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SOME EXPERIMENTS ABOUT THE OXYGEN AND HYDROGEN REACTION.

KCL EFFECT ON THE SURFACE OF STEEL.

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Introduction.

The fact that oxy-hydrogen reaction may be retarded by the existence of KCl has been often discussed by many experimenters.

For examples, Pease(1) found, when oxy-hydrogen gas passes through KCl coated pyrex tube, the H_2O_2 amount contained in exit gas decreases and the ignition temperature of oxy-hydrogen mixture becomes higher than the case of no existence of KCl.

Prettre(2) and Oldenberg(3) also found this retarding action of KCl in the pyrex glass vessels.

On the other hand, about some experiments in steel vessel, it has found that the reaction might have been proceeded by KCl.

The author and Y. Araki examined this questionable action of KCl both in steel vessels and in terex glass vessels and found the following results.

1. In steel vessels, KCl did not indicate the retarding action upon the oxy-hydrogen reaction and rather indicated the proceeding action.

There was no existence of pressure change usually accompanied with explosion wether existence of KCl or not.

2. In terex glass vessels, KCl retarded considerably the slow reaction and lowered the upper limits of explosion. The coated KCl showed the strong after effects, then to cleaning it off from the wall of the vessel, frequent washing by chromic acid mixture, caustic soda, pottasium permanganate, benzene and alchol was demanded.

This after effect predicted that the surface of the wall had any relations to the explosion as well as the slow reaction.

These results may indicate for us that the actions of KCl in steel vessels are different from that in glass vessels.

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1) Pease, *J. A. C. S.*, **52**, 5106 (1930).

2) Prettre, *Comp. rend.*, **200**, 1321 (1935).

3) Oldenberg and Sommer, *J. Chem. Phys.*, **8**, 468 (1940), **9**, 114, 432 (1941).

The author, then, in further experiments, discussed this different actions of the KCl on the steel surface.

Apparatus and Expermental methods.

The reaction vessel was a terex glass tube (16.5 cm. length and 2.8 cm. outer diameter).

A piece of soft steel plate (10 × 10 × 1 mm.) was put in this reaction vessel.

The temperature of the reaction vessel was measured by Alumel-Chromel thermoelement inserted in the electric furnace cross contacting to the reaction vessel.

The proceedings of the reactions were measured by the pressure changes of Hg manometer directly connected to the reaction vessel. The dead space between the reaction vessel and the Hg manometer was heated to about 100°C to mininize the condensation of the reaction products.

Before each experiment, the reaction vessel was heated about 540°C for several hours, at first exhausting the air by oil pump, then filling up with hydrogen gas.

After two or three times of this procedure, the gas in the vessel was again exhausted by oil pump for about an hour and the temperature of it brought about to the experimental temperature.

Into this pretreated vessel, a definite amount of hydrogen was filled, then oxygen (half amount of hydrogen) was added. This instant we defined the starting point of the reaction.

Results.

(1) The reactions in the terex glass vessel, containing a piece of steel plate.

The results are indicated in fig. 1.

The experimental conditions

Temperatures, 496°, 447°, 397°C.

Initial pressures, 740, 500, 250 mm.-Hg.

At high temperatures, the reactions of lower initial pressure indicate higher ratios of pressure change than that of higher initial pressure.

This fact is the same as the preceeding experimental results in the steel vessel and may be suggested for us the strong adsorption of the reaction products by the steel surface.

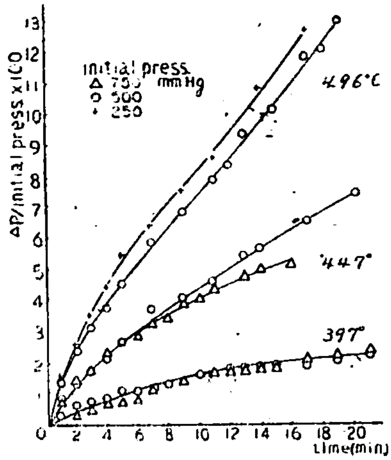


Fig. 1.

From the shapes of the curves, it is shown that the reaction initially proceeds at high velocities, then becomes slowly. (About 15 minutes later from the initial point, pressure changes again become large, but this phenomena are thought to be the condensation of the reaction products, even if the dead space of the reaction vessel are heated up to about 100°C.)

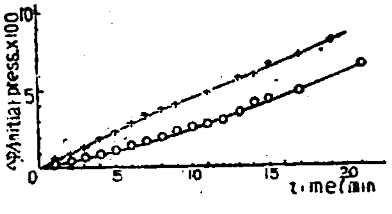
(2) The reactions in the KCl coated terex glass vessel containing a piece of steel plate.

The vessel used in the above experiments was washed with nitric acid, chromic acid mixture and water and coated by saturated KCl solution.

