

than -5600 cal. Now, assuming that the entropy of nitrogen tetroxide is equal to or less than that of nitrogen pentoxide, then the total increase in entropy is equal to or less than 24 units, the entropy of $1/2\text{O}_2$. Using these values in the equation

$$\Delta F^\circ = \Delta H - T\Delta S^\circ$$

we obtain for ΔH a value equal to or less than 1600 calories.

The value given for ΔH in the "International Critical Tables" is 2690 cal. Either this value is too high or the entropy of nitrogen tetroxide is greater than that of nitrogen pentoxide, which would be surprising.

It was not feasible, with the apparatus used, to go higher than 1000 atmospheres' pressure.

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THE PHOTO-REACTION OF HYDROGEN AND IODINE MONOCHLORIDE

Sir:

In a recent communication [THIS JOURNAL, 52, 2793 (1930)] Rollefson and Lindquist criticize our conclusions [*Nature*, 127, 93 (1931)] regarding the photo-reaction of hydrogen and iodine monochloride, namely, that excited chlorine atoms *may* not be necessary for it to take place. They maintain that, as our hydrogen pressure was large compared with the pressure of iodine monochloride, the chlorine atoms (*excited to the 2P_1 state by collisions*) would have more chance of reacting with the hydrogen than with the iodine monochloride. Nevertheless, we have been able to bring about the reaction with hydrogen pressures (*circa* 70 mm.) comparable with the pressure of iodine monochloride.

We used Merck's crystalline iodine monochloride contained in a small glass tube which was subsequently broken in the reaction vessel. Hydrogen passing through a palladium tube was brought to the required pressure in the reaction vessel, which was then sealed up. The pressure was recorded on a glass spiral gage, and no contact with impurities, tap-grease, etc., was permitted [Ashley and West, *Nature*, 127, 308 (1931)]. The vessel was then irradiated with a mercury vapor lamp through a filter of quinine sulfate solution, and also through a filter of picric acid and cupric sulfate, transmitting only the 5461, 5764 and 5791 Å. lines. The reaction is slow but measurable, and the rate of iodine formation increases when the initial hydrogen pressure is increased. If the chain mechanism suggested is correct, the reaction, even under the most favorable conditions, could only have roughly 1/500,000 the speed of the hydrogen-chlorine reaction. Doubtless the reaction $\text{ICl} + \text{Cl} = \text{Cl}_2 + \text{I}$ takes

place as Rollefson and Lindquist suggest, but it would be unwise to infer from any of these experiments that the chlorine atom is unexcited.

Rollefson and Lindquist give only a few details of their experimental conditions, gas pressures, etc., but they mention one significant fact, namely, that their chlorine pressure was always large compared with the pressures of hydrogen and iodine monochloride. In these circumstances the iodine compound in the vapor phase may have been mainly iodine trichloride. This substance is of a lighter color than iodine monochloride, and must have an altogether different absorption spectrum. We have found that the vapors of iodine monochloride and chlorine react very readily, and, indeed, Rollefson and Lindquist themselves admit that they froze out iodine trichloride in the solid phase.

We do not wish to make any further statement until we have completed the study of the reaction kinetics.

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CATALYTIC REDUCTION OF MIXTURES OF PARA-NITRO- AND NITROSO-PHENOLS WITH KETONES

Sir:

It has recently been shown by the writer that *p-sec.*-alkylaminophenols are formed by the catalytic reduction of mixtures of *p*-nitro- or nitrosophenol and ketones at room temperatures [Major, THIS JOURNAL, 53, 1901 (1931)]. The suggestion was made that the reaction probably involved formation of *p*-hydroxy-phenylhydroxylamine as an active intermediate product of the reduction and that this compound condensed with the ketone and finally that the condensation product was reduced to the alkylaminophenol. Vavon and Krajićinović have reported that they have been able to make the condensation product between benzaldehyde and phenylhydroxylamine, $C_6H_5CH=N(O)C_6H_5$, by the catalytic reduction of a mixture of nitrobenzene and benzaldehyde [Vavon and Krajićinović, *Compt. rend.*, 187, 420 (1928)].

However, it was noted that heat was formed during the catalytic reduction of mixtures of *p*-nitro- and nitrosophenol and acetone. There remained, then, the possibility that the heat of the reaction between *p*-nitro- or nitrosophenol and hydrogen was sufficient to cause the *p*-aminophenol which formed to condense with the ketone. This condensation product would then be readily reduced to *p-sec.*-alkylaminophenol.

Evidence which apparently favored this point of view was obtained when a solution of 0.1 mole of *p*-aminophenol in acetone was heated to