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

The Interaction of Bis-(ethylenediamine)-palladium(II) Iodide with Potassium and Potassium Amide in Liquid Ammonia[1]

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The reaction of bis-(ethylenediamine)-palladium(II) iodide with potassium amide in liquid ammonia at −33.5° has been shown to yield [Pd(en)(en-H)]I and $[Pd(en-H)_2]$. The weakly basic properties of the former and the strongly basic properties of the latter have been demonstrated by their respective reactions with water, dilute acids and potassium tetraiodomercurate(II). The thermal decomposition of these substances also is described. The reduction of $[Pd(en)_2]I_2$ and [Pd(en)(en-H)]I with potassium in liquid ammonia at −33.5° has been shown to yield impure palladium metal.

It was reported previously[2,3] that at least three protons could be removed successively from the coordinated amino groups of bis-(ethylenediamine)-platinum(II) iodide by reaction with appropriate mole ratios of potassium amide in liquid ammonia. Also, the reduction of the iodide with potassium in ammonia was shown to yield a variety of products containing platinum in apparent oxidation states $< 2+$. Similar reactions of the palladium analog, bis-(ethylenediamine)-palladium(II) iodide and the properties of the products, have been investigated and are reported below.

Experimental

Unless otherwise indicated, all experimental materials and methods, including procedures for carrying out reactions in liquid ammonia and the measurement of physical properties of reaction products, were the same as those described elsewhere.[4]

Bis-ethylenediamine-palladium(II) iodide was prepared from palladium(II) iodide[5] by suspending 3.69 g. of PdI_2 in 100 ml. of water, adding 5 ml. of 90% ethylenediamine solution and heating on a steam-bath until solution was complete. The solution was concentrated to about 100 ml. and 200 ml. of absolute ethanol was added to effect immediate precipitation of the complex. After cooling for 1 hr., the product was separated by filtration and washed with absolute ethanol; the yield was 4.92 g. or 75%.

Anal. Calcd. for $[Pd(en)_2]I_2$; Pd, 22.2; I, 52.8. Found: Pd, 22.0; I, 52.8; X-ray diffraction data for this compound are included in Table I.

Potentiometric Titration of $[Pd(en)_2]I_2$ with KNH_2.—A solution of 0.3946 g. of $[Pd(en)_2]I_2$ in 100 ml. of ammonia was titrated with a 0.0828 *M* solution of KNH_2. A yellow precipitate formed after the addition of 5 ml. of titrant and continued to form until about 10 ml. was added. Although the data did not correspond exactly to the reasonably anticipated reaction ratios, significant changes in potential that approximated the reactions of one and two moles of amide per mole of iodide were observed (calcd.: 9.9 and 19.8 ml. Found: 11.3 and 22.5 ml.).

TABLE I

X-RAY DIFFRACTION DATA

$[Pd(en)_2]I_2$		[Pd(en)(en-H)]I		$[Pd(en-H)_2]$	
d, Å.	I/I_0	d, Å.	I/I_0	d, Å.	I/I_0
4.83	0.3	5.30	1.0	8.72	1.0
4.23	.3	4.79	0.8	4.90	0.9
3.93	.8	4.13	.8	3.60	.5
3.62	1.0	3.86	.2	3.34	.2
3.18	0.3[a]	2.70	.1[a]	2.56	.1[a]

[a] Less intense lines not included here.

The Reaction between $[Pd(en)_2]I_2$ and KNH_2 (1:1).—The first reaction indicated by the potentiometric titration data was carried out on a larger scale in order to isolate and characterize the yellow solid product. The iodide, 2.1161 g., was dissolved in 40 ml. of ammonia, and the potassium amide formed from 0.1789 g. of potassium dissolved in 15 ml. of ammonia was added dropwise and with stirring over a period of 20 min. The yellow product which formed immediately was allowed to settle, filtered, washed 5 times with 20 ml. portions of ammonia and dried *in vacuo* at room temperature for 2 hr.

