Hydrierung mit molekularem Wasserstoff.

Von

E. B. Maxted, Bristol.

With 22 figures.

Inhaltsverzeichnis.

A. General Introduction.

1. Historical.

Although the systematic investigation of catalytic hydrogenation may be regarded as beginning with the discovery of the hydrogenating properties of the metals of the nickel group by Sabatier and Senderens during the years immediately preceding 1900, a number of isolated examples of catalytic hydrogenation, principally with platinum or palladium, occur in the literature at considerably earlier dates. Thus, Debus[1], in 1863, studied the catalytic reduction of hydrocyanic acid to methylamine in the presence of platinum, de Wilde[2] hydrogenated both acetylene and ethylene to ethane, and Saytzeff and Kolbe[3] reduced a large number of organic substances, including nitrobenzene, nitromethane, nitrophenol and benzoyl chloride, by passage, in vapour form, over platinum or palladium. Early work on the reduction of inorganic salts, in solution, by means of palladium containing occluded hydrogen also exists[4]; and the activity of platinum in bringing about the union of hydrogen and oxygen had been known even in the early years of the nineteenth century.

Sabatier and Senderens confined themselves almost exclusively to a hydrogenation technique involving the passage of bodies in vapour or gas form, together with hydrogen, over nickel, copper, cobalt, iron or, in some cases, platinum; and the development of hydrogenation in the liquid phase, including the treatment of bodies in solution, is to a large degree due to the work of Paal, Skita, Willstätter and, especially in the case of hydrogenation under pressure, Ipatiev.

2. The Catalytic Activation of Hydrogen.

Catalytic hydrogenation is based on the activation of hydrogen at metallic and other surfaces, the activation process leading to the acquisition by the hydrogen of reactive properties similar to—but in many cases exceeding in intensity—those of the gas in a nascent state. Thus, while both nascent and catalytically activated hydrogen readily saturate a number of simpler ethylenic compounds, the nascent method fails completely with bodies of high molecular weight, such as long-chain olefinic acids and, above all, with benzenoid rings, all of which are easily saturated catalytically; indeed, the general hydrogenation of unsaturated bonds of all types only became possible with the introduction of catalytic methods, the most important immediate outcome of Sabatier and Senderens' original work being probably, as already mentioned, the direct hydrogenation of benzene. It may be noted, however, in connection with this preliminary comparison of hydrogenation by nascent and by catalytically activated hydrogen, that—while the latter method is of universal application—there is no strict parallelism between the ease of reduction by the two methods. Thus, as a contrast to the examples already given, the hydrogenation of a ketonic or an aldehydic group to an alcohol, in spite of the ease and rapidity with which this particular reaction occurs with nascent hydrogen, often takes place curiously slowly when carried out in the presence of ordinary metallic catalysts. In modern practice, however, while reduction by nascent hydrogen has not completely disappeared, it has at any rate been relegated to a subordinate position not only by the universality of the catalytic method but also

---

[1] Liebigs Ann. Chem. 128, 200 (1863).

[2] Bull. Soc. chim. France 5, 175 (1866); 21, 446 (1874); Ber. dtsch. chem. Ges. 7, 353 (1874).

[3] J. prakt. Chem. 4, 418 (1871); 6, 128 (1872).

[4] e.g. Graham: Liebigs Ann. Chem., Suppl. 5, 57 (1866).

by the quantitative yields and freedom from side reactions which are usually associated with the latter method.

The general scope of catalytic hydrogenation may be illustrated by the following reaction classes, the list being, however, not exhaustive:

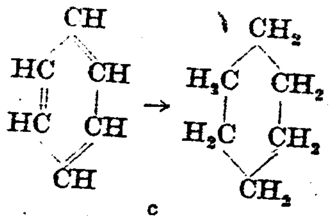
1. Saturation of Various Unsaturated Linkages:

$$R \cdot CH : CH \cdot R' + H_2 = R \cdot CH_2 \cdot CH_2 \cdot R'.$$

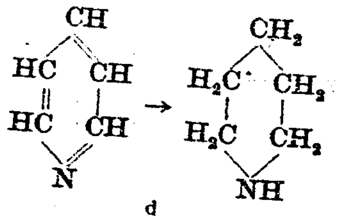
a

$$R \cdot C \vdots C \cdot R' \rightarrow R \cdot CH : CH \cdot R' \rightarrow R \cdot CH_2 \cdot CH_2 \cdot R'.$$

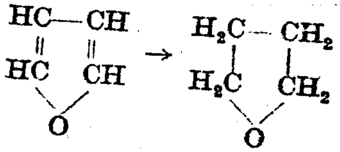
b



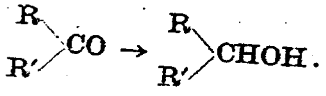
c



d



e



$$\genfrac{}{}{0pt}{}{R}{R'}\!>\!CO \rightarrow \genfrac{}{}{0pt}{}{R}{R'}\!>\!CHOH.$$

f

$$CO \rightarrow CH_3OH \text{ etc.}$$

g

$$R \cdot C \vdots N \rightarrow R \cdot CH_2 \cdot NH_2.$$

h

$$Ph \cdot N : N \cdot Ph \rightarrow Ph \cdot NH \cdot NH \cdot Ph.$$

i

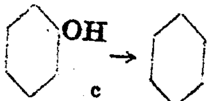
2. Reduction with Elimination of Oxygen etc.

$$CO_2 \rightarrow CO \rightarrow CH_4.$$

a

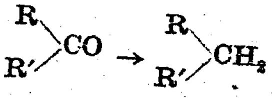
$$R \cdot CH_2OH \rightarrow R \cdot CH_3.$$

b



c

(In which the ring is either benzenoid, hydroaromatic or heterocylic.)



$$\genfrac{}{}{0pt}{}{R}{R'}\!>\!CO \rightarrow \genfrac{}{}{0pt}{}{R}{R'}\!>\!CH_2$$

d

$$R \cdot COOH \rightarrow R \cdot CH_2OH \rightarrow R \cdot CH_3.$$

e

$$R \cdot NO_2 \rightarrow R \cdot NH_2.$$

f

$$R \cdot CH_2Cl \rightarrow R \cdot CH_3.$$

g

The ordinary hydrogenation catalysts—nickel, cobalt, copper, iron and the platinum metals generally—occur, with the exception of copper, in Group VIII of the periodic system. All these metals adsorb hydrogen specifically; indeed, their activity is obviously bound up with this common property.

