277. *The Catalytic and Electrical Properties of Metallic Surfaces. Part I. A Silver Surface catalysing the Combustion of Carbonic Oxide.*

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A SERIES of investigations by Finch and Stimson (*Proc. Roy. Soc., A.*, 1927, **116**, 379; 1928, **120**, 235; 1929, **124**, 356; 1931, **132**, 192), Stimson (*ibid.*, 1934, **144**, 307), and Finch and Bradford (*ibid.*, 1934, **144**, 320) has lead to the development of methods for the study of catalytic surfaces based upon their electrical properties. These electrical methods have now been further developed and applied to the study of the combustion of carbonic oxide at a silver surface.

The experiments fall into two groups. The catalytic and electrical properties of a virgin silver surface in contact with moist or dry ($2CO + O_2$) mixtures were first determined over a wide range of temperature, and slow changes in catalytic activity due to normalisation and sintering and also the effects of alternate introduction and removal of water followed. In the second group, the kinetics of the reaction and the effects of pre-treatment of the thoroughly temperature-normalised catalyst with one or other of the reacting gases were investigated.

The catalytic properties of the silver surface, unlike those of gold (cf. Finch and Bradford, *loc. cit.*), were remarkably mobile, and were much affected by the previous history of the metal (*i.e.*, heat treatment, or contact with various gases or with moisture): at high temperatures a hitherto unobserved type of instability appeared. Furthermore, moisture, which has been shown to accelerate the combustion of ($2CO + O_2$) mixtures on gold (Finch and Bradford, *loc. cit.*), was found to exert an almost equally pronounced retarding effect in the case of silver. The kinetics of the reaction were such as to afford a view of the condition of the metallic surface and the types of adsorption thereon which could be correlated with the electrical properties; the latter were reflected not only in the comparatively slow variations in activity due to normalisation and sintering, but also to other more transient effects outlined below.

EXPERIMENTAL.

The experiments consisted in circulating either moist or phosphoric oxide-dried mixtures of carbonic oxide and oxygen over the surface of a heated silver gauze mounted on a quartz rod and connected to a Lindemann electrometer. Carbon dioxide was, according to circumstances, either absorbed in soda-lime, or condensed by liquid air, and the reaction velocity measured manometrically. Fuller details have been given elsewhere (Finch and Bradford, *loc. cit.*).

Results.

The following properties of the surface were determined:

(1) *The rate of catalytic reaction.* Although the rates of combustion of ($2CO + O_2$) mixtures were only approximately of the first order, the instantaneous unimolecular reaction coefficients, $k = (dp/dt)/2{\cdot}303$, formed convenient indices of reaction rate, and are employed throughout except where otherwise stated: the values of k usually refer to the dry gas mixture at a pressure of 100 mm.

(2) *The equilibrium surface potential, A,* measured in volts. Since the surface potentials observed throughout were without exception negative, the sign has been omitted in setting forth the results.

(3) *The rate of electrical charging, PC,* expressed in terms of micro-microcoulombs per minute per volt. As with gold, it was found that the rise of surface potential followed the relation $v = A(1 - e^{-Pt})$, where v is the instantaneous surface potential at the time, t, after insulation, A is the final equilibrium potential, and P is a constant for given conditions of temperature, gas composition and pressure, and of surface activity. The product PC, where C is the capacity of the surface-electrometer system, then affords a specific measure of the rate of electrical charging.

The Combustion of ($2CO + O_2$) *Mixtures.*—It became evident at an early stage that the silver surface exhibited in its behaviour as a catalyst certain peculiarities not met with in the previous study of gold, and the experiments were accordingly prolonged in order to elucidate

TABLE I.

(Experiments of first moist group.)

