

When using an ammonia atmosphere and a tip of gold brazed onto a water-cooled copper cathode, the oscillating arc completely suppressed the spectra of these metals, and intensified the 3361-3372 Å. line of the titanium impurity in the copper. The above phenomena suggested the use of the Poulsen Arc as a means of detecting small traces of impurities of even atomic number in such metals as copper, gold and silver.

A quantitative analytical method involving these phenomena is now being worked out in this Laboratory.

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#### COAGULATION OF PURE FERRIC HYDROXIDE SOLS

*Sir:*

In a recent article Judd and Sorum [THIS JOURNAL, 52, 2598 (1930)] have stated that with highly purified sols of ferric hydroxide, which are practically free from chloride ions, the amount of univalent coagulating ion decreases as the concentration of the sol increases.

In several publications [*J. Phys. Chem.*, 26, 701 (1922); 28, 313 (1924); 29, 435, 659 (1925); *Kolloid.-Z.*, 34, 262 (1924); 36, 129 (1925)] from these Laboratories we have shown that ordinarily purified sols of ferric hydroxide require larger amounts of univalent electrolytes for coagulation when the concentration of the sol is increased. In a recent communication Dhar and Gore [*J. Indian Chem. Soc.*, 6, 31 (1929)] have shown that even highly purified sols of ferric hydroxide containing a very small amount of chloride ion follow the general rule that the greater the concentration of the sol, the greater is the amount of electrolyte necessary for coagulation irrespective of the valency of the coagulating ion. It appears, therefore, that the results of Judd and Sorum are not in agreement with previous work and need confirmation.

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#### A CONTINUOUS (OR BAND) FLUORESCENCE EMISSION SPECTRUM WHICH ACCOMPANIES A CHANGE OF COLOR

*Sir:*

An interesting phenomenon has been observed in a study of the Raman effect with a number of liquids listed later. A continuous (or band) emission spectrum (Fig. 1) has been found to appear on the plate in each case in which the colorless liquid becomes colored, and not to appear if there

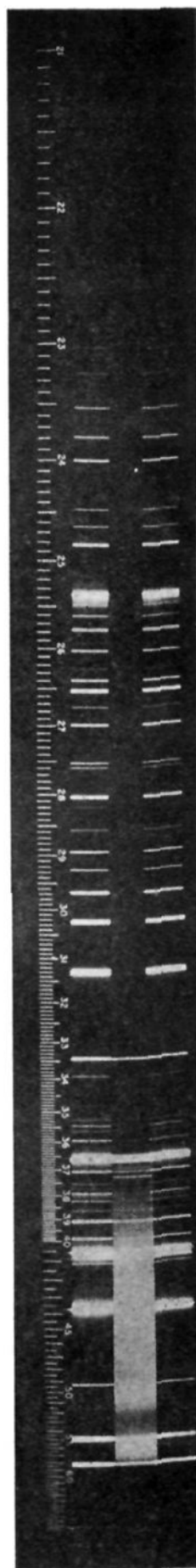
is no color change. The incident radiation of the mercury arc light appears to excite the molecules of the substance, and a part of the energy of excitation is released as a fluorescence radiation. A few of the details of this work are given below.

The Raman effect has been observed for a number of bromides: normal butyl bromide, secondary butyl bromide, isobutyl bromide, tertiary butyl bromide, normal propyl bromide, isopropyl bromide, normal amyl bromide and isoamyl bromide. The liquids were purified by distillation.

