290.16	6.395	69.09
99.88	5.598	29.23	296.50	6.837	69.86
101.86	4.208	29.76			

the points represents the heat capacity from 30 to 300°K. to within a few tenths of a per cent. From 16 to 30°K. the points are probably accurate to no more than a few per cent, due to the falling off of the temperature coefficient of gold resistance thermometers. In Fig. 1 the values of Giauque and Clark are indicated by circles and those of this research by solid black dots. It is evident that the results of Giauque and Clark show excellent agreement with this research from 16 to 200°K. Divergence does occur between 200 and 300°K. where the heat exchange corrections mentioned above become appreciable. The results of this research are given in Table I.

The experimental work reported here was performed in the Chemical Laboratory of the University of California. The calculations involved were in great part completed at The Johns Hopkins University.

### Summary

The specific heat of  $Gd_2(SO_4)_3 \cdot 8H_2O$  has been determined from 16 to 300° Absolute.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

## The Identity of Fermi's Reactions of Element 93 with Element 91

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### Introduction

The interesting experiments recently performed by E. Fermi and his collaborators,<sup>1</sup> on the bombardment of uranium with neutrons, have led him to conclude that elements with an atomic number above 92 are formed. He specifically assumes that his product, with a period of thirteen minutes, which is precipitated from a highly oxidizing and acid solution together with manganese, is the highest homolog of the latter or element 93; furthermore, in a later paper<sup>1b</sup> he assumes that his product with a period of ninety to one hundred minutes, which is partially (50–60%) precipitated with rhenium sulfide from a highly acid solution, is isotopic with the thirteen minute product.

(1) E. Fermi, (a) *Nature*, **133**, 898 (1934); (b) *Proc. Roy. Soc. (London)*, **146A**, 483–495 (1934).

However, since we have to expect, according to the *periodic law*, other properties<sup>2</sup> for the highest homolog of manganese, we have repeated Fermi's chemical experiments, using protactinium, the longest lived isotope of element 91, as an indicator and obtained results described below.

### Materials and Procedure

**Materials.**—The following solutions were prepared, using c. p. grade of chemicals in all cases: (1) a water solution of uranyl nitrate containing 2.763 g. of  $U_3O_8$  per 50 cc.; (2) a manganese nitrate solution containing 0.1179 g. of  $MnO_2$  per 10 cc.; (3) a 15% solution of sodium thio-sulfate; (4) a water solution of potassium perrhenate containing 0.1609 g. of  $KReO_4$  per 25 cc.; (5) a 4% sulfuric acid solution of protactinium pentoxide, equivalent to 900  $U_3O_8$  units of pure protactinium<sup>3</sup> per 5 cc., and containing also 5 mg. of ferric oxide in 5 cc.

(2) Grosse, *THIS JOURNAL*, **57**, 440 (1935).

(3) A. V. Grosse and M. S. Agruss, *ibid.*, **56**, 2200 (1934).

**Procedure**

**Manganese Dioxide as Carrier.**—To 50 cc. of the uranyl nitrate solution was added 50 cc. of concentrated (70%) nitric acid, 5 cc. of the protactinium solution and 10 cc. of the manganous nitrate solution. This mixture was heated to boiling and 0.1 g. of sodium chlorate was added rapidly in small portions, after which the precipitated manganese peroxide hydrate was boiled for two minutes before filtering. Unless otherwise stated, the alpha activity of the ignited  $Mn_2O_3$ , painted on aluminum disks, was measured in an ordinary Rutherford alpha electroscope. The activity remaining in the uranyl nitrate filtrate was precipitated with zirconium phosphate and its alpha activity was also measured after ignition.

**Rhenium Sulfide as Carrier.**—In the rhenium experiments, 25 cc. of the  $KReO_4$  solution was diluted to a final volume of 200 cc. containing 15% hydrochloric acid, and a definite amount of protactinium added. The rhenium was precipitated as the sulfide by adding an excess (10–15 cc.) of the sodium thiosulfate solution. After boiling for fifteen minutes, the rhenium sulfide was filtered and washed with hot 5% hydrochloric acid. The precipitate was impregnated with a solution of zirconium oxychloride, fumed with sulfuric acid, ignited and its alpha activity was measured as mentioned above. The protactinium activity remaining in the filtrate was isolated with zirconium phosphate as in the above experiment with manganese. Similarly to Fermi's experiments, the rhenium is not completely precipitated and a small amount remains in solution.

**Results**

The results obtained are shown in the tables.

TABLE I

RESULTS WITH MANGANESE AS THE CARRIER

Pa added, $U_3O_8$ units.....	900	900	900 <sup>a</sup>	900 <sup>b</sup>
Pa in $MnO_2$ , $U_3O_8$ units.....	835	885	800	860
Pa in filtrate, $U_3O_8$ units....	8.4	2.3	103.0	65.0
% of total activity in filtrate:	0.9	0.2	12.0	7.0
% of total activity in ppt., by diff. <sup>c</sup> .....	99.1	99.8	88.0	93.0

<sup>a</sup> Boiled pptd.  $MnO_2$  for ten minutes before Pa was added. <sup>b</sup> Boiled for one hour before adding. <sup>c</sup> This is more reliable than measuring the activity of the precipitate because of the error introduced by the absorption of the alpha rays.

TABLE II

RESULTS WITH RHENIUM AS THE CARRIER

Pa added, $U_3O_8$ units.....	1250	850	3200
Pa in rhenium sulfide, $U_3O_8$ units....	780	350	1720
Pa in filtrate, $U_3O_8$ units.....	460	490	1470
% of total activity with precipitate...	63	42	54

**Discussion.**—The data of Tables I and II are compared with Fermi's reactions of element 93 in the following table.

Reaction	Pptn. of $MnO_2$ with $NaClO_3$	Pptn. of rhenium sulfide with $Na_2S_2O_3$
Behavior of Element 91	99–100% pptd. in hot 30% $HNO_3$	40–60% pptd. in hot 15% $HCl$
Behavior of Fermi's Element 93	Large % of activity pptd. in hot concd. $HNO_3$	About 50% of activity pptd. in hot concd. $HCl$

It can be seen that they are identical within experimental error, and the conclusion was made<sup>4</sup> that Fermi's element 93 is a new isotope of element 91.

In the meantime "the evidence to the contrary," mentioned in our letter,<sup>3</sup> has been provided and the indications are that our conclusion is erroneous.

Following our suggestion E. Fermi has tested whether his artificial radioelements are precipitated together with zirconium phosphate, the coprecipitation being a very clear and definite reaction for element 91. Fermi found<sup>5</sup> that the zirconium phosphate precipitate is inactive and that his active products remain in solution. This result is the first definite evidence showing that Fermi's products are not isotopes of element 91. On the other hand, Fermi finds<sup>5</sup> that his products are precipitated from alkaline solutions, contrary to the predicted properties<sup>2</sup> of element 93, which should remain in solution as alkali perkarhenate. In view of these contradictions it is best to await further experimental evidence. It might be that the Szilard-Chalmers<sup>6</sup> isotope separation effect introduces difficulties in the correct interpretation of the chemical reactions of neutron products.

Much light on the transmutation of uranium would be shed by first determining the chemical nature of thorium products; this should prove an easier task, since the chemistry of elements 91 and 92 is known.

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CHICAGO, ILL.

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(4) A. V. Grosse and M. S. Agruss, *Phys. Rev.*, **46**, 241 (1934).

(5) E. Fermi, private communication.

(6) Szilard and Chalmers, *Nature*, **134**, 462 (1934).