			Initial stage.			First intermediate stage.				Second intermediate stage.				Final stage.			
Series.	Temp.	Previous temp.	*k*.	*A*.	$PC\times10^{-3}$.	Time.	*k*.	*A*.	$PC\times10^{-3}$.	Time.	*k*.	*A*.	$PC\times10^{-3}$.	Time.	*k*.	*A*.	$PC\times10^{-3}$.
B	338°	257°	0·0086	1·58	0·0030	1	0·0116	0·96	0·00255	3	0·0101	2·63	0·00134	8	0·0056	0·80	0·00851
L	532	582	0·864	0·231	20·4	1	0·693	—	—	2	0·600	0·232	25·0	3	0·608	0·162	26·5
M	523	20	0·395	0·257	16·6	1	0·426	0·207	15·0	3	0·375	0·186	7·61	7	0·316	0·169	7·50
O	520	575	0·226	0·210	9·50	2	0·181	0·248	7·10	4	0·210	0·265	6·83	9	0·162	0·210	6·39
R	464	396	0·0528	0·240	1·52	1	0·0644	0·259	1·41	2	0·0619	0·264	1·19	4	0·0645	0·234	1·28

Note. "Initial stage" in the above refers to experiments carried out immediately following attainment of steady temperature; "Time" in the following stages refers to the periods elapsing after initial stage.)

TABLE II.

First Moist Group	*E*	517	465	0·303	0·308	0·0580	1	0·819	0·547	0·0611	4	0·428	0·515	0·032	6	0·223	0·524	0·0150
	H	522	543	0·376	0·182	2·31	3	0·350	0·228	2·24	4	1·60	—	—	8	1·29	0·260	5·96
	T	583	533	0·715	—	—	1	0·819	0·280	27·4	2	2·83	0·447	59·9	7	1·89	0·412	48·0
	U	535	583	0·664	0·343	16·8	2	0·653	0·321	12·3	2·5	2·52	0·408	14·6	7	2·42	0·426	14·8
First Dry Group	*A*	528	528	1·34	0·268	9·30	1	2·22	0·322	13·7	—	—	—	—	5	2·11	0·354	13·3
	G	575	516	1·78	0·325	9·71	2	1·60	0·295	9·1	3	3·70	0·344	33·0	7	3·60	0·312	27·4

(See *Note*, Table I.)

TABLE III.

Series.	Temp.															
Dry I : *M*	469°	0·417	0·254	3·25	—	—	—	—	—	—	—	—	2	0·295	0·269	2·70
Moist II : *A*	469	0·235	0·206	3·05	1	0·230	0·191	3·20	4	0·164	0·212	2·00	7	0·110	0·164	1·50
H	550	0·535	0·260	—	—	—	—	—	—	—	—	—	2	0·546	0·237	16·2
Dry II : *A*	550	0·575	—	—	1	0·587	0·220	14·1	2	0·619	0·212	14·7	4	0·695	0·197	8·06

(See *Note*, Table I.)

the factors responsible for such apparently anomalous behaviour. In all, 8 months were occupied by this first series of combustions, and during this time the surface was always in contact with either moist or dry ($2CO + O_2$) mixtures.

The results set forth in Table I show clearly the effect of prior heat treatment upon the properties of the surface. On proceeding from one temperature to another, the change in the catalytic and electrical activities (k and PC respectively) of the surface took place exceedingly slowly, the surface accommodating itself very gradually to its new temperature conditions. This behaviour is so striking that it negatives at once any suggestion of the combustion's occurring, even in part, either homogeneously or by a chain mechanism starting at the surface; there appears to be no escape from the conclusion that it is the structure of the surface which in the main determines its catalytic and electrical properties.

These results also bring out the fact that, in addition to the heat-treatment effect, the surface underwent the type of change ascribed to sintering, which in a series of experiments at successively increased temperatures is opposed to the temperature-normalisation effect. Thus, whilst at first, on changing from one temperature to another, k in general reflected almost exclusively the effects of previous heat treatment, in the final stages of each series at constant temperature the rate of change in the value of k had become linear, and was therefore due entirely to sintering.

