22. *The Heterogeneous Combustion of Carbonic Oxide on Quartz: Water as a Negative Catalyst.*

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Although it is well established that the effect of rigorously drying a gold surface catalysing the combustion of carbon monoxide–oxygen mixtures is considerably to reduce the rate of reaction (Bone, *Proc. Roy. Soc.*, 1926, **112**, *A*, 474) and simultaneously to increase the apparent heat of activation (Finch and Bradford, *ibid.*, in the press), yet there is some conflict of evidence regarding the influence of moisture on the heterogeneous reaction catalysed by a quartz surface. Topley (*Nature*, 1930, **125**, 560) investigated the combustion in heated silica bulbs and found that reaction was apparently homogeneous; the rate was approximately proportional to the concentration of water vapour, and was immediately reduced by drying. More recent experiments by Hadman, Thompson, and Hinshelwood (*Proc. Roy. Soc.*, 1932, **137**, *A*, 87) gave somewhat similar results, but further established that in the dry the reaction was chiefly heterogeneous, and in the presence of moisture, largely homogeneous.

In the course of Finch and Bradford's investigation (*loc. cit.*), an electrically heated, transparent quartz reaction tube (diam. 4·2 cm.; heated length 50 cm.) was dried for 4 months at a maximum temperature of 600° by circulation of a $2CO + O_2$ mixture in a closed system which included a liquid-air cooled trap and several 2 m. long phosphoric oxide drying tubes; the rates of combustion of the gaseous mixture were then determined at a series of temperatures. The quartz tube was next put in communication with an alternative circulation system, and rates of combustion similarly determined in the presence of a constant partial pressure of water vapour. The following results were obtained; in all cases the rates of fall of pressure closely followed a unimolecular law, of which the coefficient k is given:

	Dry.					*Moist* ($p_{H_2O} = 15$ mm.).				
Temp.	333°	457°	508°	571°	602°	350°	502°	550°	567°	580°
$k \times 10^4$	0	1	11	47	63	0	1	2	7	12

(Explosion occurred in the moist system at 588°, at a total pressure of 90 mm., a result in fairly good agreement with the lower explosion limit determined by Kopp, Kovalsky, Sagulin, and Semenov, *Z. physikal. Chem.*, 1930, **6**, *B*, 307.) It is clear from the above results that the apparent heat of activation was higher in the moist than in the dry. The practicable range of temperature was insufficient to allow of more than an approximate determination : substitution in the Arrhenius equation indicates a value of about 25,000 cal. in the dry, and 40,000 cal. in the moist.

The characteristics of both the moist and the dry reaction were consistent with heterogeneous combustion. The rates of reaction in the dry system correspond in magnitude to those observed in comparable conditions by Hadman, Thompson, and Hinshelwood (*loc. cit.*), whereas in the moist system the rates are 50—100 times less, the former comparison being made with a heterogeneous, and the latter with a homogeneous reaction. The catalytic properties of quartz at temperatures in the neighbourhood of 600° are well known to be capable of extensive variation (Cosslett and Garner, *Trans. Faraday Soc.*, 1931, **27**, 176), and it may be supposed that, in the present case, the long period of heating in the dry affected the quartz in such a way as to diminish very considerably, or to eliminate completely, the spreading of reaction into the homogeneous moist phase. Whether this view be tenable or not, however, the above results make it clear that water does not accelerate the combustion of a $2CO + O_2$ mixture on the surface of quartz, but on the contrary, considerably retards it.

The properties of quartz in this respect are therefore similar to those of the series of non-metallic catalysts examined by Bone (*loc. cit.*) at temperatures sufficiently low to preclude the possibility of homogeneous reaction. The rates of combustion of $2CO + O_2$ mixtures on surfaces of nickel oxide, copper oxide, firebrick, and porcelain were found to be invariably higher in the dry than in the moist, a result which has been attributed by Bone to reduction of available catalytic area by adsorbed water—a so-called "lagging" effect. In order to apply such an explanation to the results described above, it is necessary to suppose that while only 1 unit in 11 of available area was unoccupied by adsorbed water at 500°, the proportion increased to 1 in 4 at 580°, and further, that the difference between the apparent energies of activation in moist and dry systems is to be wholly accounted for by the net energy of desorption of water. It appears more probable that in the presence of moisture the combustion was composite, occurring partly as a 'dry' oxidation, and partly as a reaction negatively catalysed by water, the relative importance of these two reactions being determined by temperature, and by the surface density of adsorbed water. In general, such composite reactions are characterised by apparent energies of activation which increase with increasing temperature : if an effect of this kind operated in the present experiments, the practicable range of temperature was insufficient to reveal it. This negative catalytic effect of water adsorbed on a quartz surface may be compared with the well-known fact that the water-gas reaction occurs with great ease on the surfaces of most metals and reducible oxides, but with considerable difficulty on non-metallic and non-reducible surfaces such as porcelain. (For the case of quartz, see Hadman, Thompson, and Hinshelwood, *loc. cit.*) It may be concluded that the condition of water molecules adsorbed on such non-metallic surfaces is fundamentally different from that on metallic surfaces, the type of binding in the former case being inimical to, and in the latter favourable to, chemical reactivity.

In the majority of instances in which water has been shown to catalyse heterogeneous gaseous combinations, some specific association of water with one or more of the reactants is known to be possible; *e.g.*, the combination of ammonia and hydrogen chloride in a glass vessel (Baker, J., 1894, **65**, 611; Hinshelwood, "School Science Review," 1927, No. 31, 169), or the oxidation of sulphur dioxide by oxygen on the surface of either manganese dioxide or platinum at ordinary temperatures, for which the presence of water is essential (Russell and Smith, J., 1900, **77**, 346). Few reactions not involving such combination or association with water have been studied : the combustion of electrolytic gas first investigated by Baker (J., 1902, **81**, 400), however, falls into this category. In this case, water was found to catalyse the reaction either in a heated glass tube, or on the surface of an electrically heated metallic wire. It is uncertain to what extent homogeneous reaction occurred in the former instance, and, moreover, the electrical properties of glass at high temperatures show that in such circumstances it may approximate to the behaviour of a metal. Were it found possible to study the heterogeneous combustion of electrolytic gas on quartz unaccompanied by homogeneous reaction, there is reason to suppose that the catalytic effect of water would prove to be negative.

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