Anal. Calcd. for [Pd(en)(en-H)]I: Pd, 30.3; I, 36.0; N, 15.9. Found: Pd, 29.7; I, 36.2; N, 16.0.

The combined filtrate and washings was found to contain 0.5581 g. of iodine, or 49.0% of that used as $[Pd(en)_2]I_2$. X-ray diffraction data are given in Table I.

The Reaction between $[Pd(en)_2]I_2$ and KNH_2 (1:2).—Although a change in potential was observed in the above titration after the addition of approximately two equivalents of potassium amide solution, subsequent experiments showed that it was necessary to employ excess potassium amide in order to obtain an iodine-free ammonia-insoluble product. Accordingly, 2.4219 g. of the iodide was dissolved in 40 ml. of ammonia and a solution of KNH_2 corresponding to 0.5956 g. of K in 20 ml. of ammonia was added over a period of 30 min. The mixture was stirred for an additional 2 hr. at −33.5°. The color of the initially yellow precipitate changed slowly to cream-white. This product was filtered, washed and dried as described above.

Anal. Calcd. for $[Pd(en-H)_2]$: Pd, 47.6; N, 25.0. Found: Pd, 46.2; N, 25.1.

X-Ray diffraction data are given in Table I. This product was iodine-free, and 99.1% of the iodine used as $[Pd(en)_2]I_2$ was found in the combined filtrate and washings.

Reactions of [Pd(en)(en-H)]I and $[Pd(en-H)_2]$.—The following reactions were investigated in order further to characterize the products of the reactions between $[Pd(en)_2]I_2$ and KNH_2.

Reaction with Water.—Upon contact with water, [Pd(en)(en-H)]I first becomes sticky, then slowly dissolves to form a yellow solution. The product $[Pd(en-H)_2]$ however dissolves rapidly and exothermally to form a colorless solution. Both of these solutions are basic. The absorption spectrum of a 3.9×10^{-6} *M* aqueous solution of [Pd(en)(en-H)]I is given in Fig. 1 as a function of time. The broad absorption maximum at 325 mμ decreases in intensity as the solution ages, thus indicating a slow reaction with the solvent. The spectrum of $[Pd(en-H)_2]$ (2.83×10^{-3} *M*) in water shows little absorption in this region and is stable with respect to aging. The spectra of 4.85×10^{-5} *M* solutions of $[Pd(en)_2]I_2$ are identical in water and in 1.0 *N* sodium hydroxide and show no significant absorption in this region.

Reaction with Aqueous Acids.—A sample of [Pd(en)(en-H)]I, 0.2411 g., was dissolved in 200 ml. of water and titrated with 0.1023 *N* HI and the *p*H was observed after each addition. The curve so obtained (Fig. 2) is characteristic of the titration of a weak base with a strong acid; one equivalent of acid is consumed (calcd., 6.71 ml.; found, 6.25 ml.). The portion of the curve below *p*H 7 is obscured, owing to the precipitation of PdI_2. This precipitate was removed by filtration, and the brown solid obtained by evaporation of the filtrate was shown, by X-ray diffraction patterns, to consist of a mixture of PdI_2 and $[Pd(en)_2]I_2$.

Similarly, $[Pd(en-H)_2]$, 0.1064 g., was titrated with 0.1093 *N* H_2SO_4 rather than HI in order to avoid precipita-

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

[2] G. W. Watt, R. E. McCarley and J. W. Dawes, THIS JOURNAL, **79**, 5163 (1957).

[3] G. W. Watt and J. W. Dawes, *ibid.*, **81**, 8 (1959).

[4] G. W. Watt, *et al.*, *J. Inorg. & Nuclear Chem.*, **9**, 311 (1959); *J. Electrochem. Soc.*, **98**, 1 (1951); **102**, 454 (1955).

[5] A. Gutbier and H. Krell, *Ber.*, **38**, 2385 (1905).