In addition to the lines of modified wave length, a continuous spectrum, which lies within the limits  $\lambda = 4000 \text{ \AA.}$  and  $\lambda = 5800 \text{ \AA.}$ , was obtained with each liquid. The continuous spectrum was always accompanied by the appearance of a yellow color in the liquid. Usually an exposure of forty-eight hours sufficed for the production of the continuous spectrum; this, however, was not the case with *n*-propyl bromide, *n*-butyl bromide and secondary butyl bromide, since none of these showed either a continuous spectrum or a discoloration after being exposed to the mercury arc for forty-eight hours. If the time of exposure was extended to seventy-two hours or more, the continuous spectrum and the color change were observed for each of these liquids. In all cases where the exposure was long enough to give an intense continuous spectrum, the latter contained two regions of maximum intensity, one lying between the mercury lines at  $\lambda = 4358 \text{ \AA.}$  and  $\lambda = 4916 \text{ \AA.}$ , and the other between the lines at  $\lambda = 5460 \text{ \AA.}$  and  $\lambda = 5769 \text{ \AA.}$

Methyl and ethyl alcohols saturated with ammonia were studied for Raman spectra. The solutions were exposed to the mercury arc for ten to twelve hours. Methyl alcohol saturated with ammonia gave a continuous spectrum which was similar to that of the bromides in character and in position; the solution turned yellow during the exposure. Ethyl alcohol saturated with ammonia did not give a continuous spectrum or a color change. Neither of these two accompanying phenomena was observed in the case of the pure alcohols.

Fig. 1.—In the middle is the continuous fluorescence spectrum and the Raman spectrum of an alkyl bromide. The mercury comparison spectrum is shown above and below.



An attempt was made to ascertain whether the exclusion of oxygen would affect the color change and the continuous spectrum. A brisk stream of nitrogen was bubbled through isoamyl bromide for forty-five minutes prior to exposure and the Raman tube was closed by means of a stopcock; no diminution of the intensity of the continuous spectrum or of the color, was found.

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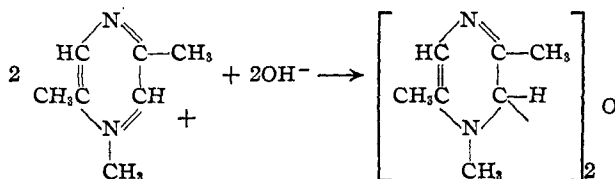
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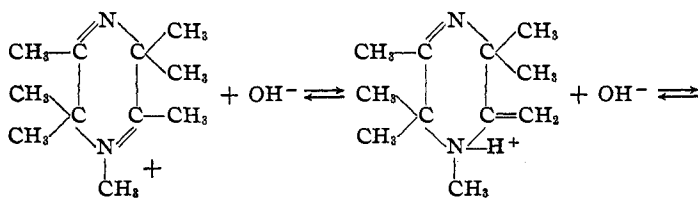
### THE BASE FROM 2,5-DIMETHYLPYRAZINE-METHYL IODIDE

Sir:

Recently Princivale<sup>1</sup> has reported unsuccessful attempts to isolate the base liberated from 2,5-dimethylpyrazine-methyl iodide. In connection with some work on pseudo bases, part of which has already been submitted for publication, the author has studied the action of alkali on this salt. Although the base isolated could not be obtained pure and gave analyses varying from C, 53.2; H, 6.94, to C, 49.5; H, 6.63, a kinetic study of the reaction using a conductimetric method has made it seem probable that the net reaction taking place is



The salts 1,2,2,5,5-pentamethyl-2,5-dihydropyrazinium iodide and 1,2,2,3,5,5,6-heptamethyl-2,5-dihydropyrazinium iodide have also been prepared and their behavior with aqueous alkali studied. From these two salts the bases isolated were, respectively, 1,2,2,5,5-pentamethyl-6-hydroxy-1,2,5,6-tetrahydropyrazine (m. p. 110°) and 1,2,2,3,5,5-hexamethyl-6-methylene-1,2,5,6-tetrahydropyrazine (b. p. (6.5 mm.) 78°). Certain evidence has been obtained to show that the latter base was formed by an enolic change



<sup>1</sup> Princivale, *Gazz. chim. ital.*, 60, 298-301 (1930); *C. A.*, 24, 3792 (1930).