The results in Table II bring to light a remarkable type of increase in the activity of the surface, which was only found to occur at temperatures over 510°, but was independent of the presence of steam or otherwise in the reacting mixture. This took the form of an abrupt, and sometimes even five-fold increase in the value of k and was reflected, though to a lesser extent, by a parallel change in the electrical activity. The suggestion that such sudden increase in activity might be spurious and, in effect, due to the starting of reaction chains at the surface and their propagation into the body of the gas, is excluded by the facts that when the surface was in such an abnormally highly active condition an abrupt reduction in temperature revealed a persistent enhanced activity at lower temperatures, and that the values of k at such lower temperatures fell only slowly in a manner characteristic of the coming into play of temperature-normalisation and sintering forces. Thus, *e.g.*, before Series E, the surface had been heated to 465°, at which the value of k was 0·11. After heating at 517° and higher temperatures in Series *F*, *G*, and *H*, the value of k was now found to be 0·49, from which it fell gradually in the course of 3 days to 0·31. An even more remarkable change was observed in the experiments carried out before and after Series *U*. In this case, the immediately previous value of k at 465° was 0·06, and after completion of the experiments at 535°, on reduction of temperature again to 465°, the abnormally enhanced activity of the surface was reflected in the exceedingly high value of $k = 1{\cdot}25$.

The effect of steam on the reaction velocity is shown by the results incorporated in Table III. The change from the dry to the moist system entailed a loss in activity and *vice versa*; this behaviour is the contrary to that previously observed in the case of gold. The reduction in activity is most pronounced at the lower temperatures, but as was previously found to be the case with gold, the moist and the dry system activities tended to become equal with increasing temperature. In the case of gold, the increase in activity on changing from dry to moist conditions was attributed to the indirect process whereby correlative oxidation and reduction of carbonic oxide and steam occurred, the hydrogen thus liberated being burnt in its turn by oxygen. As will be shown later, the behaviour of silver, which at first sight appears to be radically different from that of gold, admits of a similar interpretation.

The Kinetics of the Reaction.—At the conclusion of the foregoing series of experiments the kinetics of the reaction were studied by determining the rates of reaction of various mixtures of carbonic oxide, oxygen, and carbon dioxide. Prolonged contact with mixtures containing appreciable excess of either carbonic oxide or oxygen was found to bring about semi-permanent changes in the behaviour of the surface, and for this reason each experiment was bracketed by rate measurements in the standard ($2CO + O_2$) mixture, appropriate corrections then being applied for the change in general activity brought about by the different treatments to which the surface had been subjected. The results of the experiments with mixtures of carbonic oxide and oxygen in different proportions are summarised in Figs. 1 and 2, and of those with added carbon dioxide in Table IV, in which col. 3 gives the unimolecular rate of reaction at 100 mm., calculated on the partial pressure of ($2CO + O_2$). These experiments were all carried out at a temperature of 550° : a few experiments were made at lower temperatures, with substantially similar results, but the slow rates of reaction at such temperatures precluded a more complete investigation.

TABLE IV.

Condition.	Composition of gaseous mixture.	Unimol. rate.	*A*.	Condition.	Composition of gaseous mixture.	Unimol. rate.	*A*.
Moist	$2CO + O_2$	1·25	0·334	Dry	$2CO + O_2$	2·66	0·398
	$2CO + O_2 + \frac{3}{2}CO_2$	1·18	0·290		$2CO + O_2 + \frac{3}{2}CO_2$	2·55	0·281
	$2CO + O_2$	1·27	0·323		$2CO + O_2$	2·57	0·415

It will suffice for the present purpose to point out the following conclusions from these results : (i) the reaction was not retarded by carbon dioxide; (ii) neither carbon monoxide nor oxygen was strongly adsorbed over the whole of the surface—either gas when in excess displaced the other; (iii) water accelerated the reaction at low partial pressures of either reactant, and retarded the reaction at higher partial pressures; its catalytic effect was therefore relatively feeble, and only contributed appreciably to the total rate of reaction in conditions of sparse adsorption of carbonic oxide or oxygen (or of both). The reduced rates of reaction in the presence of water at high partial pressures of carbonic oxide and oxygen are probably to be attributed to displacement of the two gases by adsorbed water.

FIG. 1.

Rates of reaction of mixtures containing constant partial pressures of oxygen diluted with various pressures of carbonic oxide.

