209. *Thermionic Emission during the Catalytic Combination of Carbonic Oxide–Oxygen Mixtures on a Platinum Surface.*

By Bernard William Bradford.

The relation of the various electrical phenomena which frequently accompany chemical reactions to the mechanism of such reactions has been the subject of speculation and experiment since the time of Davy. The majority of recent investigations in this field have been directed to a study of negative emission from heated catalysts; the occurrence of positive and negative ionisation during homogeneous and heterogeneous reactions has, however, also received some attention. Bibliographies of the published work on the subject have been given by Richardson ("The Emission of Electricity from Hot Bodies," 2nd ed., 1921), Rideal (*Ann. Reports*, 1928), Dhar (*Trans. Faraday Soc.*, 1928) and Dushman ("Reviews of Modern Physics," 1930, **2**).

It is well established that the emission of positive ions from metallic wires is increased by the presence of a number of gases, independently of any heterogeneous reactions which may occur thereon. The nature of the ions was investigated by Richardson (*op. cit.*, p. 241) and Thomson (*Proc. Camb. Phil. Soc.*, 1908, **15**, 64), and it was proved that the emission current is carried by charged atoms or molecules of the gases concerned. Early investigations (see Richardson, *op. cit.*) showed that in many cases, surface oxidation of a number of metals by oxygen or subsequent reduction by hydrogen brought about a further increase in such emission. More recently, Brewer (*J. Physical Chem.*, 1928, **32**, 1008) has found that the emission of both positive and negative charges is a specific property of a number of different types of heterogeneous gaseous reaction, and that such ionisation originates at the catalyst surface, upon the nature of which its magnitude depends. It has also been shown in these laboratories by Finch and Stimson (*Proc. Roy. Soc.*, 1927, **116**, 379; 1928, **120**, 235; 1929, **124**, 356) that many metals, including platinum, acquire characteristic potentials when heated in atmospheres of various gases: the possible significance of this phenomenon in the process of heterogeneous catalysis has been pointed out by those authors.

Preliminary experiments having indicated that the catalytic combination of a gaseous mixture of the composition $2CO + O_2$ on nickel, gold, platinum, and other surfaces was, in every case, accompanied by the emission of positive ions, the following investigation was undertaken with the object of determining the relationship, if any, between the rate of gaseous combination upon, and the thermionic emission from, platinum.

EXPERIMENTAL.

Apparatus.—The combustion vessel resembled a diode valve and consisted essentially of a filament of platinum wire, 6 cm. long by 0·012 cm. in diameter, stretched along the axis of a well-insulated cylindrical nickel electrode (1·5 cm. in diameter) supported in a glass vessel. The latter formed part of a circulatory gas system which also included a manometer, a circulating pump, and an absorption tube partially filled with caustic potash solution.

The filament formed one arm of a high-current-carrying Wheatstone bridge, by which its resistance and hence its temperature could be determined. Current was supplied to the bridge from an accumulator battery through a graded rheostat permitting of close control. Filament temperatures were calculated from the well-known relationship, $R_t = R_0(1 + at + bt^2)$, and the end-corrections, as derived by Langmuir (*Trans. Faraday Soc.*, 1922, **17**, 634), were applied in order to determine the true temperature of the central part of the filament. The filament and bridge circuit was completely insulated from earth, and could be raised to any desired potential up to ± 400 volts by means of a battery.

In order to measure the ionisation currents flowing to the insulated electrode, the latter was connected to the needle of a Lindemann electrometer. Emission currents of less than 10^{-13} amp. were measured by direct electrometer deflexion, suitable known capacities being added to the electrical system. Higher currents were determined by the null method devised by Townsend (*Phil. Mag.*, 1903, **6**, 598) and modified by Campbell (*ibid.*, 1912, **23**, 668), the drop in potential caused by the passage of the ionisation current through an alcohol–xylene resistance of approximately 10^{10} ohms being balanced by means of a potentiometer.

Preparation of Gases.—Oxygen and carbonic oxide were prepared in the manner previously outlined (*Proc. Roy. Soc.*, 1929, *A*, **124**, 306), and were mixed in equivalent combining proportions, the purity of the gases and the composition of the mixture being checked by analysis in a Bone–Newitt apparatus.

Experimental Procedure and Results.—Throughout all experiments, the observations of catalytic activity and thermionic emission were made simultaneously. For the sake of clarity in what follows, the observed catalytic phenomena will be first described; the facts established with regard to the thermionic emission and its relation to the heterogeneous reaction follow in a later section.