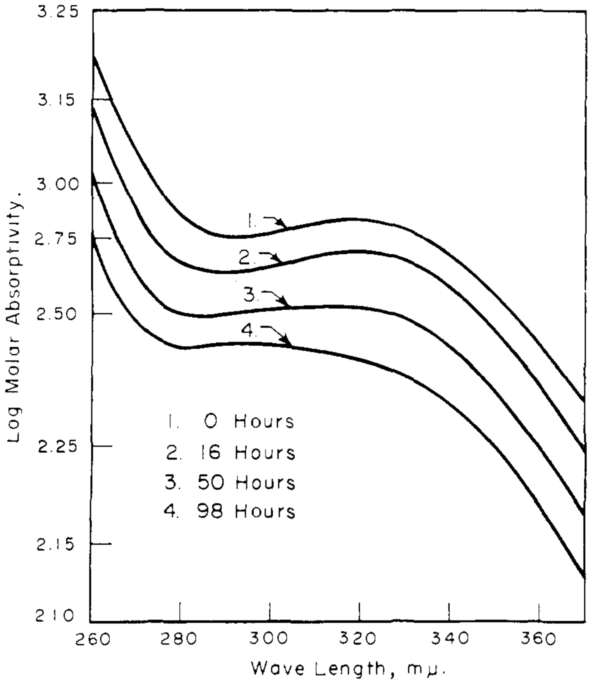

Fig. 1.—Absorption spectra of [Pd(en)(en-H)]I.

tion of PdI_2. The resulting data (Fig. 2) are characteristic of the titration of a strong base with a strong acid; two equivalents of acid was consumed (calcd., 8.66 ml.; found, 8.60 ml.). There was no indication of the intermediation of a product corresponding to the consumption of one equivalent of acid. Another sample was dissolved in water and the *p*H was adjusted to 7 by addition of 0.1 *N* HI. This solution was evaporated to dryness and the resulting tan solid gave an X-ray diffraction pattern that was characteristic of that for $[Pd(en)_2]I_2$ and which included no extraneous lines.

Reaction with Potassium Tetraiodomercurate(II).—The $[Pd(en)_2]^{2+}$ ion is precipitated quantitatively from aqueous solution as $[Pd(en)_2](HgI_4)$ upon addition of $K_2(HgI_4)$.[6]

The precipitation of $[Pd(en)_2](HgI_4)$ from a solution of [Pd(en)(en-H)]I is slow and incomplete. However, the reaction may be followed potentiometrically utilizing a calomel reference electrode and a platinum indicator electrode and allowing 5 to 10 min. after each addition to obtain a constant voltage. A solution of 0.0971 g. of [Pd(en)(en-H)]I was titrated with a 0.0788 *N* K_2HgI_4 solution that was standardized against $[Pd(en)_2]I_2$. The equivalence point was found to be 34.5 ml. as compared with the calculated value of 34.9 ml.

The $[Pd(en)_2]^{2+}$ ion was precipitated rapidly and quantitatively from an aqueous solution of $[Pd(en\text{-}H)_2]$.

Decomposition of [Pd(en)(en-H)]I and [Pd(en-H)₂].—Freshly prepared [Pd(en)(en-H)]I decomposes within 8 to 10 hr. in a dry helium atmosphere; the course of the decomposition was studied as follows. The compound was prepared, transferred to a tared tube in a dry helium atmosphere, reweighed and allowed to decompose. The volatile products were removed with a Toepler pump through a trap maintained at −78°. The non-condensible gas consisted only of helium in a volume corresponding to the known volume of the tube; ethylenediamine was found in the trap and was identified as the picrate. The tube was reweighed and the weight loss was attributed to ethylenediamine. The black solid residue was examined by X-ray diffraction and found to contain Pd and $[Pd(en)_2]I_2$. After the solid had remained under reduced pressure at room temperature for 8 hr., the temperature was raised slowly to 100°, whereupon a white sublimate deposited just above the black residue. This sublimate was found to contain ethylenediammonium iodide (Table II) and one or more

