LX.—*Hydrogenation of Cyclic Compounds under Pressure in Presence of Osmium and Other Catalysts.*

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When certain cyclic compounds (*e.g.*, benzene, naphthalene, pyridine, quinoline) were hydrogenated under pressure in Ipatiev's apparatus, it was found that the rate of absorption of the gas was dependent upon both the temperature (exhibiting a definite optimum) and the type of catalyst, particularly when platinum, palladium, iridium, or osmium was used on a supporting substance such as asbestos. Moreover, the concentration of the metal on the surface affected the rate of reaction.

We have therefore made comparative measurements of the effects of the above metals on the hydrogenation of pyridine and quinoline under pressure, and have also studied a number of subsidiary factors.

The efficiency of a given catalyst may be assessed according to the rate of the reaction, *i.e.*, from the quantity of hydrogen absorbed during equal intervals of time. As the reactions only proceed within certain temperature limits, the volumes have to be read at high temperatures (250—320°) and are therefore affected not only by thermal expansion but also by the partial pressures of other substances. The total amounts of hydrogen absorbed as shown by the manometer (at room temperature) therefore differ according to the temperature of the bomb; nevertheless the rate of decrease of hydrogen pressure at a definite optimal temperature was sufficiently well defined to enable the reaction to be followed and also to indicate certain peculiarities in the catalysts.

EXPERIMENTAL.

50 G. of the substance under investigation are placed in a glass tube, and on the surface of the liquid is placed a plug containing the catalyst (6 g. of asbestos coated with the metal), the plug being kept in position by means of a copper net. The tube is then put into the Ipatiev apparatus, which is closed and filled with hydrogen up to a pressure of about 100 atm. After the valve has been shut, the apparatus is allowed to stand for several hours in order to ensure that it is air-tight, as judged by the constancy of the manometer reading, and then heated to the optimal temperature, which should by determined by means of preliminary tests and is usually about 80° above the boiling point of the substance being hydrogenated. The experiment is considered as beginning only when the changes in the manometer readings have reached their maximal value within the given optimal temperature range, such readings being taken every 15 minutes. Usually the experiment was continued on several successive days, being interrupted over-night; it was regarded as being completed when the decrease of pressure became negligible.

Hydrogenation under such conditions differs somewhat from that in an open tube, as in Sabatier and Senderens's method, and also from that under pressure, as in Ipatiev's method. In our experiments, the catalytic mass is not distributed throughout the liquid (as in the latter method of Ipatiev), but forms a separate layer, penetrated both by the vapour of the liquid undergoing hydrogenation and by the hydrogen. Such conditions are favourable in that they prolong the time during which the substance is kept within the contact zone and also secure intimate contact. Thus, the necessity of mechanically intermixing the liquid with the catalyst is avoided. Hydrogenation is effected in the vapour phase, as in the Sabatier process, but also under pressure, as in Ipatiev's process. Such a combination is rendered still more effective if the low-boiling products are condensed in a subsidiary apparatus such as will be described in a later paper.

Preparation of Catalysts.—Osmium–asbestos. Washed and ignited asbestos (asbestos cotton) is shaken into a pulp with water and an aqueous solution of the required amount of osmium tetroxide is added, followed by solutions of sodium hydroxide and hydrazine hydrochloride until the liquid is completely decolorised; the whole is then heated in the water-bath to secure precipitation of metallic osmium upon the asbestos, which is drained, well washed in hot water, and dried first at 70—80° and finally in a vacuum desiccator over phosphoric anhydride.

Osmium–cerium–asbestos. A solution of osmium tetroxide and cerium nitrate in the required ratio is poured over asbestos pulp, and a small quantity of ammonia and 1 c.c. of hydrogen peroxide for every 0·1 g. of cerium salt are added. The whole is then boiled with solutions of caustic potash and hydrazine hydrochloride and treated as before.

