

# The Mechanism of Electrode Erosion in Electrical Discharges

## PHYSICAL BASIS OF THE LOW EROSION RATE OF THE PLATINUM METALS

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*This paper outlines the nature of the various classes of electrical discharges—the high voltage capacitative spark discharge, the normal arc discharge, and the low voltage arc that occurs at electrical contacts—and discusses the physical processes that determine the dependence of the rate of electrode erosion on the physical properties of the metal. It is concluded that the most important properties conducive to low erosion rates are high boiling point, high thermal conductivity and high density, so providing the physical reason for the low erosion rates observed for the platinum metals when used as electrodes and electrical contacts.*

Most of the technical applications of electrical discharges through gases are those which employ electrodes to establish the required electric field, and in such cases the electrodes themselves then play an important role in the discharge processes. The cathode suffers positive ion bombardment and sputtering often results; also when arcing occurs, hot spots are formed and the very high temperatures that result can produce evaporation. Such evaporation has at least two effects which are sometimes highly undesirable, namely, the production of the vapour of the electrode metal thus changing the ambient gas atmosphere, and the erosion and wearing away of the metal itself. An

instance when the latter effect is undesirable in practice is that of the well-known sparking plug of internal combustion engines, and an article referring to this effect has recently appeared in this journal (1). Electrical contacts of various types represent other examples in which the deleterious effects of electrical discharges lead to the erosion of the electrode metals (2), and Want (3) in an article in this journal has discussed the design of light duty contacts. Consequently, an understanding of processes that result in the erosion of electrode materials can be of considerable technical as well as fundamental physical interest.

### Types of Erosion

There are various processes by which metal electrodes can erode or wear away. First, there is the obvious one of chemical attack such as oxidation or corrosion. When the products of chemical action are volatile the erosion can be rapid at high temperatures. Another process is that of the actual disintegration of the structure under atomic or ionic bombardment; and, thirdly, there is the process of electrical erosion by the action of an electrical discharge. It is well known that at local regions of an electrode in a discharge tube hot spots at very high temperatures can be produced. The anode undergoes bombardment by electrons while the cathode suffers bombardment by positive ions leading to sputtering and evaporation. High temperatures can also be produced in

some gases by gas-atomic association which may involve the liberation of a great deal of heat; this produces more evaporation, but the release of energy of the electrical discharge by electronic or ionic bombardment of the electrodes is a primary cause of the production of hot spots and resulting erosion.

It is to a consideration of this latter phenomenon that this paper is devoted, with particular reference to platinum and the platinum group metals. It has long been realised that these metals appear to have a peculiar resistance to erosion by electrical discharges, and the physics of the phenomena of electrical erosion will now be discussed in an attempt to elucidate the process.

In any practical device involving electrical discharges, properties other than that of simple resistance to electrical erosion have to be taken into account. Some of these, hardness for example, naturally concern the suitability of the metal for the required practical fabrication process. Many of the required properties of a contact material and assembly are closely interrelated, and in a practical device it is often not possible to change one characteristic without altering others. However, this paper will be concerned only with the question of erosion due to an electrical discharge.

## **Electrode Processes in Contact Discharges**

A discussion of the various mechanisms of electrode bombardment occurring at an opening contact has been given previously by the present author (4). Briefly, there are different phases of operation of the arc discharge depending upon the state of development of the arc itself and therefore upon the gap separation and power dissipated.

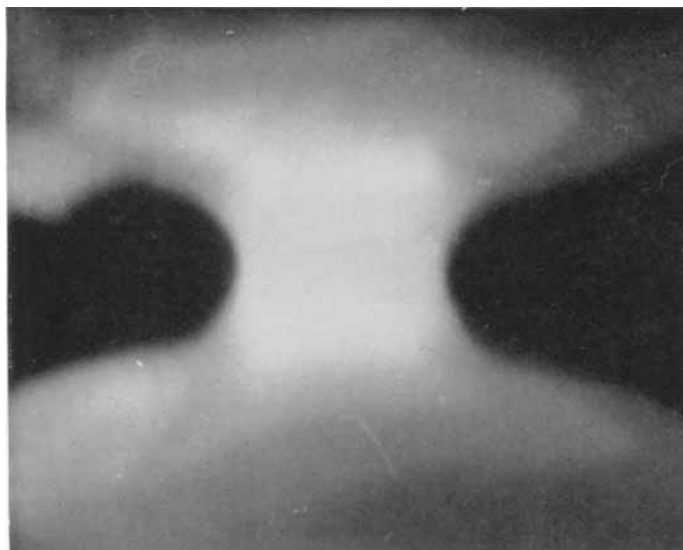
First, the arc is formed when the microscopic molten metal bridge blows up and the metal contact is replaced by a gaseous and vapour region between the electrodes (2). Since the cathode is at a high temperature ( $\geq$  melting point of the metal) it thermally emits electrons which are attracted to the

anode; the energy released there (eV) by this electron bombardment is clearly dependent upon the actual value of the contact voltage  $V$  which, on account of the presence of local self-inductance, can be greater than the static contact voltage. This bombardment can remove metal from the anode.

