experimental conditions are made more and more favorable for the induced reaction. These have accordingly been classed as examples of "induced catalysis," rather than as examples of "simple coupling." The results support the theory that oxygen reactions in general are chain reactions.

In a systematic investigation of the amount of the reaction between oxygen and iodide ion (R) which is induced during the reduction of vanadic acid (O_α) in acid solution, the induction factor has been raised from 0.01 to 12. Evidence that this is a case of induced catalysis is presented in Table I and Fig. 2.

Bäckström in 1927 studied the induced reaction between oxygen and sulfite ion under favorable conditions. His results show that induction factors as high as 48 and 1400 were attained when the oxidizing agents were hydrogen peroxide and peroxysulfate ion, respectively (Table III).

Credit for the discovery of induced catalysis belongs to Lenssen and Löwenthal, who in 1862 studied in detail the induced reaction between oxygen and stannous chloride in acid solution when the oxidizing agent was dichromate ion. They extended their investigation to include many other combinations of reducing and oxidizing agents (Table II).

In cases in which the reaction between oxygen and a reducing agent is induced while oxygen is reacting with a second more reactive reducing agent, examples of both simple coupling and induced catalysis are known.

BERKELEY AND LOS ANGELES
CALIFORNIA

RECEIVED DECEMBER 5, 1932
PUBLISHED JUNE 6, 1933

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Influence of Temperature on Certain Properties of Zirconium Oxide Sols

BY FRANCIS J. ROBINSON AND GILBERT H. AYRES

According to the method of preparation, zirconium oxide or hydroxide hydrosols have been found to show large variations in their properties as evidenced by the variety of sols, including so-called "ortho" and "meta" forms, described in the literature.[1] In this investigation the flocculation values, relative viscosities, *P*H values and intensities of scattered light of zirconium oxide sols which had been heated to temperatures ranging from 100 to 273° were determined.

Ayres and Sorum[2] have shown that the viscosities of pure ferric oxide sols which had been heated to temperatures above 100° decreased with

---

(1) Gmelin and Kraut, "Handbuch der anorganischen Chemie," Vol. VI (1), p. 698; Mellor, "A Comprehensive Treatise on Inorganic Chemistry," Longmans, Green and Co., New York, 1927, pp. 129–134; Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., Inc., New York, 1926, pp. 241–244.

(2) Ayres and Sorum, *J. Phys. Chem.*, **34**, 875, 2629, 2826 (1930).

increasing temperature of treatment, and from this they concluded that pure ferric oxide sols which had been heated to higher temperature were less hydrated than those heated to lower temperatures.

Mecklenberg[3] noted the diminished hydrophilic character of stannic oxide sols prepared at higher temperatures. Ghosh and Dhar,[4] however, report that zirconium oxide sols prepared in hot and cold solutions have practically the same viscosity. They also conclude that stability is not associated with hydration. Previously, they found that the viscosity of the closely related cerium oxide hydrosol prepared in cold solution was much larger than that prepared in hot solution.[5]

Experimental

Preparation of Sols.—A concentrated solution of pure $ZrOCl_2 \cdot 8H_2O$ was allowed to drop slowly into four liters of vigorously boiling distilled water. The sols were purified by warm dialysis (65–75°), using collodion bags and a continuous flow of distilled water, until small amounts of jelly had formed in the bottom of the dialysis bags. The sols were then carefully decanted into a flask. Portions of the dialyzed sol were diluted with distilled water, and left undisturbed for three weeks at room temperature to ensure separation of coarse material. Further dilution with water gave sol "C," while dilution with dilute hydrochloric acid gave sol "D"; sol "B" was a portion of the original, undiluted sol. Sol "A" was prepared in a manner similar to "C" but from a separate dialysate.

Analysis of Sols.—ZrO_2 was determined by precipitating the sol with ammonium hydroxide solution, drying at 115° for several hours and igniting the oxide. Chlorine was determined gravimetrically by the silver nitrate method after the sol had been digested with 3 *M* nitric acid for several hours. The analyses are given in Table I.