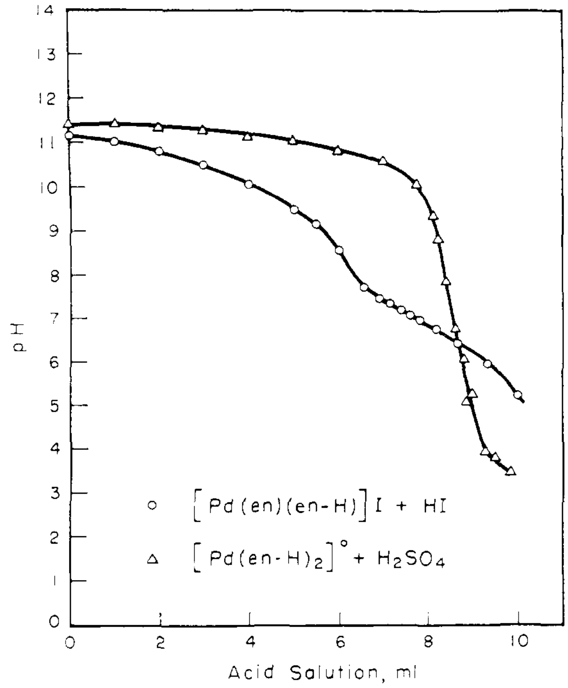

Fig. 2.—Potentiometric titration of palladium ethylenediamine complexes with acids.

unidentified components. This mixture was not investigated further since it was available in only milligram quantities.

A sample of the black residue was extracted with ethanol in a Soxhlet extractor and the soluble fraction was identified as $[Pd(en)_2]I_2$.

Anal. Calcd. for $[Pd(en)_2]I_2$: Pd, 22.2; I, 52.8. Found: Pd, 22.2; I, 52.3.

The ethanol filtrate was evaporated to dryness and provided a very small quantity of brown oily residue that was not investigated further. After thus establishing the presence of $[Pd(en)_2]I_2$ in the black residue, a weighed sample was extracted with water and the resulting water-insoluble palladium and water-soluble $[Pd(en)_2]I_2$ were determined. These data led to the mole ratios: en/[Pd(en)(en-H)]I = 1.03; Pd/[Pd(en)(en-H)]I = 0.76; $[Pd(en)_2I_2]$/[Pd(en)(en-H)]I = 0.28.

Table II

X-Ray Diffraction Data for Ethylenediammonium Iodide

$C_2H_8N_2 \cdot 2HI$		Sublimate[a]	
d, Å.	I/I_0	*d*, Å.	I/I_0
7.81	0.4		
4.86	.6	4.90	0.7
3.90	.8	3.88	0.9
3.62	1.0	3.61	1.0
2.56	0.6	2.55	0.6
2.25	.2	2.29	.3
1.64	.4	1.65	.3

[a] Unassigned lines (relative intensities in parentheses): 9.00 (0.8), 7.43 (1.0), 5.91 (0.8), 5.38 (0.9), 4.55 (0.5), 3.64 (0.3), 2.64 (0.2).

Other samples of [Pd(en)(en-H)]I were exposed to dry air for periods up to several months without visual evidence of decomposition; the fact that the sample was stable was confirmed by both X-ray diffraction patterns and analysis. The thermal decomposition of air-exposed samples led to results substantially identical with those described above for helium-exposed samples, except that the decomposition temperature was found to be 100–110°.

The compound $[Pd(en\text{-}H)_2]$ decomposed slowly in a helium atmosphere at room temperature and completely in

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(6) G. W. Watt, D. M. Sowards and R. E. McCarley, *Anal. Chem.*, **28**, 556 (1956).

8 hr. at 50°. Quantitative data for this decomposition were obtained by essentially the same procedure as that described before; again, ethylenediamine was the only volatile product. The black residue from the decomposition was found to contain palladium (62.9%) and X-ray diffraction patterns showed the presence of one or more unidentified components. Mole ratios were calculated from the data from these experiments: en/$[Pd(en\text{-}H)_2]$ = 1.35; en/Pd = 1.34 (assuming complete decomposition to Pd). Efforts to separate the components of this mixture by extraction with water, ethanol and benzene were unsuccessful.