Activation of Catalysts.—The catalyst may undergo an alteration in its degree of dispersion owing to the temperature employed, or it may become enveloped by difficultly volatile by-products of the reaction, or, further, its efficiency may be impaired in consequence of the oxygen of the oxides becoming involved in organic complexes; such occurrences may cause either a definite poisoning of the catalyst or a temporary fatigue. After a certain time, or after having transformed a definite quantity of substance, the catalyst therefore requires artificial reactivation, which may be effected by supplying it with oxygen for the purpose of forming an active surface rich in oxides. This may be accomplished either by heating it at 400° in a current of oxygen, or by subjecting it to the action of hydrogen peroxide at room temperature, the latter procedure being preferable as causing less disturbance in the state of dispersion: the catalyst is put into water, a few c.c. of hydrogen peroxide are added and rapidly drained off, and the catalyst is dried in the desiccator. The presence of a certain amount of water in the catalyst often increases its activity, so that, alternatively, drying may be effected at 105°. Any traces of organic matter are removed from the surface of the mass by thorough extraction with alcohol or ether in a Soxhlet apparatus.

Curves 1, 2, and 3 (Fig. 1) illustrate the hydrogenation of quinoline in presence of 20% platinum on asbestos at 320°, the fall

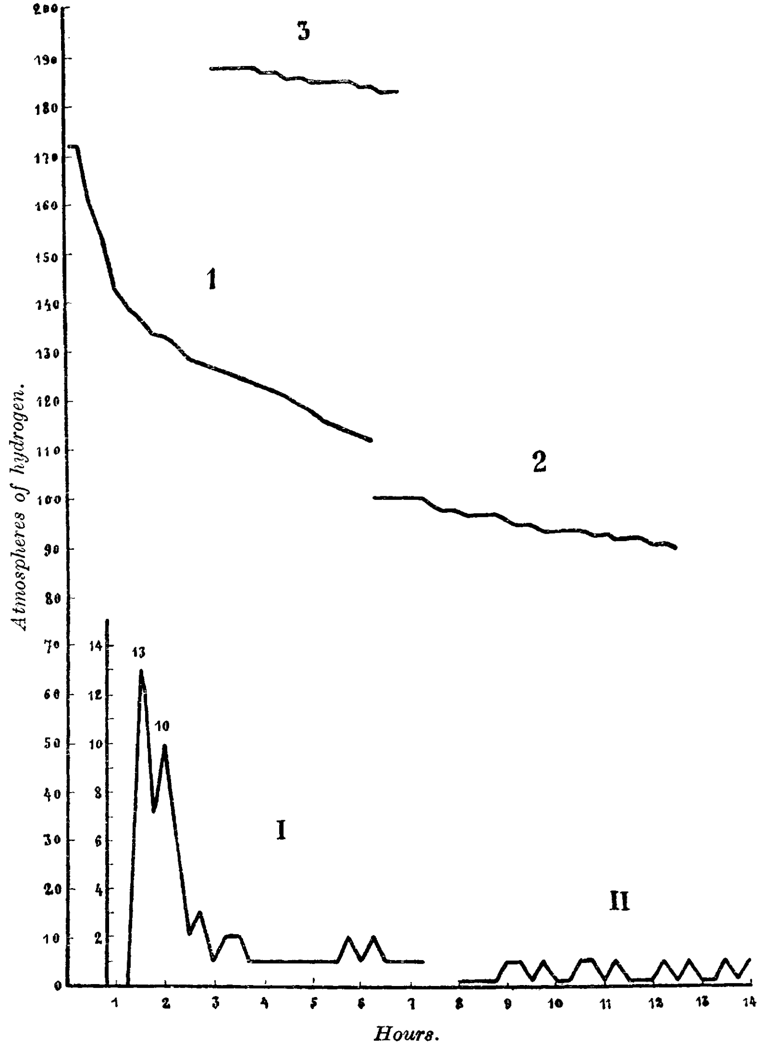
TABLE I.

Quinoline; 20% Pt on asbestos; 320°.