TABLE I

	ZrO_2		Cl		
Sol number	Grams per liter	Moles per liter	Grams per liter	Moles per liter	Ratio, moles ZrO_2:Cl
A	2.5124	0.0204	0.0771	0.0022	9.4
B	5.8420	.0475	.2730	.0077	6.2
C	2.5350	.0206	.1167	.0033	6.2
D	2.3962	.0195	.4095	.0114	1.7

Heating of Sols.—The sols were heated in a steel autoclave.[6] Pressure readings were converted to temperatures by means of data in steam tables.[7] Sols in series A were heated in a 150-ml. Pyrex Erlenmeyer flask covered with a closely fitting Pyrex cup and surrounded by a small amount of distilled water. Before and after heating, the sols were weighed; in only one case was there a loss of water greater than 5%. An amount of water equal to that lost in ebullition was added in each case.

The sols of series B, C and D were sealed in Pyrex test-tubes, and those of the same numbers in these series were heated simultaneously.

Viscosity.—Viscosities of the sols were determined at 25 ± 0.02° by means of an Ostwald viscometer, the time of efflux being taken with a stop watch reading to 0.2

---

(3) Mecklenberg, *Z. anorg. Chem.*, **64**, 268 (1909); **74**, 207 (1912).

(4) Ghosh and Dhar, *J. Ind. Chem. Soc.*, **5**, 303 (1928).

(5) Chakravarti, Ghosh and Dhar, *Z. anorg. allgem. Chem.*, **164**, 63 (1927).

(6) Ayres and Sorum, *J. Phys. Chem.*, **34**, 875 (1930).

(7) Moss and Callendar, "The Enlarged Heat Drop Tables," Longmans, Green and Co., New York, 1925.

second. The relative viscosities are shown in Fig. 1. The viscosities did not change during a period of several months. In this respect the behavior of zirconium oxide sols is similar to that of aluminum oxide sols (*P*H less than 6.5) studied by Yoe and Freyer.[8]

Flocculation Value.—Two ml. of sol was pipetted into Pyrex test-tubes, and sufficient distilled water and electrolyte solution were added to bring the mixture to a constant volume of 10 ml. After stoppering and uniform shaking, the sols were allowed to stand undisturbed for twenty-four hours. The coagulates from sols which had been heated to temperatures below 195° were usually of a transparent gelatinous character which were readily precipitated, however, as compact flakes on centrifuging the samples at 500 r. p. m. Flocculation was considered complete when no Tyndall beam was visible in the supernatant liquid.

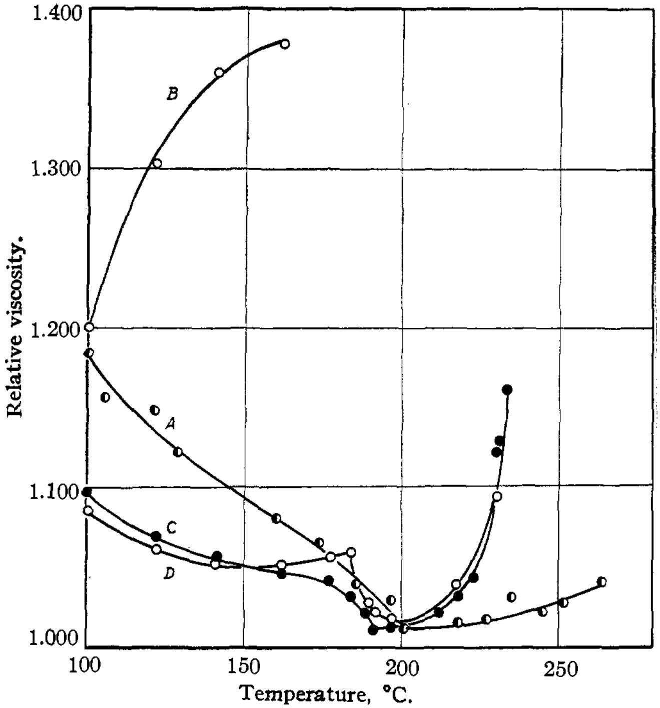

Fig. 1.