So far as the author is aware, the catalytic combustion of moist mixtures of the composition $2CO + O_2$ on any metallic or non-metallic surface hitherto examined has proved to be of a normal unimolecular type (compare Bone and Andrew, *Proc. Roy. Soc.*, 1925, *A*, **109**, 539; Bone, *ibid.*, 1926, **112**, 474). In the present experiments with a platinum catalyst, however, it soon became evident that the heterogeneous reaction was self-retarding to a high degree. The catalytic activity usually proved so short-lived that extended kinetic observations were only possible in a few cases.

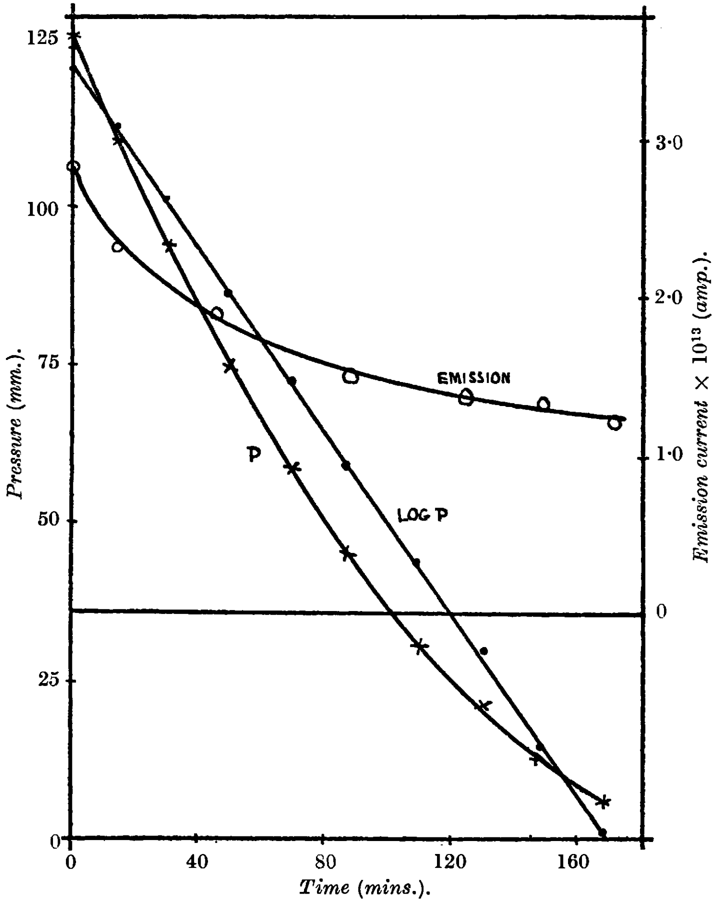
A number of different specimens of platinum wire were employed during the investigation: all of these behaved similarly, and the following results were obtained with a typical specimen. The procedure adopted throughout the experiments was as follows. After some definite preliminary treatment of the wire (such as evacuation or heating), the gaseous mixture was admitted to a pressure of 100 mm., the circulating pump was set in operation, and the temperature of the filament slowly raised by suitable increments, the manometer reading being closely observed throughout. At the first indication of catalytic activity, the filament temperature was maintained constant, and the course of the ensuing reaction followed.

When experiments were commenced with a new filament, the rate of reaction obeyed the normal unimolecular law, as is shown by the following results (the curve log *p* in Fig. 1 shows the linear relationship between log *p* and *t* for a similar combustion) :

Filament temperature, 600°.

Time, mins.	0		1		2		5		10		13
Pressure, mm.	139		124		112		79		39		27
Unimolecular constant, k_1		0·050		0·044		0·050		0·061		0·053	

Fig. 1.



This type of pressure fall persisted for approximately two weeks of continuous use, during which several experiments were carried out each day. With no preliminary indication, however, a combustion then occurred in which the gaseous pressure fell asymptotically to a value considerably above zero, in the manner indicated by the following :

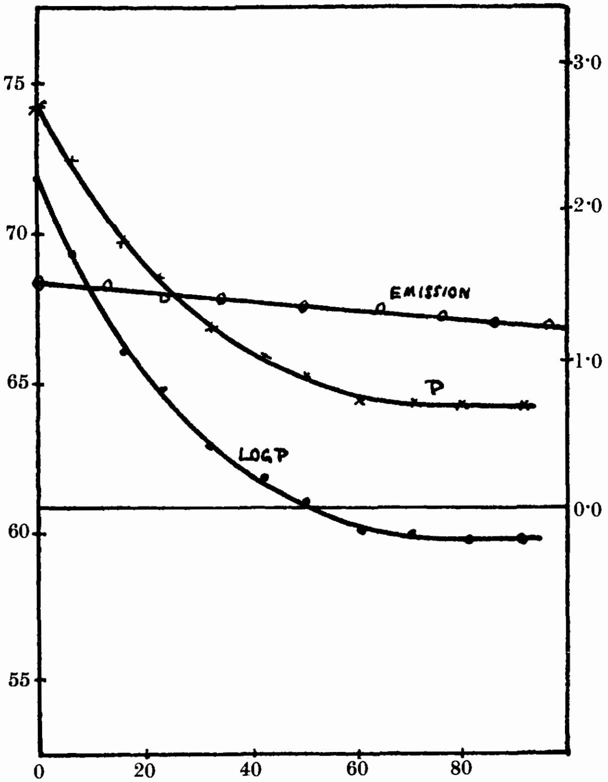
Filament temperature, 410°.

