

[CONTRIBUTION FROM THE BUTTERFIELD CHEMICAL LABORATORY, UNION COLLEGE]

Studies on the Hydrogel of Titania. I. The Effect of Temperature on Time of SetBY CHARLES B. HURD, WILLIAM J. JACOB¹ AND DAVID W. GODFREY²**Introduction**

The discovery of a hydrogel of titanium dioxide over one hundred years ago by Rose³ opened a field of study which has been very much neglected. A comparison of the literature of this field with the literature concerning silicic acid gels will show a great contrast. In particular, very little information on the time of set of these hydrogels of titania is available.

Since recent studies of the effect of temperature on the time of set of silicic acid gels have made it possible to calculate what we have called the energy of activation of the setting process, we have believed that similar measurements and calculations for the corresponding titanium compounds would prove valuable. The relation of silicon and titanium in the periodic table makes these results the more interesting.

The present paper is a report of some results which seem significant.

Historical.—In the case of hydrogels of titania, as is also true with silicic acid gels, most methods of preparation of the hydrogel start with the preparation of the hydrosol. Under suitable conditions of concentration, the hydrosol will go over into the hydrogel.

Methods for preparing the hydrosol of titania are described elsewhere.⁴ In general, they consist of the hydrolysis of titanium compounds such as the tetrachloride, the sulfate, the tartrate or tetraethyl orthotitanate. The solution resulting from the hydrolysis may be dialyzed. This process, of course, raises the pH of the solution. A number of methods have been used where the pH of an acid solution containing titanium has been raised by the addition of an alkali. This was done by Pfordten⁵ and, more recently, by Klosky and Marzano.⁴ They dissolved an alkali titanate in hydrochloric acid and then partially neutralized the solution with an alkali carbonate. This method was used in the present paper.

We should note here that the commonest method for preparing silicic acid gels in investi-

gations on the time of set, namely, the mixing of solutions of sodium silicate and an acid, is impossible with titanium compounds since sodium titanate is practically insoluble in water. This is unfortunate, since that method with sodium silicate solution and an acid gives very accurate timing.

Experimental

The preparation of hydrogels of titania is rendered the more difficult since hydrated titanium dioxide shows different behavior under different conditions. The statement is encountered that titanic acid exists in two forms, the one known as α -titanic acid or orthotitanic acid, and the other known as β -titanic acid or metatitanic acid. These terms are not exact and cause confusion. Although Weiser and Milligan⁶ have shown that the α -acid and the β -acid give the same results on X-ray analysis, namely, that of the mineral anatase, and appear to consist of anhydrous titania and adsorbed water, it is evident that the two forms show a very different chemical activity. The α -acid is easily soluble in dilute acids and is readily peptized by alkaline solutions to give stable sols. The α -form changes slowly in cold solutions and rapidly in hot solutions into the granular β -form, which is practically insoluble in dilute acids.

From the "glow phenomenon," it is concluded that the α -form contains considerably more energy than the β -form. The marked tendency to change from the α - to the β -form does cause trouble in the study of hydrogels of titania.

We may note here that Brintzinger⁷ believes that molecular titanic acid results momentarily during the hydrolysis of tetraethyl orthotitanate, but that this condenses very rapidly. His idea is similar to the one which has been suggested for silicic acid.⁸

After a study of the various methods available for preparing the hydrosol and hydrogel of titania, it was decided that the method of Klosky and Marzano,⁴ with some modification, offered the best opportunity for obtaining the time of set. There is one serious difficulty with this method, namely, that during the addition of the alkali carbonate to the solution of sodium titanate dissolved in hydrochloric acid, a precipitate is apt to form. This has been mentioned by several workers. They stressed the fact that the solution must then be shaken vigorously until the precipitate is dissolved or peptized.

The sodium titanate used in our investigation was obtained from the Titanium Alloy Manufacturing Company. It contained 60.0% TiO₂, 0.50% SiO₂, 36.0% Na₂O, with 3.5% loss on ignition and miscellaneous impurities. A total of 1000 g. of this sodium titanate was dissolved in 2700 g. of c. p. concentrated hydrochloric acid. The titanate was added very slowly, in small portions, with con-

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(3) Rose, *Gilbert's Ann.*, **73**, 67 (1823).(4) Klosky and Marzano, *J. Phys. Chem.*, **29**, 1125 (1925).(5) Pfordten, *Ber.*, **17**, 727 (1884).(6) Weiser and Milligan, *J. Phys. Chem.*, **38**, 513 (1934).(7) Brintzinger and Brintzinger, *Z. anorg. Chem.*, **196**, 44 (1931).(8) Hurd, *Chem. Rev.*, **23**, 408 (1938).

stant stirring. The beaker containing the acid was cooled in an ice-bath and the temperature was kept below 50° to prevent formation of metatitanic acid. The solution, although yellow, was slightly milky and was filtered through an asbestos layer in a Gooch crucible. The clear solution was of a strong lemon-yellow color.

