

Bismuth.—Classen and Strauch¹⁸ converted weighed quantities of redistilled bismuth triphenyl into bismuth oxide by treatment with an excess of oxalic acid and gradual heating to 750°. Weights are corrected to a vacuum. C = 12.001. H = 1.0077.

Aston¹⁹ has obtained evidence concerning the isotopic character of several elements not previously analyzed.

ISOTOPIC CHARACTER OF ELEMENTS				
Element	Atomic number	Atomic weight	Minimum number of isotopes	Mass number in order of intensity
Fe	26	55.84	2	56,54
Sr	38	87.63	2	88,86
Zr	40	91.2	4	90,94,92,96?
Cd	48	112.41	6	114,112,110,113,111,116
In	49	114.8	1	115
Te	52	127.5	3	128,130,126
Ba	56	137.37	1	138
La	57	138.90	1	139
Ce	58	140.25	2	140,142
Pr	59	140.92	1	141
Nd	60	144.27	4	142,144,146,145
Er	68	167.7	?	164-176
Bi	83	209.00	1	209

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THE REDUCING ACTION OF HYDROGEN ADSORBED IN SILICA GEL

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It has long been known that certain charcoals reduce to the metallic state the ions of such metals as silver, gold and platinum. Early investigators concluded that carbon acted as the reducing agent but Green¹ decided that carbon monoxide and hydrogen in all probability caused the change. Others such as W. W. Taylor in his "Chemistry of Colloids" have said that the negatively charged surface of the charcoal neutralized the positive ion, causing the metal to precipitate.

Since silica gel resembles charcoal in so many ways as a porous substance the authors felt that it would be possible to determine definitely the reducing action of hydrogen adsorbed in porous bodies and incidentally

¹⁸ Classen and Strauch, *Z. anorg. allgem. Chem.*, **141**, 82 (1924).

¹⁹ Aston, *Nature*, **113**, 192, 856; **114**, 272, 717 (1924); also articles in *Phil. Mag.*

¹ Green, *Bull. Inst. Mining Met.*, **109** (1913).

observe the effect of opposite charges upon positive ions by using silica gel.

The following experiments show that hydrogen adsorbed in silica gel will reduce to the metallic state certain of the ions of metals which lie below it in electrochemical series.

Experimental Part

The silica gel used in the experiments was made by the method described by Patrick,² and the granules averaged 1 to 2 millimeters in diameter. The reagents used in making up the solutions were of the highest purity obtainable and no further attempt was made to purify them.

The silica gel was found in electro-endosmose experiments to be negatively charged toward water. A 0.1 *N* silver nitrate solution was added to this silica gel but no deposit of silver occurred even after the liquid had stood for several days in contact with the gel. This would indicate that a negative surface alone would not neutralize the positive ion and cause deposition of metal.

The method finally used in reducing the metal ions by adsorbed hydrogen may best be described by taking the reduction of the silver ion as an example. About 20 g. of a good clear silica gel was placed in a Pyrex glass tube constructed for the purpose and evacuated for three to four hours at a temperature of about 400° and a pressure of less than 0.01 mm. While still evacuated the tube containing the silica gel was cooled to -20° in a salt-ice bath. Electrolytic hydrogen was then admitted under atmospheric pressure and allowed to remain in contact with the gel for at least 30 minutes. This hydrogen had been slowly bubbled through an alkaline permanganate solution and then passed through anhydrous calcium chloride before reaching the gel. The gel was then covered with 0.2 *N* silver nitrate solution. The gel began to turn brown almost at once. The tube was removed from the ice-bath, placed in the dark to eliminate photochemical effects and allowed to remain for several hours. At the end of this time the gel had become dull black. The solution was drained from the gel, and the latter was washed and dried.

Microscopic examination of the granules showed that the entire surface of the gel was well covered by the black deposit. Crushing of granules demonstrated that the deposit was distributed throughout the granule. The black deposit gave chemical tests for metallic silver and not for silver salts or oxides. In some of the experiments the solution contained a yellowish material after the reaction was complete. This appeared to be colloidal silver. In other cases very minute, shiny particles appeared most of which would pass through filter paper. The solution after treatment always gave a bright Tyndall cone.

² Patrick, U. S. pat. 1,297,724.

Since the silver ion was so easily reduced by adsorbed hydrogen, ions of other metals might conceivably also be reduced in like manner. Samples of silica gel were therefore treated in the same manner with solutions of copper, gold, platinum and palladium salts. In each case a reduction of the metal ion occurred. In the case of cupric salts reduction to the cuprous condition was observed with very small traces of metallic copper.

When cupric chloride solution was used a precipitate of cuprous chloride was obtained. Solutions of auric chloride gave some metallic gold as a yellow deposit but most of the gold flaked off from the gel on shaking, so that the solution drained from the gel contained a great number of minute gold particles. The gel became distinctly yellow after this treatment.

Some reduction of chloroplatinic acid was noted when a solution of this substance was added to silica gel treated with hydrogen in the manner described. When the chloroplatinic acid was first reduced to the platinous condition by sulfur dioxide and the gel treated with this solution, a fine black deposit formed, having much the appearance of the silver deposits. In the same way an excellent coating of palladium was obtained, using a solution of ammonium chloropalladite. All attempts to reduce nickel solutions by this method failed.

It is evident from these experiments that adsorbed hydrogen actively reduces the ions of certain metals which lie below it in the electrochemical series. The bonds between the atoms of the hydrogen molecule must be weakened by adsorption so that the atoms may act independently. The action which proceeds may be as follows: $H + Ag^+ = Ag + H^+$. The character of the deposit indicates a very fine state of division and this would follow if the above reaction were true. Reactions of the type indicated may explain in part the ability of charcoals to reduce metallic ions.

These metallized silica gels, in preliminary experiments, give every indication of being very active catalysts.

Summary

1. Negatively charged silica gel does not reduce the silver ion to molecular silver.
2. Hydrogen adsorbed in silica gel reduced the ions of copper, silver, gold, platinum and palladium.

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