Time, mins.	0	4	9	14	17	29	49	65	79	100
Press., mm.	80	78	76·5	75·5	73	72	71	70·5	70	70

The rate of reaction decreased more rapidly than that corresponding to the unimolecular law, and combustion eventually ceased, and the pressure remained constant at 70 mm. for ½ hour. No subsequent treatment to which the wire was subjected restored the original unretarded type of pressure fall, although periods of rapidly diminishing catalytic activity could be induced by means which are described later. It thus became clear that, in its final stable condition, the heated platinum surface in contact with the gaseous mixture 2CO + O_2 was catalytically inactive, and therefore, in order that combustion should occur at all, it was necessary to bring the wire initially to an

Fig. 2.

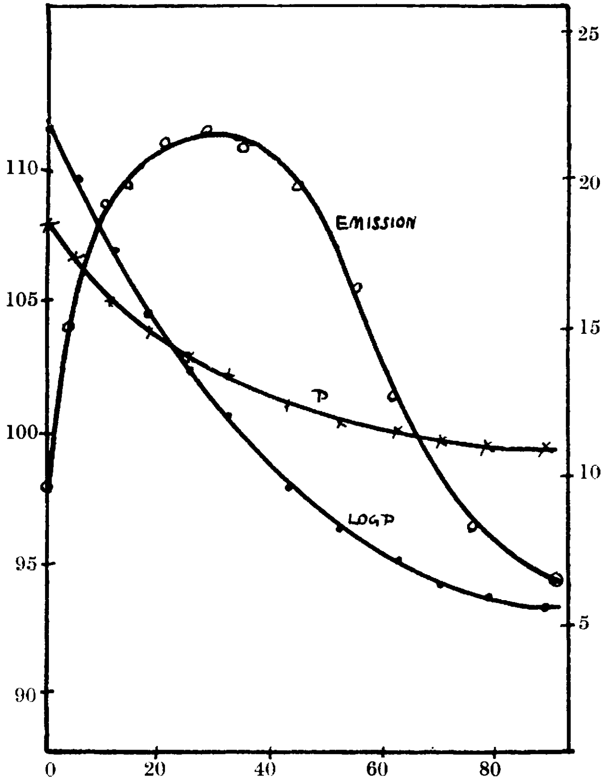
[*Left-hand ordinates represent pressure* (*in mm.*), *and for right-hand ordinates the unit is amps.* × 10^{-13}. *Abscissæ represent time* (*in mins.*).]



unstable active condition. The nature of the factors which affected this initial activity, and the kinetics of the reversion to the stable state of inactivity are described below.

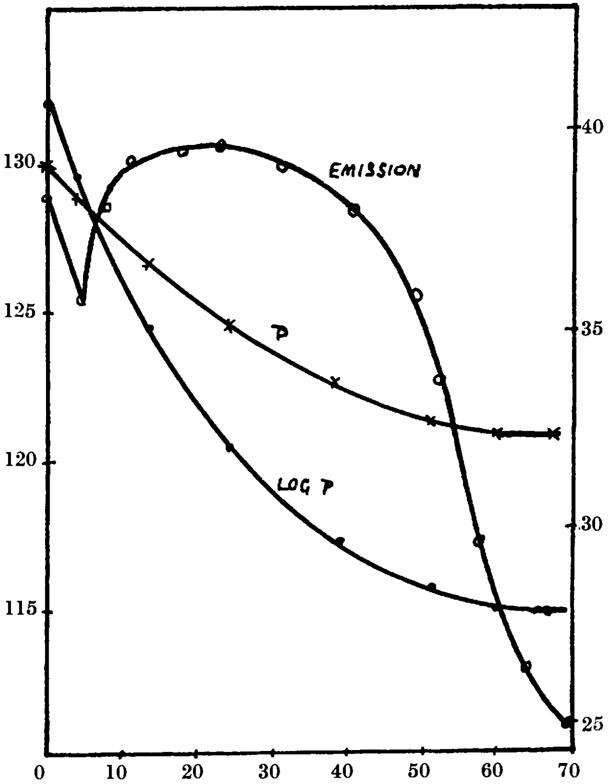
A measure of the initial activity of the surface was obtained by noting the lowest filament temperature at which the gaseous pressure first diminished perceptibly in a given experiment. With the few exceptions described in a later section, the rate of reaction usually fell so rapidly that the pressure became sensibly constant after several seconds. In general, the activity of the surface when poisoned in this way was restored by raising its temperature to some higher value, at which poisoning again rapidly ensued. Periods of catalytic activity and inactivity succeeded one another as the temperature was increased in stages, until finally, at between 610° and 620°, incandescent surface combustion set in, usually terminating in ignition.

