[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

Electrification and Luminescence Phenomena Accompanying Desorption of Gases from Metals

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Berliner[2] found that metals sputter (zerstäuben) on giving up sorbed gases. Likewise it is well known[3] that metals and some other solids become electrically charged on desorption or high temperature evacuation.

In 1922 and 1923,[4] it was found that hydrogen immediately after desorption from platinum or palladium, reacts with copper oxide or sulfur and is partly ionized, as shown by a gold leaf electroscope.

Polyakov[5] found that a luminescence occurs at as much as thirty centimeters away from palladium, nickel or iron, over which hydrogen is passed. Furthermore, tungstic oxide and copper oxide were reduced at low temperatures only in the region of luminescence.

Our own experiments have been conducted with various gases passed over platinum and nickel in a tube of fused silica. We have confirmed the occurrence of the luminescence. When the metal is heated to between 1000 and 1500° and then pure hydrogen admitted to the cooling metal, a flow being maintained by means of a vacuum pump, a greenish-blue glow, visible in a darkened room, appears on the inside wall of the silica tube beyond the catalyst. It may extend over a distance of as much as fifty-two centimeters length of tubing, and some may appear faintly on the inlet side of the catalyst. The luminescence is strongest at first, and moves slowly away from the catalyst. The process may be repeated as desired, and the metal may be restored to full power by treating it with hydrogen at 1000°. Nickel containing gas may even be melted and yet produce this effect on cooling. An extremely thin film of nickel was almost as effective as a piece of nickel sheet. The room must be darkened to observe the luminescence. The vacuum pump need only be used initially, to degas the catalyst before admitting further gas to the cooling metal. The luminescence was observed at pressures from between three millimeters and eight hundred millimeters of mercury without change in intensity. Luminescence did not occur on Pyrex tubing or on a coating of nickel inside the quartz tube.

Luminescence was produced when for hydrogen we substituted oxygen, air, natural gas, water vapor, methyl alcohol and carbon tetrachloride vapor. The tubing becomes very appreciably heated where the luminescence is occurring. In our experiments the metal became negatively charged.

Discussion

We therefore have the following phenomena during sorption and desorption of gases by metals (a) luminescence on the silica walls; (b) heating of silica tubing; (c) electrification; (d) sputtering.

The explanation finally arrived at was that sorption and desorption can dislodge infinitesimal charged particles of the metal. Their potential is increased as they are carried by the gas away from the catalyst. They slowly diffuse to the walls of the tube. and the resultant voltage is high enough to ionize the gas along the walls of the tube, producing the luminescence and accounting for any enhanced reactivity.

It is well known that many metals become porous and friable and disintegrated during sorption and desorption. Whytlaw-Gray and Patterson[6] report: "Another type of very fine particular system is produced when a stream of filtered air is passed through the metallic heater in absence of the boat. The formation of this system is apparently not due to traces of volatile material on the metal, as no amount of previous

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[1] Thesis by C. I. Glassbrook, "The Activation of Hydrogen in Contact Catalysis," Stanford University, May, 1936, available in bibliofilm through the Department of Agriculture.

[2] A. Berliner, *Wied. Ann. Physik*, **33**, 289 (1888).

[3] For references see J. W. McBain, "The Sorption of Gases and Vapors by Solids," George Rutledge and Sons, London, 1931, pp. 265–267.

[4] P. Anderson, *J. Chem. Soc.*, **121**, 1153 (1922); Y. Venkataramaiah and M. V. N. Swamy, Proc. Sci. Assoc. Maharajah's College, Vizianagram, December, 1922, p. 23; Y. Venkataramaiah, THIS JOURNAL, **45**, 261 (1923); A. E. Mitchell and A. L. Marshall, *J. Chem. Soc.*, **123**, 2448 (1923); H. S. Taylor, *Chem. Rev.*, Vol. IX, no. 1, 15–21 (1931); P. N. Kohanenko, *Acta Physicochim. U. R. S. S.*, **9**, 93 (1938).