In addition to these more usual catalysts, certain other elements, for instance, zinc, have been used for catalytic hydrogenation generally, although to a limited degree; and a number of other metals, including silver, gold, lead, tin and thallium, possess slight hydrogen-activating properties, which permit their employment for relatively easy reactions such as the reduction of nitrobenzene to aniline, but which are insufficient in intensity for their general use. Moreover, in place of using catalysts which merely form an adsorption complex with hydrogen, it is also possible to induce hydrogenation by employing elements whose union with hydrogen is usually associated with the formation of definite chemical hydrides. Thus, calcium will catalyse ordinary hydrogenation, for instance the reduction of ethylene to ethane; and special hydrogenation reactions may even be catalysed by the alkali metals. These less common catalysts will be dealt with later in the present section.

Another class, which is of greater importance from the standpoint of practical hydrogenation than those mentioned in the preceding paragraph, contains oxides such as those of chromium, manganese or zinc. These, apparently even in the unreduced oxide form, enter into chemisorptive union with hydrogen and induce its activation; but, under the normal conditions of their use, it is difficult to say whether incipient reduction to metal also occurs and to what extent their activity at high temperatures is due to this metal content. This difficulty is enhanced by the fact that they are far more frequently employed in conjunction with other components in such a way that they also act as carriers. Thus, catalysts such as nickel chromite or copper chromite may be regarded as consisting, under the conditions of use, of metallic nickel or copper supported on a possibly also partly reduced chromium oxide, which, in addition to exerting some inherent activity, derives its high efficacy as a carrier from the intimate degree of the mutual dispersion of the nickel and of the chromium oxide, the use of a body such as a metallic chromite as a starting material being merely a very convenient and effective method of securing the initial lattice penetration which is conducive to intimate contact between the components even after reduction: indeed, it has been shown, for such two-component catalysts, that abnormal activation usually only occurs in cases in which X-ray examination gives evidence of such lattice penetration. This view of these catalysts is supported by the fact that few, if any, reactions which can be carried out with nickel chromite or copper chromite cannot also be effected with nickel or copper alone. Thus, the reduction of carboxylic acids to alcohols or to hydrocarbons, which was for some time regarded as being specific to catalysts of the above complex type, can also be induced by copper or nickel on an external, in itself inactive, carrier, such as kieselguhr, in place of on an internal and active carrier such as chromium oxide. Zinc chromite, which is, in general, a mild hydrogenating catalyst, which easily hydrogenates a carboxyl group to give an alcohol but does not readily induce the saturation of an ethylenic or of a benzenoid bond between carbon atoms, can also be viewed from the same standpoint. Finally, there exists an increasingly important class of high-temperature hydrogenation catalysts containing the oxides and sulphides of metals such as molybdenum or tungsten. These are tolerant to sulphur and to catalyst poisons generally, and can consequently be used for impure materials. They are of special use for the elimination of hydroxyl from phenols and for hydrogenation generally in the case of bodies, such as naphthalene, which are sufficiently stable thermally to permit the use of the very high temperatures (400—500°) which these catalysts require. They also find extensive commercial application for the hydrogenation-cracking of fuel products such as tars or creosote, or hydrocarbon oils generally, in such a way as to produce lower-boiling degradation products.

3. Mechanism of the Activation of Hydrogen.

The nature and probable sequence of the processes involved in hydrogenation, particularly in the presence of metals, are more fully discussed in other sections in connection with the mechanism of catalysis generally; and, for this reason, the subject will here only be treated briefly and in outline.

In the first place, the action of ordinary catalysts in hydrogenation is obviously bound up with their power of activating hydrogen itself, quite apart from any adsorptive or other reaction between the body hydrogenated, on the one hand, and either the catalyst itself or its adsorption complex with hydrogen, on the other. Thus, hydrogenating catalysts, as a class, are also active for reactions involving hydrogen alone, such as the ortho-para hydrogen conversion.

This emphasis on the activation of hydrogen, as distinct from any activation of the second component, has led to the postulation by many authors of a modification in the molecular form of hydrogen adsorbed by catalytically active metals. **Polanyi**[1] regards the dissociation of hydrogen into atoms on the catalyst surface as the essential factor in the activation of the reacting molecules, the activity of the catalyst being due to its dissociating power and to its preferential adsorption of free atoms. It is pointed out that the dissociation of hydrogen by a catalyst should, in spite of the high dissociation heat (100,000 cals.), be facilitated by the high heat of adsorption of atomic hydrogen.

This hypothesis of atomic hydrogen as the active agent in catalytic hydrogenation by metals has been taken a stage further by O. **Schmidt**[2], who has put forward the view that the activation of hydrogen by metals such as those of the nickel or platinum groups takes place in the metal by the formation of positive hydrogen ions and that catalytic hydrogenation occurs in the micro-pores of the catalyst which, for high activity, must be porous. The hydrogenation of, for instance, ethylene, is thus regarded as a process which may be written:

$$C_2H_4^{2\bar{e}} + 2H^+ = C_2H_6 .$$

Schmidt makes a sharp distinction between such micro-pores and the rather indefinite term internal surface, since, in the former, the adsorbed species may be regarded as being completely surrounded by the catalysing metal. If the rate-controlling factor in a hydrogenation reaction is, in accordance with **Schmidt**'s views, the diffusion of the substrate into the micro-pores, the reaction velocity should be influenced above all by the diffusive mobility of the substance hydrogenated. This was, in general, found by **Schmidt**, on the basis of changes in the unsaturated body and in the solvent, to be the case; but it should be pointed out that diffusion rates also play an important part—especially in liquid systems—in determining the rate of supply, both of the molecular species hydrogenated and of the hydrogen itself, to a catalytic surface in the ordinary sense, in addition to any possible further diffusion into micro-pores. It may be noted further that **Schmidt**[3] considers that, in the hydrogenation of ethylene by catalysts such as calcium, the activation of hydrogen also occurs ionically, but through negatively charged hydrogen in place of through protons, and on the surface in place of in the interior, as with nickel or platinum.

The possibility of the influence of a further factor, namely that of molecular distortion, on the stability, and consequently on the reactivity, of bodies adsorbed on catalysts has been advanced by A. **Balandin**[4], who postulates, for instance in dehydrogenation, a state of strain in the molecules of the body to be dehydrogenated, due to their adsorption on more than one surface element of the catalyst, this strain being sufficient in some cases to induce actual cleavage. **Balandin** has developed this strain or multiplet hypothesis in such a way as to involve an actual connection between the geometrical structure and dimensions of the catalysing surface and of the molecule catalysed. Some difficulties in the rigid application of the theory have recently been discussed by H. S. **Taylor**[5] on the basis of the observed hydrogenation of cyclopentene and cycloheptenes by catalysts configurationally unsuitable from the standpoint of the multiplet hypothesis.