The results are shown graphically in Fig. 2; the flocculation values are calculated as the number of millimoles of potassium sulfate necessary to cause complete precipitation of the zirconium oxide in one liter of sol plus electrolyte mixture in twenty-four hours.

Hydrogen-Ion Concentration.—The *P*H values for the sols were determined with a glass electrode of the type described by MacInnes and Dole,[9] using a Partridge vacuum tube potentiometer.[10] After every third *P*H determination on a sol, the electrode was checked with a buffer solution the *P*H of which had been ascertained with a hydrogen electrode.

The results are shown in Fig. 3.

---

(8) Yoe and Freyer, *J. Phys. Chem.*, **30**, 1389 (1926).

(9) MacInnes and Dole, THIS JOURNAL, **52**, 29 (1930).

(10) Hazel and Sorum, *ibid.*, **53**, 49 (1931).

Intensity of Scattered Light.—The intensity of light scattered by sols of the same zirconium oxide content was determined from readings with a nephelometer. Procedures outlined by Yoe[11] were followed in correcting the original values for light scattered by the instrument and dispersion medium. For each sol four or five readings were taken and averaged. These readings deviated not more than 10% for any one sol, although average values for different sols of the same ZrO_2 concentration showed differences as high as 300-fold. The relative intensities of the scattered light are expressed in terms of that of Sol C-6 which is taken as unity. The results are shown in Fig. 4.

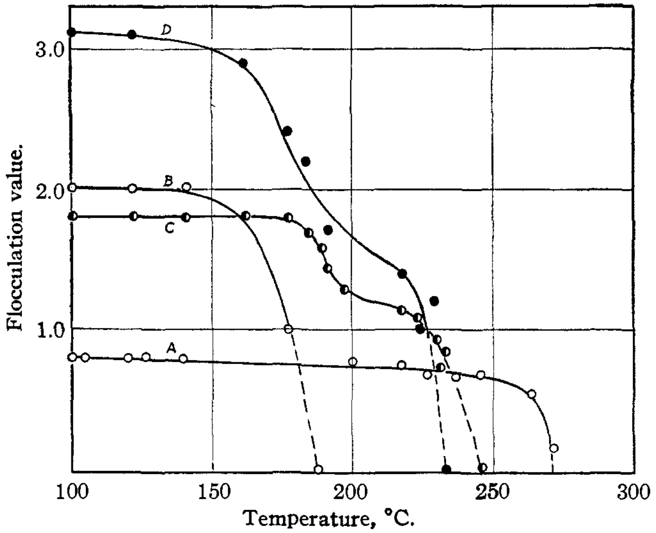

Fig. 2.

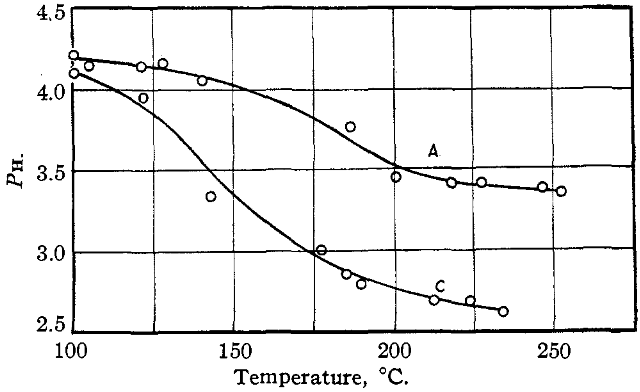

Fig. 3.

Figure 5 represents in composite form the effect of heat treatment on the *P*H, viscosity, flocculation value and intensity of scattered light of sols of series C.

---

[11] Yoe, "Photometric Chemical Analysis," John Wiley and Sons, New York, 1928, Vol. II.