Reactions of $[Pd(en)_2]I_2$ and [Pd(en)(en-H)]I with Potassium in Ammonia at − 33.5°.—A solution of 1.9859 g. of $[Pd(en)_2]I_2$ in 40 ml. of ammonia was treated dropwise with 20 ml. of ammonia solution containing 0.3391 g. of potassium. When the first drop of potassium solution was added, the blue color was discharged rapidly and a black, finely-divided precipitate formed. After the final addition, the precipitate was allowed to settle, the product was filtered, washed 6 times with 25 ml. portions of ammonia and dried *in vacuo* for 2 hr. at room temperature.

Anal. Found: Pd, 90.7.

The combined filtrate and washings was found to contain 98.3% of the iodine introduced as $[Pd(en)_2]I_2$.

The compound [Pd(en)(en-H)]I was prepared as described above from 2.8085 g. of $[Pd(en)_2]I_2$. The yellow solid product was resuspended in 40 ml. of ammonia and treated with 0.3572 g. of potassium in 20 ml. of ammonia solution. All procedures, observations and results were essentially the same as in the reduction of $[Pd(en)_2]I_2$.

Anal. Found: Pd, 87.5.

The filtrate from the preparation of $[Pd(en)(en\text{-}H)]I_2$ was found to contain 48.6% of the iodine used as $[Pd(en)_2]I_2$, and 44.9% was found in the filtrate following the reduction with potassium.

Discussion

The data given above show that some of the reactions of, and products from, bis-ethylenediamine-palladium(II) iodide are substantially identical with those reported[2,3] for the corresponding platinum compound, *e.g.*, the reactions with potassium amide in ammonia

$$[Pd(en)_2]I_2 + KNH_2 \longrightarrow [Pd(en)(en\text{-}H)]I + KI + NH_3 \quad (1)$$

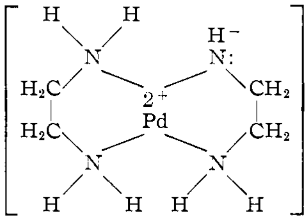
$$[Pd(en)(en\text{-}H)]I + KNH_2 \longrightarrow [Pd(en\text{-}H)_2] + KI + NH_3 \quad (2)$$

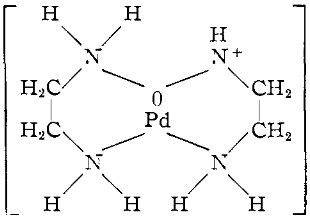
The product of reaction 2 is similar to the platinum analog in that it is a strong base which reacts instantaneously with water to form $[Pd(en)_2{}^{2+}]$, as evidenced by both the aqueous titration data and the reaction with K_2HgI_4. The differences in the properties of [Pd(en)(en-H)]I and [Pt(en)(en-H)]I, however, are quite pronounced. The platinum compound is white and dissolves readily in water to form a strongly basic solution. The corresponding palladium compound is yellow and dissolves very slowly in water to provide a weakly basic solution. The rate of the reaction of [Pd(en)(en-H)]I with water, in which a proton is transferred to the palladium complex, is obviously a function of the basicity of the latter

$$[Pd(en)(en\text{-}H)]I + H_2O \longrightarrow [Pd(en)_2]^{2+} + I^- + (OH)^- \quad (3)$$

and the rate of reaction 3 also controls the rate of precipitation of $[Pd(en)_2](HgI_4)$ which has also been demonstrated to be quite slow. Neutralization of [Pd(en)(en-H)]I with aqueous acid consumes one equivalent of acid and $[Pd(en)_2]I_2$ is recovered from the resulting solution. Since the reaction of acid with $[Pd(en)_2]I(OH)$ would be expected to be rapid and yield a titration curve characteristic of a strong base, the acid must react predominantly with unchanged $[Pd(en)(en\text{-}H)]^+$ in solution. This conclusion is quite reasonable in view of the fact that the existence of [Pd(en)(en-H)]I in aqueous solution is demonstrated by the data given above.