A fundamentally different method of approaching the action of catalysts in hydrogenation consists in considering the energetics of the hydrogenation process as a whole, especially by taking into consideration the possible contri-

---

[1] Z. Elektrochem. angew. physik. Chem. 35, 361 (1929).
[2] Z. physik. Chem. 118, 193 (1925); Abt. A 165, 209 (1933); Abt. A 176, 237 (1936).
[3] Ber. dtsch. chem. Ges. 68, 1098 (1935).
[4] Z. physik. Chem., Abt. B 2, 289 (1929); 3, 167
[5] J. Amer. chem. Soc. 60, 630 (1938).

bution of the heat of adsorption—or of a heat of association generally—to the energy of activation of the process.

On grounds of its heat of adsorption, hydrogen, or, in general, any other adsorbed species such as ethylene, will, on adsorption, acquire additional free heat energy liberated as the result of the adsorption process and corresponding in magnitude with the adsorption heat, Q. This heat, which is initially resident in the adsorption complex, will, in the absence of the reaction of this complex with another adsorbed or free molecular species, gradually become dissipated by radiation or by energy redistribution through the adsorbing lattice: consequently, this additional energy in the adsorption complex may, according to the time which elapses between the actual formation of the complex and its participation in a reaction, have any value between zero and Q; and, by virtue of this contribution of adsorption heat towards the energy of activation, only the balance, namely, $E - \Sigma Q$, in which ΣQ is the sum of the contributions from the adsorption heats, will be required to raise the energy to the value necessary for reaction. This leads to an expression for the reaction velocity of the type[1]

$$k = a e^{-(E - \Sigma Q)/RT},$$

in place of the ARRHENIUS relationship,

$$k = a e^{-E/RT},$$

in which E is the normal energy of activation, the probability of reaction, and with it the reaction velocity, being thus increased by the reduction—by the ΣQ term—of the energy hill to be surmounted. This view is borne out by experimental evidence based firstly on the reversal of the temperature coefficient of hydrogenation reactions as soon as a certain critical temperature, dependent on the system, has been passed, and, secondly, on the change of kinetic form of the reaction, with the temperature; and it would seem that, under the conditions which obtain in catalysis, the effective contribution may approximate in value to the normal adsorption heat of either one or both reactants (hydrogen and unsaturated body) according to the conditions.

4. The Kinetics of Hydrogenation.

It is found in practice that the general kinetics of liquid-phase hydrogenation at a constant hydrogen pressure correspond, according to the conditions, with the two alternative types of reaction path shown diagrammatically in Fig. 1. In the first place, the reaction may be approximately of zero order, the rate of absorption of hydrogen remaining approximately constant until a stage in the neighbourhood of saturation is reached, when the velocity decreases relatively rapidly and suddenly owing to a deficiency in the available supply of the unsaturated body. It should be noted that a linear reaction path may be masked by the presence of impurities in the substance hydrogenated, in that impure organic liquids frequently give a curved reaction path which, after purification of the liquid, becomes linear[2]; and it is probable in such cases that the curvature observed is due not to the inherent kinetics of the process but to the presence of clogging poisons or reaction residues which are deposited on the catalyst as the reaction proceeds.

---

[1] ZUR STRASSEN: Z. physik. Chem., Abt. A 169, 81 (1934). — SCHWAB: Ebenda 171, 421 (1934). — MAXTED, MOON: J. chem. Soc. [London] 1935, 393, 1190.

[2] ARMSTRONG, HILDITCH: Proc. Roy. Soc. [London], Ser. A 96, 137 (1919); 98, 27 (1920); 99, 490 (1921). — MAXTED: J. chem. Soc. [London] 119, 225 (1921).

A zero order reaction with respect to the unsaturated body involves a concentration of this body in the free—and consequently also in the adsorbed—state in excess of the value required by the reaction velocity imposed by the other factors, in such a way that this velocity remains relatively unaffected by the disappearance of the unsaturated substance. As soon, however, as the concentration falls below the critical value at which the supply of unsaturated body begins to be an effective factor in controlling the reaction velocity, namely as saturation is approached, the velocity will diminish more or less rapidly with the falling off of the supply of this body.

On the other hand, the conditions under which the hydrogenation is carried out may be such that the concentration of the unsaturated substance—and the disappearance of this by reaction—exercises an effective influence on the velocity from the start, or even from an intermediate stage. This will give, respectively, continuously curved or initially linear reaction graphs of the types shown diagrammatically by curves II and III of Fig. 1. Curves of Type III are not common, but were observed by **Armstrong** and **Hilditch** in some cases. Further, since the distribution of the unsaturated body between the free and the adsorbed phase is adversely affected, from the adsorption side, by increasing the temperature, it should be possible, by increasing the reaction temperature, to produce conditions such that a hydrogenation which is linear at a low temperature becomes curved as the temperature is raised. Examples of this will be given later.

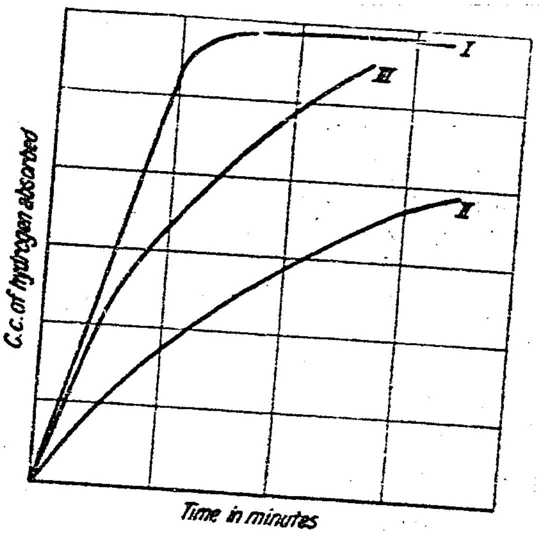


Fig. 1. Types of reaction curves.

Under conditions in which the velocity is controlled by the concentration of the unsaturated body, **Schwab** and his collaborators[1] have rightly laid emphasis on the importance of the adsorbed rather than on the free concentration. Thus, in a case such as the liquid-phase hydrogenation of ethyl cinnamate by nickel, it was found that the rate of disappearance of the unsaturated substance could be based on a **Langmuir** adsorption isotherm[2] of the type:

$$\sigma = \frac{bc}{1 + bc},$$

in which σ is the fraction of the surface covered, b is the adsorption coefficient and c is the concentration of the ester. The close agreement of the observed and of the calculated change in velocity at various stages during the reaction is shown in Table 1, the calculated values being derived from the relationship:

$$\frac{-dc}{dt} = \frac{kc}{1 + bc},$$

The hydrogenation was carried out at 50° in alcoholic solution. By the hydrogen equivalent of the ester is understood the volume of hydrogen, in c.c., required for saturation.

---

[1] **Schwab, Brennecke**: Z. physik. Chem., Abt. B **24**, 393 (1933).