I. .... 0, 13, 7, 10, 2, 2, 3, 1, 2, 2, 1, 1, 1, 1, 1, 1, 1, 1, 2, 1, 2, 1, 1, 1, 1.
II. .... 0, 0, 0, 0, 1, 1, 0, 1, 0, 0, 1, 1, 0, 1, 0, 0, 0, 1, 0, 1, 0, 0, 1, 0, 1.

Product of reaction: 91% tetrahydroquinoline.

FIG. 1.



of the pressure of hydrogen being measured every 15 min. at 320°. Curve 1 denotes rapid hydrogenation, which quickly slackens owing to fatigue of the catalyst. Table I (I) and Curve I show the amounts of hydrogen absorbed (in atmos.) in successive intervals of 15 mins., and it will be noted that the absorption proceeds discontinuously, the curve showing undulations.

Curve 2 represents the course of hydrogenation after 12 hours' interruption (the bomb having been cooled to room temperature and subsequently re-heated to the optimal temperature of 320°); Table I (II) and Curve II show the successive absorptions and indicate considerable fatigue of the catalyst. On the first heating (I), an absorption equal to 59 atm. occurred during 6¼ hours, whereas during the second heating the amount absorbed for an equal lapse of time only reached 10 atm. Now, in the first case the fluctuations in the quantities of hydrogen absorbed give evidence that periods of fatigue alternate with periods of partial reactivation of the catalysts, and similar renewal of activity may also be observed in the second case where values of 1 atm. alternate with inactivity.

Finally, in the third case (curve 3) a state of extinction of the catalyst is attained, notwithstanding the optimal temperature, the excess of hydrogen re-introduced (188 atm.), and the incomplete hydrogenation of the quinoline (only 91% of tetrahydroquinoline).

20% Palladium–asbestos produces a more uniform and extensive hydrogenation of quinoline. After a short induction period (15 minutes), at the optimal temperature, absorption starts and soon attains a maximum of 5 atm. in 15 mins., followed by oscillations from 3 to 2 atm. in 15 mins.; thus, during the first hour 15 atm. were absorbed, whilst in the course of the following 4½ hours the absorption was only 6·9 atm. per hour. Heating anew after cooling gave an absorption of 3 atm. per hour (21 atm. in 7 hours). These two ranges gave the following values for absorption in successive periods of 15 mins. :

I. ... 0, 4, 5, 3, 3, 3, 1, 2, 2, 3, 3, 2, 1, 0, 2, 3, 1, 1, 2, 1, 1, 1, 2.
(5¾ hours; 46 atm.)

II.... 0, 0, 1, 2, 1, 0, 0, 1, 1, 1, 1, 1, 1, 0, 0, 1, 1, 2, 0, 1, 0, 1, 0, 1, 1, 1, 1, 1.
(7 hours; 21 atm.)

The powerful catalytic effect of osmium, which is effective in a concentration of only 1% on asbestos, is due to the ease of formation of its oxide in contact with the air, or when exposed to the action of hydrogen peroxide. With the above concentration at 320°, the following ranges were obtained for the hydrogenation of quinoline;

I. 0, 4, 4, 5, 5, 5, 5, 2, 3, 3, 1, 3, 2, 3, 1, 1, 1, 0, 2, 1, 2, 1, 1, 2, 0, 0. 1, 0, 1, 1.
(60 atm. in $7\frac{1}{2}$ hrs. = 8 atm./hr.)

