

Letters to the Editor.

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Influence of Hydrogen on Chemical Changes in Silica Vessels.

CHEMICAL literature has of late contained several references to the influence of adsorbed hydrogen on silica on chemical changes taking place in silica vessels. At the same time the fact that silica, at moderately high temperatures, takes up very large quantities of hydrogen is stressed, and it is assumed that this hydrogen is adsorbed, that is to say, exists as a film on the gas-glass interface. However, the following experiments seem to indicate that this is only a part of the story.

During the past year we have been studying the condensation of ethane at 600°, by heating the pure gas, generally at concentration of 0.025 gram molecules per litre, in sealed silica tubes for periods up to eight hours. During the first few minutes a part of the ethane is decomposed into ethylene and hydrogen; but when equilibrium conditions are approached this reaction slows down, so that the hydrogen content of the tube varies but little or not at all during the latter periods. Hydrogen plays no direct part in the secondary reaction, or reactions, which lead to the formation of methane and a condensate of aromatic compounds.

Now, though hydrogen plays no direct part in the secondary processes, it plays a very important indirect part; for if hydrogen is added to the ethane to increase the hydrogen content of the reaction mixture by a small amount, the rate of formation of condensate diminishes rapidly, and a relatively small increase in the hydrogen condensate inhibits the formation of condensate altogether. However, we will only refer to this point in passing.

Down to a few weeks ago we had carried out a large number of experiments, using about twenty different silica reaction tubes, and had come only to the conclusion that the hydrogen played some part in the reactions, which we were absolutely unable to understand or to control. We were unable to reproduce experimental results, though in two series of experiments an apparent regularity nearly misled us to the conclusion that the condensation of ethane was primarily a unimolecular process.

Reasons which we cannot set forth in detail led us, however, to adopt a method of experiment which gave results which we believe to be both new and interesting. We observed that the results were more erratic when we used thin silica tubing than when moderately thick walled tubing was used, suggesting that, since hydrogen can pass fairly rapidly through silica at 600°, the solubility of the hydrogen in the silica was a factor which must be reckoned with, since the hydrogen in the adsorbed layer must obviously be in equilibrium with the hydrogen in the glassy and gaseous phases. We therefore carried out two series of experiments. In one, we used a very thick-walled reaction tube, and heated it for 15 hours when full of hydrogen to the reaction temperature, before exhausting, cooling, and filling with ethane for an experiment. The other was a thin-walled tube, but it was enclosed in an outer tube, and the space between the tubes was filled with hydrogen during the pre-treatment and during the actual experiment. The results were now absolutely reproducible, and those obtained with the two tubes were sensibly identical.

We suggest that the idea which led us to carry out these experiments is a correct one, and that in dealing with such materials as silica and palladium, through which hydrogen passes readily, the equilibrium system is rather a complex one, and consists of:

Glassy phase :: Glass-gas interface :: Gas-glass interface :: Gas phase

It is possible that in the solid or glassy phase the hydrogen may be more highly dissociated than in the gaseous phase, so that we have to consider the equilibria:

Glassy phase | Glass-gas interface | Gas-glass interface | Gas phase
 $H_2 \rightleftharpoons 2H$ | $[H_2 \rightleftharpoons 2H]$ | $H_2 \rightleftharpoons 2H$ | $[H_2 \rightleftharpoons H_2]$ | H_2 | $[H_2 \rightleftharpoons H_2]$ | H_2

The hydrogen atoms in equilibrium in the gas-glass interface and in the gas phase may be so small as to be negligible; however, the life of hydrogen atoms passing out from the glass-gas interface into the gas-glass interface may be long enough to effect those processes which are commonly attributed to atomic hydrogen in the adsorbed layer (gas-glass) on the silica.

Now that we have been able to stabilise the silica-gas system, and to obtain reproducible results, we have been able to study another phenomenon, which is rather striking. The process of condensation of ethane with formation of methane and condensate appears to be catalysed and accelerated, so that, representing the amounts of product obtained as ordinates and time as abscissæ, the curve representing the change, in either case, has an upward tendency. Now over a range between 570° and 610° C., and at concentrations between 0.025 and 0.0125, and whether in the thick-walled tube or in the double-walled tube, the rate of formation of condensate or of methane undergoes so sudden a change after a period which is always almost exactly 2½ hours from the commencement of the experiment, that one is inclined to connect the phenomenon with some change of an explosive character such as all forms of silica undergo when changing from the α to the β form, or vice versa. What the nature of the change is we do not know, but we suggest that it may be a chemical change, facilitated by the fact that the silica surface, like the interior surface of all tubes, is in tension, when, as we now know, reactions can take place which general thermodynamic data would indicate to be impossible.

These matters are the subject of further investigations.

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The Composition of the Blood of Aquatic Animals and its Bearings upon the Possible Conditions of Origin of the Vertebrates.

Forty years ago a suggestion was made (Bunge)¹ that the sodium chloride in the human tissues might be a relic, an inherited feature of some aquatic marine ancestor. The same idea was expressed in certain papers by Quinton,² who stated that so far as salinity is concerned the blood of most animals is an altered sea water. In 1903,³ Macallum, then unaware of the suggestions of Bunge and Quinton, advanced the theory "that the blood plasma of vertebrates and invertebrates with a closed circulatory system is, in its inorganic salts, but a reproduction of the sea water of the remote geological period in which the prototypic representative of such animal forms first made their appearance". He regarded the differences between the blood salinity of the higher vertebrates and the