[2] **Schwab**: Z. physik. Chem., Abt. A **171**, 421 (1934).

Table 1.

Concentration of ester expressed as its hydrogen value	$-\frac{dc}{dt}$ (observed)	$-\frac{dc}{dt}$ (calculated)	Concentration of ester expressed as its hydrogen value	$-\frac{dc}{dt}$ (observed)	$-\frac{dc}{dt}$ (calculated)
123	23	20.2	41.5	8.9	9.5
100	18.4	17.9	33	7.9	7.9
82	14.9	15.7	18	5.2	4.6
66	13.6	13.5	10	2.7	2.7
52	11.1	11.3	5	1.4	1.4

Similar considerations apply to gas-phase hydrogenation. Thus, the kinetics of the hydrogenation of ethylene itself, as the simplest unsaturated hydrocarbon, have been widely studied[1], it being found that the reaction velocity is, at atmospheric pressure, in general proportional to the hydrogen partial pressure and independent of the partial pressure of the ethylene. As has been pointed out by SCHWAB and ZORN[2], this independence on the ethylene pressure is, as in the liquid systems dealt with above, obviously due to observations of the kinetics under conditions which include an effective saturation range in the adsorption isotherm of ethylene on the catalysts employed (platinum, nickel, copper etc.).

If, however, the ethylene reaction is carried out under conditions outside the saturation range for this gas, for instance, at low pressures or at high temperatures, the hydrogenation velocity may, in addition to varying with the hydrogen pressure, also vary with the partial pressure of the ethylene. Conditions of this type were obtained by ZUR STRASSEN[3], and SCHWAB[4] has treated the kinetics of ethylene hydrogenation under these conditions from the standpoint of the adsorbed concentrations in a similar manner to that given above for liquid systems. It should be noted that the possibility of calculating the change in the reaction velocity, as the reaction proceeds, on the basis of simple LANGMUIR adsorption isotherms may be regarded[5] as additional evidence of the catalytic action, in such cases, of a range of energetically homogeneous catalysing points.

The temperature coefficient of hydrogenation processes is of considerable interest since, by virtue of the dependence of the reaction velocity on adsorbed concentrations, a reversal in the sign of the coefficient, namely, a decrease in velocity as the temperature is increased, may occur at high temperatures. This reversal, with production of a negative temperature coefficient, has been noticed, for instance, in ethylene hydrogenation, by a number of workers[6], and has been studied in detail by KLAR[7] and SCHWAB[8]. KLAR, who observed a temperature of maximum velocity at 130° in the hydrogenation of ethylene on nickel, regards the increase in the adsorption rate of ethylene with increasing temperature as a responsible factor in the positive temperature coefficient under the conditions in which the kinetics are controlled by the ethylene adsorption, this influence of the adsorption rate being—if the temperature is

---

[1] RIDEAL: J. chem. Soc. [London] **121**, 309 (1922) — PEASE, HARRIS: J. Amer. chem. Soc. **49**, 2503 (1927). — PEASE: Ebenda **54**, 1876 (1932). — DOHSE, KÄLBERER, SCHUSTER: Z. Elektrochem. angew. physik. Chem. **36**, 677 (1930).

[2] Z. physik. Chem., Abt. B **32**, 169 (1936).

[3] Z. physik. Chem., Abt. A **169**, 81 (1934).

[4] Z. physik. Chem., Abt. A **171**, 421 (1934).

[5] SCHWAB, BRENNECKE: loc. cit. — SCHWAB, STAEGER, v. BAUMBACH: Z. physik. Chem., Abt. B **21**, 65 (1933); **25**, 418 (1934).

[6] RIDEAL: J. chem. Soc. [London] **121**, 309 (1922). — GRASSI: Nuovo Cimento (6) **11**, 147 (1916). [7] Z. physik. Chem., Abt. A **168**, 215 (1933).

[8] Z. physik. Chem., Abt. A **171**, 421 (1934).

increased sufficiently—ultimately dominated by the influence of quantity adsorbed, which decreases with temperature; and, on studying the velocity of the adsorption of ethylene on nickel at low pressures and at various temperatures, maxima both in the effective rate and in the quantity absorbed were found at 130°, namely, at the reversal point.

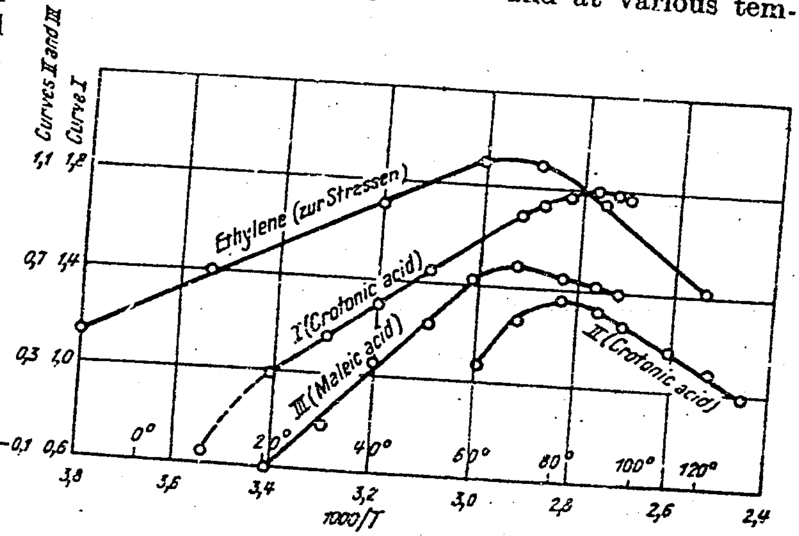


Fig. 2. Temperatur-velocity curves.

According to the views of zur Strassen and Schwab, the reversal in the sign of the temperature coefficient in the hydrogenation of gaseous ethylene is regarded as being due to the falling—as the temperature range corresponding with reversal is reached—of the adsorbed concentration of ethylene to a value which is insufficient to render the progress of the reaction independent of the adsorbed concentration of this gas, in the manner already discussed, the ratecontrolling factor being thus hydrogen adsorption at low temperatures and ethylene adsorption plus hydrogen adsorption at higher temperatures. This is apparently supported by the change in the form of the reaction kinetics as the temperature is raised. Thus, zur Strassen, who investigated the hydrogenation of ethylene on a nickel ribbon catalyst at low pressures and at various temperatures, found that, while the reaction velocity was, at all the temperatures studied (—10° to + 130°), proportional to the hydrogen pressure, its independence, at low temperatures, on the ethylene pressure disappeared as the temperature was raised, until, at high temperatures, it was also approximately linearly proportional to the ethylene pressure.