Fig. 3.



The initial activity of the surface, when first heated from room temperature, was found to be affected by the following factors: (1) Previous reduction of the gaseous pressure for several hours to 5 mm. or less with the wire at room temperature resulted in a low initial activity. (2) Previous exposure of the cold wire for a similar period of time to the gaseous mixture at a pressure of about 150 mm. resulted in increased initial activity. These two effects are illustrated by the following results :

Fig. 4.



Preliminary treatment of the cold wire.	Temperatures at which first perceptible reaction occurred.							
Evacuation	565°	570°	480°	565°	560°	460°	520°	565°
Exposure to $2CO + O_2$ at 150 mm............	225	485	310	310	330	560	450	460

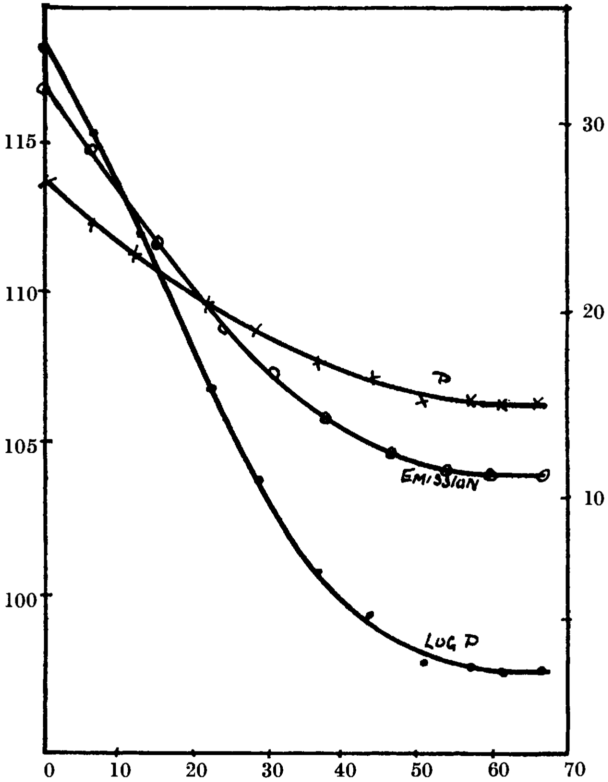
(3) The effect of heating the filament to 700° or above immediately before testing considerably increased the initial catalytic activity : it was immaterial whether the wire was heated in a vacuum or in an atmosphere of carbon dioxide. (4) Previous heating and

cooling in oxygen at 150 mm. increased, and in carbon monoxide decreased, the initial activity of the surface.

Kinetics of the Combustion.

In a number of instances, the catalytic activity of the platinum persisted for periods of time, varying from 5 mins. to 2 hours, sufficient for a number of simultaneous pressure and time observations to be made. Pressure–time and log pressure–time curves typical of the results obtained are shown in Figs. 2, 3, 4, and 5. The exact mathematical forms of these curves are considered later; as a preliminary step, in order to compare the chief characteristics of the experimental observations, parabolic functions were roughly fitted to the rapidly falling portions of the pressure–time curves. If the relation of the pressure, p, and the time, t, is given by $p = at^2 + bt + c$, then the values of $(1/p) \, . \, dp/dt$ and the differential of this with regard to t may be taken as representing the rate of

Fig. 5.



reaction and the rate of poisoning respectively at any time. Hence, the ratio of the initial rate of poisoning to the initial rate of reaction is given by $2a/b$.