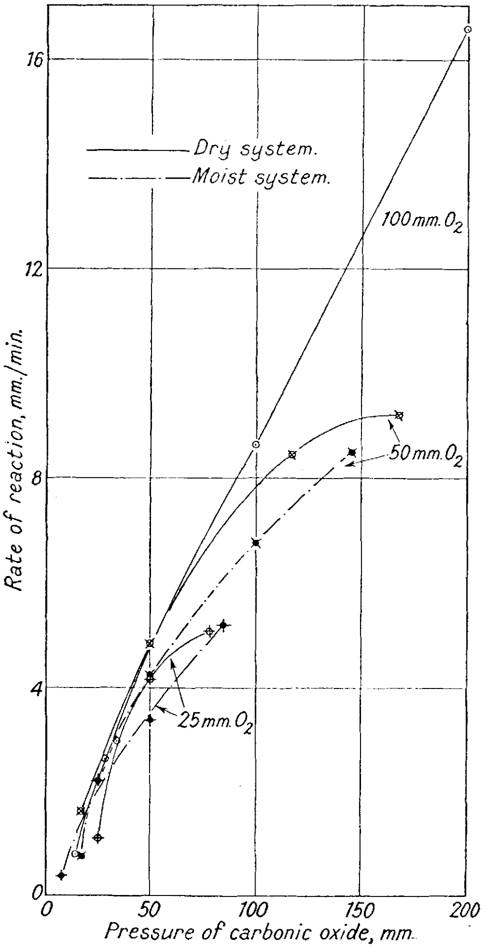
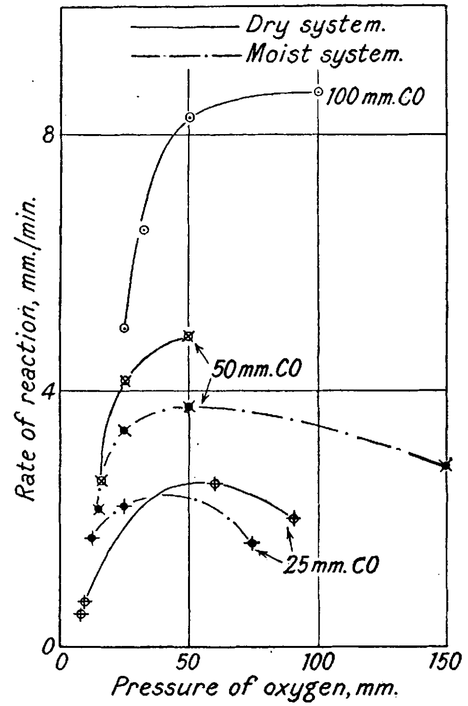


FIG. 2.

Rates of reaction of mixtures containing constant partial pressures of carbonic oxide diluted with various amounts of oxygen.



Effects of Pre-treatment of the Catalyst with Carbonic Oxide or Oxygen.—A further study of pre-treatment effects was carried out, with results which may be summarised as follows [it should be borne in mind that ($2CO + O_2$) was employed throughout as a reference mixture] :

(1) *In the dry system*, at all temperatures, the catalytic activity of the surface was increased by treatment with carbon monoxide, decreased by treatment with oxygen, and unaffected by carbon dioxide. For instance, at 440°, when the surface was brought into contact with CO and O_2 for periods of 1 hour each in the following order : CO, CO, O_2, O_2, CO, the rates of combustion of ($2CO + O_2$) mixtures—initially 0·651 on the thoroughly normalised surface—had the successive intervening values : 2·84, 2·65, 1·30, 2·65. Prior contact with carbon monoxide increased the rate of combustion by a factor of 4; subsequent carbon monoxide treatment brought about no further increase, but oxygen treatment slowly and continuously reduced the resultant abnormal activity, which could, however, be immediately restored by a short exposure to carbon monoxide. Contact with ($2CO + O_2$), either circulating (*i.e.*, carbon dioxide-free) or stagnant (*i.e.*, highly diluted with dioxide), gradually restored normal activity following either carbon monoxide or oxygen treatment. Similar results were obtained at a temperature of 550°.