Discussion

Sols A, B and C are relatively pure if we compare the chlorine content with that of sols used by other investigators. Thus Hüttig and Wehling obtained a *weight Cl : weight Zr* ratio of 1:20; Ghosh and Dhar, 1:7; and Adolf and Pauli, 1:8.[12] Sols with a relatively smaller chloride content may be prepared by decreasing the zirconium content. A less gelatinous type of zirconium oxide sol can be prepared by heating a solution of zirconium oxychloride to temperatures above 130°. If a loose white precipitate is formed, it may be peptized by water to give a sol which has a clear orange-red appearance by transmitted light, but appears a bluish milky white by reflected light. Ruer[13] described a somewhat similar sol prepared by repeatedly boiling down an aqueous solution of $ZrOCl_2$. This "meta-zirconic oxide sol" appeared to require less peptizing electrolyte than the "ortho" or hydroxide form and resembled the ferric oxide sols more closely than did the so-called "ortho-zirconic oxide" sol.

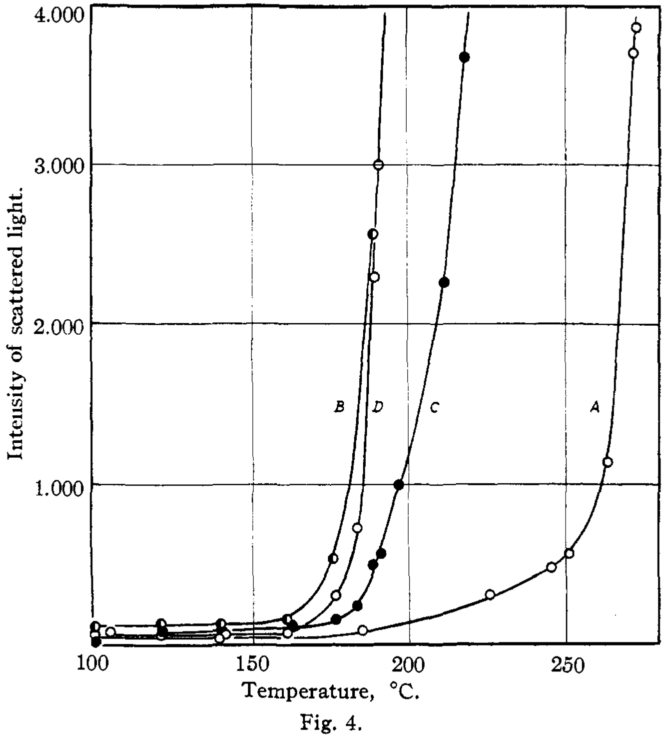

Fig. 4.

Samples of Sols A, B and C were observed with the slit ultramicroscope. Those of series A and C which had been heated to temperatures up to

---

(12) Hüttig and Wehling, *Kolloidchem. Beihefte*, **23**, 365 (1927); Ghosh and Dhar, *J. Ind. Chem. Soc.*, **6**, 31 (1929); Adolf and Pauli, *Kolloid-Z.*, **29**, 173 (1921).

(13) Ruer, *Z. anorg. allgem. Chem.*, **30**, 1389 (1926).

approximately 200°, and samples of series B which had been heated to temperatures up to about 160°, appeared quite similar. The particles gave bright, slowly scintillating iridescent images against a dark background; they appeared to be relatively few in number since it was unnecessary to dilute the sol with more than five volumes of water to secure well separated images. Sols which had been heated to temperatures higher than 200° showed a different ultramicroscopic image; the entire cone was brightly illuminated and still remained bright after the sol was greatly diluted; its color, compared with that of the bluish cone shown by ferric oxide sol, appeared to be much whiter. A marked increase in the number of visible particles and a "grainy" appearance indicated what probably were a large number of particles too small to give distinct diffraction images.

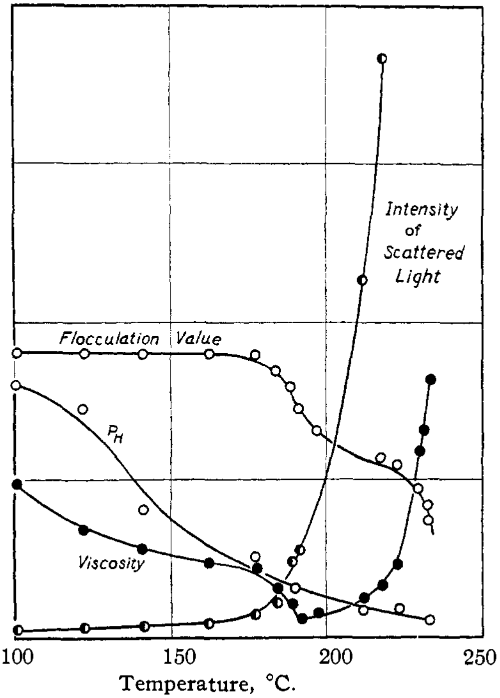

Fig. 5.