Secondly, as the gap widens and the concentration in it of metal vapour increases, this vapour becomes ionised by the electron stream, so producing positive ions. These are attracted towards and bombard the cathode thus leading to loss of material from the cathode. Because of the presence of electrons, and ions as well as gas atoms, a plasma or positive column is formed, direct high energy electron bombardment of the anode is reduced and, as the gap lengthens, a normal arc discharge is set up. The energy released at the cathode is then of the order  $eV_c$ , where  $V_c$  is the cathode fall of potential between the electrode and the plasma column. In this stage the release of energy at the cathode can exceed that at the anode.

Clearly, for the fully developed arc and when a high current is passed, considerable bombardment of both electrodes can occur. In such conditions considerable energy is also dissipated in the positive column itself where very high temperatures can be attained. However, in the present discussion attention is mainly directed to the simple states of the contact discharge during the earliest stages of its development and when the gap separation is short. This separation  $d$  is approximately that of the largest molten metal bridge and is of the order of  $10^{-3}$  cm. Two types of short arc have been classified and the term "anode arc" is given to the case of predominant anode loss of material, and "cathode arc" to the case when the loss is confined to the cathode (5).

So far the post-contact arc has been considered, but it is also known that a pre-contact arc can occur with cold electrodes (6). Consideration of the electron emission activity (7) of the cathode surface shows that this can be initiated when the gap separation



*Photomicrograph ( $\times 420$ ) of a molten metal bridge between pure platinum contacts operating in air, showing the stable nodoid form. The temperature of the glowing metal ranges from about  $2000^{\circ}\text{K}$  at the ends to about  $4500^{\circ}\text{K}$  near the middle of the bridge*

*(Photograph by F. Llewellyn-Jones and Michael Price)*

is of the order of  $10^{-4}$  cm and must be initiated by an electron avalanche ( $n$  electrons each of charge  $e$ ) striking the anode and releasing energy in some cases as much as  $n$  eV.

Again, as in the case of a spark discharge passed between two cold electrodes of self capacity  $C$ , the energy of the spark released by particle bombardment of the electrodes must be some fraction of the total energy ( $\sim CV^2/2$ ) of the gap which is discharged by the spark current.

Thus in all the cases considered, whether a spark, or the pre-contact or post-contact micro-arc, electrical discharges have this basic feature in common in that a fraction of the total energy available in the charged spark gap is released at either or both of the electrodes.

Thus, from elementary considerations of the discharge mechanism, it can be seen that particle bombardment, whether electronic or ionic, of electrodes can occur, and it is now necessary to consider the consequences to the electrodes of this release of discharge energy.

The first important factor to appreciate is the great rapidity with which a significant amount of energy can be released at an electrode surface. If the total energy  $W$  of a discharge were released at a slow rate over a

long period, any rise in electrode temperature, and therefore consequent evaporation, would be negligible. Now, the initial stage of the setting up of the discharge takes place in times of the order of the electron and ion transit times  $t_t$  and is therefore  $\sim d/W_+$ , where  $W_+$  is the ionic drift speed this is  $10^5$ , giving  $t_t$  of the order of  $10^{-9}$  sec. Clearly then, the practical consequences of an extremely rapid release of discharge energy  $W$  ( $\sim$  kinetic energy of ions and electrons plus the potential energy of the ions and less the work required in the secondary emission of electrons) is a rapid rise in temperature over the "hot spot" area and throughout a small volume of electrode underneath.

### **Electrode Hot Spot and Energy Balance**

Thus it seems reasonable to regard the main consequences of the electrical discharge (neglecting chemical effects) as far as the electrode is concerned as being due to the sudden release of energy over a certain small area of either electrode, and clearly the magnitude of that release is a matter of physical significance.