Experiments with mixtures of carbon monoxide and oxygen in various proportions, admitted to the surface for a few minutes only, showed further that the extent of enhancement or depression of activity was dependent upon the relative excess of the one or the other gas.

(2) *In the moist system*, at low temperatures ($< 470°$), contact with either carbon monoxide or oxygen immediately decreased the catalytic activity of the surface. At high temperatures, however, the effect of such pre-treatments was negligible. Carbon dioxide was without effect in any conditions.

The results in the dry system indicate that the surface, when in equilibrium with the gaseous mixture ($2CO + O_2$), was covered to the extent of about 75% by an inactive layer of oxygen, which may be termed " pseudo-oxide," formed slowly in oxygen, but immediately removed by carbon monoxide, and that the normal reaction occurred only on the remaining bare metallic surface. Despite the thermodynamic instability of silver oxide in the conditions of the present experiments (cf. Lewis, *J. Amer. Chem. Soc.*, 1906, **28**, 139, and Keyes and Hara, *ibid.*, 1922, **44**, 479), there is strong evidence for the existence of such an oxide film on the surface of silver (see Chapman, *Proc. Roy. Soc.*, *A*, 1925, **107**, 92; Finch and Stimson, *loc. cit.*; Benton and Drake, *J. Amer. Chem. Soc.*, 1932, **54**, 2186). The introduction of moisture further complicated the condition of the surface, and the results may be taken to indicate the formation of a strongly bound film of water in addition to surface oxide.

Electrical Properties of the Surface.

The close connexion which has previously been noted between the catalytic and the electrical properties of heated metallic surfaces (Finch and Bradford, *loc. cit.*) prompted a thorough study of the changes in electrical potential and electrical activity (*A* and *PC* respectively) brought about by different experimental conditions. The general conclusions only can be indicated.

The surface potential, A, was determined by two factors, (i) the state of the metallic surface, and (ii) the composition of the adsorbed film of gas. Thus, at a given temperature, the values of *A* were considerably higher in the early stages of the experiments than after prolonged heat treatment. The general trend of surface potential is shown in Figs. 3 and 4; rapid diminution of *A* was practically confined to the initial period of heating, during which the temperature of the metal was raised to a maximum of 580°. The most rapid diminution occurred, moreover, in the temperature range which Beilby (" Aggregation and Flow of Solids," London, 1921) has shown to be associated with the rapid recrystallisation of cold-drawn silver wire.

Minor changes in the catalytic activity due to reaction- and temperature-normalisation were also accompanied by slight displacements of surface potential. Sintering at constant temperature was without effect; the important fact was established, however, that abrupt high-temperature increase of activity was invariably accompanied by abrupt increase in *A* values (see Fig. 3, Series *T*).

Comparison of surface potentials in carbon monoxide and oxygen with those in the mixture ($2CO + O_2$) (Figs. 3 and 4) and in other mixtures of different composition, together with the data on rates of charging summarised in Fig. 5, leads to a conclusion in accordance with the kinetic experiments, that although oxygen was the more strongly adsorbed, yet carbon monoxide also played an important part in the adsorbed gas film. Other observations which need not be further detailed confirmed the view previously advanced that oxygen was bound in at least two states, chemically inactive and active respectively, entry into the former of which was slow, even at 550°. The presence of moisture had little effect on surface potential.

The rate of electrical charging, PC, probably because of the relatively small differences between the rates of charging of the three gases concerned, was comparatively insensitive to changes in the composition of the adsorbed gas layer, and served primarily to indicate alterations in the state of the metallic substrate. Accordingly, the rates of charging of the (2CO + O_2)-normalised surface closely paralleled its catalytic activity. Reaction- and temperature-normalisation, sintering, and abrupt high-temperature increase were all accompanied by corresponding changes

FIG. 3.

(*Abrupt increase of activity occurred during series* T.)