Two sols of series A and C which had been heated to 185–200° and left undisturbed at room temperature for several months, showed the formation of irregularly shaped transparent plates approximately 0.1 to 0.5 mm. in length and having a thickness of the order of the wave length of light, since they could be seen only when iridescing. A sample of a sol showing this phenomenon was evaporated at 90°, leaving a residue containing some colorless, transparent needle-like crystals. Examination of one of these crystals with the petrographic microscope revealed that it was birefringent, biaxial. A portion of this residue was examined by the Hull, Debye–Scherrer powder method of x-ray analysis, but the interference bands obtained were few and indistinct. No definite conclusions may be drawn from these few data.

Ruff and Ebert[14] in a review of the crystalline structure of zirconium oxide mention no definite hydrate. Simon and Fischer[15] also show that the ordinary precipitated hydroxide loses water continuously when dried

---

(14) Ruff and Ebert, *Z. anorg. allgem. Chem.*, **180**, 19 (1929).

(15) Simon and Fischer, *ibid.*, **185**, 130 (1930).

in vacuum. Haber, and Böhm and Niclassen[16] could detect no crystalline structure in the freshly precipitated zirconium hydroxide nor in the hydroxide which had been precipitated and dried below 400°. No x-ray analyses of the aged sol have been reported, although Weiser[17] points out that aged sols usually assume micro-crystalline form while the corresponding hydrous oxides when first prepared are entirely amorphous.

The authors are indebted to Dr. C. Harvey Sorum and Dr. Fred Hazel for numerous suggestions during this investigation, and to Dr. Hazel also for valuable assistance in making the *P*H determinations.

Summary

1. Zirconium oxide hydrosols have been prepared and heated to temperatures up to 275°.

2. Measurements have been made on their relative viscosity, flocculation value, *P*H and intensity of scattered light.

3. High temperature was found to produce a decrease in viscosity, flocculation value and *P*H, and an increase in the intensity of scattered light.

4. The data presented indicate that the sols heated to higher temperatures are less hydrated than those heated to lower temperatures.

---

(16) Haber, *Ber.*, **55**, 1717 (1922); Böhm and Niclassen, *Z. anorg. allgem. Chem.*, **132**, 1 (1924).

(17) Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., Inc., New York, 1926, p. 238.

MADISON, WISCONSIN RECEIVED DECEMBER 5, 1932
PUBLISHED JUNE 6, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Nature of the Sorption of Water by Charcoal

JAMES W. McBAIN, J. L. PORTER AND R. F. SESSIONS

It is commonly supposed that water is not sorbed by charcoal but is taken up by capillary condensation of the liquid as such;[1] all ordinary estimates of the surface of charcoal are based upon this assumption. Our experiments appear to disprove this point of view. When activated sugar charcoal is exposed to water vapor, the charcoal undergoes linear expansion instead of the contraction that would be necessitated by the assumption of capillary columns with concave menisci. Part I of this communication describes experiments (by J. L. P.) on the expansion of charcoal caused by exposure to the vapors of water, benzene and heptane, respectively.

Part II describes isotherms for the sorption of water by charcoal. The sealed up sorption balance admits of far more rigorous evacuation than any hitherto employed. The result is that sorption of water vapor sets

---

(1) For example, Lowry, THIS JOURNAL, **46**, 837 (1924); Cude and Hulett, *ibid.*, **42**, 391 (1920); Knudson, Dissertation, State University of Iowa (1924); Brown, *Phys. Rev.*, [2] **17**, 700 (1921); Lavine and Gauger, *Ind. Eng. Chem.*, **22**, 1226 (1930); Kreulen and Ongkiehong, *Brennstoff-Chem.*, **10**, 317 (1929).