The considerations put forward above of the basic processes in the establishment of an arc discharge show that the area of the

electrode significant in the bombardment processes is the area over which either the electron avalanche or the positive ion avalanche will strike the appropriate electrode. Theoretical estimates of these areas have been made by the present author (8) for certain cases of practical interest, such as that of the sparking plug of an internal combustion engine, and it is found that very high current densities  $\sim 10^7$  amp  $\text{cm}^{-2}$  can occur at "hot spots" about  $10^{-7}$   $\text{cm}^2$  in area.

The energy balance following this sudden release of energy at areas on the electrode of this order must now be considered. A certain (microscopic) volume of metal lying under this area will be suddenly heated, and part of this heat must be dissipated by thermal conduction through the bulk of the metal; the rate at which this can occur has been given previously (8). Heat will also be lost by thermal radiation from the hot spot surface of area  $A$  and temperature  $T^\circ$  K at a rate proportional to  $AT^4$ .

Considerations such as these lead to the conclusion that the mass of metal beneath the hot spot will play a vanishingly small part in the energy balance there which determines the processes of disposal of the energy released, and part of which may even involve boiling of some metal. Thus, the boiling of the electrode material involves the energy of the discharge current and not the current directly considered simply as a transport of charge. It follows that these processes of disposal must include the processes of the thermal conduction through the metal itself away from the surface of the hot spot; the process of the heating up of a small volume of metal underneath the hot spot, first to the melting point, followed by melting; if sufficient energy is available, there occurs the further heating of the volume of molten metal up to the boiling point; and, finally, evaporation or boiling can occur when there is further excess available, this leading to removal of metal from the electrode.

The author has previously obtained an expression (8) relating the rate of boiling of

metal to these processes and therefore to physical properties of the metal. This is

$$v = \frac{\alpha V^2 - \beta T^4 - \gamma \lambda (T - \theta)}{\rho \{ (T - \theta)s + 2T/A \}} \quad (1)$$

$v$  = volume of electrode metal eroded, or boiled off, per elementary discharge

$\rho$  = density of metal

$T$  = boiling point of the metal

$\lambda$  = thermal conductivity

$A$  = atomic weight

$s$  = specific heat

$V$  = effective discharge potential difference

$\alpha = f(C)$  = function of the local capacity  $C$  and discharge conditions which determine the fraction of the total energy released at the electrodes and available

$\beta$  = a constant which includes Stefan's constant and the area of the hot spot

$\gamma$  = a geometrical factor related to the rate of thermal conduction of energy through the metal

$\theta$  = the steady temperature (in  $^\circ\text{K}$ ) at points remote from the hot spot.

The erosion equation can also be written in a simplified form by noting that  $T \gg \theta$  and  $\alpha$  is a constant in any given circuit when electrical parameters are given; further,  $\alpha V^2$  can be replaced by a constant  $\alpha'$  when the gap voltage is given and remains constant for different electrode materials, so that

$$v = \frac{\alpha' - \beta T^4 - \gamma \lambda T}{\rho (s + 2T/A) T} \quad (2)$$

## The Erosion Equation

Before discussing experimental data that may be used to test the validity of this equation, it is of interest to consider what guidance this relation gives concerning the behaviour of metals with different physical properties when exposed to an electrical discharge.

Inspection at once brings out the importance of the boiling point, the density and the thermal conductivity, high values of which should lead to low values of electrode erosion; a high boiling point is clearly of the greatest significance in considering those physical properties of a metal for which low electrical erosion is desired. Another factor of impor-

tance is the first term,  $V^2 f(C)$  or  $\alpha'$ , representing the amount of electrical energy released at the electrodes. When this is comparatively small, the amount of resulting erosion, being given by the difference of two terms, is not necessarily proportional to the energy released; but when the energy term  $\alpha'$  greatly exceeds the other terms and the erosion is great, the volume rate of erosion  $v$  is then very approximately proportional to  $\alpha V^2$ . Further, in cases of comparatively prolonged arcs as distinct from short, almost instantaneous, discharges of the gap and local circuit capacity, the gap or arc potential  $V_a$  can be almost constant, and then the arc energy dissipated  $V_a \times I_a \times t$  has become roughly proportional to the arc current  $I_a$  and also to  $I_a t$ , i.e. to  $Q$ , the total charge passed.

Clearly, the highest possible values of these quantities lead to the lowest possible rate of matter erosion; further, it would appear that the most important property, for any given amount of energy released, is that of high boiling point. The physical reason for this is, of course, that high values of this property lead to high dissipation of energy, so reducing the amount of excess energy available for actual boiling of metal.