Into this vessel, the same steel plate was inserted and sealed.

Before each experiment, the vessel was pretreated in the same manner as above mentioned.

In this case, the reactions were considerably retarded and the surface of the steel plate covered with a yellow brownish material. Then using this vessel without steel, we repeated the oxy-hydrogen reaction and found that it was very much retarded, and further more we found this retarding effect was never swept off by washing the vessel with concentrated nitric acid, chromic acid mixture and etc.



initial press.
o 500 mmHg
+ 250 mmHg

Fig. 2.

The reaction in this strongly poisoned vessel containing the clean steel plate is indicated by fig. 2.

These curves may perhaps represent that the reaction on the surface of the steel plate have two different forms.

One is an autocatalytic one and another the one sugesting a catalytic reaction on steel surface.

Also from both curves, we find that the ratio of pressure changes to the initial pressure is smaller in the former than in the latter in spite of the initial pressure of the former is half of the latter.

(3) The reactions when both vessel and steel plate are coated with KCl.

The steel plate used in the above experiments was coated with sat. KCl solution and dried in the air without heating.

In these KCl coated vessels with steel plate, the reaction proceeds as shown in Fig. 3.

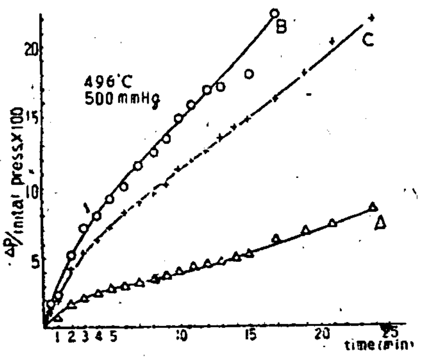


Fig. 3.

In this figure, the curve A, B and C indicate the order of experiment, i. e. A is the reaction which is pretreated by heating for several hours at 500°C at first in vacuum and next in the presence of hydrogen. B is the reaction pretreated as before after the experiment A. C is the reaction after B (the same pretreatments as B).

The experimental temperature and the initial pressure are 496°C and 500 mm. Hg. respectively.

From these curves, we can see that the repetition of the reaction becomes difficult by means of KCl coating on the steel, but these reactions proceed initially, then are retarded ; and also in the cases of B and C reactions, there occur larger pressure changes than without KCl.

The fact that the pressure change caused by the reaction increases by means of the coating of the steel plate with KCl is quite different from the glass vessel alone.

Discussions.

The oxy-hydrogen reaction in terex glass vessel containing a steel plate may be suggested from the pressure change caused by the catalytic actions of Steel.

From the strong remaining effect of KCl, we can consider that KCl may combine chemically with glass surface, particularly in the existence of steel.

The oxy-hydrogen reaction on steel plate may be shown in Fig. 2 and in this case it is very much retarded. This reaction also indicates the surface catalytic action of steel and suggests a strong adsorption of reaction products from the inverse action of initial pressure on the pressure change.

In this case, it is interesting to mention that the autocatalytic reaction may proceed at higher pressure.

The facts that the reaction on the KCl coated steel which is inserted in the KCl poisoned glass vessel lacks very much the repetition of reactions and the pressure changes in this case are much remarkable in comparison with the steel without KCl, may be interpreted by the secondary reaction on the steel surface of KCl. For example, if the condition of KCl coated on the steel is different from that of KCl on the glass, and KCl coats the steel coarsely, the reacting gas will diffuse freely along the intergranular space of KCl into the surface of steel and react catalytically on the surface. Then there, the reaction products will react with KCl, as it is not easily left off from the surface. Accordingly the condition of the steel surface will change from time to time and it will be deduced that the repetition of reaction is difficult and the pressure changes also become considerably large. About the difficulty of the desorption of the reaction products, we can see from the strong adsorption of it and about this strong adsorption, we can see from the strong adsorption of it and about this strong adsorption, we can see from the inverse action of the increase of the initial pressure on the reaction and the necessity of the pretreatment for several methods.

If such secondary actions on the KCl coated steel surface are introduced in our considerations, we can easily understand that the pressure changes in the KCl coated steel vessel should become large in comparison with that in a glass vessel.

The reaction on a steel vessel may be a surface catalytic reaction and that of a glass vessel may be an autocatalytic reaction, as many authors have induced.

These conclusions may be justified by examining the remaining effects of KCl on the steel surface. It will be shown later.

Conclusion.

KCl effects on oxy-hydrogen reaction are examined in the terex glass vessel containing the steel plate.

Catalytic reaction of the steel surface may arise and KCl may react with the reaction products.

This secondary reaction may proceed considerably fast, so that pressure changes following the reaction may proceed faster than the case of no KCl.

We express our gratitude to Prof. Horiba and Prof. Goto for their kind guidance.

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