In the following table, the results of a number of reactions are arranged in order of increasing initial activity :

Expt. No.	Temp.	Initial press., mm.	$b \times 10^4$.	$2a \times 10^5$.	$200a/b$.	Period of perceptible combustion, mins.
9	315°	114	273	73	2·7	70
6	565	130	350	100	2·9	50
1	315	80	400	80	2·0	80
5	515	108	444	89	2·0	70
11	315	53	600	222	3·7	40
8	400	88	630	860	13·6	8
12	315	94	717	300	4·2	30
4	515	100	900	200	2·2	30
2	315	74	958	634	6·6	20
3	595	72	1,160	324	2·8	35
10	480	63	1,400	400	2·8	35
13	315	79	2,275	4,060	17·7	7
7	580	68	6,166	6,166	10·0	10
14	595	68	12,126	16,880	13·9	7

(The numbers used to distinguish experiments in the above indicate chronological sequence.)

It is clear from the above results that the initial rates of reaction did not vary systematically with the age of the wire, or with the initial pressure of the gaseous mixture; it is furthermore evident that the temperature of the wire was not the controlling factor in determining the magnitude of the initial rate of reaction. In the majority of the combustions, particularly those in which the catalytic activity was low, the initial rate of poisoning was roughly proportional to the initial rate of reaction, as is shown by the approximate constancy of $2a/b$. When the catalyst was in a more highly active condition, however, the rate of poisoning was relatively greater.

If it be assumed that this proportionality applied not only to the initial stages of all the combustions, but also operated throughout the duration of each, then the relation of pressure and time should be given by $dp/dt = k \, . \, d^2p/dt^2$, where k is a constant for a given combustion. On applying the condition that when t is infinitely great, p is equal to the final constant pressure, p_f, one obtains the solution

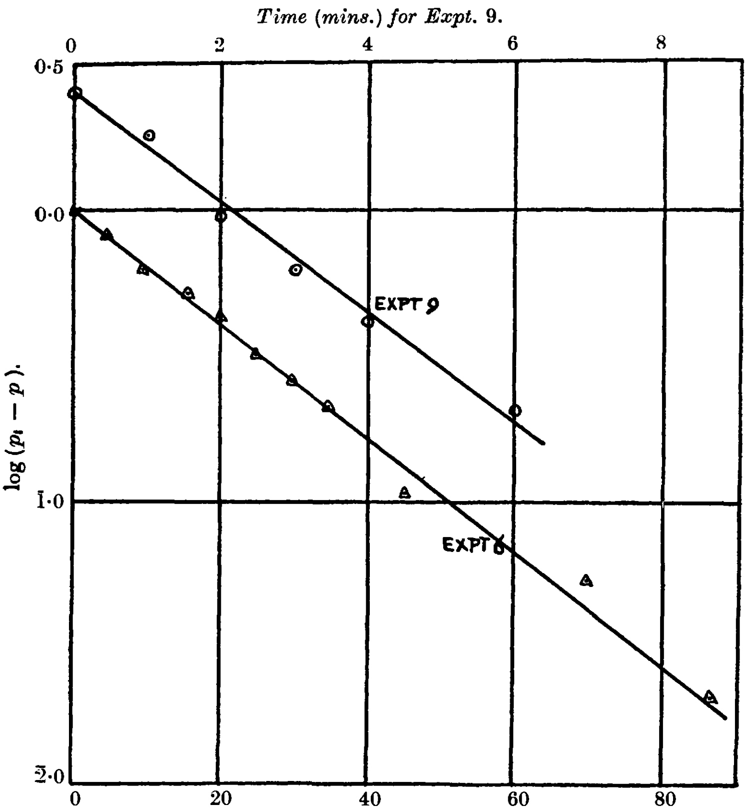
$$p_t = Ae^{-t} + p_f$$

$$i.e., \log (p_t - p_f) = \log A - t$$

where A is a constant equal to $\log (p_0 - p_f)$.

Typical graphs of $\log (p_t - p_f)$ against t are shown plotted in Figs. 6 and 7. The majority of the combustions give good linear relationships. In two cases (Expts. Nos. 10 and 14) the plotted points deviate markedly from a straight line; examination of the log p–t curves for these two experiments shows that they were exceptional in that retardation did not occur uniformly throughout the reaction, but set in only towards the end.