Now these properties are precisely those associated with metals such as platinum and iridium, which have very high boiling points as well as high densities compared with those of other metals. Thus the theory of electrical erosion due to electrical discharges briefly outlined above indicates the physical reasons for the peculiar property of platinum and iridium in resisting erosion by an electrical discharge and therefore for their general suitability as contact or spark gap electrodes, as far as that particular property is concerned.

It can also be seen that approximate measurements in certain special conditions, for example with constant arc voltage  $V_a$ , can lead to the result that erosion appears to be proportional to the total charge passed, as would be the case in "ionic transfer" of matter from one electrode to the other (9, 10). This line of thought indicates that the physical

interpretation, on the basis of fundamental physical processes, of experimental results must be carried out with some care when considering the dependence of erosion directly on current or total charge passed. On the other hand, in the case of comparatively high-voltage, short-time or capacitative spark discharges, the energy released could depend on the square of the initial spark gap voltage  $V_s$ , and this then becomes an important parameter. This condition applies to the case of the ignition spark discharge of an internal combustion engine, in which turbulence and other factors lead to rapid arc quenching and the discharge itself takes the form of a succession of high voltage sparks (8).

### Applications and Test of Erosion Equation

The expression derived above for the rate of volume erosion in terms of the physical properties of the electrode has been applied in a number of different cases for which experimental data on spark erosion are available. Since these cases were concerned with widely different experimental and physical conditions, it may be of interest to describe them. The three distinct sets of discharge conditions were:

- (a) the high voltage "capacitative" electrical spark as employed at sparking plugs of internal combustion engines,
- (b) the erosion of electrical contacts by the normal arc discharge at break, and
- (c) the erosion of electrical contacts by the low-voltage ( $V \sim 4$  volts) arc at break and occurring immediately after the rupture of the molten metal contact bridge.

(a) If the constants  $\alpha$ ,  $\beta$  and  $\gamma$  in any given contact circuit were known, it would be possible to calculate the mass or volume eroded per spark for any particular metal when sustained low-voltage arcing and chemical reaction are negligible. However, such detailed calculations are not possible at present since neither the precise time during

which the hot spots were maintained in the development of the spark discharge nor the precise areas of the hot spots are known.

The procedure in such cases is then to find the constants  $\alpha$ ,  $\beta$  and  $\gamma$  empirically by applying the expression to the particular experimental data for three materials of known, preferably differing, physical properties. This procedure has in fact been followed for the metals platinum, nickel and austenitic steel, which have been employed in experimental sparking plugs and used in aero engines (8). The three simultaneous equations were then solved, and the values obtained were

$$\begin{aligned}\alpha &= 0.95 \times 10^{-12} \text{ F,} \\ \beta &= 2.00 \times 10^{-20} \text{ cal per } (0^\circ\text{K})^4, \\ \gamma &= 0.95 \times 10^{-8} \text{ cm sec.}\end{aligned}$$

Inspection then showed that these values for the particular conditions were physically reasonable. On the basis of these values it could be deduced, for instance, that for these sparking plug discharges only 11 per cent of the total spark energy was actually released at the two electrodes, the remainder being dissipated in the gas.

(b) Consider next the second example of practical application. Ittner and Ulsh (11), at the IBM laboratories, New York, measured the erosion of a large number of contact

