[CONTRIBUTION NO. 538 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

The Vapor Pressure of Thulium Metal

BY F. H. SPEDDING, R. J. BARTON AND A. H. DAANE

RECEIVED MAY 18, 1957

The vapor pressure of thulium has been measured by two modifications of the Knudsen effusion method, covering the temperature region from 809 to 1219°K. The results may be expressed by eq. 3. This represents a heat of sublimation of -57.44 ± 0.20 kcal. for this temperature region, which is somewhat lower than would be expected for a normal trivalent rare earth element, but appears reasonable for thulium in which the binding may perhaps be weaker due to the nearly filled 4f shell in this metal.

In the study of the rare earth elements being carried out in this Laboratory it has been shown that in the metallic state, there are differences among the properties of members of this group of elements that are quite large in some cases.[1,2] For example, the vapor pressures of some of the rare earths have been found to be different by factors of over 10^6.[1,3] From metallurgical experience in the preparation of thulium metal,[4] it was known that thulium is one of the more volatile rare earth metals; this paper describes the results obtained from a detailed study of the vapor pressure of this element.

Because of the convenient activity that could be formed by neutron irradiation of the metal, the radio-tracer modification of Knudsen's effusion technique of measuring vapor pressures was selected for this work.[5] To remove some of the uncertainty that sometimes accompanies the use of this method, the vapor pressure also was determined by measuring the direct weight loss from an effusion cell, similar to the method used by Harteck to study the vapor pressure of silver.[6]

Apparatus and Experimental Procedure

A. **Weight Loss Method.**—A tantalum effusion vessel, with a 0.2077 cm. diameter orifice in the lid, was loaded with redistilled thulium metal, and weighed and placed in the vacuum furnace assembly shown in Fig. 1; the graphite crucible served both to maintain an even temperature around the effusion vessel, and to prevent back-scatter of thulium vapor by the formation of stable, non-volatile thulium carbides. The junctions of the chromel–alumel and platinum–platinum, 13% rhodium thermocouples, calibrated against the freezing points of copper, silver and the copper silver eutectic, were placed in a molybdenum block that also held the effusion vessel. The vacuum in the system was maintained at 5×10^{-5} mm. or better during outgassing and at 1×10^{-6} or better during the measurements. To make an exposure the system was extensively torched and a Kanthal wound resistance furnace, at a temperature above the desired exposure temperature, was raised around the tube containing the effusion vessel with about 15 minutes being required for the vessel and furnace to come to thermal equilibrium. The exposures were terminated by lowering the furnace. This procedure gave an estimated maximum uncertainty of five minutes in starting time and three minutes in stopping time, or a total timing uncertainty of about 3% for the shortest exposures. The vessel was weighed before and after each run to determine the amount of thulium vapor that had left the vessel.

B. **Target Condensation Method.**—To extend the range of pressure covered and to be able to later investigate the partial pressure of thulium over some of its alloys, a second apparatus was built, shown in Fig. 2, which employed the target condensation modification of the effusion method. Many of the essential features of this method have been described by other workers.[6,7] The tantalum effusion vessel was placed in a graphite holder which helped maintain a uniform temperature around the vessel and trapped all of the effused material except a small beam that escaped through the hole in the lid. This formed a well defined beam that covered an area slightly larger than the hole in the cooled collimator plate, and prevented any stray material from striking portions of the apparatus from which it might re-evaporate and reach the target. The tantalum targets, held in aluminum cassettes by soft iron snap rings, were thick enough to act as infinite back-scatterers of the radiation from the Tm^{170}. Because of the magnetic nature of the snap rings, the targets could be moved by external magnets after their ejection from the target holder by a rack and pinion device that was operated by a winch through a standard taper joint. The temperature of the furnace was maintained constant to ±1° during all of the exposures by means of an electronic temperature controller operating on a resistance bridge principle.[8] The temperature of the furnace was measured by means of chromel–alumel and platinum–platinum, 13% rhodium thermocouples placed at the side of the effusion vessel in the graphite crucible.

