427. *Septum Hydrogenation.*

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Hydrogenation of molecules can be carried out by the uptake of hydrogen discharged electrolytically and diffusing through a metal septum. Thermodynamics indicates that septum hydrogenation should provide a possible alternative to catalytic hydrogenation at high pressures. Practical limitations to this possibility throw new light on the mechanism of catalytic hydrogenation, and on the chemical state of hydrogen dissolved in metals.

Possibilities of Septum Hydrogenation.—When hydrogen ions are discharged at certain metal electrodes, such as iron, platinum, or palladium, the hydrogen is found to diffuse through the metal. Various lines of evidence indicate that diffusion occurs in the form of atoms. If the electrode forms a septum, for example, a cylinder or plate separating two media, discharge of ions on the one side can be followed by the appearance of gaseous hydrogen on the other side of the septum. The pressure of gas built up depends on such factors as the current density, and the solubility and rate of diffusion of hydrogen atoms through the metal.

It is noteworthy that comparatively very high pressures of gas can be built up by means of relatively small current densities. These high pressures appear to be responsible for certain characteristic cracks, which are formed when the gas is evolved at minute fissures within the metal. A quantitative relationship established empirically by Borelius and Lindblom for iron septa (*Ann. Physik*, 1927, **82**, 201) gives

$$p = 17{,}000\, I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where p is the pressure in atmospheres on one side of the septum, corresponding with a current density I amp./sq. cm. of hydrogen ions discharged on the other side of the septum. Values of p up to 16 atm. have been reported by Borelius and Lindblom, who do not however discuss at what limiting pressures this relationship would break down.

This supply of hydrogen to the septum face from within the metal is of considerable interest for a number of physicochemical investigations. Two related problems which are discussed in the present paper are: (i) How far septum hydrogenation might be used to replace hydrogenation by gaseous hydrogen at high pressures. (ii) How far the catalytic activity of hydrogen arriving at the septum face from within the metal differs from the catalytic activity of hydrogen adsorbed on the metal surface from the gas phase.

Reduction Potentials in Septum Hydrogenation.—Owing to their technological importance, the pressures of hydrogen set up on the gas face of metal septa, particularly of iron, during electrolysis have been investigated by a number of authors. Other transitional metals have also been studied (Borelius and Lindblom, *loc. cit.*; Aten and Zieren, *Rec. Trav. chim.*, 1930, **49**, 641; Morris, *J. Soc. Chem. Ind.*, 1935, **54**, 7T; Barrer, *Trans. Faraday Soc.*, 1940, **36**, 1935).

The magnitudes in the empirical equation (1) may be correlated with Tafel's equation which relates the over-voltage E_S for discharge of hydrogen ion with the current density I:

$$E_S = a + b \log I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

A general argument about the thermodynamics of irreversible processes may be developed without going into all the complexities which arise in connection with the discharge of hydrogen at electrodes (cf. Bockris, *Chem. Reviews*, 1948, **3**, 526). Attention may be fixed on the layer of freshly discharged hydrogen at the electrolyte face of the septum. This layer supplies both the hydrogen in the gas bubbles which are evolved on the electrolyte side of the septum, and the hydrogen which diffuses through to the gas face of the septum. On account of the irreversibility of discharge of gas bubbles, there is at most electrodes an " overpotential " between this freshly discharged hydrogen and the hydrogen in the gas bubbles. The small effect of surface tension on gas pressure in the bubbles being neglected, once the hydrogen comes off in a bubble it is at 1 atm. pressure.

Whatever the physicochemical origins of the irreversibility on the electrolyte side of the septum, the difference $\Delta\mu$ in thermodynamic potential between the hydrogen freshly discharged at the septum face and hydrogen at 1 atm. pressure in the gas bubbles cannot exceed the maximum free energy which could be obtained from a potential difference E_S if utilised in a reversible process, *i.e.*,

$$\boldsymbol{F}E_S \geqslant \Delta\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where E_S is in volts and $\boldsymbol{F} = 96{,}494$ coulombs. Again, on the gas side of the septum, the maximum pressure p of hydrogen (in atm.) cannot exceed the value which would give the same thermodynamic potential to the hydrogen on both sides of the septum. It may be substantially smaller, if irreversible processes are involved to an important extent in the transfer of hydrogen through the septum, *i.e.*,

$$\Delta\mu \geqslant \boldsymbol{RT} \ln p \qquad (4)$$

Combination with (3) gives

$$E_S \geqslant [\boldsymbol{RT}/\boldsymbol{F}] \ln p \qquad (5)$$

Insertion of the empirical relation (1) for iron septa gives

$$E_S \geqslant \boldsymbol{R}T[\ln 17{,}000 + \ln I]/\boldsymbol{F}$$

and introduction of numerical constants at 25° leads to

$$E_S \geqslant 0{\cdot}25 + 0{\cdot}06 \log I \qquad (6)$$

Although the constants in Tafel's equation do not appear to be free from controversy in the case of iron (Bockris, *loc. cit.*, p. 537), the numerical values in equation (6) are in line with values for other transitional metals.

