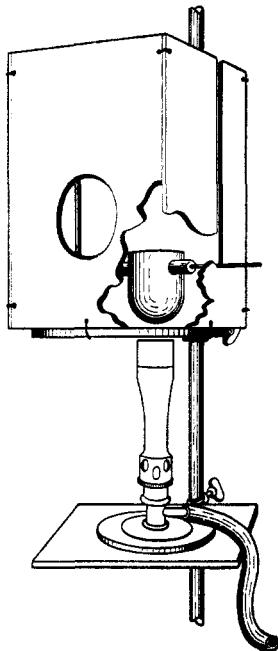


## NOTES.

**A New Type of Sodium Lamp for Polarimetry.**—To those persons who make use of a polariscope in their work the need of a constant and intense source of sodium light is one that is greatly felt. In this respect the authors believe that they have made a decided improvement by devising a simple arrangement which has served their purpose most admirably. Instead of any modification of the schemes used heretofore<sup>1</sup> they employ an alundum thimble or crucible as a reservoir for the salt which should preferably be sodium chloride. The thimble is exposed to the flame and as a result the sodium chloride melts, flows through the pores of the thimble and is vaporized in the flame so as to give a very intense illumination. The supply of material is large enough to insure a continuous source of light over a period of observation even to the extent of 5 or 6 hours if necessary. It is to be remarked, however, that in using this flame as with other sodium flames it is necessary for very precise work to use a dichromate light filter.



The general arrangement is portrayed in the accompanying sketch; while the details are discussed in the text under the three captions of shade, thimble and burner.

**Shade.**—The shade of the lamp is constructed of hard asbestos boarding about 3 to 4 mm. in thickness, the sides being bound by nickel or nickel-chromium wire passing through holes bored for this purpose. This shade is 14 cm. in height and 7.5 cm. square. A hole 3 cm. in diameter and 3.5 cm. from the bottom is cut in front, and constitutes the window for the light. On each side of the shade, 2.5 cm. from the back and extending to within 3.5 cm. from the bottom, are cut slits which allow the wire and suspended thimble to be lifted up and down, or removed and replaced at will. The whole shade is fastened at its bottom edge by wires to an iron ring which is movable up or down on a ring stand. This arrangement allows the adjustment of the shade with respect to the optical axis of the polariscope.

**Thimble.**—The alundum thimble should have a medium porosity; if the pores are too fine the molten sodium chloride filters through the thimble so slowly that the rate of vaporization is not enough to give proper intensity to the light; if the pores are too large the molten salt filters through the alundum more rapidly than it is vaporized and drops on the burner below. The thimble is suspended primarily by means of a silica tube which passes over a stout nickel or nickel-chromium wire.<sup>2</sup> The tube not only

<sup>1</sup> For a description of the various types of sodium light sources the reader is referred to Landolt, "Optical Rotation of Organic Substances," 1898, pp. 393-399. Browne, "Handbook of Sugar Analysis," 1912, pp. 147-149. Bur. Standards, *Bull.* No. 44 (Polarimetry), pp. 14-15 and 30-33 (1918).

<sup>2</sup> The silica tube can be obtained from a triangle made of this type of tubing.

protects the salt from contamination by the wire, but also protects the wire from the heat of the flame, thus preventing sagging. The holes in the alundum thimble, through which the silica tube passes, are easily and quickly bored with a rat-tail file or other sharp instrument, while the thimble itself can be cut down quickly to any size by means of a triangular file. The height of the thimble should be such that its top is in the same horizontal plane as the bottom of the window in the shade.

**Burner.**—The burner, which should preferably be of the Meker type, rests upon a movable platform attached to the same ring stand as the shade. The burner should be placed in such a position with respect to the thimble that the flame is not distorted by too close proximity, and so that the rear portion of the flame encounters the front part of the thimble.

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**The Thermal Ionization of Metallic Vapors.**<sup>1</sup>—In a preceding paper,<sup>2</sup> the author has shown that the entropy of electron gas may be calculated from the same theoretical equation as for the other monatomic gases, namely,

$$S = \frac{5}{2} R \ln T - R \ln p + \frac{3}{2} R \ln M + S_1$$

where  $M$  is the molecular weight of the monatomic gas and  $S_1$  has the same value for all monatomic gases. Taking  $p$  in atmospheres,  $S_1$  has the value  $-3.2$  calories per degree.

This new theoretical knowledge may be used in predicting the thermal ionization of metallic vapors, a matter of some interest from the point of view of physical chemistry and astronomy.

**Derivation of Free Energy Equation for Ionization.**—Consider a metallic vapor which can dissociate into a positive ion and an electron in accordance with the reaction,



For the heat of the reaction of constant pressure and at temperature  $T$  we may evidently write,

$$\Delta H = \mathbf{EF} + \frac{5}{2} RT \quad (2)$$

where  $\mathbf{E}$  is the ionization potential of the metal in question,  $\mathbf{F}$  is the value of the faraday,  $\mathbf{EF}$  being the increase in the heat content of the system at the absolute zero, and  $\frac{5}{2} R T$  the value of  $\Delta C_p T$ .