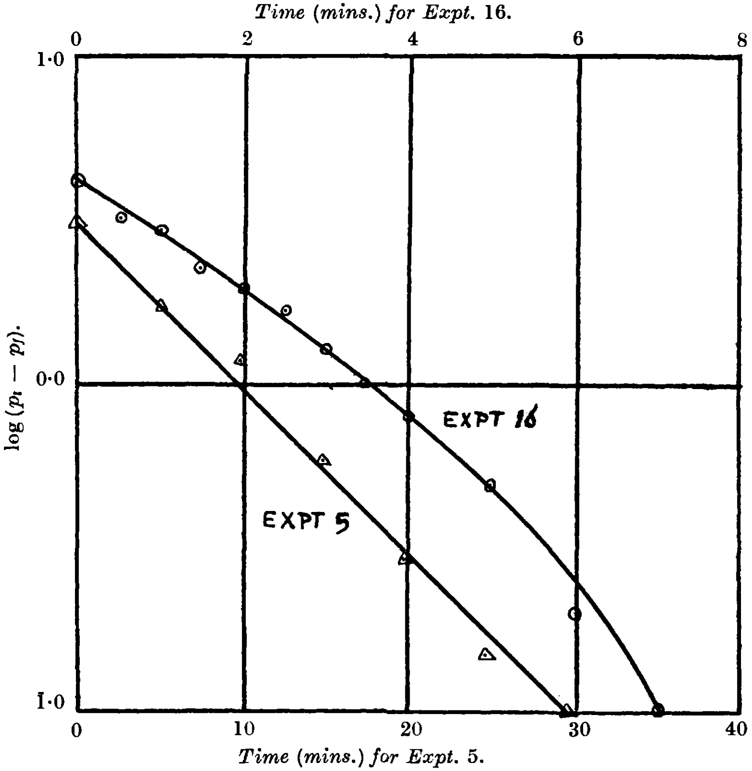
FIG. 6.



Summary and Discussion.

It has been shown in the foregoing that the rate of combination of the moist mixture $2CO + O_2$ on a new platinum surface corresponded to the unimolecular type of reaction, but that after a short period of time the course of the reaction changed, and became strongly self-retarding. The effects of the auto-poisoning were so marked that temperature had little or no influence on the rate of heterogeneous reaction. In the majority of combustions, the rate of poisoning followed a general and simple exponential law, being directly proportional to the rate of reaction, and furthermore the ratio of the two rates was approximately constant for many, and of the same order for all, of the experiments. The physical significance of this generalisation is not, however, clear : it may readily be shown that the exponential type of retardation may result either from selective adsorption in an inactive form of any species present in the gaseous phase, or alternatively, that it is due to changes in the superficial condition of the catalyst occasioned by, and proportional to, the heterogeneous reaction.

FIG. 7.



Faraday (" Experimental Researches," 1849, **1**, 165) first proved that carbonic oxide poisons the surface of platinum for the combustion of electrolytic gas. More recent experiments by Langmuir (*Trans. Faraday Soc.*, 1921—22, **17**, 634), conducted at gas pressures less than 0·1 mm., led to the conclusion that carbonic oxide forms an inactive layer on the surface of platinum, the production of carbon dioxide occurring only on patches of the metallic surface left bare by evaporation. Consideration of Langmuir's results indicates that at the pressures and temperatures of the present experiments, the inactive carbonic oxide film would almost completely cover the surface of the metal, and the rate of reaction should be scarcely appreciable. Although this conclusion agrees with the fact, brought to light in the course of the experiments outlined above, that the stable condition of a hot platinum surface in the mixture $2CO + O_2$ is catalytically inactive, yet the occurrence of rapid reaction in many cases, and the prolonged periods of time frequently required for reversion to inactivity, show that the mechanism of combustion in the conditions of the present experiments differed in several important respects from that at the low pressures of Langmuir's investigation. The occurrence of an initial period of normal unimolecular reaction and the effects of preliminary evacuation and heat treatment of the catalyst point, furthermore, to the conclusion that deeply occluded, as distinct from superficially adsorbed, gases play an important part in determining the activity, an observation which may be compared with similar cases investigated by Bone (*Phil. Trans.*, 1906, *A*, **206**, 1; *Proc. Roy. Soc.*, 1925, *A*, **109**, 459).

Although, as Hinshelwood and Pritchard (J., 1925, **127**, 806) have shown, the possibility of retardation of the reaction by carbon dioxide cannot be excluded from consideration, it was frequently found during the present experiments that the accumulation of the products of combustion in the vicinity of the wire did not result in an exceptionally high rate of poisoning.

Thermionic Emission from the Platinum Wire.

It is well known that most metals exhibit a relatively high but rapidly decaying rate of positive emission when heated for the first time in a vacuum or in a gaseous atmosphere (see Richardson, *op. cit.*, p. 226). To eliminate this effect as far as possible, the wires used in the present experiments were heated in carbonic oxide or oxygen to 600°, and the behaviour of the emission was followed, for several days before observations in the combustible mixture $2CO + O_2$ were commenced. Throughout the whole period of the experiments with a given wire, moreover, the emission currents in carbonic oxide and oxygen separately were frequently measured, in order to follow changes in the emissivity of the wire.

