

COMMUNICATIONS TO THE EDITOR

THE ABSORPTION OF WATER VAPOR BY COTTON CELLULOSE

Sir:

In a paper by L. M. Pidgeon and O. Maass entitled "The Adsorption of Water by Wood" [THIS JOURNAL, 52, 1053 (1930)], figures are given for the adsorption of water vapor by purified cotton cellulose. The method of measurement was one that was selected by the authors after a consideration of the possible sources* of error, since, they say, "Little of the work which has been done is entirely free from objection . . . and . . . in even the most careful determinations of the adsorption by cotton cellulose the amount of adsorption was measured indirectly."

The absorption of water vapor by cotton has formed the subject of systematic investigations extending over eight years by my colleagues, the late Dr. A. M. Williams and Dr. A. R. Urquhart. The methods used were submitted to critical examination, and the results of the investigation, which derive from observations on some hundreds of samples of cotton, are contained in the *Shirley Institute Memoirs*, and are being published in a series of communications to the "Journal of the Textile Institute," nine of which have so far appeared since 1924. A complete absorption and desorption isotherm for pure cotton cellulose at 25° is given in one of these communications [*J. Text. Inst.*, 15, T433 (1924), or *Shirley Institute Memoirs*, 3, 197 (1924)], the latter of these two references being quoted by Pidgeon and Maass in their paper.

Since these authors have omitted to do so, and since the *Shirley Institute Memoirs* do not possess the wide circulation among scientific readers enjoyed by the *Journal of the American Chemical Society*, it seems desirable to call the attention of your readers to the fact that, at high relative humidities, there are gross discrepancies between the results of Pidgeon and Maass and those of Urquhart and Williams. Only one isotherm is given by Pidgeon and Maass, namely, at 23°, but this can be compared with the isotherm obtained by Urquhart and Williams at 25°, since it is clear from the work of both laboratories that this small difference of temperature can have no significant effect on the moisture absorption at a given relative humidity. The value obtained by Urquhart and Williams exceeds that given by Pidgeon and Maass by 11% at saturation, by 4% at 90% relative humidity, and by 2% at 80% relative humidity.

It is to be hoped that an attempt will be made to discover the source of the discrepancy, which must lie either in the technique of measurement or in the samples of "pure cotton cellulose." In this connection, it must be pointed out that the chemical attack of cotton cellulose by bleaching or otherwise, which increases its solubility in sodium hydroxide solutions, or reduces its so-called " α -cellulose" content, does not increase its moisture

absorption at constant humidity, as Pidgeon and Maass would appear to expect on theoretical considerations, but has the opposite effect.

From the purely scientific aspect, the absolute values of the absorption may appear of less importance, as any errors of technique affecting all measurements would not necessarily invalidate conclusions drawn from the comparative behavior of different materials. Absolute values of the moisture absorption of cotton are, however, of the highest commercial and technical importance, since cotton is bought and sold on an agreed average moisture content, which can be defined from the absorption isotherm when the average conditions with respect to humidity and temperature are known. From this point of view alone it seems advisable to place on record the fact that the low figures of Pidgeon and Maass at high humidities—which will certainly surprise many technical workers experienced in the cotton processing industries—are much below those of other workers who have also devoted themselves to a long and critical examination of the subject.

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THE SUPERPOSITION OF ELECTRON CHARGES IN MOLECULES AND α -PARTICLES

Sir:

In their paper on the hydrogen molecule, Heitler and London¹ went to great length to stress the fact that the valence forces were not the ordinary coulomb forces, but were due to an exchange phenomenon involving the pair of electrons. Recent work by Slater,² Zener,³ Bartlett⁴ and others, raises the question as to whether Heitler and London have not over-emphasized the importance of the exchange phenomenon. When we consider the exchange phenomenon we find that it has little objective significance; it may be described as a resonance effect in wave functions. On the other hand, the work of Slater and the others referred to above makes it clear that the bonding force between atoms is due to the overlapping or superposition of electron charge, the electron charge being treated as a distributed charge, whose density is proportion to $\psi\bar{\psi}$. In atoms with more than one valence electron, where the charge distribution is not spherically symmetrical, there is the possibility of a considerable

¹ Heitler and London, *Z. Physik*, **44**, 455 (1927).

² Slater, *Phys. Rev.*, **36**, 57 (1930).

³ Zener, *ibid.*, **36**, 51 (1930).