If this correlation between Tafel's equation and the septum equation (1) is accepted, important conclusions for the possibilities of septum hydrogenation are:

(*a*) Very high hydrogenation pressures should be equivalent to quite accessible current densities, especially if the irreversible processes in transferring hydrogen through the septum do not lead to the dissipation of much of the free energy of the hydrogen.

(*b*) The maximum free energy of the hydrogen available is determined by the overvoltage which can be realised at the electrolyte face of the septum. For example, experiments (Bockris, *loc. cit.*, p. 546) indicate that poisoning of the iron face by arsenic or mercury can substantially increase this overpotential. Such poisoning should correspondingly raise the potential of hydrogen available. Support for this conclusion is obtained from the fact that the diffusion pressures of hydrogen through iron septa are *increased* on poisoning the electrolyte face with mercury or arsenic (Aten and Zieren, *loc. cit.*). Limitation to the possible usefulness of septum hydrogenation arise from the fact that potential barriers may hinder the entry of hydrogen into the metal, and also the exit of hydrogen from the metal. The significance of these exit barriers is further discussed below. A further limitation is that, except at high temperatures or for very thin septa, the rate of hydrogen transfer is rather slow.

EXPERIMENTAL.

Experiments on Septum Hydrogenation.—Attempts to measure the electrode potential of hydrogen diffusing through a metal septum have been reported by various authors (cf. Bodenstein, *Z. Elektrochem.*, 1922, **28**, 517; Aten and Zieren, *loc. cit.*; Bockris, *loc. cit.*, p. 541).

As is illustrated below, more detailed information about septum hydrogenation can be obtained by investigating specific hydrogenation reactions. The experiments were carried out to obtain a preliminary survey of the practical possibilities of septum hydrogenation, for example, as a means of circumventing the need for pressure hydrogenation of certain organic substances which are available only in small quantities. Various forms of apparatus were tested.

Fig. 1 illustrates apparatus with which many experiments were made. Two condensers were used in view of the fact that hydrogenation was normally investigated at the boiling point of the solutions, in order to keep the solutions stirred, and to secure maximum diffusion rate for the hydrogen. Various authors have established the dependence of the diffusion coefficient of hydrogen D through a metal

$$D = (k/d) \exp[-E/\boldsymbol{RT}]$$

where k is a constant characteristic of the metal, d is the thickness, and E is the activation energy for diffusion. This makes it desirable to accelerate diffusion of hydrogen by working at the highest possible temperature.

The electrolyte vessel, containing either 10% sulphuric acid or 10% sodium hydroxide, and the hydrogenation vessel were heated by means of nichrome wire carrying a current. They were separated by a septum whose construction is detailed in Fig. 1*a*. It consisted of a circular plate of copper 0·1″ thick. This plate had a central oblong aperture approx. 4 × 5 cm., in which a thin metal sheet, the "septum," was hard soldered. The whole surface except the two faces of the septum was thickly plated with silver and then gold to protect it from corrosion.

The metal sheets available for use as septa were: "Shim" steel 0·04 mm. thick, palladium 0·02 mm. thick, and platinum 0·01 mm. thick.

Gaskets of polythene 0·2 cm. thick gave satisfactory resistance to leakage, if the screws were tightened whilst the system was hot. Polythene was considered to be fairly unobjectionable on chemical grounds.

