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THE CHEMICAL PROPERTIES OF MENDELEVium

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THE CHEMICAL PROPERTIES OF MENDELEVIUM

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In the earlier observances in this series commemorating the discovery of new elements, a profusion of information on the chemical properties of the elements 97 (Bk), 98 (Cf), 99 (Es), and 100 (Fm) was available 25 years after their discovery. Many properties obtainable from bulk samples had been measured and we therefore knew of the structure of their metals and simple compounds, their vapor pressures, densities, magnetic susceptibilities, and energy levels in their atoms and molecules. Such information was obtainable only because milligram amounts of Bk, Cf, and Es could be manufactured by neutron irradiation of the lighter actinides. Beginning with Md, a greatly reduced amount of knowledge is and will ever become available for the reason that the synthesis of these heaviest of the known elements is only possible by ion bombardment of lighter actinide target nuclei. Even with the most intense ion beams and the largest available quantities of target isotope, about 10^6 atoms at a time is all the Md that can be produced for chemical studies. This lack of sufficient sample size coupled with the very short lifetimes of the few atoms produced has severely restricted the gathering and the broadness of our knowledge concerning the properties of Md and the heavier elements. To illustrate, the literature contains a mere eleven references to the chemical studies of Md, and none of these deal with bulk properties associated with the element bound in solid phases.

The isotope ^{256}Md is nearly always employed for chemical studies of this element. Besides having a convenient half life of 77 min, this nuclide can be made with millibarn cross sections by a number of nuclear reactions between light or heavy ions with actinide target nuclei. We have found that the bombardment of fractions of a microgram of ^{254}Es with intense alpha-particle beams will produce $\sim 10^6$ atoms of ^{256}Md in one to two hours of irradiation time. The ^{256}Md is most easily detected through spontaneous fission arising from the ingrowth of its electron-capture daughter ^{256}Fm . A difficulty with using spontaneous-fission counting to determine the Md content of samples is that the growth and decay of fission radioactivity in each sample must be followed with time in order to resolve the amounts of Md and Fm initially present. However, alpha-particles of a distinctive energy coming from a 70% alpha-decay branch can also be used to identify ^{256}Md in a mixture of actinide tracers.

Mendelevium and Fm metal was found to be more volatile than other actinide metals. In the numerous thermochromatographic studies by Zvara and coworkers (1), the evaporation of Fm and Md tracer from molten La at 1750°C was compared with the behavior of other selected lanthanides and actinides. The volatility of Md and Fm was found to be greater than that of Cf and Cf was about equivalent to Yb and Eu, and all were much more volatile than Am. The volatilities are correlated by the number and energy of the valence bonds minus the energy needed to promote electrons to the valence bands in the metals. Therefore, within the normally trivalent lanthanides and actinides, the more volatile elements are

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associated with the divalent metals. The unusual volatility of Fm and Md was then construed by Zvara as evidence for divalency in the metallic state.

There are no experimental verifications of the electronic structure of Md, but this has been calculated by several methods to be $5f^{13}7s^2$ in which the ground state level is $^4F_{7/2}$ (2).

The separation of Md from the other actinides can be accomplished either by reduction of Md^{3+} to the divalent state (3) or by chromatographic separations with Md remaining in the tripositive state. Historically, Md^{3+} has been separated in columns of cation-exchange resin by elution with α -hydroxyisobutyric acid solutions (4). This method is still widely used even though extraction chromatography requires less effort and attention to technique. Horwitz and coworkers (5) developed a highly-efficient and rapid separation of Md^{3+} by employing HNO_3 elutions of columns of silica powder saturated with an organic extractant, bis(2-ethylhexyl)phosphoric acid. The separation of Md from Es and Fm could be completed in under 20 minutes and had the advantage of providing final solutions of Md free of complexing agents that might be an interference in subsequent experiments.

When the divalent state of Md was first discovered, extraction chromatography was used to prove that the behavior of Md^{2+} was dissimilar to that of Es^{3+} and Fm^{3+} (3). The extractant, bis(2-ethylhexyl)phosphoric acid (HDEHP), has a much lower affinity for divalent ions than it does for the tri- and tetravalent ones. Thus, the extraction of Md^{2+} is much poorer than the extraction of the neighboring tripositive actinides as indicated by the results shown in Table 1. This became the basis for a separation method in which tracer Md in 0.1 M HCl is reduced by fresh Jones' Reductor in the upper half of an extraction column containing HDEHP absorbed on a fluorocarbon powder in the lower half. Mendelevium, in the dipositive state, is rapidly eluted with 0.1 M HCl whereas the other actinides are retained by the extractant. The separation is quickly performed, but the Md contains small amounts of Zn^{2+} from the Jones' Reductor and also Eu^{2+} , which was added prior to the elution to prevent reoxidation of Md^{2+} by the extractant.