The thulium-170 activity was prepared at the Oak Ridge National Laboratory by neutron bombardment of 1.96 g. of thulium turnings prepared in the laboratory. The irradiated turnings were homogenized by melting them together with 2.52 g. of lanthanum and 1.03 g. of inert thulium. The lanthanum served to provide a lower melting medium in which the two samples of thulium could dissolve and equilibrate, and promoted homogenization by reducing any thulium oxide present. The pure homogeneous thulium was obtained as a distillate by heating the alloy in a high vacuum to 1500°; previous work with inert thulium had shown the absence of any lanthanum in such a distillate. The loosely sintered condensate was crumbled to give a sample with a large surface area in the effusion vessel. The specific activity of the thulium was determined by standard radiochemical techniques, using targets identical with those employed in the vapor pressure work. By counting these samples with each set of targets, the need for counter geometry or half-life corrections was eliminated.

To make a run, the loaded effusion vessel and targets were put into place, and the apparatus was outgassed to a vacuum of 1×10^{-6} mm. or better as the temperature was slowly raised. At the desired temperature, the bottom target was ejected and a timed exposure was begun on the next target as it fell into place. At the end of the exposure, this target was ejected, the temperature adjusted for the next exposure and the next "spacer" target ejected to start the next exposure. About seven seconds were required to eject a target, which contributed an uncertainty of less than 0.1% to the exposure time. After the series of exposures was completed, the targets and the specific activity plates

---

[1] F. H. Spedding and A. H. Daane, *J. Metals*, **6**, 504 (1954).

[2] F. H. Spedding, A. H. Daane and K. W. Herrmann, *Acta Cryst.*, **9**, 559 (1956).

[3] A. H. Daane, Atomic Energy Commission Report AECD-3209, 1950.

[4] F. H. Spedding, A. H. Daane and J. E. Powell, *Nucleonics*, **12**, 37 (1954).

[5] H. M. Schadel, Jr., and C. E. Birchenall, *J. Metals*, **2**, 1134 (1950).

[6] P. Harteck, *Z. physik. Chem.*, **134**, 1 (1928).

[7] T. E. Phipps, N. D. Erdway, L. O. Gilpatrick, Z. V. Jasaitis, F. D. Johnson, G. W. Sears, R. L. Seifert and O. C. Simpson, Atomic Energy Commission Report CN-3223, 1954.

[8] H. J. Svec, A. A. Read and D. W. Hilker, Atomic Energy Commission Report ISC-585, 1955.

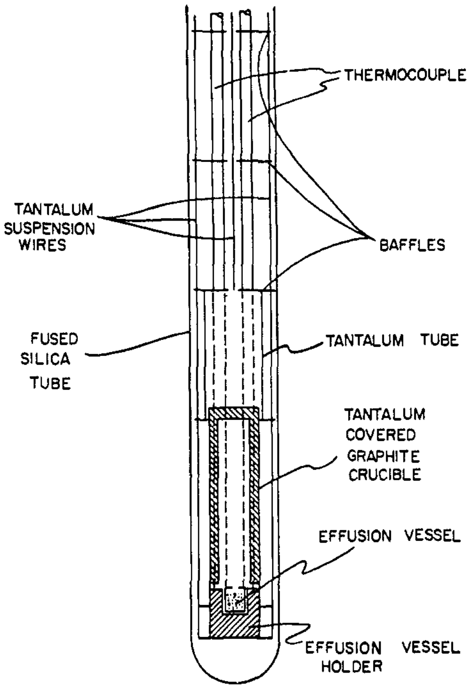

Fig. 1.—Direct weight loss vapor pressure apparatus.

were counted three times, the weight of material on the targets was calculated and the values were averaged and corrected for the small amount of isotopic fractionation that occurred during the effusion process.

Results

The data obtained from runs using both methods are given in Tables I, II and III. For the weight loss method, the pressures given in Table I were calculated using the equation

TABLE I

VAPOR PRESSURE DATA FOR THULIUM BY THE WEIGHT LOSS MODIFICATION (RUN I)

Diameter of orifice, 0.2077 cm.; orifice area, 3.3904 × 10^{-2} cm.^{2}; $P = 3.89014 \times 10^1 G\sqrt{T}/t$.