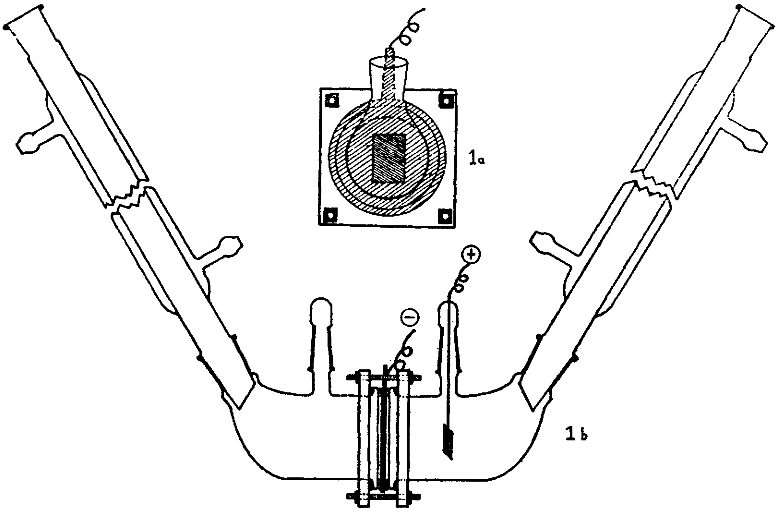
A more elegant apparatus for septum hydrogenation avoided the need for any gaskets, by carrying out the electrolysis in a nickel test-tube about 1·5 cm. in diameter and 15 cm. long which was immersed in the solution undergoing reduction. The top of the test-tube fitted into a condenser to permit the use of boiling electrolyte. Part of the walls of the test-tube was replaced by platinum or palladium septa, and the remainder was heavily silver-plated and coated with bakelite varnish to prevent attack of the nickel.

On the electrolyte side of this " test-tube " the metal was made cathodic, and a central platinum anode completed the circuit. By this means the septa formed windows for letting reducing hydrogen into the solutions under investigation. Technical difficulties arose in the construction of such test-tubes, which had a rather short life. On account of the limited supply of metal foils available, the bulk of the experiments were carried out with the simpler septa with sealing gaskets, described above.

Even when used in plate form, both the iron and the palladium septa had comparatively short lives owing to recrystallisation and chemical action, leading to tearing. The platinum septum was much more durable.

To explore the kind of behaviour to be expected, three main types of reduction were followed. The progress of hydrogenation was ascertained in (i) by observing colour changes and in (ii) and (iii) by withdrawing aliquot portions of solution from the hydrogenation side of the septum, and carrying out appropriate analyses.

FIG. 1.



APPARATUS FOR SEPTUM HYDROGENATION

(i) *Reduction of aqueous solutions of organic molecules.* Approximately M/100-aqueous solutions were used of methylene-blue, of the zinc chloride complex with malachite-green, and of neutral and acid benzoquinone. In no case was complete decoloration achieved even on prolonged reduction for several hours, using a current density of approx. 1 amp./sq. cm. and a palladium septum. Benzoquinone solutions in water or aqueous alcohol rapidly developed a deep brown quinone–quinol colour, and appeared to reach a steady state in about 3—4 hours. A less highly coloured steady state was reached with the acid solutions. This might be expected if the reduction reaches an end-point determined by the thermodynamic potential of the hydrogen available at the septum face.

(ii) *Reduction of organic molecules in organic solvents.* (*a*) Oleic acid gave evidence of some reduction at 100°, a platinum septum being used with a current density of 0·3 amp./sq. cm., and the unsaturation being determined with Wijs's reagent. However, a complicated side reaction also took place, which led to the formation of dark by-products and made it difficult to analyse the amount of stearic acid formed.

(*b*) Nitrobenzene in glacial acetic acid at about 118° was reduced through a platinum septum. Unchanged nitrobenzene at the end of an experiment was estimated by pouring into water. The observed reduction (calculated as aniline) corresponded with a rate of transfer of approximately 6×10^{-6} g.-atom of hydrogen per sq. cm./min. at 118° for a current density of 0·3 amp./sq. cm.

(iii) *Reduction of inorganic compounds in aqueous solution.* (*a*) The reduction of iodine dissolved in aqueous potassium iodide could readily be followed by titration with sodium thiosulphate. Rapid diffusion of hydrogen was observed in the case of iron septa, but since the metal also appeared to be attacked by the iodine no quantitative data could be obtained on the rate of transfer of reducing hydrogen through the septum. With a palladium septum, the reduction rate corresponded to a transfer of approximately 4×10^{-6} g.-atom of hydrogen per min. per sq. cm. for a current density of 0·9 amp./sq. cm. at about 30°. These experiments were carried out with an " immersion test-tube " type of apparatus.

(*b*) Reduction in sulphuric acid solution, $Fe^{\cdot\cdot\cdot} \longrightarrow Fe^{\cdot\cdot}$, with a platinum septum was followed under various conditions, by titrating ferrous ion produced with potassium permanganate. The maximum rate of transfer of hydrogen observed was when the septum on the electrolysis side was first activated. For this purpose it was made anodic for about 10 minutes, at a current density of 1 amp./sq. cm., before being made cathodic.

