

bonding force, without the exchange phenomenon. When the exchange phenomenon is taken into account, a redistribution of charge is obtained with an increase in bonding energy, but this increase is in some cases a small fraction of the total energy. It seems entirely probable that the "residual affinity" which has been invented to explain compounds such as B_2H_6 may be a result of overlapping of charge, without the exchange phenomenon.

It is perhaps not realized by chemists how revolutionary the idea of superposition of electron charges is, and how completely it removes the old difficulties with electrical charges and coulomb forces. The combination of two protons and two electrons in a stable arrangement is an impossibility; if the two electrons are superposed the repulsive forces between electrons disappear and a stable configuration is possible.

Of course, the complete superposition of charge does not occur ordinarily but one may wonder if it is not approached in the α -particle. The idea of the tetrahedral structure of the α -particle has suggested itself to many, and Latimer⁵ has recently developed the idea in formulating a lattice structure for the nucleus. It is evident that a pair of electrons surrounded by four protons is subject to extraordinary forces and the superposition of the two electron charges might be nearly complete. The solution of this problem seems to lie within the present possibilities of wave mechanics, and the result would be of great interest.

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ZIRCONIUM. III. THE REACTION BETWEEN AMMONIA AND METHYL ALCOHOLIC SOLUTIONS OF ZIRCONIUM SULFATE

Sir:

The fact that solutions of zirconium salts yield, upon the addition of ammonium hydroxide, a white gelatinous precipitate of zirconium hydroxide quite insoluble in water or in an excess of the precipitant has been known since the days of Berzelius. The results of recent work in this Laboratory tend to show, however, that under special conditions a compound other than the hydroxide may be precipitated by ammonium hydroxide if the zirconium sulfate be dissolved in methyl alcohol.

A methyl alcoholic solution of zirconium sulfate was treated with ammonium hydroxide or ammonia gas. Under ordinary conditions only the hydroxide would have been precipitated. If the solution be quite fresh, that is, if it has been prepared for only a matter of two or three minutes,

⁵ Latimer, *THIS JOURNAL*, **53**, 981 (1931).

a white precipitate is obtained which is, strangely enough, quite soluble in water or in an excess of the precipitant. If the solution be allowed to stand for from five to ten minutes, only the hydroxide is precipitated. It was thought possible that the alcohol, employed as a solvent, either went into a direct chemical reaction, or prevented hydrolysis from taking place as would have been the case if water had been employed as a solvent and to this end it was decided to carry out the experiments with a fresh water solution of zirconium sulfate in which hydrolysis had not taken place to any great extent. A solution of the age of three minutes yielded only the hydroxide upon precipitation with ammonia, and it was thought to be possibly too old. To this end the entire procedure of the preparation of the solution and precipitation by ammonia was reduced to ten seconds, then to five, but even in these cases only the hydroxide was obtained. It was considered that the amount of hydrolysis which could take place in five seconds would be very slight, and certainly would have had no great influence upon the reaction. Consequently it was considered that the presence of methyl alcohol was necessary for the reaction. Naturally this consideration does not account for the fact that old methyl alcoholic solutions yield only the hydroxide, and this will be discussed later.

A water solution of the precipitate was treated with the following reagents: ammonium hydroxide, ammonium carbonate, citric acid, and oxalic acid, all of which give characteristic precipitates with the zirconium ion. In no case was any reaction observed. When the solution was treated with barium chloride, however, a precipitate of barium sulfate was filtered off, and the filtrate resulting from this reaction readily gave precipitates with ammonium hydroxide and the other reagents mentioned above. When the usual analytical precautions were taken it was found that the precipitate lost 87.52% by weight on ignition over a Fisher burner for forty-five minutes. Since the sample turned black during the course of ignition it was suspected that organic matter was present in the compound.

The fact that only fresh methyl alcoholic solutions of zirconium sulfate yield the soluble precipitate tends to indicate that some intermediate, and probably very complex, compound is formed between methyl alcohol and zirconium sulfate. Under ordinary conditions this compound probably decomposes very readily, but if the solution be used when fresh and treated with ammonium hydroxide, the ammonia enters the compound and forms a complex with zirconium in the anion. These conclusions, while not necessarily final, are supported by the evidence given above.

It is interesting to note that this phenomenon appears to take place with certain other elements such as aluminum and zinc, while such substances as magnesium and iron give no such reaction.

Work is now going on to the thorough study of these phenomena. Since the results are rather novel, however, this preliminary report has been

prepared with the hope in mind that it might prove of some interest to those working with zirconium, especially since the complete research will not appear for some months.

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THE ORTHO-PARA-HYDROGEN CONVERSION AT SURFACES

Sir:

Bonhoeffer and Harteck [*Z. physik. Chem.*, 4B, 113 (1929)] found that nickel possessed a negligible activity for the reconversion of para-hydrogen to the ortho-para mixture even at room temperatures. Still less might one expect it to function as an agent for para-hydrogen formation at liquid-air temperatures. The data of Benton and White [THIS JOURNAL, 52, 2325 (1930)] showed adsorption of hydrogen on nickel even at -110° in an activated form [Taylor, THIS JOURNAL, 53, 585 (1931)]. We have, therefore, carried out experiments on para-hydrogen formation with a very active nickel (10% nickel on kieselguhr) showing specific adsorptions for hydrogen of a much higher order of magnitude than the material employed by Benton and White. With this material we have shown it possible to produce the equilibrium concentration of 50% para-hydrogen at liquid-air temperatures as readily as on charcoal. That the surface activity was the important factor was readily shown by experiments with small fragments of nickel wire. With such, there was no measurable para-hydrogen formation.

We have extended these measurements to oxide surfaces since it has been found in adsorption studies [Garner and Kingman, *Nature*, 126, 352 (1930); Taylor and Williamson, THIS JOURNAL, 53, 813 (1931)] that below 0° there is no evidence of an activating adsorption of hydrogen but marked adsorption of molecular hydrogen. Our results on para-hydrogen conversion confirm this. Neither with an active zinc oxide nor with the more active hydrogenation agent zinc-chromium oxide is there any para-hydrogen formed at liquid-air temperatures even after fourteen hours' contact. On the contrary, in the temperature region where, on these surfaces, activated adsorption of hydrogen sets in, namely from 0° upwards, there is an immediate activity in the reconversion of the 50% para-hydrogen to the normal 1:3 mixture. The relative activities in this respect are exactly parallel with the influence of composition on the velocity of activated adsorption. Thus, with zinc-chromium oxide, the reconversion is complete in fifteen minutes' contact time at room temperature. With the less active zinc oxide it is barely perceptible in the same time at the same temperature and is not quite complete at 100° with the same time of con-