arsenite. Transfer the contents of the cylinder to a beaker and mix thoroughly. Filter, and wash the residue free from alkali. Test the residue for arsenite and the filtrate for arsenate.

(2) **Detection of Arsenite.**—Dissolve the residue of silver arsenite (1) by pouring a 5-cc. portion of 6 N hydrochloric acid repeatedly through the filter and add hydrogen sulfide to the clear solution obtained. If a dark precipitate is obtained showing the presence of heavy metal sulfides insoluble in hydrochloric acid, it may be tested for arsenic according to the usual methods.

(3) **Detection of Arsenate.**—The filtrate from (1) contains the arsenate which may be separated by acidifying with acetic acid and adding uranyl acetate in slight excess. The arsenate is precipitated as uranyl hydrogen arsenate, UO_2HAsO_4. If the precipitate should be colloidal or finely divided it may be collected and readily filtered by shaking with a pinch of asbestos fiber. The uranyl arsenate is readily soluble in hydrochloric acid from which it may be precipitated as sulfide by means of hydrogen sulfide.

The method has been successfully used by the author's classes in qualitative analysis as a means of detecting arsenate and arsenite either alone or in the presence of each other.

Summary.

A procedure is described for the separation and detection of arsenate and arsenite.

The separation is based on the relative solubility of their silver salts in sodium hydroxide.

Data in support of the procedure are furnished. The method is capable of detecting 1 mg. of either ion in the presence of 450 mg. of the other.

RENO, NEVADA.

NOTES REGARDING THE CONSTRUCTION OF PLATINUM RESISTANCE THERMOMETERS AND IMMERSION HEATING COILS OF LOW LAG.[1]

BY T. S. SLIGH, JR.

This paper describes briefly some recent modifications in the construction of platinum resistance thermometers which have been found desirable on account of a gain in accuracy, simplification of construction, or of greater mechanical strength.[2]

Strain-free Thermometers.

All thermometers are of the potential terminal type as the use of this type with a potentiometer or a wheatstone bridge with reversing commutator offers complete elimination of the effects of lead resistance.

Changes in the construction of the strain-free type of thermometer from that described in Bureau of Standards *Bulletin* **6**, p. 150 (1909),

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[1] Published by permission of the Director, Bureau of Standards.

[2] See *Scientific Paper* No. S-407 of the Bureau of Standards for a more detailed treatment of this subject.

consist in the sealing of the thermometer tube to prevent condensation of atmospheric moisture in the thermometer at low temperatures, the use of a neater and simpler thermometer head, (K, Fig. 1), composed of a brass shell with bakelite base and cap, and the use of thermometer leads (J, Fig. 1) consisting of a 4-strand cable insulated with a double silk wrapping and a silk braid. Each strand of this cable consists of 3 No. 28 insulated copper wires twisted together and double silk covered. The lead terminals (h, Fig. 1) are cut and formed from thin sheet copper. This form of thermometer lead possesses sufficient flexibility and is far superior in point of constancy of resistance to the fine strand lamp-cord leads previously used.

Calorimetric Thermometers.