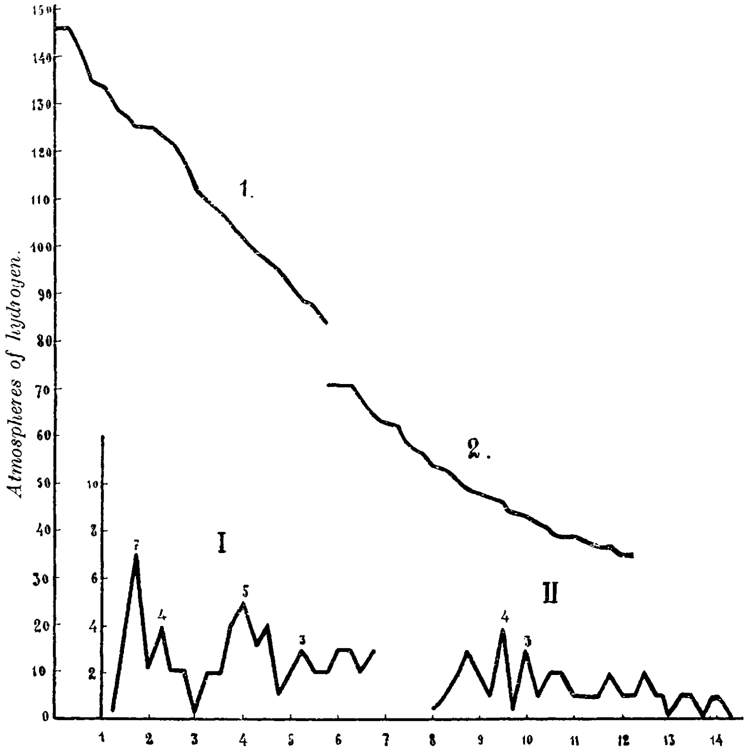
II. 2, 0, 1, 0, 1, 0, 0, 1, 0, 1, 1, 0, 0, 1, 0, 1, 0, 0, 1, 0, 0.
(10 atm. in $5\frac{1}{4}$ hrs. = 1·9 atm./hr.)

93% of tetrahydroquinoline was produced.

For 20% osmium-asbestos at 300° the following ranges were obtained (see Fig. 2):

Fig. 2.

Quinoline. 20 % Os *on asbestos;* 300 .



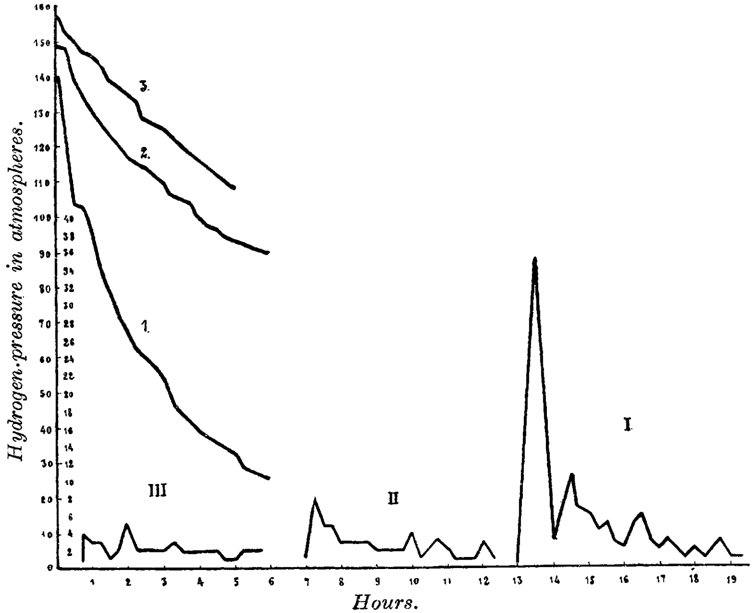
I. ... 0, 4, 7, 2, 4, 2, 2, 0, 2, 2, 4, 5, 3, 4, 1, 2, 3, 2, 2, 3, 3, 2, 3.
(62 atm. in $5\frac{3}{4}$ hrs. = 10·8 atm./hr.)

II. ... 0, 1, 2, 3, 2, 1, 4, 1, 3, 1, 2, 2, 1, 1, 1, 2, 1, 1, 2, 1, 0, 1, 1, 0, 1, 0.
(35 atm. in $6\frac{1}{4}$ hrs. = 5·6 atm./hr.)

If only 1% of ceric oxide be added to the foregoing 20% osmium-asbestos, considerable initial acceleration and increased intensity result (see Fig. 3):

FIG. 3.

Quinoline. Osmium 20% + CeO_2 1% *on asbestos;* 320°.