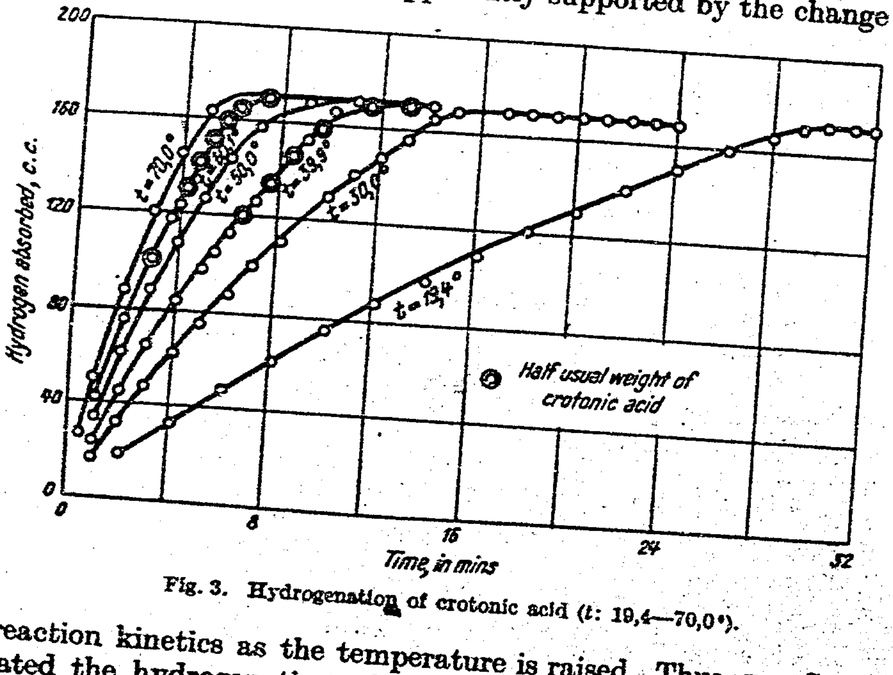


Fig. 3. Hydrogenation of crotonic acid (t: 19,4—70,0°).

Similar maxima in the temperature-velocity curves and a similar change in the kinetic form with increasing temperature have also been observed[1] in the liquid-phase hydrogenation of ethylenic derivatives. The variation with temperature in the velocity of hydrogenation of crotonic acid and maleic acid under varying conditions is shown in Fig. 2, in which are also included, for comparison, ZUR STRASSEN's results with gaseous ethylene.

The change in the kinetic form as the temperature is raised is illustrated by the next two figures which, as before, refer to the hydrogenation of crotonic acid, dissolved in a solvent, in the presence of platinum. Fig. 3 relates to temperatures below the reversal point. Under these conditions, the reaction path is in each case approximately linear; and all the graphs show the relatively sudden and complete cessation of reaction which is characteristic of processes of zero order. Fig. 4 shows the fundamental change in the kinetic form at higher temperatures. Following a transition type during the temperature range corresponding with reversal (80—90°), the reaction path became evenly curved, lost its characteristic phase of sudden cessation and, at these higher temperatures, was found to be very nearly of the first order with regard to the crotonic acid, i. e., under these conditions the rate was approximately proportional to the concentration of the unsaturated body. This corresponds with results in gasphase hydrogenation in which the velocity has, as already stated, been found under some conditions to vary directly with the partial pressure of the ethylene: moreover, a first order curve may be regarded as derived from the simplest form of adsorption isotherm, namely, from a region in which the adsorbed concentration varies approximately linearly with the free concentration.

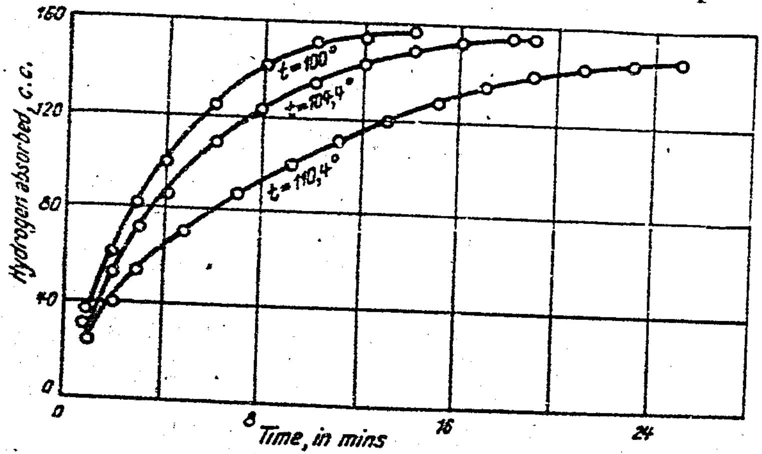


Fig. 4. Hydrogenation of crotonic acid (t: 100—110,4°).

a) *Influence of Pressure.*

In the above treatment of liquid-phase—as distinct from gas-phase—hydrogenation, some account has been given of the variation of the velocity of hydrogenation with the concentration of the unsaturated body without considering variations in the concentration of the hydrogen, since the hydrogen pressure is usually kept constant during the hydrogenation of a liquid. The general effect of hydrogen pressure on the velocity is, however, of considerable importance from the standpoint of practical hydrogenation, particularly since a number of hydrogenations only take place at a reasonable rate at a high pressure.

Under many conditions, the rate of hydrogenation of liquids is approximately directly proportional to the hydrogen pressure[2]; but deviations from this

---

[1] MAXTED, MOON: J. chem. Soc. [London] 1935, 1190; 1936, 635.

[2] MOORE, RICHTER, VAN ARSDEL: Ind. Engng. Chem. 9, 541 (1917). — MAXTED: J. Soc. chem. Ind., 40, 169 T (1921). — ARMSTRONG, HILDITCH: Proc. Roy. Soc. [London], Ser. A 100, 240 (1921).

simple relationship also occur. According to the experimental results of Armstrong and Hilditch, normal (i. e. direct) variation with the pressure occurs provided, firstly, that the concentration of the catalyst is not too low (in general, not below 0.1 per cent with nickel) and, secondly, that the body hydrogenated does not contain certain substituent groups. Thus, Table 2 shows the variation for pinene, at 160°, in the presence of 0.2 per cent of nickel; and a similar relationship was observed for ethyl cinnamate and for ethyl linoleate.

Table 2.

Partial pressure of hydrogen (Atm.)	Relative rates of hydrogenation
1	1.00
2	2.08
3	3.05

If, however, the percentage of the nickel was reduced substantially below 0.1 per cent, subnormal variation with pressure occured, i. e. the hydrogenation rate increased less rapidly than the pressure. This is illustrated by Table 3, which refers to the hydrogenation of ethyl cinnamate at 140°.

Table 3.