Exposure	Time × 10^{-4} (sec.)	Temp. (°K.)	Wt. loss (g.)	$10^4/T$	P
1	3.12	974.4	0.00564	10.263	2.195×10^{-4}
2	1.71	1058.2	.02652	9.450	1.963×10^{-3}
3	1.80	1033.6	.01358	9.675	9.436×10^{-4}
4	8.28	949.9	.00619	10.527	8.963×10^{-5}
5	2.52	1005.9	.00912	9.941	4.465×10^{-4}
6	1.80	1092.9	.06144	9.150	4.390×10^{-3}
7	1.83	1021.7	.01221	9.788	8.296×10^{-4}

$$P(\text{mm}) = \frac{(2\pi RT)^{1/2}}{M}\frac{G}{at} \qquad (1)$$

where "G" is the weight of vapor lost from the cell, "R" is the gas constant, "M" is the molecular weight of the vapor (a monatomic species was assumed for this study), "a" is the orifice area, "t" is the exposure time in seconds and "T" is the temperature in degrees Kelvin. The pressures determined by the target condensation method (see Tables II and III) were calculated using the equation

$$P(\text{mm}) = \frac{(2\pi RT)^{1/2}}{M}\frac{G_{\ominus\,168.94}}{at}\sin^2\theta \qquad (2)$$

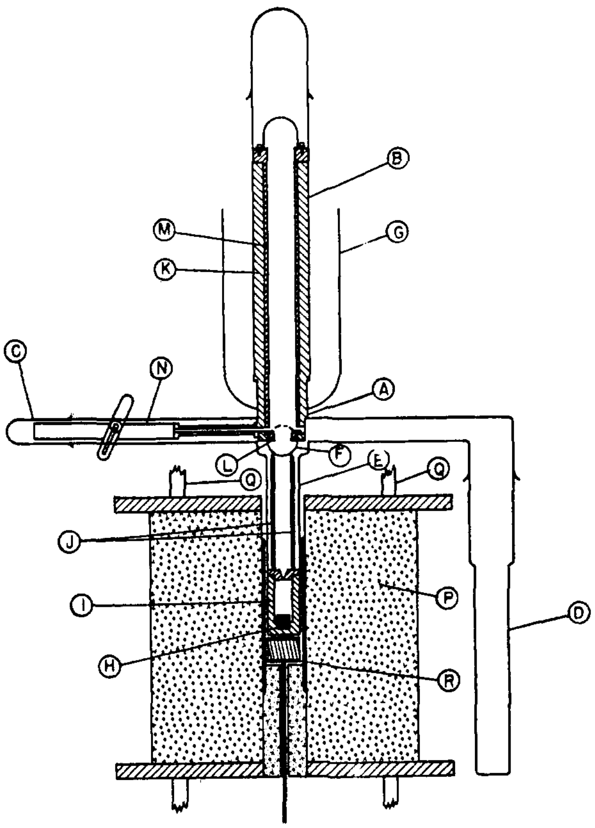

Fig. 2.—Radio-tracer vapor pressure apparatus: A, target holder support tube; B, target holder jacket; C, target ejector tube; D, target collector; E, furnace tube; F, lead to vacuum pump; G, Dry Ice target cooling trap; H, effusion vessel; I, effusion vessel holder; J, thermocouples; K, copper target holder support; L, collimator; M, target holder; N, target ejector; P, furnace; Q, furnace guide rods.

where the letter designation is the same as in eq. 1, and "$G_{\ominus\,168.94}$" is the weight of material, corrected to the normal atomic weight, condensed on the target

TABLE II

VAPOR PRESSURE DATA FOR THULIUM BY THE TARGET CONDENSATION MODIFICATION (RUN II)

Diameter of orifice, 0.2459 cm.; orifice area, 4.6721 × 10^{-2} cm.^{2}; $P = 1.05977 \times 10^4 G\sqrt{T}/t$; collimator diameter, 15.259 mm.; orifice to collimator distance, 147.63 mm.