Calorimetric thermometers of the type described in Bureau of Standards *Bulletin* **9,** p. 483 (1913), have been found to show values of the δ constant in the Callendar difference formula of about 1.47 as against a δ value 1.495, for a strain-free thermometer wound of the same wire. The effect of this difference upon the scale defined by the thermometer in the range 0–100° was not sufficiently large to warrant an
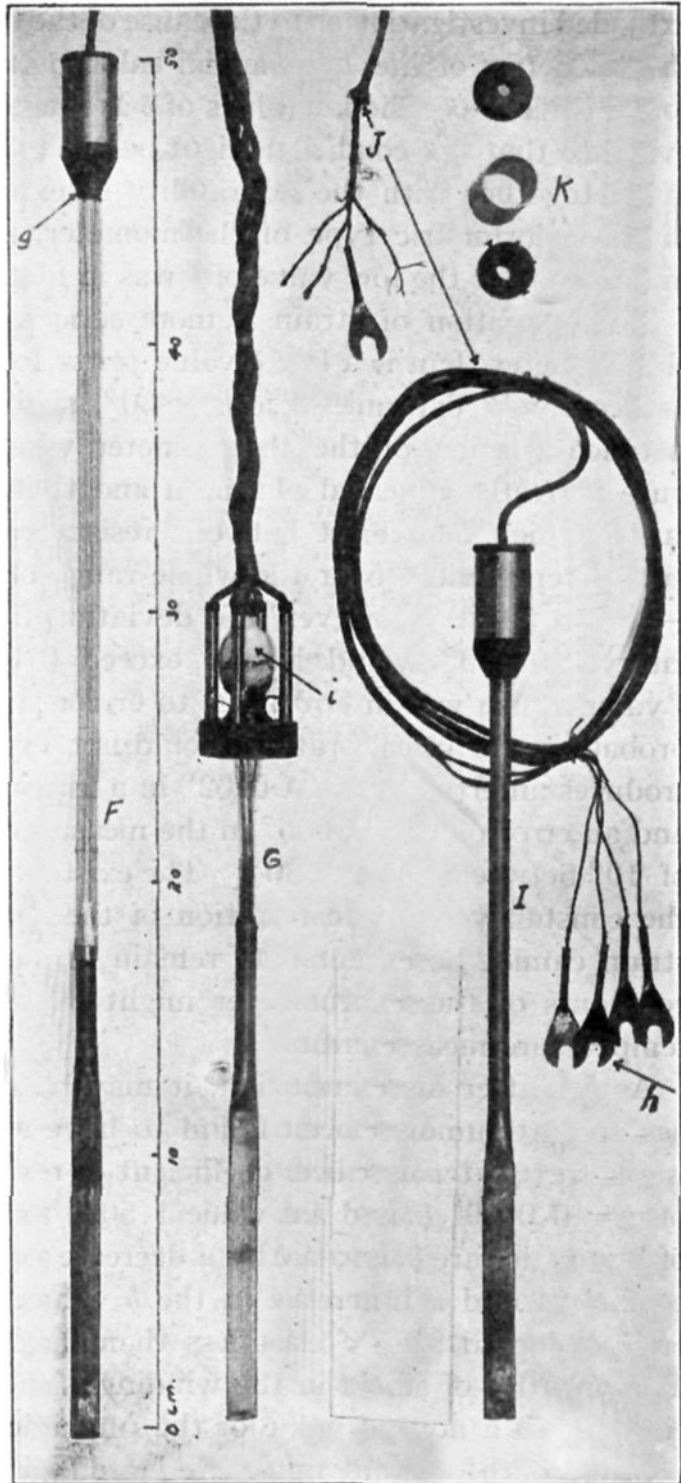

Fig. 1.—Types of platinum resistance thermometers. F, Calorimetric thermometer B. S. No. Pt.7 for use at temperatures up to 500°. G, commercial form of calorimetric resistance thermometer; I, calorimetric resistance thermometer B. S. No. Pt.11 with German silver case and without drying head. j, flexible lead for resistance thermometers; k, new style thermometer head of the size shown at "F" and "I."

extended investigation as to the cause of the low value of δ. However, some thermometers of the commercial calorimetric type G, Fig. 1, were later found to show occasional values of δ as low as $\delta = 1.4$, and there was some evidence that this condition might be due to strains in the winding. These facts, together with the desirability of extending the temperature range of the calorimetric type of thermometer, led to an investigation which indicated that the low value of δ was in fact due to a strained winding.

This condition of strain is more serious in the case of a calorimetric thermometer than is a low δ value *per se* for a low value, *e. g.*, $\delta = 1.45$ as accurately determined at say $30°$, signifies that the temperature re- sistance relation of the thermometer wire differs *slightly* from that of pure perfectly annealed platinum and that, as mentioned above, the re- lation which does exist between resistance and temperature cannot be *exactly* represented over the whole range of the standard platinum scale, —$40°$ to $500°$. However, the deviation from the standard scale in the interval $0–100°$ would hardly exceed $0.002°$. Further, the use of a δ value which was in *error*, due to errrors in calibration, by 0.1 (and the probable error in calibration should not exceed 0.005 in the δ value) in- troduces an error of about $0.02°$ in a measurement of temperature at $50°$ and an error of only $0.005°$ in the measurement of a temperature interval of $10°$ between $20°$ and $30°$. The existence of strain, however, threatens the constancy of the calibration of the thermometer because a state of strain cannot be expected to remain stable. An unnoted change in the constants of the thermometer might obviously result in large errors in temperature measurement.

