383. *Catalysis of an Interface Reaction by Adsorbed Molecules.*

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The rate of the reaction $CuSO_4,5H_2O = CuSO_4,H_2O + 4H_2O$ is increased by the presence in the reaction interface of adsorbed hydrogen chloride molecules. This is established by comparing the rates at which a given crystal of the pentahydrate loses water molecules into a stream of hydrogen, (*a*) alone, and (*b*) carrying a small partial pressure of hydrogen chloride : hydrogen alone has no catalytic effect upon the dissociation (Smith and Topley, *Proc. Roy. Soc.*, 1931, *A*, **134**, 224).

The results recorded below were obtained by means of the apparatus previously described (*loc. cit.*). Pressures are in mm. Hg, reaction rates in mg. H_2O/sq. cm./min., at 22·25°.

	p_{H_2}.	p_{H_2O}.	p_{HCl}.	Rate.
Crystal A.	1·71	0·00313	0	0·022
	1·49	0·0131	0·0562	0·15
Crystal B.	3·39	0·00307	0	0·021
	2·92	0·0211	0·0554	0·11

The partial pressures of water vapour are those set up in the stationary state by the dissociating crystal itself, except that in the second part of the B experiment extra water vapour amounting to 0·0099 mm. was added to the gas stream along with the hydrogen chloride, making the total of 0·0211.

Analysis of the partly decomposed crystals after the rate measurements in hydrogen chloride showed that this gas is adsorbed, but after ½ hour's heating at 100° no chloride remained in the solid. The sulphate is therefore not converted into chloride under the experimental conditions.

The absolute rates in the first part of each experiment (*i.e.*, without hydrogen chloride) agree well with those previously determined. The increase under the catalytic action of the gas is 7-fold in the first experiment and 5-fold in the second, where more water vapour was also present. Thus in the presence of the same partial pressure of hydrogen chloride, the increase from 0·0131 to 0·0211 in partial pressure of water vapour decreased the rate by a factor of nearly 1·5; this is close to the analogous factor found in the absence of the catalyst (see *Phil. Mag.*, 1932, **14**, 1080).

The strong catalytic influence of the hydrogen chloride was qualitatively confirmed by further experiments in which it was also found that larger pressures have a somewhat greater influence. When the hydrogen chloride is introduced into the hydrogen stream, the reaction rate does not immediately adjust itself to the new value, but rises slowly over an interval of about an hour up to a maximum. It may be that this effect is caused by slow adsorption of hydrogen chloride on the amorphous solid product; no correction has been applied for the weight thus adsorbed, so the recorded rates of the catalysed reaction are *minimum* values.

If, as seems most likely, the " autocatalytic " phenomenon in salt hydrate dissociations is to be attributed to the lowering of the activation energy of the rate-controlling stage (see *Proc. Roy. Soc.*, 1932, *A*, **136**, 413) by the action of the attraction across the reaction zone of water molecules by the ions of the lower hydrate phase, then the possibility suggests itself that very polar molecules present in the reaction zone as the result of adsorption from the gas phase might act in a similar way. We already know a case in which a salt hydrate decomposition ($MnC_2O_4,2H_2O = MnC_2O_4 + 2H_2O$) is strongly catalysed by adsorbed water molecules (Topley and Smith, *Nature*, 1931, **128**, 302). We have therefore examined the effect of small partial pressures of sulphur dioxide, ammonia, and methyl alcohol. The first made no observable difference to the reaction rate when added at a pressure of 0·4 mm.; the second at 0·36 mm. reduced the rate by 40%, and the last at 0·1 mm. reduced it by 20%. On the basis of dipole moment only, the molecules of these three substances and of hydrogen chloride and water are similar. It is evident that the catalysis is a phenomenon showing specificity with respect both to the particular salt hydrate and to the adsorbed substance.

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