Exposure	Time (sec.)	Temp. (°K.)	Wt. loss (g.)	$10^4/T$	P
2 B	3.96×10^4	869.2	0.6694	11.505	5.282×10^{-6}
2 D	5.04×10^4	849.0	.4587	11.779	2.810×10^{-6}
2 G	2.25×10^4	889.7	.8364	11.240	1.175×10^{-5}
2 J	1.08×10^4	911.2	.9450	10.974	2.799×10^{-5}
2 L	3.42×10^4	878.0	1.0354	11.390	9.507×10^{-6}
2 N	1.53×10^4	899.8	1.0139	11.114	2.107×10^{-5}
2 Q	2.25×10^4	890.5	0.9024	11.230	1.268×10^{-5}
2 S	2.43×10^1	870.9	.4257	11.482	5.479×10^{-6}
2 U	5.40×10^4	828.8	.1999	12.066	1.130×10^{-6}
2 W	7.20×10^4	819.4	.1435	12.204	6.046×10^{-7}
2 Y	11.16×10^4	809.0	.1753	12.361	4.735×10^{-7}
2 AA	4.68×10^4	840.2	.2356	11.902	1.547×10^{-6}
2 AC	1.26×10^4	912.3	.9702	10.961	2.456×10^{-5}
2 AE	5.40×10^3	931.5	.6404	10.735	3.836×10^{-5}
2 AG	3.60×10^4	951.0	1.1562	10.515	1.050×10^{-4}
2 AK	1.80×10^3	969.2	0.8555	10.318	1.568×10^{-4}
2 AM	1.80×10^4	990.6	1.5283	10.095	2.832×10^{-4}
2 AP	1.80×10^3	1006.6	2.7622	9.934	5.150×10^{-4}
2 AR	1.80×10^3	1000.1	1.9494	9.999	3.443×10^{-4}

which subtends a solid angle θ at the orifice; $\sin^2\theta$ is given as

$$\sin^2\theta = \frac{D^2}{4Z^2 + D^2}$$

where "Z" is the orifice to collimator distance and "D" is the collimator diameter.

In these experiments, three different crucibles with different orifice areas were used, and in each case, the mean free path of the thulium atoms was greater than ten times the orifice diameter. The good agreement obtained in the data from these measurements is shown in Fig. 3, in the logarithmic plot of pressure *versus* $1/T$°K., where the points from both methods fall together, indicating that the vapor phase in the effusion vessel was saturated in all of these experiments. The agreement in results from the two methods and the absence of thulium activity on the top of the collimator plate and other places out of the direct beam indicated that complete condensation on the targets had been achieved. The very thin tantalum sheet (1.97×10^{-4} cm.) used for the crucible lids made corrections for a "canal" effect in the orifice negligibly small.

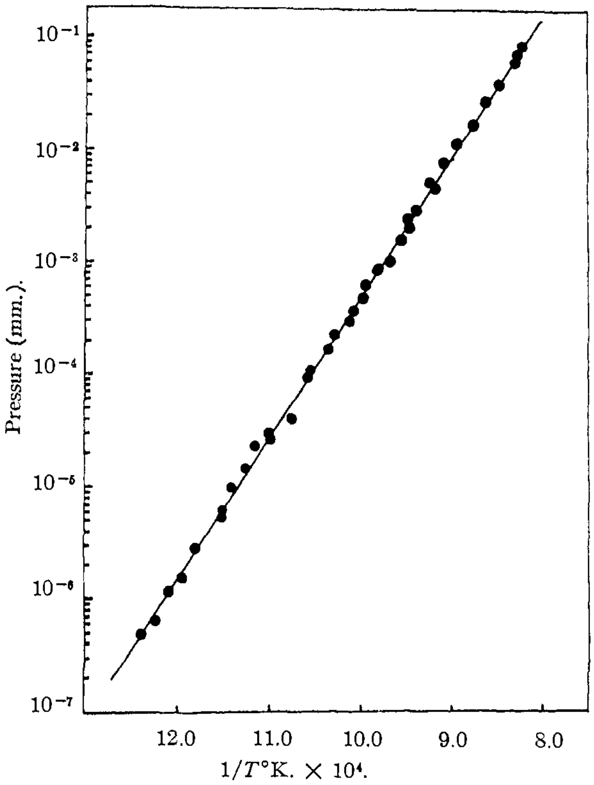

Fig. 3.—Vapor pressure of thulium.

