

plate prevented them from extending their measurements further.

In view of these contradictory reports, it was decided to investigate the surface ionization of cesium by a different method. Copley and Phipps [*Phys. Rev.*, **45**, 344 (1934); **48**, 960 (1935)] found that the use of an atomic ray instead of saturated vapor almost entirely eliminated the photoelectric current in the case of potassium, and they were able to determine its degree of ionization up to a temperature of 2800°K. An apparatus similar to the one described by Copley and Phipps was constructed, its furnace was filled with carefully purified cesium, and the measurements were taken in the same manner as was described in the case of potassium.

According to statistical mechanics, the degree of ionization of cesium on tungsten is given by the expression

$$\frac{1}{1 + 2 \exp [(I - \phi)\epsilon/kT]} \quad (1)$$

where  $\phi$  is the work function of tungsten at the temperature  $T$ , and  $I$  is the ionization potential of cesium. Curve A in Fig. 1 was obtained by

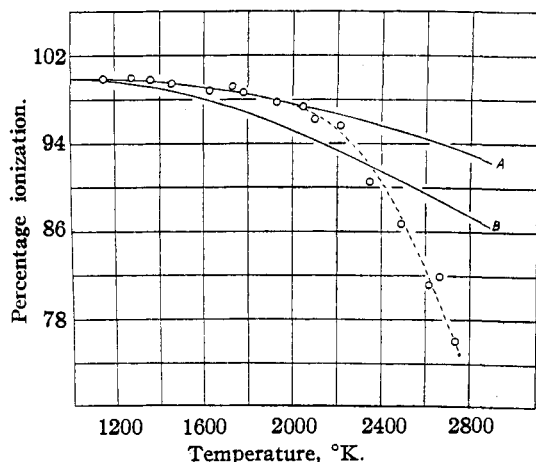


Fig. 1.—The percentage ionization of cesium on tungsten versus temperature.

plotting Eq. 1 with  $\phi$  replaced by  $\phi_0 + \alpha T$  where  $\phi_0$  is the work function at absolute zero and  $\alpha$  is its temperature coefficient. The numerical values used for these constants (4.514 v. e. for  $\phi_0$  and  $5.6 \times 10^{-5}$  v. deg.<sup>-1</sup> for  $\alpha$ ) are the same as those which were found necessary to account for the results obtained with potassium. It is evident that the experimental values for the degree of ionization of cesium below 2000°K. are in satisfactory agreement with curve A. Furthermore, our results confirm those found in the low tem-

perature range by Taylor and Langmuir. Curve B, which is shown for comparison, was obtained by plotting Eq. 1 assuming a negligible temperature coefficient of the work function.

Above 2000°K. the experimental values for the degree of ionization fell off too rapidly to agree with curve A. This behavior may be accounted for in part by experimental error caused by a photoelectric current, which, in spite of the use of the atomic ray, was present in this range of temperature. A similar rapid falling off of the ionization of potassium at temperatures above 2000°K. has been observed. This phenomenon is being further investigated by using atomic rays of potassium and sodium. Since these metals have higher ionization potentials than cesium, their surface ionization in the high temperature range may be more accurately measured.

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JULIAN GLASSER

RECEIVED APRIL 17, 1936

#### KINETICS OF THERMAL CIS-TRANS ISOMERIZATIONS

Sir:

Kistiakowsky and Smith [*THIS JOURNAL*, **58**, 766 (1936)] have shown that the *cis-trans* isomerization of butene-2 appears to be of approximately first order during a run but of second order with respect to initial pressure. The purpose of this communication is to point out that when the equilibrium constant is approximately 1 as in this reaction, the rate in a given run for a bimolecular reaction would be indistinguishable from that calculated for a first order reaction.

If  $x$  is the concentration of the *trans* isomer, the net rate for a bimolecular reaction may be expressed by the equation  $-dx/dt = Kx^2 - (1-x)^2 = (K-1)x^2 + 2x - 1$  where  $K$  equals  $K_1/K_2$ , the ratio of the rate constants for the forward and reverse reactions. If the equilibrium corresponds to  $x = 0.5$ , then  $K = 1$  and  $-dx/dt = +2(x - 0.5)$ , which is the expression for a first order reaction. The deviations from this result are considerable for equilibrium mixtures differing only slightly from 50%, so it is desirable to make a calculation for the experimental value of  $x = 0.528$  at equilibrium. This rate is given by  $-dx/dt = -0.20x^2 + 2x - 1 = (x - 0.528)(-0.20x + 1.894)$ . The first order rate would be proportional to  $(x - 0.528)$  so the variations in

the second term correspond to the deviations from the first order rate. For example, if a velocity constant for a first order reaction were calculated for  $x = 1$ , the observed rate would be about 11% high when  $x = 0$ .