Three methods of adding the sodium carbonate solution to the acid titanate solution were used. In the first method, 8.0 cc. of 0.75 *N* sodium carbonate solution was added to 2.0 cc. of the acid titanate solution. Then, to this mixture was added 26 cc. of 0.19 *N* sodium carbonate solution. No precipitate formed and the mixtures were reproducible. The mixture was placed in three 6" × 5/8" test-tubes, the tubes were stoppered and placed in a water filled, electrically controlled thermostat. A sample was also taken to determine the pH at 25° with a quinhydrone potentiometer. The time of set was determined by the "Inverted Tube" method of Flemming.⁹ Since frequent testing disturbs the gel, two of the three tubes were used to roughly determine the time of set, thus preserving the third tube for an accurate determination. The averages of a number of determinations at three temperatures are shown in Table I as Series I.

In the second method, 7.0 cc. of a 0.75 *N* sodium carbonate solution was added to 2.0 cc. of acid titanate solution. This was allowed to stand for twenty-four hours. Then 6.0 cc. of 0.21 *N* sodium carbonate solution was added, the mixture thermostated, and time of set and pH were determined. The results are in Table I, Series 2.

A third method, namely, addition of 15.0 cc. 0.21 *N* sodium carbonate solution to 2.0 cc. acid titanate solution in one step only gave mixtures which were immediately thermostated. Time of set was determined as before. Table I, Series 3, gives the time of set. These mixtures were more acidic, but ran at higher temperature. Control of temperature was not so close as in Series 1 and 2.

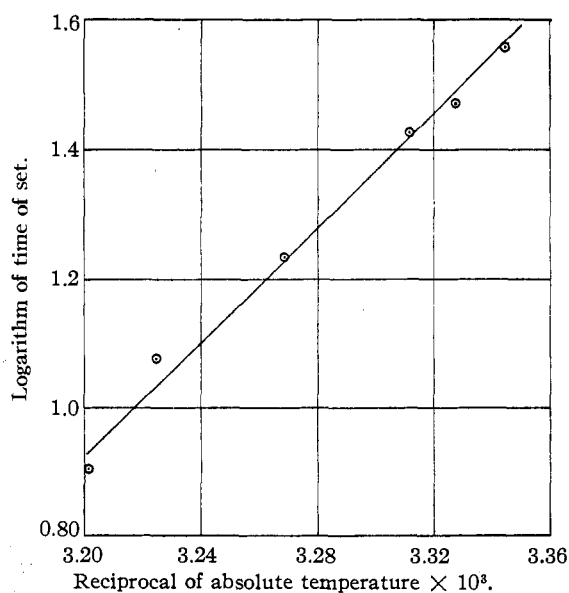


Fig. 1.—Effect of temperature on time of set of hydrogels of titania.

(9) Flemming, *Z. physik. Chem.*, **41**, 427 (1902).

The compositions and pH values for the mixtures are given in Table II.

TABLE I
TIME OF SET (IN MINUTES) OF HYDROGELS OF TITANIA

Series 1		Series 2		Series 3	
Temp., °C.	Time of set	Temp., °C.	Time of set	Temp., °C.	Time of set
13.0	615	26.0	37	70	16.0
26.0	95	27.5	30	80	7.0
32.2	37.1	29.0	27	90	2.75
		34.0	17	100	1.25
		37.5	12		
		39.0	8		

TABLE II
COMPOSITIONS AND pH VALUES OF MIXTURES SHOWN IN TABLE I

	TiO ₂	Na from titanate	HCl	Na ₂ CO ₃ added	pH
Series 1	0.15	0.23	0.39	0.14	1.90
2	.35	.54	.64	.22	2.75
3	.31	.48	.56	.09	<2.75

From the data of Table I were determined the logarithms of times of set. By plotting these against the reciprocal absolute temperatures the energy of activation may be obtained by multiplying the slope by 2.30*R*, as was first shown by Hurd and Letteron¹⁰ for silicic acid gels. Linear curves were obtained for the three series as shown by Fig. 1 for Series 2, which is the most complete. Values for the energy of activation, *Q*, are given in Table III.