Hydrogen pressure (Atm.)	Relative rates of hydrogenation with		
	0.085 % Ni	0.017 % Ni	0.008 % Ni
1	1.00	1.00	1.00
2	2.08	1.93	1.32
3	3.00	2.26	1.35
4	3.95	2.53	1.43

It will be seen that, with these low catalyst concentrations, the rate of supply of molecular hydrogen in the gaseous—and consequently, in the liquid—phase is no longer the directing factor in the determination of rate.

With a number of unsaturated alcohols or free acids, on the other hand, Armstrong and Hilditch observed a greater increase in the hydrogenation rate than that corresponding with the direct increase in the pressure. Thus, with geraniol, an increase in the hydrogen pressure from 1 to 4 atmospheres raised the hydrogenation velocity to almost six times its original value. A variation of the same type was given by oleic acid, and is summarised in Table 4. This behaviour should be contrasted with the normal variation given by an ester such as ethyl oleate or by a glyceride of oleic acid, the abnormal variation being apparently dependent—at any rate with nickel, which cannot be regarded as a good hydrogenation catalyst for a free acid on account of the possibility of chemical attack—on the presence of a free carboxyl group.

Table 4.

Hydrogen pressure (Atm.)	Relative rates of hydrogenation with	
	0.375 % Ni	0.15 % Ni
1	1.00	1.00
2	2.26	2.83
3	3.74	4.88
4	5.23	6.53

On the whole, these results of Armstrong and Hilditch, especially those on normal and subnormal variation, are in agreement with the experience of other workers. Thus, the author found a close linear variation of velocity with presure during the hydrogenation of olein, and a similar variation was observed by Moore, Richter and van Arsdel for the hydrogenation of cotton oil; but subnormal variation, which in some cases may approach the dependence of the rate on the square root of the pressure, has been reported by Thomas[1] and may apparently also occur during the hydrogenation of liquid films which are caused to flow over a stationary catalyst.

Under modern conditions, there is a tendency, with bodies which can be hydrogenated only with difficulty, to employ far higher pressures, for instance,

---

[1] J. Soc. chem. Ind. 39, 120 T. (1920).

of the order of 100—300 atm. While many data exist for the time required at these high pressures, little systematic work has been done on the quantitative comparison of these rates with those at lower pressures.

b) *Influence of the Solvent.*

In many cases, especially where small quantities of a substance are hydrogenated, it is convenient to treat a solution of this in a suitable solvent rather than to hydrogenate the substance alone. Accordingly, the use of organic solvents such as acetic acid, alcohol, or ether is common in hydrogenation practice. Water can also in some case be used, although, on grounds of the limited solubility of the organic substances ordinarily hydrogenated, this is not common.

The hydrogenation velocity varies considerably with the solvent taken. Thus, **Willstätter** and **Hatt**[1] found that the hydrogenation of naphthalene with platinum took place far more rapidly in acetic acid than in ether, and this effect was confirmed by **Kelber** and **Schwarz**[2], who went to the length of making colloidal palladium containing a protective colloid stable in acetic acid in order to allow the use of this solvent.

Some observations by the author and **Stone**[3] of the relative rates of hydrogenation of a standard unsaturated body (crotonic acid) in various solvents are given in Table 5. The system hydrogenated consisted in each case of 1 g. of crotonic acid, 9 c.c. of the solvent and 0.1 g. of a standard preparation of non-colloïdal platinum containing 0.0085 g. of metal. Hydrogenation was carried out at 20°, in a mechanically driven shaker. The rate of reaction, k, is expressed in c.c. of hydrogen absorbed per minute, the reaction course being approximately of zero order. Specially purified poison-free solvents were employed.

Table 5.

Solvent	k	k, corrected for vapour pressure of solvent	Solubility of hydrogen α_{20}	Viscosity of solvent η_{20}
Acetic acid	18.7	19.0	0.0563	1.24
Ethyl acetate ...	17.7	19.6	0.0758	0.45
Chloroform	15.2	19.3	0.0596	0.56
Ethyl alcohol ...	14.1	15.0	0.0766	0.56
Cyclo-hexane	11.6	12.9	—	1.72
Ethyl ether	11.2	26.8	0.118	0.96

The concentration of the dissolved hydrogen in the solvent will be a function of the partial pressure of hydrogen in the gas phase and of the solubility coefficient; and, in addition, the rate of transport of the gas from the gas phase, through the solvent, to the catalytic surface will vary with the viscosity and with other—for instance mechanical—factors which determine the rate of diffusion or mixing: accordingly, the respective values for α, the **Bunsen** solubility coefficient for hydrogen, at 20°, in the solvents in question, and for the viscosity of the solvent, η, in poises, have also been inserted in the table. It will be seen that, after correction of the hydrogen pressure for the partial pressure of solvent vapour in the gas phase, there is little difference in the rate in acetic acid, ethyl acetate or chloroform. The somewhat lower rate in ethyl alcohol may to some degree be due to the high value of the viscosity, and the higher corrected velocity in ether to the higher hydrogen solubility and lower viscosity. The quantitative influence of the viscosity and of the solubility is

---

[1] Ber. dtsch. chem. Ges. 45, 1471 (1912).
[2] Ber. dtsch. chem. Ges. 45, 1946 (1912).
[3] J. chem. Soc. [London] 1988, 454.

not known sufficiently to justify the insertion of the appropriate corrections for these; but it seems justifiable to assume a saturated hydrogen-solvent layer at the gas-liquid interface, the hydrogen concentration in which is proportional to the solubility at the partial pressure in question and from which the transport of dissolved gas to the catalyst—both by diffusion and by mechanical mixing—is facilitated by a decrease in the viscosity.

In connection with the solubility of hydrogen in the solvent, it may be noted that this increases (not decreases) with increasing temperature throughout the temperature range ordinarily used in hydrogenation[1]. The variation in the **Bunsen** solubility coefficient, α, for a number of solvents, based on measurements of the author and **Moon**, is shown in Fig. 5.