As a matter of information, it may be stated that pure perfectly an- nealed platinum has been found to have a fundamental coefficient, that is an average temperature coefficient of resistance in the interval $0–100°$ of $c = 0.00391+$ and a δ value $1.50—$ and that in general the presence of impurities are indicated by a decrease in the value of the fundamental coefficient and an increase in the δ value. The permissible limits gen- erally adopted are "c" not less than 0.00388 nor δ greater than 1.52. The presence of strain in the winding is indicated by a low δ value asso- ciated with a normal value of the fundamental coefficient.

Strain in the winding may be reduced to a negligible factor by thoroughly annealing the wire before winding the coil, by winding under *very light* tension on a mica core plate not less than 0.5 mm. thick in order to avoid the strain due to bending the wire around a sharp corner, by flash-anneal- ing the winding both before and after placing it in the case, and by avoid- ing pressures on the sheath large enough to strain or deform the winding.

The flash-annealing is accomplished by repeatedly connecting the wind- ing to a voltage sufficiently great to bring the winding to a temperature of approximately $1000°$ before the mica has time to reach its dehydra-

tion temperature (700°). This annealing is specially valuable after the sheath has been flattened down on the coil.

It has been found possible to raise the δ value of commercial calorimetric thermometers from values as low as 1.44 to values as high as 1.50 by flash annealing without opening the thermometer case. This fact indicates that the use of a thick mica core may not be absolutely essential and that thermometers which have become strained through mishandling or accident may be easily annealed. The annealing, of course, necessitates re-calibration.

The all-metal thermometer case (I, Fig. 1) which is made of German-silver tubing 0.75 cm. in diameter by 0.02 cm. thick with the lower end flattened into a sheath for the winding is much more robust and is fully as effective in eliminating the effects of thermal conduction down the leads and the stem as was the original case with a metal sheath and a glass stem. The 4 cm. of the internal leads immediately above the winding are flattened and placed between thin strips of mica upon which the sheath is pressed tightly.

German silver was selected for the sheath (I, Fig. 1) on account of its low thermal conductivity, its freedom from excessive oxidation, and its availability in the desired form. It is evident that any metal of low thermal conductivity, if not subject to corrosion, could be used. As a matter of fact, there are several such metals which are superior to German silver in some respects, but they are not at present available in the form of thin-walled tubing. For use in chemical reagents the sheath could well be made of platinum or some of its alloys, the latter having in general the advantage of greater stiffness and lower thermal conductivity.

The head and internal leads are as described above. The drying-head previously used (i, Fig. 1) has been found to be unnecessary where the thermometer case is tight and the initial drying has been complete.

Sheath Type Heating Coils.

A type of heating coil (B, Fig. 2) constructed by winding resistance ribbon on a flat strip of mica, insulating by means of thin mica sideplates,

Fig. 2.—Sheath heating coil sectioned. Note that copper leads are flattened and wound a few turns on the core before joining the resistance winding. Leads insulated by mica. Cap of bakelite cemented to the lead duct.

and enclosing in a flattened copper tube or sheath has been found to be very convenient for general laboratory use.