It was found that the thermionic emissivities of the platinum filaments passed through complex changes during the period of their use as catalysts. In general, the emission current from a new wire was relatively high, but decayed rapidly to a minimum during the progress of the experiments, and finally rose again to a steady value. Tests for emission of negative sign were made on many occasions, but no such emission was found to occur at temperatures below 750°. The positive ionisation currents measured during the experiments were therefore unaffected by losses due to recombination.

Emission in Carbonic Oxide and Oxygen Individually.—The emission currents from new wires were high, but diminished rapidly at constant temperature. The emission was partially restored by allowing the wire to remain at room temperature for 2 or 3 hours, but a general decay continued for several weeks. When a condition had been reached in which further decay was imperceptible during periods of 10—15 minutes, the observations on catalytic activity were begun.

The following table shows the variation of the emission current in oxygen at a pressure of 150 mm. at different stages in the history of the wire :

Time from beginning of experiments.	Emission (amp. × 10^{-13}) at 500°.	600°.	A.	$B \times 10^{-4}$.
3 days	40	—	$3{\cdot}0 \times 10^{24}$	2·6
6 weeks	0·6	3·8	$5{\cdot}0 \times 10^{24}$	3·1
12 ,,	3·8	50·0	$7{\cdot}2 \times 10^{18}$	1·73
20 ,,	4·0	53·0	$0{\cdot}69 \times 10^{18}$	1·53

The magnitudes of the emission currents in an atmosphere of carbonic oxide in similar conditions were practically identical with those in oxygen; the following are the values in the former gas at a pressure of 150 mm. :

12 weeks	4·8	49·0	$1{\cdot}6 \times 10^{18}$	1·59

It was found that the variation of positive emission with temperature between 250° and 650° was accurately represented by Richardson's well-known function, $AT^{\frac{1}{2}}e^{-B/T}$. Values of the numerical constants are tabulated above. The value, $1{\cdot}53 \times 10^4$, of the exponential coefficient for the fully normalised wire in oxygen compares with that obtained by Richardson (*op. cit.*, p. 231), *viz.*, $1{\cdot}52 \times 10^4$.

The emission currents tabulated above were measured with a P.D. of 200 volts between filament and plate. The currents approached a condition of saturation with this voltage, but it was not possible to obtain complete saturation, except at gaseous pressures lower than 5 mm., with a P.D. less than that at which ionisation by collision occurred.

It would appear that the decrease of emissivity during the initial period of 8 weeks is attributable to the decay of the random positive emission from the new wire, and that the subsequent growth and final constancy of emission resulted from the slow establishment of equilibrium between the metal and the gaseous atmosphere in which it was heated. In this connexion it may be recalled that, as the experiments of Wilson ("The Electrical Properties of Flames and Incandescent Solids," 1912) and of Richardson (*op. cit.*, p. 117) have shown, a somewhat similar change occurs in the electronic emission from a platinum wire when heated in hydrogen for long periods. The former author has attributed the change to a slow diffusion of the gas into, or combination with, the metal, a hypothesis which is applicable to the present case.

Positive Emission during Catalytic Combustion.—As a general conclusion from the results for emission during catalytic combustion, it may be stated that when the surface was in a fully poisoned condition, the magnitude of the emission was identical with that in carbonic oxide or oxygen at the same temperature, and underwent the same series of changes during the history of the wire as those which have been previously described for the emission in the individual reacting gases. For the sake of brevity, this latter value will be referred to in the following as the "characteristic value" of the emission. While reaction was proceeding with measurable velocity on the surface of the wire, the emission was invariably higher than the characteristic value. Conditions were, however, frequently realised in which the emission was greater than the characteristic value, although no reaction was perceptible. No simple relation was found to exist between the magnitude of the emission current and the rate of catalytic reaction: the variation of the one with the other was complex, and the type of variation changed during the history of the wire. The changes which occurred may be traced in Figs. 2—5; the following table shows how the type of variation altered with the gradual changes in the characteristic emission from the wire:

Time from beginning of experiments.	Type of catalytic reaction.	Characteristic emission.	No. of Fig. showing emission during reaction.
1 week	Unimolecular	Rapidly decaying	1
1—6 weeks	Self-retarding	Slowly decaying	2
7 ,,	,,	Minimum	2
8 ,,	,,	Slowly rising	Transition from 2
8—11 ,,	,,	,,	through 3 and 4 to 5
12—20 ,,	,,	Constant	5

The variation of emission during periods of catalytic activity was the same in the preliminary period of decaying emission as in the final period of constant emission. In both these periods, the highest emission occurred at the commencement of a period of activity, and fell as the rate of combustion decreased (*e.g.*, compare Figs. 1, 2, and 5). In the intervening period, however, the emissivity during reaction changed from this normal type to that shown in Fig. 3, finally reverting again to normal. Fig. 4 illustrates a stage in the reversion : a complete series of such intermediate steps was experimentally realised.