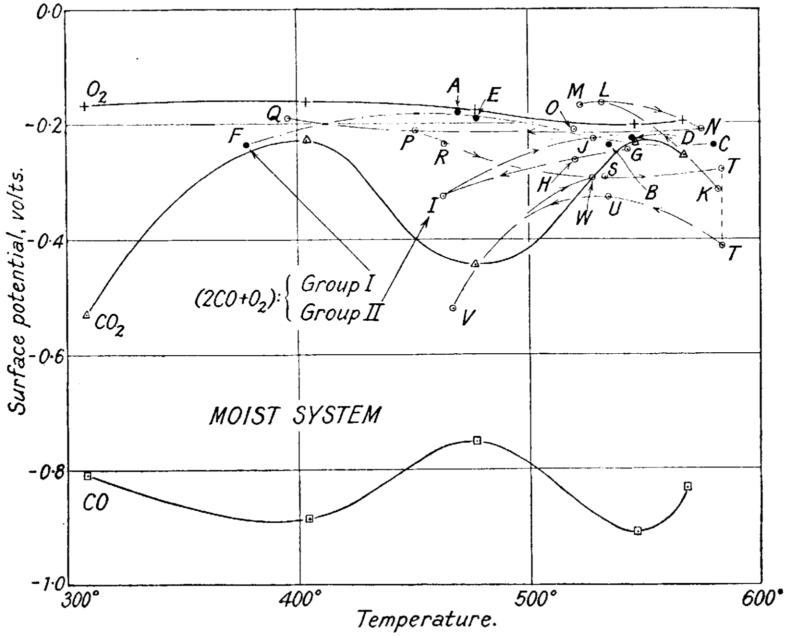
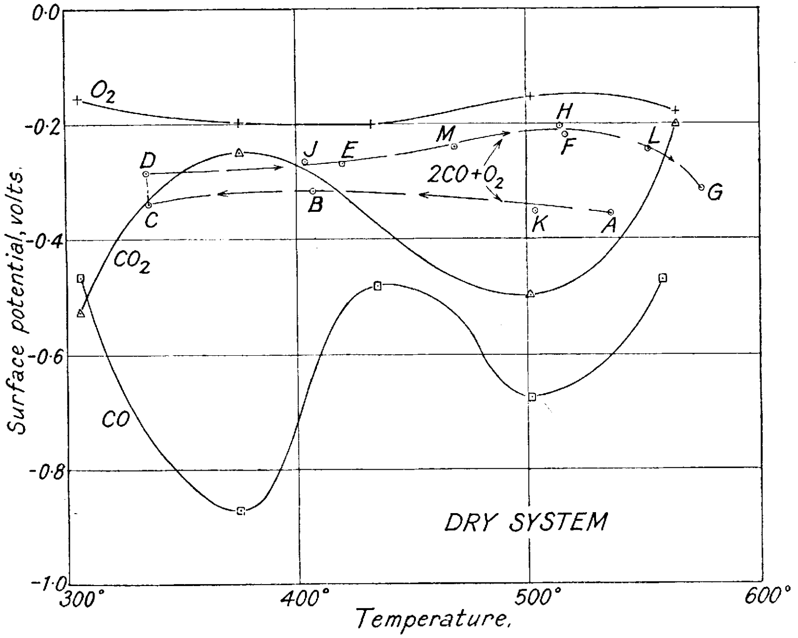