The rates of transfer ranged from approximately 2×10^{-7} to 5×10^{-7} g.-atom of hydrogen per min. per sq. cm. at 100°, for a current density of 0·37 amp./sq. cm.

DISCUSSION.

(i) *Scope of Septum Hydrogenation.—End-point of reduction.* Although the experiments were only exploratory, they serve to illustrate the fact that septum hydrogenation can be carried out to a satisfactory end-point only for reactions involving moderate reduction potentials. The reason for this became apparent in the course of the work. As is explained above (equation 6), the maximum reduction potential available in this type of hydrogenation has as upper limit the overpotential for evolution of hydrogen at the electrolysis side of the septum.

Rate of reduction. The rate of septum hydrogenation is rather slow since it is limited by the rate of diffusion of hydrogen through the septum. Higher temperatures of reduction than those used in the present work could be realised without too much difficulty, particularly with the test-tube apparatus. It should also be possible to devise alloys more permeable to hydrogen than pure platinum and not so liable to cracking as pure palladium.

Efficiency of reduction. An important consideration for the fundamental theory of catalysis is the efficiency of septum hydrogenation. One definition of this efficiency is the ratio

$$r_1 = \frac{\text{g.-atoms of } H_2 \text{ effecting reduction in unit time}}{\text{g.-atoms of } H_2 \text{ arriving at the septum face in unit time}} \quad . \quad . \quad . \quad . \quad (7)$$

In order to calculate this efficiency, a knowledge is required of the rate of arrival of hydrogen atoms at the inner face of the exit side of the septum. A *lower* limit to this rate can be obtained experimentally from measurements of the rate of evolution of gaseous hydrogen when the exit side of the septum is exposed to vacuum. If no activation process were required for the reaction

$$\text{H (dissolved in metal)} \longrightarrow H_2 \text{ gas (exit side of septum)} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

the rate of gas evolution into a vacuum should be identical with the rate of arrival at the inner face of the septum. On the other hand, if there is a potential barrier, this barrier may be substantially lower for the combination of hydrogen atoms with molecules adsorbed on the exit side of the septum in a process such as

$$\text{H (dissolved in metal)} \longrightarrow \text{H–M (combined with molecules adsorbed on septum face)} \quad . \quad . \quad (9)$$

than for the evolution of hydrogen molecules. What this would imply experimentally is that the rate of transfer of hydrogen atoms effecting reduction according to (9) may be many times as large as the rate of transfer of atoms leading to evolution of gaseous hydrogen according to (8).

Obviously, such a possibility is of great interest in elucidating the mechanism of catalytic hydrogenation. Although data are not yet available for estimating the efficiency according to (7), experimental data permit the calculation of the related ratio

$$r_2 = \frac{\text{g.-atoms of } H_2 \text{ effecting reduction in unit time}}{\text{g.-atoms of } H_2 \text{ evolved as } H_2 \text{ under comparable conditions}}$$

Fully conclusive evidence can only be obtained by experiments on the same septum, in which the rate of evolution of gaseous hydrogen and the rate of reduction of various molecules can be directly compared. Such experiments are not, of course, restricted to reduction in liquid systems. It has not yet been possible to carry out such parallel experiments on the same septum. Comparisons may, however, be made with experiments by other authors, as follows.

Palladium. Data are given by Barrer (*Trans. Faraday Soc.*, 1940, **36**, 1235) on the permeability P, measured in c.c. of gas (at N.T.P.) transferred per sq. cm. per sec. through a plate 1 mm. thick for a current density of 1 amp./sq. cm. A range of values is observed according to the activity of the metal. The highest permeability observed by Barrer, when recalculated for a current density of 0·9 amp. per sq. cm., would correspond to $9{\cdot}3 \times 10^{-6}$ g.-atom of hydrogen per sq. cm. per min. for reaction (8) as compared with 4×10^{-6} for reaction (9) in the present experiments, for the reduction of iodine in potassium iodide. So far as this evidence goes, there are thus no grounds for expecting large differences between processes (8) and (9) for palladium septa, at any rate for the reduction of iodine. Further evidence is however desirable in view of the interest of the problem.

Platinum. No direct measurements appear to be available on the rate of evolution of gaseous hydrogen from the exit side of a platinum septum when the entry side is charged electrolytically. It seems likely that this rate is small.