The solution chemistry of the trivalent oxidation state has not been investigated beyond its behavior in the separation procedures described above. All observations indicate that Md^{3+} is a "normal" actinide with an ionic radius slightly less than that of Fm. As might be expected, attempts to oxidize Md^{3+} with sodium bismuthate failed to show any evidence for Md^{4+} (3).

The divalent oxidation state was the first found for any member of the actinide series (3,6) and, therefore, stirred a strong theoretical and experimental effort to establish the reasons for the unexpected stability of this state in Md, and subsequently, in the adjacent actinides. We shall summarize the interpretations for divalency in the heaviest actinides in a later section, but in this section, only the known properties of Md^{2+} will be presented.

In the earliest experiments with Md^{2+} , rough measurements were made of the reduction potential for the half-reaction

The first measurement gave a reduction potential of -0.2 V with respect to the standard hydrogen electrode (3). This value was obtained from determining the equilibrium concentration of each metal ion in the reaction

and then calculating the equilibrium constant. After entering the equilibrium constant into the Nernst equation, it was found that V^{3+} was a better reducing agent than Md^{2+} by about 0.07 V. In other experiments, Maly observed the complete reduction of Md^{3+} with V^{2+} but the reduction was incomplete when Ti^{3+} was used (6). From these observations, he concluded the standard reduction potential of Md^{3+} was close to -0.1 volt. The standard potentials obtained by both groups are in reasonable agreement and, most importantly, they conclusively show that the stability of Md^{2+} is greater than any lanthanide(II) ion. This finding was surprising since divalency in the lanthanides is mainly associated with the special stability given by the half-filled and fully-filled f-electron shell. Divalent Md ions are at least one electron short of the stable $5f^{14}$ configuration.

Additional experiments which may not be clearly relevant to the divalent oxidation state, include the reduction of Md^{3+} to $\text{Md}(\text{Hg})$ by sodium amalgams and by electrolysis (7). Both the extraction experiments with Na amalgams and the electrolysis at a Hg cathode indicated a large enrichment of Md in the Hg phase relative to that of Np, Pu, Am, Cm, and Cf. The percentages of Es and Fm in the sodium amalgam were not greatly different from the percentage of Md. But a clear enrichment of Md was obtained in the electrolysis experiments as shown in Figure 1. The initial rate of amalgamation is much larger for Md than for Es and Fm.

Recently, new electrochemical experiments were carried out with Md in which controlled-potential electrolysis was used to study the reduction of Md^{3+} to the metallic state in a Hg amalgam (8,9). Half-wave potentials were measured by radiocoulometry and radiopolarography in the presence of noncomplexing and weak and strong complexing agents. The radiopolarogram obtained for Md in a noncomplexing media is presented in Figure 2. The half-wave potential for Fm was remeasured at the same time as that of Md because of its presence as a decay product of ^{256}Md . The results showed that the reduction potential of Md is about 10 mV more negative than Fm and that no significant difference is observed upon changing the medium from ClO_4^- to Cl^- . In citrate solutions, a shift of 90 mV was obtained for Md which is about the same shift seen with Fm and Ba ions in a citrate medium. The slope of the logarithmically transformed wave was 30 mV for Md and Fm.

The electrochemical reaction taking place at a reversible electrode can be deduced from the slope of the polarographic wave. Specifically, the number of electrons exchanged at the electrode, based on the Nernst equation, is obtained from this slope. From their analysis of the polarograms, there were three electrons involved in the electrochemical reduction of the trivalent ions of the elements Am through Es and only

two electrons for the reduction of Fm and Md. This implies that Md^{3+} was first reduced to Md^{2+} before being further reduced to the metal. The III $\rightarrow$ II reduction step is not detected by this radiopolarographic technique because both the III and II ions are in the solution phase; whereas, the measured parameter is the distribution of the tracer between the aqueous and Hg phase.

These results demonstrate that the electrochemical behavior of Md is very similar to that of Fm and can be summarized in the equation

The half-wave potentials measured by this method include the amalgamation potential of the metal-mercury reaction. The amalgamation potential was estimated to be 0.90 V by using the metal radii as a correlating parameter and interpolating within a series of divalent elements with known amalgamation potentials (10). This correlation is shown in Figure 3. The standard electrode potential is then given as -2.40 V for the $Md^{2+} + 2e^- = Md^0$ reaction. The authors' estimated 5 mV accuracy for the measured half-wave potential seems reasonable, but there is a much larger uncertainty in the estimated amalgamation potential. Because the amalgamation potential represents a large correction in obtaining the standard potential, caution should be exercised in combining this standard potential with other data to calculate additional thermodynamic properties.

In addition to the di- and trivalent ions of Md, a stable monovalent ion was reported by Mikheev et al. in 1972 (11). This oxidation state was indicated in the cocrystallization of Md with CsCl and RbCl after the coreduction of Md^{3+} and Sm^{3+} with Mg in an ethanol-7 M HCl solution. Mendelevium was also found enriched in Rb_2PtCl_6 precipitates, a specific carrier for the larger ions of the alkali metals. These results were explained by a stabilization of the monovalent ion due to completing the f shell which would give the $5f^{14}$ electronic configuration.