Since 11% is not more than the experimental error in Kistiakowsky and Smith's velocity constants, it seems that all of their results, with the exception of the two runs at 1440 mm., are consistent with the hypothesis of a bimolecular mechanism for the isomerization. Probably the simplest way to test this hypothesis would be to investigate the effects of inert gases but negative results would be inconclusive because collisions of butene with inert molecules would not necessarily have the same effect as collisions with molecules of their own kind.

It is believed that the assumption of a bimolecular mechanism eliminates some of the difficulties involved in explaining the low energy of activation and in postulating a chain mechanism of unknown nature.

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RECEIVED MAY 21, 1936

#### THE N-ALKYL GROUP OF ACONINE (ACONITINE)

Sir:

Since the first applications of the Herzig-Meyer method for N-alkyl determinations to aconine [H. Schulze, *Arch. Pharm.*, **244**, 165 (1906)], it has been commonly assumed that aconitine (aconine) possesses an N-methyl group. This has apparently not been questioned in the interpretations given by a number of workers to the results obtained in alkyl determinations on aconitine, aconine, etc. [among others, R. Majima and S. Morio, *Ann.*, **476**, 194 (1929); A. Lawson, *J. Chem. Soc.*, 80 (1936); although Henry and Sharp, *J. Chem. Soc.*, 581 (1931) considered the possibility of the presence of an N-ethyl group but rejected it as unprecedented].

In the course of work which is now in progress in this Laboratory on the structure of the aconite alkaloids, we have found that when aconine hydrochloride is fused with potassium hydroxide in an atmosphere of hydrogen, the principal volatile amine formed is ethylamine, which was readily identified as the *picrate*, m. p. 166° [*Anal.* Calcd. for  $C_8H_{10}O_7N_4$ : C, 35.02; H, 3.59.

Found: C, 35.43; H, 3.46], and as the *ethyl phenyl thiourea*, m. p. 100–100.5° [*Anal.* Calcd. for  $C_9H_{12}N_2S$ : C, 59.93; H, 6.72. Found: C, 59.93; H, 6.58]. Since this result appeared to contradict the long-standing statement of Ehrenberg and Purfürst [*J. prakt. Chem.* [2], **45**, 604 (1892)] that dimethylamine results on fusion of aconine with barium hydroxide, we have also repeated this experiment. Here again only ethylamine could be identified as before. The so-called dimethylamine derivative of Ehrenberg and Purfürst was unquestionably a double platinum salt of ethylamine. These results therefore strongly indicate the presence of an N-ethyl group in aconine and its parent alkaloid, aconitine.

This conclusion was confirmed by a study of the products of the decomposition of aconine hydrochloride with hydriodic acid under the conditions of the usual alkyl determination. After removal of the methyl iodide which comes from the methoxyl groups, the succeeding iodide originating from the N-alkyl group was shown to be ethyl iodide by identification as *ethyl trimethyl ammonium iodide* [R. Willstätter and M. Utzinger, *Ann.*, **382**, 148 (1911)]. *Anal.* Calcd. for  $C_8H_{14}NI$ : C, 27.91; H, 6.56; I, 59.02. Found: C, 28.42; H, 6.49; I, 58.48. It is not likely that the ethyl iodide could have had another origin, *e. g.*, in a larger grouping to which the cyclic N atom is attached.

Further, in the similar study of oxonitine, which different workers have examined for N-methyl with unconvincing indications, our own determinations have been negative. It is to be concluded that in the transformation of aconitine into oxonitine by oxidation the reaction involves in some way the N-ethyl group which is thus removed. Possibly the acetaldehyde which has been previously reported as a by-product of the reaction may have its origin in this group. Oxonitine may be of betaine or lactam character.

Finally, in the preparation of oxonitine a second, possibly isomeric substance of m. p. 261°, with decomposition, and  $[\alpha]^{26D} -98^\circ$  in chloroform has been isolated as a by-product. *Anal.* Found: C, 61.40, 61.45; H, 6.69, 6.75; N, 2.57, 2.42;  $OCH_3$ , 19.18, 19.07;  $N(CH_3)$ , trace.

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