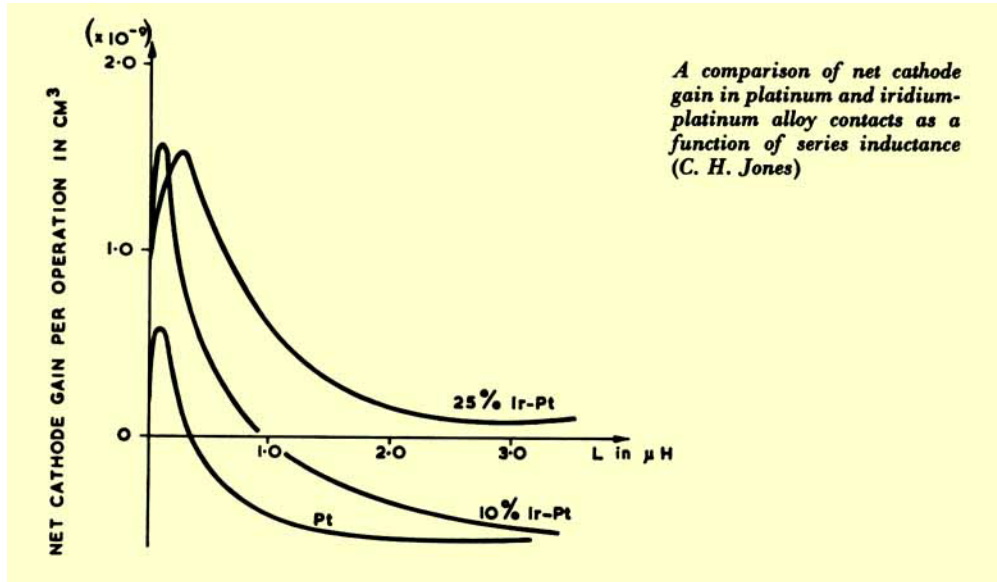
materials. In their experiments, the arc current  $I_a$  lay in the range 1–5 amp and the gap arc voltage  $V_a$  remained constant at about 50 V in a resistive and inductive circuit, and consequently these authors considered that the discharge obtained on opening the contacts to have been a normal arc discharge. They applied the general erosion equation in its simplified form (2) where  $v$  is the matter transfer coefficient expressed in  $\text{cm}^3$  per coulomb. The thermal conductivity  $\lambda$  is expressed in joules per second – cm per degree centigrade; the boiling point  $T$  in  $^\circ\text{C}$ , the density  $\rho$  in g per  $\text{cm}^3$ ; specific heat  $s$  in joules per  $\text{g}^\circ\text{C}$ . Ittner and Ulsh used the following values of the constants for their specific experimental conditions:

$$\begin{aligned}\alpha' &= 2.40 \times 10^{-2} \\ \beta &= 2.04 \times 10^{-17} \\ \gamma &= 2.52 \times 10^{-6}\end{aligned}$$

and with these used the expression (2) to calculate the transfer coefficient (or cathode loss as it was in their experiments).

Some of their results for metals of the platinum group are given in the table, from which they concluded that expression (2) is useful in giving a first approximation to the expected cathode arc transfer of most materials and so permits evaluation of normal arc transfer coefficients which can then be

Data on Physical Properties and Erosion							
Metal	Density g/cm <sup>3</sup>	Boiling point °C	Thermal conductivity joules/sec cm/°C	Specific heat, joules/ g°C	Atomic weight	Transfer coefficient (cathode loss) in cm <sup>3</sup> × 10 <sup>-6</sup> /C	
						Measured	Calculated
Ag	10.5	1950	4.2	0.23	108	0.33	0.34
Au	19.3	2600	2.9	0.13	197	0.34	1.1
Ir	22.4	4800	0.58	0.13	193	0.25	
Pd	12.2	2200	0.70	0.29	107	1.51	1.59
Pt	21.4	4300	0.70	0.13	195	0.43	0.41
10% Ir-Pt	21.6	4400	0.31	0.13	194	0.63	0.81
20% Ir-Pt	21.7	4500	0.18	0.13	194	0.60	0.67
35% Ir-Pt	21.8	4600	0.20	0.13	194	0.54	0.54
Rh	12.4	3880	0.88	0.24	103	0.42	0.5



used as a guide for the choice of contact materials. The table gives, for comparison, the data for more common metals in addition to those for the platinum metals.

Ittner and Ulsh also drew attention to the fact that the simplified erosion equation gives a qualitative explanation of the behaviour of the iridium-platinum alloys included in the table. The observed effect of alloying iridium with platinum was first to increase matter transfer due to arcing, but this eventually decreased as the percentage of iridium is increased. They attributed this increase in transfer with small amounts of iridium to the decrease in thermal conductivity in the alloy as compared with pure platinum.

(c) The third application of the erosion equation to the platinum metals also lies in the field of electrical contacts, but this time to a different class of electrical discharge. The contact voltage was 4V, the parallel quenching capacitance was 4μfd, and the series inductance was controllable in the range of  $10^{-8}$  to  $10^{-5}$  Henry. The erosion and net transfer produced at electrodes of platinum and iridium-platinum alloys have been investigated at Swansea, using a radio-active tracer technique, and C. H. Jones reported

some results at a recent conference in London (12). These are given in the graph and were explained on the following lines.

With low series circuit inductance  $< 10^{-7}$ H there was no region over which the transfer was constant and independent of inductance, so that the transfer was not solely due to bridge transfer; in fact, there must have been a short duration, short length post-bridge rupture arc. In that case, it is reasonable to assume that expressions (1) or (2) might be applicable. Indeed, the same argument as used for these materials by Ittner and Ulsh, who had shown that the arc transfer was greater for the alloys than for pure platinum, might be expected to apply to these materials for these discharges also.