The vapor pressure data, when fitted to a straight line by a least squares treatment taking the temperature as the independent variable, gave the equation

$$\log P(\text{mm}) = \frac{-1.2552 \pm 0.0045 \times 10^4}{T} + 9.1761 \pm 0.0457 \quad (3)$$

This gives a heat of sublimation of -57.44 ± 0.20 kcal./mole in this temperature range. This compares favorably with the value of -56.2 ± 0.4 kcal. reported by Savage[9] of this Laboratory who used a mass spectrometric method to determine the heat of sublimation. The thermodynamic data needed to permit an accurate calculation of the heat of sublimation at room temperature or to calculate the normal boiling point are not available. However, using estimated data, a ΔH_{298} of -59.1 kcal./mole and a normal boiling point of 2000°K. are obtained.

TABLE III

VAPOR PRESSURE DATA FOR THULIUM BY THE TARGET CONDENSATION MODIFICATION (RUN III)

Diameter of orifice, 0.01935 cm.; $P = 1.65423 \times 10^6 G\sqrt{T}/t$; orifice area, 2.9359×10^{-4}; collimator diameter, 15.246 mm.; orifice to collimator distance, 146.08 mm.

Exposure	Time (sec.)	Temp. (°K.)	Wt. loss (g.)	$10^4/T$	P
3 C	2.79×10^4	1051.0	0.7820	9.515	1.503×10^{-3}
3 E	5.40×10^4	1027.5	0.8885	9.732	8.725×10^{-4}
3 G	2.16×10^4	1067.1	1.0942	9.371	2.738×10^{-3}
3 J	7.83×10^4	1008.3	0.8851	9.918	5.938×10^{-4}
3 L	7.80×10^4	990.1	.4845	10.100	3.233×10^{-4}
3 N	13.68×10^4	970.1	.4640	10.308	1.747×10^{-4}
3 Q	12.78×10^4	949.5	.1841	10.532	7.342×10^{-1}
3 S	7.92×10^4	980.3	.4012	10.201	2.624×10^{-4}
3 U	3.06×10^4	1057.7	1.2960	9.454	2.278×10^{-3}
3 W	1.44×10^4	1085.5	1.2850	9.212	4.864×10^{-3}
3 Y	9.00×10^3	1105.0	1.1325	9.050	6.920×10^{-3}
3 AA	5.40×10^3	1123.6	1.0948	8.900	1.124×10^{-2}
3 AC	3.60×10^3	1144.3	1.0419	8.739	1.620×10^{-2}
3 AF	2.40×10^3	1162.6	1.0670	8.601	2.508×10^{-2}
3 AJ	1.80×10^3	1181.1	1.1328	8.467	3.578×10^{-2}
3 AM	1.80×10^3	1211.7	1.7102	8.523	5.471×10^{-2}
3 AQ	1.80×10^3	1218.9	2.4031	8.204	7.710×10^{-2}
3 AT	1.80×10^3	1210.9	2.0702	8.258	6.620×10^{-2}
3 AW	1.80×10^3	1189.7	1.4577	8.406	4.621×10^{-2}