The ratio of permeation velocities of gaseous hydrogen through palladium and platinum can be calculated from data quoted by Smithells and Ransley (*Proc. Roy. Soc.*, 1935, **150**, 172). At 373° this ratio is

$$\mathrm{Pd/Pt} = \frac{1{\cdot}18 \exp (9000/373)}{1{\cdot}41 \exp (2100/373)}$$
$$= 8{\cdot}4 \times 10^7 \text{ for reaction (8)}$$

If there were no catalytic effects at the septum face, the ratio of permeabilities to hydrogen determined according to reaction (8) should be the same as the ratio of the g.-atoms of hydrogen available for reduction under comparable conditions according to reaction (9). Although no exact ratio can yet be established, owing to the exhaustion of supply of a particular batch of palladium foil, if the ratio of reducing hydrogen atoms in (iii) is compared, differences in the reactions studied and in the current densities being neglected, this gives

$$\mathrm{Pd/Pt} = 4 \times 10^{-6}/5 \times 10^{-7}$$

a factor of about 8. Thus there appears to be a marked difference between the two septa for reaction (8) and reaction (9).

Various explanations of this difference can be suggested. The most likely seems to be that the exit of hydrogen atoms for a catalytic reduction (9) involves a much smaller barrier at the platinum septum face than the exit of hydrogen as molecules, according to (8). This contrasts with palladium, for which any barriers appear to be about the same for the two processes. Further work is needed to substantiate and develop the implications of this interesting difference.

Availability of the Hydrogen from within a Septum.—Experiments by Bodenstein (*loc. cit.*) indicate that the *atoms* within the metal of a palladium septum are not available for starting various chain reactions such as $H_2 + Cl_2$ or $H_2 + O_2$ or even for reacting with bromine. It is useful to consider briefly two alternative models for representing the processes under discussion since these orient further lines of investigation.

(a) *The interstitial proton gas/potential barrier model for septum hydrogenation.* A generalised description of the state of hydrogen atoms dissolved in a metal such as palladium or platinum is to regard the hydrogen as a proton gas, partly dissociated from its accompanying electrons, and occupying the interstitial space between the atoms of the metal. Considerations about the expansion pressures of such a gas (Ubbelohde, *Proc. Roy. Soc.*, 1937, **159**, *A*, 295; and in publication) do not wholly favour this extremely generalised description. It does, however, lend itself to the conventional formulation of potential barriers for the extraction of protons from the interior to the surface of the metal forming the septum, analogous to the barriers for extracting electrons. On this model, work is required to remove the proton and the electron to the surface. Once these have reached the surface they form hydrogen atoms which will exhibit a finite rate of recombination to molecules dependent on a number of surface factors. Combination with molecules on the surface can also occur in favourable circumstances.

(b) *The "pseudometallic hydride" model.* According to this model, specific metal atoms A form ordinary covalent bonds with H, and each "pseudo-atom" (A–H) behaves like the next atom to the right in the same row of the Periodic System (Ubbelohde, in publication). Usually these (A–H) pseudo-atoms are still capable of acting as metals, *i.e.*, they have vacant electron orbits and can form shared covalent bonds in close-packed systems of atoms (cf. Pauling's theories of metallic binding).

By way of illustration, on this view, $PdH_{0{\cdot}6}$ should be represented as $Pd_2(PdH)_3$, which should be similar in many ways to the alloy Pd_2Ag_3. In particular, any (PdH) pseudo-atom forms the same number of covalent linkages as any Ag atom, provided it is wholly surrounded by other atoms of Pd or (PdH). The composition of an alloy of particular crystal structure can usually assume a range of values.

At the surface, if the A–H bond lies within the lattice pointing downwards, the régime is analogous to that within the metal. If, however, an A atom is partly detached from the remaining atoms in the lattice, or if the A–H bond is directed outwards from the surface, it will no longer be stabilised by metallic linkages. Transfers of hydrogen atoms to other molecules can be facilitated from these partly detached (A–H) atoms.

On this model, catalytic hydrogenation at a septum can be represented by a series of chemical bond transfers such as

(A–H) interior + A (surface) → (A–H) surface, partly detached + A (interior)

$$\begin{tikzcd}[column sep=small] & \text{H}_2\text{ gas } + \text{ A (surface)} \\ \text{(A–H) surface, partly detached} \arrow[ur] \arrow[dr] & \\ & \text{H–M (combination with adsorbed molecules) } + \text{ A (surface)} \end{tikzcd}$$

Although the two models are merely to be regarded as alternative descriptions of the same process, the " pseudo-atomic " hydride model lends itself more readily to the consideration of specific chemical bond transfers such as may be influenced by local atomic impurities, and such as are operative in catalytic hydrogenation at the septum face.

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