CCCXCIX.—*An Auto-poisoning Phenomenon shown by Catalytically Active Copper at Moderate Temperatures.*

By Frederick Hurn Constable.

The author has previously shown (this vol., p. 1578) the extent to which sintering by heat treatment reduces the surface area and catalytic activity of copper, and has also provided definite evidence that the " centres of activity " collapse when the kinetic energy of the constituent atoms becomes sufficient. The heterogeneous nature of the active surface is now well recognised, and the present paper shows how the active centres may be rendered inactive during the catalysis of a chemical change, even when precautions are taken that the reactant is quite pure, and that the temperatures are below those at which sintering of the centres occurs in a vacuum, in spite of the fact that the reaction proceeds with the absorption of heat.

When a copper catalyst is used to dehydrogenate alcoholic substances at temperatures above 280°, it is found that the activity decays with time. Measurements have been made on the variation of activity with time, and on the effect of temperature on the rate of decay. The catalyst is stable when heated alone to the temperature used, so the poisoning is due to the interaction of the copper and the alcohol. It has been shown that the method of preparation of the catalyst does not alter the temperature at which the effect becomes noticeable, though it seems to have a considerable influence on the rate of poisoning, the rate of decay of the preparation from copper oxalate being about 5 times greater than that of copper reduced from oxide at the same temperature (*Proc. Roy. Soc.*, 1926, *A*, **110**, 297, Fig. 2, curve 5, and Fig. 5).

EXPERIMENTAL.

The ethyl alcohol was twice refluxed with lime, distilled through a Dufton column, and collected in a receiver fitted with a phosphorus pentoxide guard tube; it had b. p. 78·30° ± 0·01°/760 mm. The apparatus used has already been described (*Proc. Camb. Phil. Soc.*, 1925, **22**, 739). The initial stages of the reaction were always studied, and the rate of flow of the alcohol was regulated so that the concentration of the aldehyde over the catalyst was never greater than 1%. The amount of copper used as a catalyst had to be decreased as the temperature of experiment was increased. The rate of poisoning at constant temperature is not dependent on the rate of passage of the alcohol vapour when this exceeds a definite limiting value, and is therefore not dependent on the small concentration of the aldehyde in the vapour above the catalyst.

The reaction tube was filled with carbon monoxide at the constant temperature at which the decay of activity was to be measured, and the copper oxide thereby reduced. Blank experiments were made with water vapour instead of alcohol in order to determine the magnitude of the correction which had to be applied on account of the displacement of carbon monoxide from the reaction tube in the initial stages of the reaction. The correction was very large in the first few minutes after the bulk of the gas had suddenly been displaced by the admission of the vapour stream. It was found that a current of steam produced by the vaporisation of 1·28 c.c. of water per minute would take about 10 seconds to pass the glass valve B_2 (*Proc. Camb. Phil. Soc., loc. cit.*, Fig. 1), and during this time the valve condensed the gas stream and was being warmed; then followed a very rapid evolution of gas from the reaction tube, lasting about 25 seconds, which stopped suddenly when the vapour stream reached the condenser K. The gas which had escaped removal by diffusion was then evolved at a continually decreasing rate, which was carefully measured; the readings so obtained are in Table I, the time from the commencement being given in minutes, and the rate of evolution in c.c. per minute. This correction was applied to all the measurements made, but owing to variations in this quantity with the rate of flow the magnitude of the correction in the period 0—5 minutes is subject to considerable uncertainty. The measurements are thus somewhat untrustworthy except when the reaction

FIG. 1.

Decay curves at 270—350°.

(*The catalyst was produced by reduction at the temperature of experiment, the amount being varied.*)

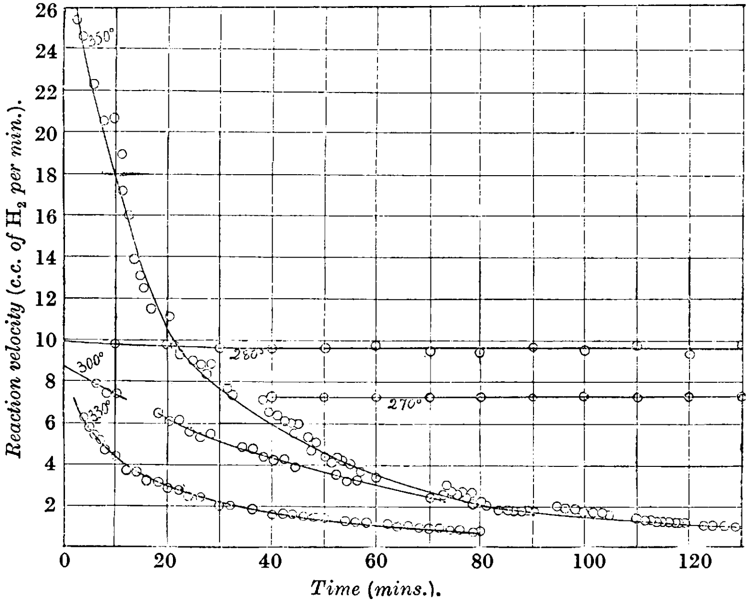


TABLE I.