Discussion

In comparison with the other rare earth metals, thulium appears to have a higher vapor pressure than might at first be expected. The five heavy rare earth elements immediately preceding thulium have quite similar vapor pressures, but thulium is much more volatile than these, and ytterbium, which follows thulium, is more volatile yet; lutetium appears to have a lower volatility than even the first five heavy rare earth elements. The weaker binding of ytterbium can be attributed to its divalent nature which results from a filled 4f shell and two electrons in the conduction band, which is essentially the configuration of the rather volatile alkaline earth metals; europium metal is also very volatile, for a similar reason, inasmuch as it has a half filled 4f shell with the two conduction electrons. An explanation of the stable divalent character of samarium with the attendant volatility of the metal is not so apparent, for atomic radii data indicate that metallic samarium should behave much like the normal trivalent metals. However, it may be proposed that the weaker binding that results may be due to the approaching of a half filled condition of the 4f shell. Thulium occupies a position toward the end of the rare earth series that might be comparable to that of samarium, and the enhanced volatility of thulium may be attributable to the approaching of a filled 4f shell

---

(9) W. R. Savage, unpublished Ph.D. Thesis, Iowa State College, Ames, Iowa, 1956.

with the attendant weaker binding of this condition. Such a similarity of thulium to samarium has been suggested by Selwood.[10] Holleck[11] has reported the existence of a divalent thulium ion when trapped in a strontium sulfate lattice. The divalent nature of thulium would appear to be a likely subject for further study.

AMES, IOWA

[10] P. W. Selwood, THIS JOURNAL, **56**, 2392 (1934).

[11] L. Holleck, *Angew. Chem.*, **50**, 819 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Compounds of Platinum in the Zero Oxidation State[1]

BY GEORGE W. WATT, ROBERT E. MCCARLEY AND JAMES W. DAWES

RECEIVED MAY 20, 1957

The reactions of $[Pt(en)_2]I_2$ with one and two molar equivalents of potassium amide in liquid ammonia at −33.5° are shown to yield $[Pt(en\text{-}H)(en)]I$ and $[Pt(en\text{-}H)_2]^0$, respectively. Certain reactions of these species in both liquid ammonia and water are described. The reduction of $[Pt(en)_2]I_2$ with one equivalent of potassium in ammonia is shown to lead to an unstable $[Pt(en)_2]I$ which decomposes at −33.5° to form $[Pt(en\text{-}H)(en)]I$ and hydrogen, and disproportionates at higher temperatures to $[Pt(en)_2]I_2$ and $[Pt(en)_2]^0$. The latter decomposes to form $[Pt(en\text{-}H)_2]^0$, hydrogen, platinum and ethylenediamine. The reduction of $[Pt(en)_2]I_2$ with two equivalents of potassium provides $[Pt(en)_2]^0$ which decomposes in the manner indicated above.

Earlier work in this Laboratory has shown that the reduction of tetrammineplatinum(II) bromide[2] and bromopentammineiridium(III) bromide[3] with solutions of potassium in liquid ammonia yields ammines of the corresponding metals in the zero oxidation state, *i.e.*, $[Pt(NH_3)_4]$ and $[Ir(NH_3)_5]$. Among compounds of the transitional metals in the zero oxidation state,[4] these species are unusual in the sense that such stability as they exhibit is not attributable to π-bonding. Accordingly, it is of interest to determine the generality of formation of this type of compound and more particularly to determine whether enhanced stability results from substitution of bi- and polydentate ligands for ammonia.

Preliminary studies on the reduction of bisethylenediamineplatinum(II) iodide showed that mixtures of reduction products were formed and that hydrogen was evolved during the course of the reactions. This suggested the formation and possible involvement of potassium amide in concurrent reactions and therefore indicated the desirability of studying the interaction of the iodide and potassium amide. It was shown subsequently, however, that the intermediate formation of potassium amide is not necessary in accounting for the observed products of the reduction reactions.