⁴ Bartlett, *ibid.*, **36**, 1096 (1930).

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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HOWARD S. GABLE

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-

tact. We are extending further this interesting method of determining the nature of hydrogen adsorbed on surfaces.

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THE ALLOMERIZATION OF CHLOROPHYLL

Sir:

When an alcoholic solution of chlorophyll is allowed to stand, a process known as allomerization takes place.¹ Allomerized chlorophyll *a* differs from the original material in that the product of hot alkaline hydrolysis is a mixture of unstable chlorins instead of the normal product chlorin *e*. The same unstable chlorins are obtained from unallomerized chlorophyll or the magnesium-free compounds (phaeophytin *a* or methyl phaeophorbide *a*) by saponification with alcoholic alkali at room temperature or below. It has recently been established² that the essential change in both allomerization and low temperature saponification ("phase test" hydrolysis) is the dehydrogenation of the grouping —CHOHCO— to —COCO—. The fate of the two hydrogen atoms was, however, uncertain. We have now been able to show by very simple experiments that the hydrogen atoms are removed by the oxygen of the air. If allomerization or "phase test" saponification is carried out in a modified Warburg apparatus,³ the absorption of oxygen is easily measured. The amount absorbed corresponds to the removal of two hydrogen atoms with the formation of hydrogen peroxide.

The dehydrogenation of chlorophyll *a* or the magnesium-free compounds in the *a* or *b* series may also be brought about by the use of potassium molybdicyanide in acetone-pyridine solution. Two equivalents of reagent are required per mole. Dehydrogenated chlorophyll *a* thus prepared is identical with allomerized chlorophyll (the ultraviolet absorption spectrum is a satisfactory method of distinguishing the dehydro compound from the original material). After removal of the magnesium from allomerized chlorophyll or chlorophyll dehydrogenated with molybdicyanide, the absorption spectrum in the visible and the ultraviolet is identical in both cases and indistinguishable from that of methyl dehydrophaeophorbide. This latter substance we have prepared in quantity by the action of molybdicyanide on methyl phaeophorbide *a*; it yields the unstable chlorins on hot alkaline hydrolysis.

¹ Willstätter and Utzinger, *Ann.*, **382**, 129 (1911).

² Conant, Hyde, Moyer and Dietz, *THIS JOURNAL*, **53**, 359 (1931).

³ Hyde and Scherp, *ibid.*, **52**, 3359 (1930).

From the facts given above, it is clear that allomerization is dehydrogenation brought about by the oxygen of the air. It is interesting that the dehydrogenation of a very easily oxidized group in chlorophyll is without pronounced effect on the color, although marked changes in color, as a rule, accompany the oxidation of a colored substance. The unusual behavior of chlorophyll in this respect is due to the fact that the chromophoric group is not the most easily oxidized group. A theory of photosynthesis has been recently suggested⁴ which is based on the presence of this easily dehydrogenated group in chlorophyll.

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NEW BOOKS

Fundamentals of Chemistry. By CARL WILLIAM GRAY, CLAUDE W. SANDIFUR and HOWARD J. HANNA. Revised and enlarged edition. Houghton Mifflin Company, 2 Park St., Boston, Massachusetts, 1929. xiv + 650 pp. 201 figs. 13 × 19.5 cm. Price \$1.80.

This book is a revised and enlarged edition of a high school text, first published in 1924.¹ The order of presentation of the subject matter, used in the first edition, remains one of the original features of the book. This unusual order is characterized in part by the introduction of metals in Chapter III, metallic oxides and ores in Chapter VI, and the introduction of carbon as the third element considered. A new chapter on the structure of matter has been introduced before the chapter on ionization, obviating one criticism of the first edition. These two chapters now constitute a good elementary presentation of the electron concept, which, however, is not afterward utilized even in discussing such topics as the periodic classification and storage batteries, and only a limited use is made of this concept in the chapter on oxidation and reduction which has been added in this edition.

Other new chapters are entitled "The Atmosphere," "Paints, Varnishes and Lacquers," and "Chemistry in Agriculture." These titles indicate that the method of treatment and the subject matter are those conventionally associated with courses for school students not in the college preparatory group. However, it cannot be said that the fundamental generalizations have suffered. The illustrative material and the order of treatment constitute the chief differences from the conventional text.

⁴ Conant, Dietz and Kamerling, *Science*, 73, 268 (1931).

¹ Reviewed in *THIS JOURNAL*, 47, 592 (1925).