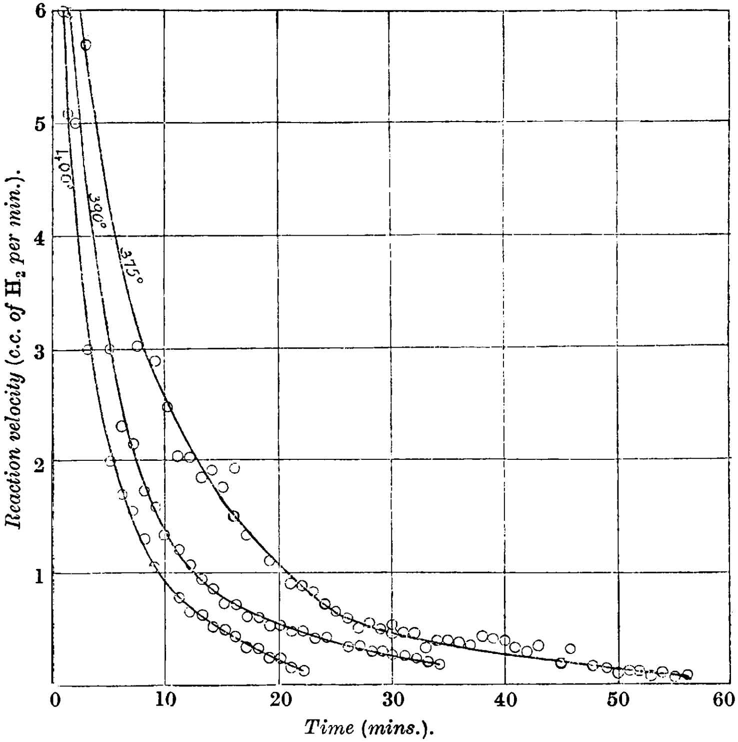
Time	5	10	15	20	25	30	35
Rate	0·80	0·45	0·33	0·30	0·22	0·20	0·18

velocity is large, and if the activity is short-lived the precise form of the curve may be doubtful, *e.g.*, at 400°.

Procedure.—The alcohol stream was turned on, and 20 seconds were allowed for the time taken by the gas stream to reach the copper, and hence for the commencement of the reaction. The gas burette T was read every 30 seconds in the first 5 minutes, and then every minute until the activity became inappreciable. The corrected results of the experiments are shown in Figs. 1 and 2, and the fractional reaction velocities during each decay are given with the corresponding temperatures in Fig. 3. The value of the initial activity was obtained by extrapolation of the measurements in the very early stages of the poisoning.

FIG. 2.

Decay curves at 375—400°.



Examination shows that the data follow neither a simple logarithmic law nor a reciprocal law. The initial logarithmic rate of decay, $d \log v/dt = 1/v \,.\, (dv/dt)$, is considerably retarded as the time proceeds. One typical set of observations at 350° is given in Table II,

TABLE II.

Time	0	10	20	30	40	50	60
Velocity	29·0	18·0	10·7	8·3	6·6	4·8	3·6
Time	70	80	90	100	110	120	130
Velocity	2·7	2·0	1·8	1·5	1·3	1·1	1·0

the time being in minutes, and the reaction velocity in c.c. of hydrogen (reduced to *N.T.P.*) evolved per minute.

It is thought that these data may represent a particular case of the selective poisoning of a distribution of centres of activity, and the question is still under investigation. In the absence of definite knowledge of the law of decay, the time required for the velocity five minutes after the commencement to fall to one-tenth of its value has been used as a measure of the rate of poisoning at various temperatures; these times (in mins.), as read from the curves, are shown in Table III.

FIG. 3.

The fractional reaction velocities.

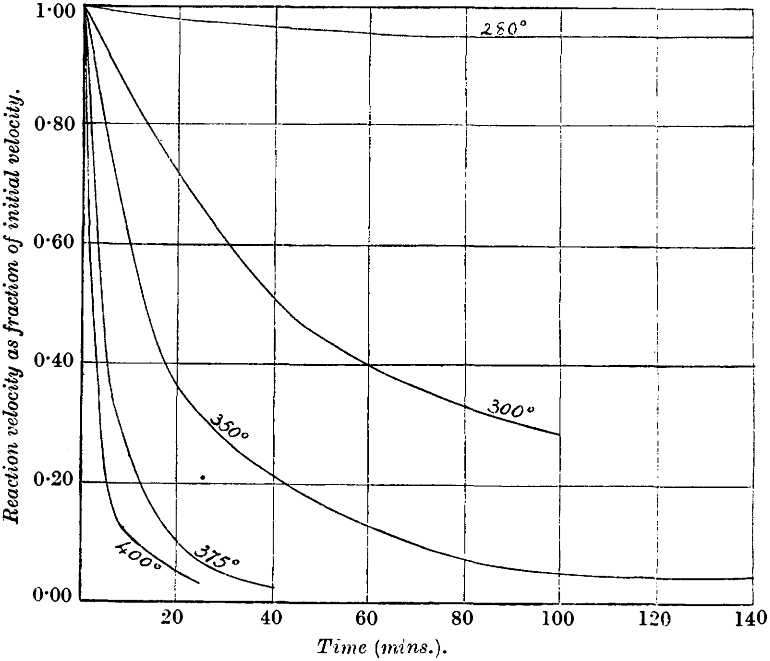


TABLE III.

Variation of Rate of Poisoning with Temperature.

Temp.	280°	300°	330°	350°	375°	390°	400°
Time	Very large	200	90	65	30	25	13

The rate of poisoning increases rapidly with the temperature, and is so fast that it can hardly be observed above 400°.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE.

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