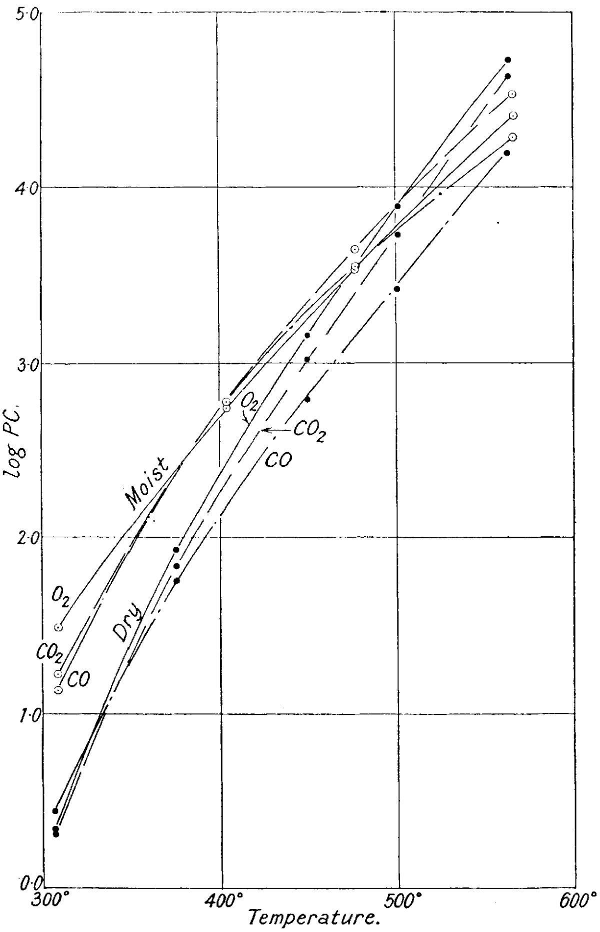
FIG. 4.

(*The surface was cooled to room temperature between* C *and* D.)



in *PC*: examples will be found in the foregoing tables. There was no evidence of either enhanced or diminished rate of charging during chemical reaction, the *PC* values of mixtures containing various amounts of carbon monoxide and oxygen lying proportionately between those of the two gases (cf. the case of gold, Finch and Bradford, *loc. cit.*). The temperature coefficients of *PC* are best considered in relation to the heat of activation of the surface reaction, and will be dealt with from that point of view in Part II, which it is hoped shortly to submit to the Society.

FIG. 5.



DISCUSSION.

A number of the factors responsible for the well-known variability of the catalytic properties of a silver surface have emerged during the present work. The most striking among these is the abrupt increase in activity repeatedly observed at temperatures in the neighbourhood of 500°. A careful search failed to reveal the presence of impurities which might possibly lead to this behaviour, such, *e.g.*, as traces of copper in the silver (cf. Stockdale, *J. Inst. Metals*, 1931, **45**, 132) or of sulphur compounds in the gases employed. Furthermore, the effect cannot be attributed to rupture or decomposition of the pseudo-oxide film, since stripping of the latter by contact with carbon monoxide increased only the surface potential, and slightly decreased the rate of charging, whereas both *A* and *PC* increased simultaneously with the increase of activity at high temperatures, thereby indicating a change in the metallic substrate rather than independent alteration in the composition of the adsorbed gas film. There appears to be no satisfactory evidence for any phase-modification of the bulk silver lattice at temperatures in the neighbourhood of 500°. It is, however, only necessary in the present case that a new phase should appear in the surface layers of the metal, and a dynamic, rather than an enantiotropic, change is indicated by the experimental results. Recent work on the surface properties of several metals at temperatures considerably below their melting points appears to indicate that the stable condition of the surface layers may in certain circumstances be amorphous, and, moreover, that this apparent surface vitrification may even occur superimposed on a regular substrate lattice (see Finch and Ikin, *Proc. Roy. Soc.*, 1934, **145**, 551). Desch (J., 1923, **123**, 291, and private communication) has shown that, certainly in the case of gold, and probably in that of silver, surface-tension forces operate quite rapidly at temperatures of 700—900°, and will, for example, gradually obscure the outlines of crystal grains, replacing the sharp boundaries by "surface markings which rather suggest a purely amorphous substance such as gelatine, than a crystalline solid." The phenomenon was observed by Desch at considerably higher temperatures than the 500—550° of the present experiments; nevertheless, the powerful forces which must have been brought into play by the reactions occurring at the surface (cf. Langmuir, *Trans. Faraday Soc.*, 1921–22, **17**, 607) might be expected to accelerate such surface modification.

The fact that the appearance of the state of enhanced activity was accompanied by *increase* of surface potential is strong evidence in favour of the occurrence of surface vitrification, since, as is well known, the polishing or cold-working of metals leads to an increase in the magnitudes of their Volta potentials (*e.g.*, see Kelvin, " Mathematical and Physical Papers," *VI*, 110 *et seq.*).

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