TABLE III
ENERGY OF ACTIVATION OF HYDROGELS OF TITANIA
Q in calories

Series 1	25,700
2	21,400
3	20,500

Discussion

The accurate determination of the times of set of various hydrogels of titania has been found to be more difficult than the same determination with silicic acid gels. Titania gels are much less stiff and elastic than are silicic acid gels of equal molar concentration. There appears to be a skin effect with the titania gels, that is, a skin forms as the gel mixture is setting which is tougher than the material in the interior. These factors interfere with the accuracy of the determination of time of set.

Some of the gels were allowed to stand for a time after they had set. Many of these broke down, giving a granular precipitate in a liquid

(10) Hurd and Letteron, *J. Phys. Chem.*, **36**, 604 (1932).

medium. This material is probably what is loosely termed β -titanic acid. An X-ray diffraction examination would probably classify this material, although such an examination was not made. The effect which produced the precipitate is apparently not syneresis, since the volume of the granular precipitate is only a small fraction of the volume of the liquid.

A peculiar effect was discovered when a gel which had set at a higher temperature was suddenly cooled. The material liquefied. If this was again raised to the higher temperature, it was found to regel. This cycle was repeated five times for one mixture which set at 80°. This phenomenon is being reinvestigated.

In spite of the peculiarities in the setting of these hydrogels of titania, we believe that the values of the energy of activation, using three different methods of mixing, are approximately correct. These hydrogels set more rapidly as the temperature is raised. A value of the energy of activation of 22,000 calories appears reasonable.

In these acidic mixtures, the gels set more rapidly, as the pH increases, for a given concentration of titania. They also set more rapidly, with a given pH , as the titania concentration increases. The behavior here resembles that of silicic acid gels.

The formation of β -titanic acid appears to prevent the formation of the gel; in fact, when the gels broke down, apparently the β -titanic acid was formed. The β -acid is thus, apparently, a

form with lower energy content than either the gelatinous α -acid or the form present in the gel. There are not sufficient data here to contribute much information to clarify relations between the α - and β -acids and the gel.

If a monotitanic acid is first formed when the alkali carbonate reacts with the acid titanate solution, as was suggested by Brintzinger,⁷ the condensation process must be rapid. It should be noted here that considerably more evidence is at hand to show the amphoteric character of titanium hydroxide than is available to show the amphoteric character of silicon hydroxide.⁸ This amphoteric nature of the hydroxide affords an easy way of explaining the condensation mechanism.

Summary

A study of some properties of the hydrogel of titania has been made.

These gels are softer than silicic acid gels of equivalent concentration. They also break down on standing to give a granular precipitate.

An approximate value of 22,000 calories for the energy of activation was obtained. This is higher than the value of 17,000 calories for silicic acid gels.

Acidic mixtures set more rapidly with increases in the pH , the titania content or the temperature.

Gels set at a higher temperature were liquefied by rapid cooling.

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RECEIVED NOVEMBER 18, 1940

[A CONTRIBUTION FROM THE PHYSICAL CHEMISTRY RESEARCH LABORATORY OF NORTHWESTERN UNIVERSITY]

The Theory of the Glass Electrode. V. The Influence of Negative Ions

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Introduction

It has long been believed that the type or relative concentration of negative ions is without influence on the behavior of the glass electrode either in acid or alkaline solutions.¹ However, we have been informed by an industrial research chemist that the use of the glass electrode in solutions containing borate or fluoride ions encounters difficulties, in the latter case in solutions too alkaline for hydrogen fluoride attack on glass

(1) A complete discussion of the theory of the glass electrode with references is to be found in the monograph by Dole, "The Glass Electrode," to be published by John Wiley and Sons, Inc.

(according to this chemist). Furthermore, no careful investigation has been carried out on the effect of the smallest negative ions such as the hydroxyl, fluoride or chloride ions which might be expected to be the negative ions most likely to interfere with the hydrogen electrode function of glass electrodes. Finally, a certain discrepancy between some of the data of Dole and of Dole and Wiener² was thought possibly to be due to a difference in the type of negative ions in their buffer solutions, as the other experimental condi-

(2) (a) M. Dole, *THIS JOURNAL*, **53**, 4260 (1931); (b) M. Dole and B. Z. Wiener, *Trans. Electrochem. Soc.*, **72**, 107 (1937).