The leads are brought out through a continuation of the sheath or through a tube soldered to the sheath and may be insulated with either silk or mica strips.   If the coil is to be used in low temperature baths (*i. e.,* below the dew-point) the lead duct must be sealed to avoid condensation of moisture in the sheath.   This sealing is unnecessary for general laboratory use.   The sheath must, of course, be tight against the bath liquid; failure to observe this point is the most common cause for failure of immersion heating coils.   Tightness is secured more easily with sheaths formed of seamless tubing, which is commercially available in diameters up to 1″ and wall thickness of 0.01″ and 0.02″, than with sheaths formed from sheet metal and soldered.   Good thermal contact which is due to the contact of the sheath with the heating element through the thin mica sideplates is best secured by the use of a relatively narrow sheath.   A width not exceeding 150 times the wall thickness insures the permanence of the good contact obtained by squeezing the well annealed sheath down on the element in a vise.   The heaters may be made of flat plates or with care may be bent into a cylindrical or helical form without injury to the winding.

This type of heating coil is probably the best form of low lag heater available and because of its small heat capacity and large transfer coefficient is specially suited for use in thermostated baths and for work involving the accurate measurement of heat supplied as electrical energy.

The coil will transfer to a bath of stirred water about 0.07 watt/cm². of sheath area per degree of difference of temperature between the *winding* and the bath liquid.   The transfer coefficient in an oil bath will depend largely upon the viscosity of the oil.   0.03 watt/cm²./° C. is probably a safe value.   The areas mentioned are the areas of sheath in contact with the bath liquid.   The spacing between successive turns of the resistance ribbon should not exceed the width of the ribbon nor should the dimensions of the sheath greatly exceed those required to accommodate the heating element.   For example, a sheath type heater 3 cm. wide by 17 cm. long by 0.15 cm. thick will transfer energy to a water-bath at 25° at the rate of 1000 watts with a winding temperature of about 140°. The average temperature of the heater as a whole is, of course, much less than this.   The water equivalent of such a coil should not exceed 10 g. and the lag of the *winding* with respect to the bath should be less than 3 seconds.   These coils have been loaded to 30 watts/cm². without injury though the loading usually assumed is about 10 watts/cm².

This sheath type coil is found to be easier to construct, especially in the larger sizes, than the types in which an insulated wire is drawn into a

small tube. In addition the electrical insulation is more permanent and the lag smaller.

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THE DISSOCIATION PRESSURES OF IRON NITRIDES.

BY ARTHUR A. NOYES AND LEIGHTON B. SMITH.

1. Introduction.

In the synthesis of ammonia from its elements on an industrial scale catalysts consisting of iron in association with other metals, especially molybdenum, have been found to be especially satisfactory. In view of the extensive empirical investigations that have been made on such catalysts, there would seem to be little hope of largely increasing their effectiveness except through theoretical knowledge of the mechanism of their action; and one of the main factors in this mechanism is probably the extent to which the nitrogen and hydrogen gases are absorbed by or combined with the metals of the catalyst. The combination of nitrogen with the iron to form a nitride, and the tendency of the latter to form solid solutions with the iron itself, seem especially worthy of further investigation; and as a contribution in that direction this research was undertaken with the view of determining the dissociation pressures of iron nitrides under different conditions.

2. Principle of the Method.

Several investigators have attempted to prepare an iron nitride directly from its elements and to estimate its dissociation pressure. Baur and Voorman[1] worked with pressures of nitrogen up to 14 atmospheres, while Maxted[2] went to 200 atmospheres without any indication that the dissociation pressure was being approached. Groebe[3] states, to be sure, that nitrogen is taken up to an extent of 0.25% by finely divided iron at 450–$850°$. It is, however, well known[4] that an iron nitride is readily prepared by the action of ammonia gas on iron, rapidly at $460°$, in accordance with the equation, $4Fe + 2NH_3 = 2Fe_2N + 3H_2$.

The study of this ammonia reaction seemed to offer the most promising method of throwing more light on the iron nitrides and to furnish an indirect means of determining their dissociation pressures. This study was therefore undertaken. The principle of the method will be first described.

[1] Baur and Voorman, Z. physik. Chem., 52, 467 (1905).

[2] Maxted, J. Soc. Chem. Ind., 37, 105 (1918).

[3] Groebe, Z. angew. Chem., 27, 334 (1914).

[4] See Fowler, J. Chem. Soc. (London), 79, 285 (1901); and White and Kirschbaum, THIS JOURNAL, 28, 1343 (1906).