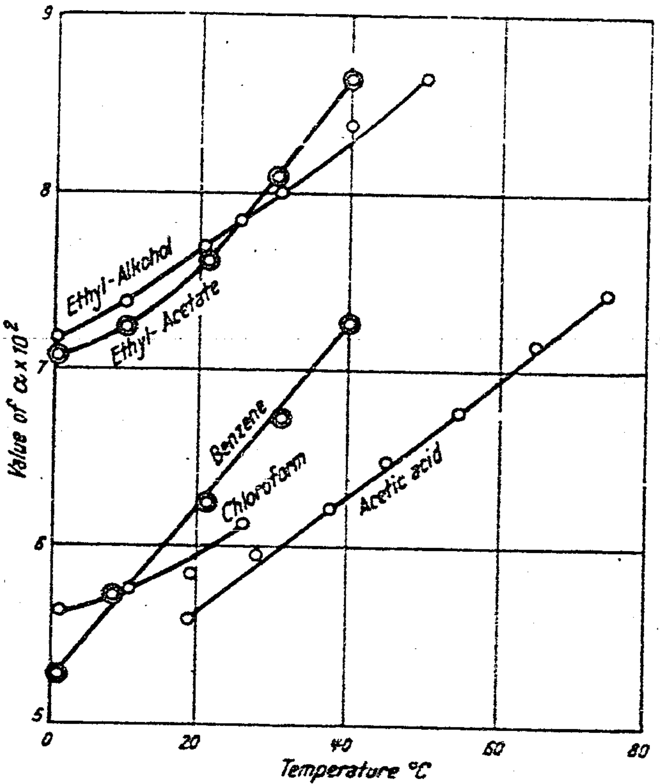


Fig. 5. The **Bunsen** solubility coefficient α for a number of solvents.

The influence of viscosity in liquid-phase hydrogenation has been examined by O. **Schmidt**[2], who has emphasised the importance of diffusive mobility as a factor in hydrogenation velocity. **Schmidt** found that the velocity of hydrogenation of a given substance in various solvents varied, in general, parallel to the variation in the viscosity of the solvent; but the velocity was apparently also influenced by the value of the heat of adsorption of the solvent on the catalyst, which is a measure of the strength of the attachment (Haftfestigkeit) of the solvent to the catalyst. This effect is shown in Table 6, which contains, in place of the heat of adsorption, the values of the heat of vaporisation, λ, of the solvent. According to A. **Eucken**[3], the heat of adsorption is equal to $a\sqrt{\lambda}$. The figures

Table 6.

Solvent	λ	η	Time of half reaction, in mins.		
			Ni	Pt	Co
Methyl alcohol	9,300	0.0061	7.3	11.4	55
Ethyl alcohol	9,580	0.0121	10.2	11.8	342
Iso-Propyl alcohol ..	9,860	0.0223	18.2	12.2	342
n-Butyl alcohol	10,610	0.028	11.8	14.8	720
Tert.-Butyl alcohol ..	9,430	—	18	20	—
Iso-Amyl alcohol ...	10,690	0.045	63	20	1,530
o-Methylcyclohexanol	10,800	0.217	73	400	—
Cyclohexane	7,340	0.009	25	10	—

---

[1] W. **Timojew**: Z. physik. Chem., 6, 141 (1890). — G. **Just**: Ebenda 37, 342 (1901). — A. **Christoff**: Ebenda 79, 456 (1917). — J. **Horiuti**: Inst. chem. Phys. Res., Tokyo 17, 125 (1931). — E. B. **Maxted**, C. H. **Moon**: Trans. Faraday Soc. 32, 769 (1936).

[2] Z. physik. Chem., Abt. A 176, 254 (1936).

[3] Ber. physik. Ges. 16, 348 (1914).

given in the table refer to the hydrogenation of the methyl ester of undecylenic acid at 20°.

It will be seen that, in the homologous alcohol series, the reaction velocity decreases with increasing molecular weight. A similar variation, from solvent to solvent, to that given above for methyl undecylenate was also observed for the hydrogenation of methyl acrylate.

While, as already mentioned, the use of water as a solvent is, if only for reasons of general solubility, not very common, special cases exist in which this is preferable to an organic solvent. Thus, J. Houben and A. Pfau[1] have shown that acetic acid may advantageously be replaced by water in cases in which the by no means negligible dehydrating action of this acid tends to cause a change in the body hydrogenated. For instance, oxy-acids, such as salicylic acid, or amino-acids, such as sulphanilic acid or p-aminobenzoic acid, are far more satisfactorily hydrogenated in water; and hydrogenation in the presence of water may also be applied—with, for instance, a non-colloidal platinum catalyst—to aqueous suspensions of bodies which are only slightly water-soluble.

c) *Influence of the Degree of Agitation.*

In liquid-phase hydrogenation, in which gaseous hydrogen is brought into intimate contact with the solution either by shaking this in hydrogen in a mechanically agitated reaction vessel or—with non-volatile liquids—by the passage of a rapid current of hydrogen through the liquid, the reaction rate will in general increase more or less rapidly with any increase in the degree of agitation, in that a more intensive agitation tends both to increase the gas-liquid interface which is the means of entry of the hydrogen into the solution and also to facilitate the mixing of this probably saturated surface layer with the bulk of the solution, thus bringing the supply of dissolved hydrogen into contact with the catalyst.

Some typical figures for the influence of shaker speed on the reaction rate[2] are given in Table 7 in order to illustrate the great dependence of the rate actually observed in practice on the degree of agitation employed; but the exact variation will, of course, differ from apparatus to apparatus. The figures given in Table 7 were obtained in an apparatus of the type illustrated in Fig. 16, with a charge consisting of 1 g. of crotonic acid, dissolved in 9 c.c. of acetic acid, and 0.085 g. of platinum, hydrogenation being carried out at 20°.

Table 7. *Variation of Hydrogenation Rate with Shaker Speed.*

Speed of shaker (Double strokes per min.)	Rate of absorption of hydrogen c.cs. per min.	Relative reaction rate
240	1.3	1.0
325	11.2	8.6
385	14.5	11.2
580	18.7	14.4
770	20.5	15.8

It will be seen that the curve rises very steeply at first but subsequently flattens as the shaking speed is increased: consequently, in quantitative measurements of rate, in general, the shaker employed should be run at a relatively high speed in order to reduce to a minimum the effect of any unavoidable variations in the shaking factor due, for instance, to variations in belt slip; or, better still, some form of direct coupling to a constant-speed motor should be employed.

d) *Influence of Structure on the Velocity of Hydrogenation.*

While the influence of the chemical structure of the substance hydrogenated varies considerably with the conditions of hydrogenation, certain regularities

---

[1] Ber. dtsch. chem. Ges. 49, 2294 (1916).
[2] Maxted, Stone: Unpublished results.

exist which to some degree connect the structure of a body with its ease of hydrogenation. In general, ethylenic and, above all, acetylenic linkages hydrogenate far more rapidly, especially at low temperatures, than either benzenoid bonds or —CO groups attached to a ring or a chain. This last point is to be noted in view of the general ease of reduction of a carbonyl group by nascent hydrogen, the use of which for the reduction of an ethylenic bond is very limited. Further, as is also found with nascent hydrogen, the velocity of hydrogenation of an ethylenic linkage decreases with the chain length of the body treated. These points, namely the lower rate of hydrogenation of a long-chain compared with a short-chain ethylenic body and the relatively low rate of hydrogenation of benzenoid bonds and carbonyl groups, are illustrated by the typical results summarised in Table 8, which refers to some observed relative rates of hydrogenation under similar conditions, in the presence of a platinum catalyst in acetic acid solution at 40°[1]. The substances were in each case carefully purified from catalyst poisons, by adsorption of these with platinum.