It has been previously suggested that the changes in the emissivity of the wire in carbonic oxide and oxygen are attributable to a slow diffusion of the gaseous components into, or combination with, the metal. It has also been shown that a number of considerations support the view that deeply occluded, as distinct from superficially adsorbed, gas is involved in the process of combustion. Hence it would appear probable that the abnormal types of emission graph such as Figs. 3 and 4 are characteristic of a non-homogeneous emitter, of which the surface-layer composition changes during the process of combustion.

The following experimental record illustrates typical variations of emission current during alternating periods of catalytic activity and inactivity, the column head C.C.E. denoting the corresponding characteristic emission (also in amps. × 10^{-13}) :

Time, mins.	Temp.	Press., mm.	Emission obs. (amps. $\times 10^{-13}$).	C.C.E.
0	315°	111	3·3	0·0
5	315	109	3·3	0·0
10	315	109	0·0	0·0
12	400	109	6·5	0·2
16	400	108	6·5	0·2
20	400	108	0·2	0·2
22	445	108	0·8	1
26	445	108	0·8	1
28	470	108	1·9	2
33	470	108	1·9	2
35	510	108	9	6
40	510	106	17·5	6
45	510	104	19	6
51	510	103	22·5	6
56	510°	102	23	6
60	510	101	23	6
65	510	100·5	22·5	6
70	510	100	22·5	6
85	510	99	22	6
105	510	98·5	14·5	6
115	510	98·5	14	6
120	510	98·5	5·8	6
125	540	99	10	14
130	540	99	13	14
132	570	100	53	26
137	570	100	36	26
145	570	100	28	26
147	600	Rapid combustion terminating in ignition.		

In the above series of observations, the normal increase of emission during periods of combustion may be observed at 315°, 400°, and 510°, and in each case cessation of activity was accompanied by decrease of emission to the characteristic value. At 445° and 470° neither combustion nor increased emission was perceptible, but at 570°, although no sensible fall in pressure occurred, the emission was considerably higher than the corresponding characteristic value for some time after the temperature had been raised, eventually falling, however, to the characteristic value. It was usually found that such a temporary increase in the emission unaccompanied by reaction was the precursor of catalytic activity at a slightly higher temperature, and in fact served as a guide in determining the rate at which the temperature was raised during an experiment. It may therefore be regarded as indicating a state of incipient activity, and was possibly accompanied by heterogeneous reaction to an extent so small as to be imperceptible on the manometer.

Summary and Discussion.

Some caution is necessary in the interpretation of data relating to thermionic emission from heated metals, since, not only is the revival of the initial positive emission readily brought about in a variety of ways, but minor variations in temperature cause large variations in emission. The precautions taken to ensure the elimination of effects due to random impurities in the metal have been previously described, and there is strong evidence for the supposition that the emission currents observed subsequent to the period of minimum emissivity were genuinely characteristic of the gaseous atmosphere surrounding the wire. The gradual transition of the type of variation of emission during combustion, the occurrence of maxima of emission in several experiments after the rate of reaction had fallen considerably, and the high emission currents frequently observed during the periods of incipient activity, render it extremely improbable that the increased emission during combustion was the result of local variations in temperature along the wire. It may therefore be concluded that the surface of the wire when in a catalytically active state was also in a state of high thermionic emissivity.

The relation between activity and emissivity was, however, by no means well defined. It was difficult to establish any wide quantitative proportionality between the rates of reaction and the corresponding emission currents, and, as has been previously noted, although the catalytic activity of the metal ceased to change after a short period of normalisation, the magnitude and behaviour of the thermionic emission continued to pass through complex changes for some time.

The explanation of this divergence is possibly to be found in the consideration that while the catalytic reaction is to a great extent determined by gas deeply occluded in the metal, the thermionic emissivity is largely dependent on the condition of the superficial layers. The occurrence of enhanced emission unaccompanied by measurable combustion lends support to this view. It is clear, however, that the condition of the metal in contact with the reacting gases was highly complex, and underwent slow and complicated changes which affected reaction and emission unequally. In the absence of more definite information regarding the mechanism of the poisoning process, and also of the gradually increasing emissivity, it is not possible at this stage to advance more definite hypotheses.

My thanks are due to Professor G. I. Finch, at whose suggestion the investigation was commenced, and to Mr. G. H. Barker, M.Sc., for his assistance in carrying out the experiments.

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