For the change in the entropy of the system when the reaction occurs at constant temperature and under the standard conditions of unit partial pressure for each of the three components, we may obviously write from Equation 1,

$$\Delta S = \frac{5}{2} R \ln T + \frac{3}{2} R \ln M_E + S_1 \quad (3)$$

<sup>1</sup> Published by permission of the Chief of Ordnance.

<sup>2</sup> Tolman, *THIS JOURNAL*, **43**, 1592 (1921).

where  $M_E$  is the molecular weight of electron gas and we have neglected the slight difference between the molecular weights of the un-ionized vapor and its positive ion.<sup>3</sup>

We have thus obtained simple expressions (2) and (3) for the heat change and entropy change accompanying the reaction in which we are interested. We have, however, the following fundamental equation of definition connecting free energy with heat content and entropy, namely,

$$\Delta F = \Delta H - T \Delta S \quad (4)$$

Introducing (2) and (3) we obtain,

$$\Delta F = \mathbf{EF} - \frac{5}{2} R T \ln T + \left( \frac{5}{2} R - \frac{3}{2} R \ln M_E - S_1 \right) T. \quad (5)$$

It is interesting to note that this equation has the same form as that of the familiar free energy equation,

$$\Delta F = \Delta H_0 - \Delta C_p T \ln T + I T$$

and the corresponding quantities have precisely the same significance.

**Calculation of Ionization Constant.**—In order to determine the degree of ionization of the vapor we may substitute Equation 5 into the well-known expression connecting free energy change with equilibrium constant,

$$\Delta F = - R T \ln K_p = - R T \ln \frac{p_{R^+} p_{E^-}}{p_R}. \quad (6)$$

We obtain,

$$\ln K_p = - \frac{\mathbf{EF}}{RT} + \frac{5}{2} \ln T - \left( \frac{5}{2} - \frac{3}{2} \ln M_E - \frac{S_1}{R} \right). \quad (7)$$

If  $K_p$  is the equilibrium constant using partial pressures expressed in atmospheres,  $\mathbf{E}$  is the ionization potential in volts,  $T$  is in degrees Kelvin, and we change to common logarithms and use the values  $\mathbf{F} = 96540$  coulombs,  $M_E = 5.44 \times 10^{-4}$  grams,  $S = -3.2$  calories per degree and  $R = 1.985$  calories per degree we obtain,

$$\log K_p = - \frac{5040 \mathbf{E}}{T} + 2.5 \log T - 6.69. \quad (8)$$

**Ionization of Calcium Vapor in the Sun's Atmosphere.**—The use of this equation in predicting the degree of ionization of metallic vapors in the electric arc or the atmosphere of the sun will be obvious.

For example, if we take the ionization potential of calcium vapor as 6.1 volts, the partial pressure of un-ionized calcium vapor in the sun's

<sup>3</sup> Equation 3 involves the assumption that we are justified in considering all three gases  $R$ ,  $R^+$  and  $E^-$  as monatomic even at the high temperatures involved. It is of course possible that the atoms of the metallic vapor would pick up rotational energy at high temperatures and hence that their entropy should be calculated from the formula for a diatomic or polyatomic gas.

atmosphere as 4 atmospheres, and the temperature as 5500° absolute, the partial pressure of calcium ion or of electron gas comes out 0.07 atmospheres corresponding to 1.7% ionization. This means that the sun's atmosphere has a very considerable electrical conductivity which can be calculated by making proper estimates of the ionic mobilities.

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**Addendum.**—In connection with my recent article on "The Ionization of Aqueous Solutions of Ammonia in the Presence of Urea," published in the December, 1920, number of THIS JOURNAL the following addendum should be made.

"This paper embodies the subject matter of a thesis presented to the Faculty of Clark University in partial fulfilment of the requirements for the Degree of Master of Arts. I wish to acknowledge my indebtedness to the Chemical Laboratory of Clark University for the use of the facilities of this Laboratory in connection with this investigation, and to Dr. Kraus for his interest and coöperation which made this investigation possible."

TOOBLER, UTAH.  
Received January 11, 1921.

WINTHROP M. BURKE.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

## AROMATIC ARSENIC COMPOUNDS. IX. DIAZO-AMINO COMPOUNDS OF ARSANILIC ACID AND ITS DERIVATIVES.

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In a former communication<sup>1</sup> there was outlined a plan for the synthesis of aromatic arsenic compounds for chemotherapeutic study in which, among other series of substances which have since been published, were mentioned the two groups of diazo-amino and azo derivatives obtained from arsanilic acid. These substances with the first which we prepared for these investigations, and although interesting results were obtained with individual compounds in the treatment of experimental trypanosomiasis, we were soon led to discontinue the study of these types because of disadvantages which seemed inherent in them, such as the general instability of the diazo-amino compounds and certain harmful toxic effects induced by both groups. We believe, however, that a presentation of our chemical studies with these compounds should not be devoid of interest.

<sup>1</sup> THIS JOURNAL, 41, 1581 (1919).