[5] M. V. Polyakov, *Naturwissenschaften*, **15**, 539 (1927); **16**, 131 (1928); *Ber. Ukrain. Wiss. Forsch.-inst. Physik. Chem.*, **2**, 55–67 (1929).

[6] R. Whytlaw-Gray and H. S. Patterson, "Smoke: A Study of Aerial Disperse Systems," Arnold and Company, London, 1932, p. 51.

heating eliminates it. The dispersoid in this case is even too fine to show appreciably in the Tyndall beam which we use, but we have been able to determine its rate of coagulation with Mr. Green's condensation apparatus."

Likewise, the electrification produced upon the disruption of materials and surfaces is well known.[7]

(7) Obreimoff, *Proc. Roy. Soc.* (London), **127A**, 294 (1930); J. Strachan, *Nature*, **139**, 803 (1937); E. Newton Harvey, *Science*, **89**, 460–461 (1939); S. C. Blacktin, *Nature*, **140**, 280 (1937).

Summary

1. When various gases are passed over a metal that is cooling during sorption and desorption, the gas stream on the outward side becomes electrified. It causes a luminescence on the walls of a silica tube.

2. The effect is ascribed to very fine electrified ultramicroscopic particles released from the metal.

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Sorption and Surface Area in Silica Aerogel

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Introduction

The discovery of a process[3] by which water can be removed from a hydrogel without the collapse of its structure has made it possible to learn facts about that structure that were formerly obscure. The present work was undertaken in 1935 as a part of a comprehensive program on the properties of gels but was interrupted after preliminary data had been taken by the departure of all three authors from the University. It had been hoped that a more complete study could be made before publication, but since no opportunity is before us, the information is here offered in its fragmentary state, since definite conclusions on some moot questions have already been attained.

Attention will be confined to silica aerogel and silica gel.

Several facts are known that should have a bearing on our conclusions. As silica gel sets, its mechanical properties strongly indicate a fibrillar nature to the elements of structure. Diffusion and electrical conductivity in the hydrogels indicate extremely free passage of particles the size of molecules through the solid framework, as does the fact that the liquid in a lump of gel at the critical temperature of the liquid can be released very rapidly without the outward rush of gas disrupting it.

Ultramicroscopic observations[4] that silica aerogel is optically empty would seem to eliminate a predominance of platelike elements of structure due to the fact that platelets with the solid volume and surface area of silica aerogel would certainly be large enough to produce visible reflections.

Some hollow structures, *e. g.*, tubules, are not excluded but probably must compose a minor fraction of the gel. Heat conductivity data[5] show that gas molecules can move freely within the structure of silica aerogel, and in flying from surface to surface travel on the average approximately 7×10^{-6} cm. between impacts. If the major portion of the structure were tubules with diameters of this magnitude they would almost certainly be visible in the ultramicroscope. In addition, they would have a combined area too small to account for the area as calculated from the heat conductivity data or as calculated from adsorption.[6]

The probable structure of silica aerogel is, therefore, a mat or felt of filaments, needles, etc., forming a three dimensional network. It can be much more accurately visualized as like a felt of glass wool in which many fibers are attached to each other at their points of contact, rather than as a system of capillaries. This picture would lead to the conclusion that the total surface area will not be much affected by compression of the aerogel to a smaller volume. References (3) and (4) show that the area of silica aerogel is of the same magnitude as that of some samples of silica xerogel (the gel prepared by drying in the usual manner).

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(2) Present address, U. S. Reduction Company, East Chicago, Indiana.

(3) Kistler, *J. Phys. Chem.*, **36**, 52 (1932).

(4) E. R. Riegel, private communication.

(5) Kistler, *J. Phys. Chem.*, **46**, 19 (1942); **39**, 79 (1935); *Ind. Eng. Chem.*, **26**, 658 (1934).

(6) Harvey, Dissertation, Princeton University, 1941.