I. ... 35, 3, 6, 1, 1, 7, 6, 4, 5, 3, 2, 5, 6, 3, 2, 3, 2, 1, 2, 1, 2, 3, 1, 1.
(105 atm. in 6 hrs. = 17·5 atm./hr.)

II. ... 1, 8, 5, 5, 3, 3, 3, 3, 2, 2, 2, 2, 4, 1, 2, 3, 2, 1, 2, 1, 1, 1, 3, 1.
(61 atm. in 6 hrs. = 10 atm./hr.)

III. ... 4, 3, 3, 1, 2, 5, 2, 2, 2, 2, 3, 2, 2, 2, 2, 2, 2, 2, 1, 1, 2, 2, 2.
(51 atm. in 5¾ hrs. = 9 atm./hr.)

Products of reaction:

Temp. range.	165—200°.	200—240°.	240—250°.	260° and above.
NH_3%	66·7	17·0	3·3	13·2

In order to emphasise the significance of the addition of ceric oxide, the two foregoing experiments are compared in the following table:

	20% Os–Asbestos.	20% Os–Asbestos + 1% CeO_2.
Maximum in the course of 15 mins. ...	7 atm.	35 atm.
Maximum in the course of 60 mins. ...	15 ,,	45 ,,
Average quantity of H_2 absorbed per hour (I)	10·8 ,,	17·5 ,,
Average quantity of H_2 absorbed per hour (II)	5·6 ,,	10 ,,
Average quantity of H_2 absorbed per hour (III)	—	9 ,,

Owing to the presence of ceric oxide, the activity of osmium undergoes a comparatively rapid restoration, and in each of the three ranges there is a total absence of zero values. In each case the initial activity is immediately followed by a temporary fatigue, and periods of activity and depression then alternate. This example clearly demonstrates the discontinuity of the hydrogenation. Oxygen doubtless participates in the reactivation, both in the layer of osmium tetroxide and in the ceric oxide which serves as a promoter or subsidiary activating agent.

Although ceric oxide, when distributed over asbestos to the extent of 20%, will facilitate the hydrogenation of quinoline, giving as much as 88% of tetrahydroquinoline, yet, in the absence of any catalysing metal, it is incapable of hydrogenating pyridine, naphthalene, or benzene; similarly, it is unable to effect further reduction of tetrahydroquinoline and hexahydroquinoline, whereas this is easily effected on the addition of osmium or nickel. Thus, although osmium and cerium jointly produce intense hydrogenation, neither of these alone is capable of giving such an effect. Similar results are obtained for the formation of low-boiling products (below 200°) when a combination of 20% CeO_2 + 1% Os is used instead of 20% Os + 1% CeO_2 (compare p. 447).

The following significant data were obtained on hydrogenating benzene or pyridine in the presence of 20% osmium–asbestos (1) alone, and (2) with the addition of ceria:

(1) Benzene; Osmium, 20% on asbestos; 250°.

I. 0, 0, 2, 8, 6, 5, 4, 4, 4, 5, 3, 3, 4, 1, 4, 4, 4, 3, 4.
II. 0, 1, 1, 2, 2, 3, 2, 2, 2, 1, 4, 4, 2, 6, 1, 1, 1, 2, 1, 1, 0, 1, 0, 0, 0, 0, 1, 1, 0, 0, 0.
III. 0, 0, 5, 7, 6, 5, 5, 4, 5, 3, 2, 5, 2.
IV. 0, 0, 0, 2, 1, 1, 1, 0, 1, 1, 1, 1, 1, 1, 2, 1, 0, 1, 0, 0, 0, 0, 1, 1, 0, 0, 1, 0, 0, 0, 0.

Pyridine; Osmium, 20% on asbestos; 250°.