Since, of the known species of this general type, [Pd(en)(en-H)]I is anomalous, it seems evident that its properties are not compatible with exclusively σ-bonding. These properties, however, can be explained in terms of the fate of the electron pair resulting from the removal of a proton from the ligand nitrogen atom. It is suggested that this electron pair may be involved in the formation of a π bond with the $5p_z$ orbital on palladium that is perpendicular to the plane of the molecule. From a crystal field standpoint, the $d_{x^2-y^2}$ is also available but it is not favorably oriented for orbital overlap. Accordingly, we may consider two structures in relation to the observed properties





If a π bond is formed, this would result in a reduction of charge density about the ligand nitrogen atom, and this should lead to a marked decrease in base strength; the weakly basic character of $[Pd(en)(en\text{-}H)]^+$ has been clearly demonstrated. Further, the effect of π bond formation should result in a shifting of the absorption band at 290 mμ in the parent compound to longer wave lengths in the π-bonded complex[7]; this also has been demonstrated. Finally, the rather remarkable stability of this substance is also compatible with these ideas. This complex is quite unstable in an atmosphere of dry helium but is stable for months in dry air. Thus, in an oxygen-containing atmosphere, the higher oxidation state of palladium is stabilized, while in the helium atmosphere the charge density is greater about the central metal atom, thus stabilizing palladium in the zero oxidation state.

On this basis, it follows that π-bonding must not be of importance in closely related complexes of this same general type since they do not exhibit the properties described for [Pd(en)(en-H)]I. If the electron density about the ligand nitrogen atom remains largely unaltered upon removal of a proton, this would account for the strongly basic properties of species such as $[Pd(en\text{-}H)_2]$, $[Pt(en\text{-}H)_2]$ and $[Pt(en)(en\text{-}H)]^+$. The lack of tendency toward

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[7] A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1956, pp. 219–224.

π-bonding in the platinum complexes may result from the much higher energy of the P_3 orbital on platinum. Apparently, the p_z orbital on palladium and the p orbital of the ligand atom are closely similar in energy.

Study of the thermal decomposition of [Pd(en)(en-H)]I has shown that the major products are Pd and $[Pd(en)_2]I_2$ in a 3:1 mole ratio, ethylenediamine, ethylenediammonium iodide and unidentified minor products that presumably arise from secondary reactions of the (en-H) ligand. The decomposition of $[Pd(en\text{-}H)_2]$ is similarly complicated; palladium and ethylenediamine are produced in a 5:3 mole ratio, together with apparently a mixture of products of reactions of (en-H). Similar data are not available for the corresponding platinum compounds (other than that they are stable at room temperature); hence a direct comparison cannot be made at this time.

Finally, it should be noted that the reactions of $[Pd(en)_2]I_2$ and [Pd(en)(en-H)]I with potassium in ammonia involve direct reduction to elemental palladium without the intermediation of isolatable lower oxidation species of the type previously described[2,3] as products of the reduction of the analogous platinum compounds.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA]

Solutions of Metals in Amine Solvents. IV. The Effect of Temperature on the Conductance of Lithium in Methylamine[1,2]

BY ARMAND J. PANSON[3] AND E. CHARLES EVERS

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The conductance of moderately dilute solutions of lithium in methylamine has been studied in the temperature range from −78 to 20°. Maxima are observed in the conductance–temperature curves for the more dilute solutions; the maximum proceeds to higher temperatures with increasing metal concentration. Phenomenologically these results are similar to those observed for solutions of normal electrolytes. It is concluded that these data provide direct evidence for the existence of mass action equilibria in metal–amine solutions.