These experiments were recently repeated and a series of new ones were performed in which attempts were made to prepare Md^+ by reduction with $SmCl_2$ in an ethanolic or fused KCl medium (12). After the reductions, the coprecipitation behavior of Md was compared with the behavior of tracer amounts of Es, Fm, Eu, Sr, Y, and Cs. A large number of experiments showed that Md consistently followed the behavior of Fm^{2+} , Eu^{2+} , and Sr^{2+} rather than the behavior of Cs^+ . The most telling experiment was the precipitation of Rb_2PtCl_6 after reduction of Md^{3+} with Sm^{2+} . The distribution of the tracer elements between the precipitate and an ~85% ethanol solution is given in the form of a ratio in Table 2. These results clearly demonstrate that Md did not coprecipitate with Rb_2PtCl_6 , whereas virtually all of the Cs did so. The overall conclusion of this work was that Md cannot be reduced to a monovalent ion with Sm^{2+} , and therefore, the earlier claim for Md^+ was unsubstantiated.

Table 2. Distribution of tracer elements after reduction with Sm^{2+} and coprecipitation with Rb_2PtCl_2 in ~85% ethanol. (Ref. 11).

<u>Fm</u>	<u>Md</u>	<u>Eu</u>	Distribution ratio for		<u>Es</u>	<u>Ce</u>
			<u>Sr</u>	<u>Y</u>		
0.004	0.005	0.006	0.012	0.017	0.033	110

This same conclusion was reached also by Samhoun et al. (8) and David and coworkers (9) on the basis of their electrochemical investigations of Md, which we described earlier. If the potential for the reaction $\text{Md}^+ + e^- \rightarrow \text{Md}$ was more positive than -1.5 V, it would have been observed in the electrochemical reductions. Furthermore, the logarithmic slope of the Md reduction waves could not be fitted to a slope of 60 mV expected for a one-electron change. And lastly, the shifts in potential caused by complexing Md with either citrate or chloride ions were consistent with it being a divalent ion and not with it being either a cesium-like or silver-like ion.

The attempts to produce a monovalent state have the positive effect of setting limits on its stability. From the limits obtained, we can then make an estimate of the stability of the $5f^{14}$ configuration relative to the $5f^{13}7s$. Presumably, the $f^{13}s$ configuration lies lower in energy than the f^{14} because there is no obvious stabilization of a monovalent state due to a possible closing of the 5f shell. The divalent ion is at least 1.3 V more stable than the monovalent.

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FIGURE CAPTIONS

- Table 1. Comparison of the extraction behavior of tracer Es, Fm, and Md after treatment with various reducing agents. The column-elution method of extraction chromatography was used with the extractant, bis(2-ethylhexyl)phosphoric acid (HDEHP) adsorbed on a column bed of a fluoroplastic powder (Ref. 3).
- Fig. 1. Percentage of actinide tracers electrodeposited in mercury as a function of time and passed charge. Current density used in this experiment was 5 mA/cm². (Reprinted with the permission of J. Mály and Pergamon Press (Ref. 7)).
- Fig. 2. Distribution of Md as a function of applied voltage between mercury in a dropping Hg cathode and 0.1 M tetramethyl ammonium perchlorate at pH = 2.4. The slope of the logarithmically-transformed line indicates the number of electrons exchanged in the electrolysis reaction. The slope of line (a) is 30 mV, and (b) is 60 mV, which corresponds to a one-electron reduction. (Ref. 9).
- Fig. 3. Amalgamation potentials, Δ_2 , derived from experimental data are plotted as a function of the atomic (metallic) radii. The amalgamation potential for Fm is obtained by using an estimated radius. (Partially redrawn from Ref. 10).

CONDITIONS FOR REDUCTION	STANDARD POTENTIAL OF REDUCING AGENT (volts)	% NON-EXTRACTED BY HDEHP COLUMN	
		Md	Es-Fm
Zn(Hg) AMALGAM, 80° ~20 min, 0.1 M HCl; Zn(Hg) AMALGAM IN UPPER HALF OF EXTRACTION COLUMN	+0.763	77	<0.10
0.01 M Eu^{2+} , 0.1 M HCl, ~2-3 min, 80°; Zn(Hg) AMALGAM IN UPPER HALF OF EXTRACTION COLUMN	+0.43	75	<0.10
0.6 M Cr^{2+} , 0.1 M HCl, ~2 min, 25°C; EXTRACTION COLUMN PRE- WASHED WITH 0.6 M Cr^{2+} IN 0.1 M HCl	+0.41	99	0.56

Table 1

Amalgamation rates (J. Maly')

Figure 1

Figure 2

Figure 3