I. 0, 5, 19, 1, 1, 1, 3, 0, 1, 3, 2, 3, 2, 3, 2, 2, 4, 4, 3, 6, 1, 2, 4, 2, 2, 3, 2, 3, 1, 3, 2, 2, 2, 1, 1, 4, 2, 2.
II. 0, 2, 1, 2, 1, 2, 10, 3, 0, 1, 2, 1, 1, 1, 0, 1, 1, 1, 1, 0, 1, 0, 1, 0, 1, 1, 1, 0.

(2) Pyridine; 20% Os + 1% CeO_2 on asbestos; 250°.

I. 0, 0, 0, 0, 2, 2, 2, 2, 2, 1, 1, 1, 1, 1, 1, 1, 2, 2, 1, 0, 1, 2, 2, 2, 1, 1, 1, 1.
II. 0, 1, 1, 1, 1, 1, 1, 2, 1, 1, 2, 2.
III. 0, 0, 1, 0, 2, 1, 1, 0, 1, 1, 1, 1, 1, 2, 1, 1, 2, 0, 1, 1, 1, 0, 2, 2, 1, 0, 1, 2, 1, 0, 1.

(1) Comparing the hydrogen absorption during successive intervals of 15 mins., we see that benzene is not so readily hydrogenated as pyridine, the maximum in the first case being 8 atm., and in the second 19 atm.; however, in the course of the first run ($4\frac{3}{4}$-hours) in each case an almost equal number of atmospheres is absorbed per hour, *viz.*, 14 atm. in the case of benzene, and 12·5 in that of pyridine. The sharp rise of the curve up to 19 atm. with pyridine causes succeeding values to be lower (1 and 2 atm.),

whereas with benzene, the initial maximum being lower (8 atm.), the subsequent values are somewhat higher (4 atm.). Further, the extinction of the catalyst's activity takes place much more rapidly in the case of pyridine than in that of benzene.

(2) The addition to 20% osmium–asbestos of 1% of ceric oxide is followed by marked lowering of the rate of hydrogenation of pyridine, whereas in the case of quinoline a pronounced increase in the rate was noted (p. 444). One and the same catalytic system when applied to different compounds may thus display entirely opposite effects. Pyridine and benzene nuclei, when taken as forming part of the quinoline complex, apparently are endowed with other properties than when taken separately.

The foregoing method of investigating catalytic systems not only affords the possibility of estimating the catalytic power of a given " symbiosis " of catalytically acting substances, but also permits a closer study of the characteristics of various kinds of bonds in cyclic formations, whereby we may establish a relationship between the speeds of hydrogenation and the properties of cyclic bonds.

Thus, support is afforded to the assumption that the activity of the catalyst depends upon some sort of association with the substance undergoing hydrogenation. The extinction of the catalyst may depend, *inter alia*, upon lack of purity and homogeneity of the matter subjected to hydrogenation, *i.e.*, upon the presence therein of impurities or of products of hydrogenation which are inimical to the catalyst.

A careful examination of the curves obtained from many hydrogenations of quinoline in the presence of osmium–asbestos containing 1% of ceria reveals the same general tendency in spite of differences in degree : the sharp rise within the first 15 mins. characteristic of osmium and greatly enhanced by the presence of cerium, seems to. denote a more or less noticeable concentration of the activity of the catalyst within this initial period. The catalyst behaves as if it were supplied with a definite initial charge of activity, which is being expended either *en bloc* during the first moments of action, or by small portions distributed throughout a number of intervals. This initial charge, after being more or less rapidly consumed, is partially restored within a short space of time, then expended anew and once more restored. The phases of accumulation are characterised by low or even zero absorption, being, as a rule, the longer the greater the previous manifestation of the catalyst's activity, and being considerably shortened in the presence of reactivating agents (*e.g.*, of ceric oxide).

It may sometimes happen, owing to causes not yet understood, that the catalyst selected gives signs of fatigue from the very beginning of the process, being endowed with a low initial charge. There are even cases in which the charge is originally so low as to require a certain period of induction (or of accumulation), this condition being expressed by zero values throughout a whole range of 15-min. intervals.