Experimental

Unless indicated to the contrary, all experimental materials and methods, including the synthesis of starting materials, procedures for carrying out reactions in ammonia, and the measurement of physical properties of reaction products were the same as those described in earlier publications.[2,3,5]

Bisethylenediamineplatinum(II) iodide was prepared from platinum(IV) iodide[6] by suspending 10.25 g. of PtI_4 in 100 ml. of water, adding 4 ml. of 90% aqueous ethylenediamine, and heating at 90° until solution was complete. The solution was evaporated to incipient crystallization, cooled, and the resulting crystals were filtered, washed with water and recrystallized from hot water after boiling with Norite. The yield was 5.82 g. or 69%. *Anal.* Calcd. for $[Pt(en)_2]I_2$: Pt, 34.3; I, 44.6. Found: Pt, 34.3; I, 44.6. X-Ray diffraction data for this compound are included in Table I.

TABLE I

X-RAY DIFFRACTION DATA

$[Pt(en)_2]I_2$		$[Pt(en)_2]ICl$		$[Pt(en)_2]Cl_2$		$[Pt(en\text{-}H)(en)]I$		$[Pt(en\text{-}H)_2]^0$	
d, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0
8.10	0.7	7.92	1.0	7.83	1.0	4.98	1.0	8.96	1.0
4.85	.7	4.83	0.4	6.42	0.7	3.78	0.8	6.37	0.5
4.45	.6[a]	4.41	.4	6.04	.5	3.45	.6	4.91	.7
4.22	1.0	4.20	.7	4.77	.5	3.14	.4	3.62	.6
3.94	0.7	3.91	.4[a]	4.50	.3[a]	2.70	.4[a]	3.33	.4[a]
3.70	.9	3.66	.5	3.87	.5	2.49	.5		

[a] Less intense lines not included here.

Although preliminary studies showed that bisethylenediamineplatinum(II) *bromide* is reduced by liquid ammonia solutions of potassium, this salt is substantially insoluble in ammonia at its boiling point.[7] In the study of reaction products corresponding to intermediate steps, the presence of solid unreacted bromide complicated the separation of ammonia-insoluble reduction products; hence the bromide was not used further as a starting material. In order to determine whether the iodide undergoes solvolysis in the presence of liquid ammonia, a sample of the pure iodide was dissolved in liquid ammonia at −33.5°, the solvent was evaporated, and the residual solid was found to give an X-ray diffraction pattern identical with that of the starting material.[7] *Anal.* Calcd. for $[Pt(en)_2]I_2$: Pt, 34.3. Found: Pt, 34.3.

Each of the cases described below is a typical example of reactions of demonstrated reproducibility.

Potentiometric Titration of $[Pt(en)_2]I_2$ with KNH_2.—A solution of 0.0374 g. of $[Pt(en)_2]I_2$ in 30 ml. of liquid ammonia was titrated at −39° with 0.0092 *M* KNH_2 solution over a period of 5 hr. After about 5 ml. of the titrant had been added, a white precipitate appeared and continued to form throughout the remainder of the titration. The data are shown in Fig. 1; the change in potential that occurred upon addition of 6.3 ml. of titrant corresponds to the reaction of one mole of the iodide with one mole of potassium amide (calcd., 7.2 ml.).

The Reaction between $[Pt(en)_2]I_2$ and KNH_2 (1:1).—In order to isolate and characterize the product of this reaction, 4.3218 g. of the iodide in 75 ml. of ammonia was treated dropwise at −38° with the potassium amide equivalent to

---

[1] This work was supported in part by the Atomic Energy Commission, Contract AT-(40-1)-1639.

[2] G. W. Watt, M. T. Walling, Jr., and P. I. Mayfield, THIS JOURNAL, **75**, 6175 (1953).

[3] G. W. Watt and P. I. Mayfield, *ibid.*, **75**, 6178 (1953).

[4] J. Kleinberg, *J. Chem. Ed.*, **33**, 73 (1956).

[5] G. W. Watt, *et al.*, THIS JOURNAL, **70**, 1197 (1948); **71**, 3833 (1949); **76**, 4742 (1954); **79**, 3315 (1957); *J. Electrochem. Soc.*, **98**, 1 (1951); **102**, 46, 545 (1955).

[6] L. Pigeon, *Ann. chim. phys.*, **2**, 496 (1894).

[7] G. W. Watt and R. E. McCarley, THIS JOURNAL, **79**, 3315 (1957).