In the case of dilute solutions of metals in ammonia,[2b,4] as well as in methylamine,[2c] it has been suggested that mass action equilibria, involving several species, are responsible for the rapid decrease in conductance and in the magnetic susceptibility with increasing concentration. Further support of this thesis is furnished by nuclear magnetic resonance measurements.[5]

Although conductance and magnetic data appear interpretable in terms of mass action equilibria, it would be of value to have other, more direct evidence for the existence of these equilibria. In seeking such data we have studied the effect of temperature on the conductance of moderately dilute solutions of lithium in methylamine. It has been found that dilute solutions of lithium behave phenomenologically very much like solutions of normal electrolytes. This would seem to bear out the mass action hypothesis; ion association is well established in the case of electrolytes dissolved in a solvent such as methylamine.[2c]

Experimental

Procedures employed in purifying and handling solvent and in preparing solutions of lithium were described previously.[2a,c] Conductance cells of approximately 300 cc. capacity were used. They were provided with bright platinum electrodes 1.5 mm. in diameter and approximately 2 mm. apart. Methods of fabricating metal-through-glass seals and of calibrating cells also have been described.[2a]

The conductance cells were provided with a thermocouple well, sealed through a cap prepared from a 24–40 standard tapered ground glass joint. The well was drawn to a thin walled tip at the bottom, which was filled with a drop of alcohol to improve heat transfer. The cap was cemented on the cell with Apiezon wax in order to withstand super-atmospheric pressure when the temperature exceeded the boiling point of the solvent. Metal was introduced through a tube carried by the cap; the tube was then sealed. All glass blowing was done using a current of dry helium or argon gas.

Resistance measurements were made with a Leeds and Northrup Co., Jones-type, a.c. conductance bridge, in conjunction with an audio oscillator and amplifier; an oscilloscope was employed as the null point detector. Resistance measurements were recorded as a function of time on solutions which were either warming or cooling. Temperatures were measured with a Leeds and Northrup Co. adjustable range (0 to 40 m.v.) and adjustable zero recording potentiometer. Immediately after measuring the resistance of a solution, the temperature and time were recorded by marking the thermocouple potential-time curve. This was done by short circuiting the thermocouple signal momentarily, which caused a "pip" to be recorded on the temperature-time chart.

The thermocouple and recording potentiometer were calibrated as follows. The 0° reference junction and measuring junction were both immersed in an ice-bath. The zero potential reading was then set at a convenient point on the potentiometer scale. The measuring junction was next removed and placed in a cooling bath of powdered Dry Ice and isopropyl alcohol. Meanwhile the latter had been covered and aged in a Dewar flask for about 2 hr. to assure equilibrium conditions. The potentiometer reading was then set to full scale. The temperatures of several Dry Ice-baths prepared in the same way were measured with a N.B.S. calibrated, platinum resistance, thermometer. The temperatures of these baths were found to be $-78.33 \pm 0.01°$; the corresponding potential for the copper constantan thermocouple is −2.71 mv. This represented full scale deflection on the potentiometer. Temperatures between −78.3 and 0° were obtained by linear interpolation. The linearity of the recorder scale and thermocouple potential were checked by measuring the temperature of various

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(1) Taken in part from a thesis by A. J. Panson, presented in partial fulfillment of the requirements for the Ph.D. degree, June, 1957.

(2) Previous papers in this series are: (a) E. C. Evers, A. E. Young, II, and A. J. Panson, THIS JOURNAL, **79**, 5118 (1957); (b) E. C. Evers and P. W. Frank, Jr., *J. Chem. Phys.*, **30**, 61 (1959); (c) D. S. Berns, E. C. Evers and P. W. Frank, Jr., THIS JOURNAL, **82**, 310 (1960).

(3) E. I. du Pont de Nemours Fellow in Chemistry, 1955–1956.

(4) (a) E. Becker, R. H. Lindquist and B. J. Alder, *J. Chem. Phys.*, **25**, 971 (1956); (b) M. F. Deigen and Yu A. Tsvirko, *Ukrain Fiz. Zhur.*, **1**, 245 (1956). References to previous work may be found here.

(5) (a) H. McConnell and C. Holm, *J. Chem. Phys.*, **26**, 1517 (1957). (b) W. Blumberg and T. Das, *ibid.*, **30**, 251 (1959).