The following results were obtained for the hydrogenation of quinoline in the presence of 20% CeO_2 + 1% Os on asbestos at 320° :

I. 3, 2, 3, 2, 6, 4, 5, 6, 5, 5, 5, 4, 5, 5, 4, 1, 4, 2, 4, 2, 2, 2, 2, 3, 2, 2, 2, 3.
II. 4, 2, 4, 2, 2, 2, 1, 3, 2, 1, 1, 3, 0, 1, 1, 1, 2, 1, 0, 1, 1, 1, 1, 0, 0, 0, 1.
III. 0, 10, 5, 6, 8, 4, 5, 3, 5, 4.
IV. 1, 4, 2, 2, 1, 3, 2 . . . 2, 0, 3, 1, 0, 1, 2, 2, 1, 0, 1, 1, 1, 1.

The initial 1-hour rate of the second period (12 atm.) is higher than that in the first period (10 atm.); also, in the third phase we have a 15-min. maximum of 10 atm., and 1-hour values of 21 and 20 atm. Thus, the deficiency in the initial increase (in the first 15 min.) is, as it were, compensated by a prolonged duration of activity, and by a more uniform expenditure of the catalytic force, which, in conjunction with a concurrent reactivation, gives the impression of a certain catalytic equilibrium.

These investigations give convincing evidence of the discontinuous character of the activity of the catalyst, which is most clearly exhibited when the easily oxidisable osmium is used in presence of ceric oxide as a promoter. Oscillations of activity are evidently closely allied with co-operation of oxygen, which regenerates the catalyst; the latter, during the process of hydrogenation, experiences a fatigue which is inherent in the nature of the catalytic process. Poisoning and complete exhaustion of the catalyst are to be considered as a mere summing up of natural moments of weariness—their accumulation in amounts high enough to exclude the possibility of automatic regeneration. But how shall we represent the oscillatory character of the catalytic activity ? New light is being shed on this matter by the work of Bredig and Weinmayr (*Z. physikal. Chem.*, 1903, **42**, 600) on periodic contact catalysis, as well as by the investigations of Hedges and Myers (J., 1924, **125**, 604, 1282; 1925, **127**, 445, 1513) on the periodic character of the dissolution of metals in acids and alkalis. In the first case, we have to deal with evolution of oxygen, and in the second with that of hydrogen. In hydrogenating cyclic compounds in presence of osmium and ceric oxide, we meet for the first time with a case of periodicity in the absorption of gas.

Moreover, the phenomena now described present many points of difference from those observed by Ostwald, Bredig, Hedges, and others, for the latter occur at comparatively low temperatures (down to 35°), under atmospheric pressure, and in aqueous media.

On the other hand, those now described occur at higher temperatures, under high pressures, and in absence of water. In each case, however, there are periods of induction, rises and falls, stages of activity and passivity, and, lastly, exhaustion of the catalyst's power due, not only to the reagents being consumed, but also to degeneration of its efficiency.

The alteration in the appearance of the catalysing metal, which has been noted by Bredig and by Hedges, is in our case beyond the possibility of observation; nevertheless, the part played by oxygen, in forming suboxides, oxides, and peroxides, especially in the system osmium + ceric oxide, should be beyond doubt: The views of Hedges as to the formation of an amorphous, gas-free, highly occluding crust of metal on heating in a vacuum do not exclude the significance of the alternate ripening and disappearance of oxide laminæ, the more so as this phenomenon closely corresponds to the rhythmic pulsations in the evolution of gases and in electric potential. The thermal preparation of the catalyst, combined with the addition of the second metallic component (promoter), gives identical results as to periodicity in the interaction of the reagents. In our cases, the thermal preparation of the catalyst assumes a permanent character owing to the fact that the reaction is being effected only within the limits of a definite optimal range of temperature. The formation of the oxide lamina is ensured both by the presence of ceric oxide and by the easy oxidisability of osmium, whereas the disappearance of the lamina (regeneration of the occluding metal) is due to the presence of hydrogen which is capable not only of hydrogenating but also of exerting a reducing influence.

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