### Conclusion

The experimental results described above show that the rate of matter erosion due to electrical discharges is, to a first approximation, given by the expressions (1) or (2). Further, the experiments involved a number of different metals, including the metals of the platinum group, which covered a wide range of physical properties. Consequently, it is reasonable to conclude that this agreement is experimental evidence in support of

the basic physical assumptions regarding the mechanism of the erosion of metal electrodes by electrical discharges. This mechanism, in cases which exclude chemical activity, corrosion and sputtering, envisages actual boiling of metal at the electrode hot spots by the energy available in excess of that dissipated by radiation and thermal conduction from the hot spot. Further, the agreement between theoretically predicted and experimentally observed erosion rates may also be regarded as evidence in support of the analysis of the different types of electrical discharges given above in the section on electrode processes.

From these conclusions, then, it follows that the dependence of the discharge erosion rate of the electrode on its physical properties is mainly on the lines indicated by the relation (1), and so substantiates the general observations given in the section on the erosion equation. This is of particular interest as far as the platinum metals are concerned, and it supplies the physical basis of the observed low erosion rates of metals of the platinum group: this also explains the low erosion rates of metals like tungsten and molybdenum in chemically inactive ambient atmospheres. These experimental applications of the erosion equation, therefore,

help to form the basis of a fuller understanding, not only of the behaviour of platinum and of other metals, but also of the erosion process itself due to electrical discharges.

### References

- 1 G. W. Shoobert, *Platinum Metals Rev.*, 1962, **6**, 92-94
- 2 F. Llewellyn-Jones, *The Physics of Electrical Contacts*, Oxford, Clarendon Press, 1957
- 3 J. G. Want, *Platinum Metals Rev.*, 1961, **5**, 42-50
- 4 F. Llewellyn-Jones, *Proc. Inst. Elec. Engrs.*, Part I, 1949, **96**, (Nov.), 305-312
- 5 L. H. Germer and W. S. Boyle, Paper D3, 8th Annual Gaseous Electronics Conference, Schenectady, N.Y., 20th October, 1955
- 6 L. H. Germer and I. L. Haworth, *Phys. Rev.*, 1948, **73**, (9), 1121
- 7 F. Llewellyn-Jones, *Proc. Inst. Elec. Engrs.*, Part I, 1953, **100**, (Jul.), 169-173
- 8 F. Llewellyn-Jones, *Nature*, 1946, **157**, (Mar. 9th), 289-299; *Brit. J. Appl. Phys.*, 1950, **1**, (3), 60-65
- 9 R. Holm, *Electrical Contacts*, Stockholm, Hugo Gebers, 1946
- 10 W. B. Ittner, *J. Appl. Phys.*, 1956, **27**, (4), 382
- 11 W. B. Ittner and H. B. Ulsh, *Proc. Inst. Elec. Engrs.*, 1957, Part B, **104**, (Jan.), 63-68
- 12 C. H. Jones, Paper read at Symposium on Electrical Contacts, organised by the Institute of Physics and Physical Society, London, 1961; see also M. R. Hopkins and C. H. Jones, *Brit. J. Appl. Phys.*, in the press.

## Electro-organic Synthesis at Controlled Potentials

### MERCURY CATHODE AND PLATINUM GAUZE ANODE

Although catalytic hydrogenation and other chemical reduction processes are employed in the synthesis of many organic chemicals, their application is sometimes limited by lack of selectivity. An alternative method of reducing organic compounds—controlled potential electrolysis—has been investigated recently by W. H. Harwood, of Continental Oil Company, and R. M. Hurd and W. H. Jordan, of Tracor Inc., using nitrobenzene as the starting material (*Ind. Eng. Chem., Process Design & Development*, 1963, **2**, (1), 72-77).

Electrolyses were carried out over the potential range -0.4 to -0.9 volt in sulphuric acid solutions, in a cell with a platinum gauze anode, a mercury pool cathode and a satur-

ated calomel reference electrode. A high current capacity potentiostat, developed recently, maintained potential control. The various proportions of *p*-aminophenol, aniline, azoxybenzene and *p*-phenetidine produced were dependent on the electrolysis time and on the potential used.

The results of this laboratory-scale investigation indicate that potential control is effective in directing the course of electrochemical reduction reactions and in producing higher yields of some reduction products than are obtainable with chemical reducing agents. On an industrial scale, this technique may have many applications in the manufacture of organic compounds.