Table 8.

Substance hydrogenated	Relative reaction velocity
Crotonic acid.	100
Oleic acid	70
Benzoic acid	5
Benzene	17.5
Acetophenone	15.5

The preferential reduction of a short ethylenic chain compared with that of a relatively long one is also exercised if both chains are contained in the same molecule. Thus, GOLENDEE[2] found that if allyl oleate or allyl elaidate is hydrogenated with, for instance, palladium, the allyl double linkage is saturated before that in the longchain fatty acid.

The influence of constitution on the ease of hydrogenation has been examined more systematically by O. SCHMIDT[3]. With corresponding compounds of the type, $CH_2 : CHR$, namely, in ethylenic compounds containing a terminal double bond, an increase in the chain length of the group, *R*, led only to a slight increase in the time required for half reduction. This is shown by, for instance, the following figures:

Table 9.

Substance hydrogenated	Time, in mins., for 50 per cent reduction in presence of		
	Ni	Pt	Co
Methyl acrylate, $CH_2{=}CH \cdot COOCH_3$	5.5	9.0	68.0
Methyl undecylenate, $CH_2{=}CH \cdot (CH_2)_8 \cdot COOCH_3$.	7.3	11.4	55.0

Further, the acids, in general, hydrogenate more slowly than their esters, as may be seen from the following results with nickel (Table 10).

The presence of phenyl groups was shown to depress, in some cases very considerably, the rate of hydrogenation of an ethylenic linkage in an attached chain, the effect being greater if additional phenyl groups are introduced. This effect of additional substitution is also caused if alkyl groups are substituted for hydrogen in the ethylene

Table 10.

Substance hydrogenated	Time, in mins., for 50 per cent hydrogenation
Acrylic acid	8.0
Methyl acrylate	5.0
Crotonic acid	11.2
Ethyl crotonate	5.0
Cinnamic acid	17.8
Ethyl cinnamate	7.5

---

[1] MAXTED, STONE: J. chem. Soc. [London] 26, 672 (1934).

[2] J. Chim. gen. (russ.) 7, 317 (1937).

[3] Z. physik. Chem., Abt. A 176, 237 (1936).

molecule. Thus, compounds of the type $R_1R_2C{=}CHR_3$, such as isoamylene, $(CH_3)_2C{=}CHCH_3$, hydrogenate especially slowly. It will be noticed that, as already mentioned, the general tendency is for complicated molecules to hydrogenate more slowly than simple ones. The effect of phenyl substitution is shown in Table 11.

Table 11.

Body hydrogenated	Time, in mins., for 50 per cent hydrogenation in presence of		
	Pt	Ni	Co
Ethyl crotonate, $CH_3 \cdot CH{=}CH \cdot COOEt$	31.6	5.0	110
Ethyl cinnamate, $C_6H_5 \cdot CH{=}CH \cdot COOEt$	307	7.5	240
Styrene, $C_6H_5 \cdot CH{=}CH_2$	—	7.1	—
Stilbene, $C_6H_5 \cdot CH{=}CH \cdot C_6H_5$	—	340	—

With cis-trans isomers, the cis form, in general, hydrogenates more rapidly than the trans form: thus, with maleic and fumaric acid in the presence of nickel, the times for fifty per cent hydrogenation were, in a typical experiment, found to be in the ratio of about 1 : 2.5.

G. DUPONT[1] has investigated a number of further regularities, using alloy-skeleton nickel at room temperature and at the ordinary pressure. Substances containing a terminal—$CH : CH_2$ group—such as styrene, $C_6H_5 \cdot CH : CH_2$, the corresponding phenyl propylene, $C_6H_5 \cdot CH \cdot CH : CH_2$, or undecylenic acid, $CH_2 : CH \cdot (CH_2)_8 \cdot COOH$—hydrogenated quickly and with linear reaction paths. The hydrogenation of a secondary double bond, —$CH : CH$—, took place in general more slowly than that of the primary grouping, $CH_2 : CH$—. This was shown, for instance, with maleic acid, $HOOC \cdot CH : CH \cdot COOH$, and cinnamyl alcohol, $C_6H_5 \cdot CH : CH \cdot CH_2 \cdot OH$. Further substitution of the ethylene residue, i. e. the presence of groupings of the type, $R_1R_2 \cdot C : CR_3H$, or even of $R_1R_2 \cdot C : CH_2$, usually decreased the hydrogenation rate to a low value and may even prevent effective hydrogenation under the above conditions.

Special interest is attached to cases where the molecule to be hydrogenated contains two or more double bonds, in that the presence of a second unsaturated linking in general raises the reactivity of the other bond. Thus, even if both unsaturated groups are tertiary, DUPONT found that one was usually reduced while the other remained unattacked. This also applies to bodies containing one tertiary and one other linking, in which case the unsaturated tertiary linkage remained unhydrogenated. For further regularities, reference should be made to the original paper.

The speed of reduction of nitro groups is of particular interest in view of the ease with which these are reduced both by relatively inactive catalysts and by nascent hydrogen. The slowness of hydrogenation of ordinary nitrobenzene in the liquid phase has, for instance, been commented on by GREEN[2]. Since, however, ordinary specimens of nitrobenzene contain many of the sulphur compounds which are present in the benzene from which they are made—possibly partly as nitro-derivatives—and may, in addition, contain traces of sulphonic acids, this slowness is probably due to poisons: indeed, it was found by MAXTED and STONE (loc. cit.) that the purification of nitrobenzene from catalyst poisons gave a product which absorbed hydrogen, in the presence of a platinum catalyst, at about 150 times the rate of absorption by the purest nitrobenzene which could be purchased and about 2.5 times the rate of absorption by carefully purified oleic acid.

---

[1] Bull. Soc. chim. France (5) 3, 1021 (1936).

[2] J. Soc. chem. Ind. 55, 52 T (1933).

e) *Competitive Hydrogenation.*

The distribution of hydrogen between two competing reactants may, in some circumstances, bear little relationship to the relative rates of hydrogenation of each reactant when hydrogenated alone. This effect has been studied by Adkins, Diwoky and Broderick[1] with a platinum catalyst, using pinene as a standard reference body. Pinene, when alone, is hydrogenated much more rapidly than cinnamic acid: however, when a mixture of these is treated, the cinnamic acid is reduced before the pinene. Again, pinene and octene are reduced at very similar rates: yet, in a mixture, about three-quarters of the reduction takes place in the octene. As yet another example, allyl alcohol is hydrogenated at about one seventh the rate of pinene; but, in competitive hydrogenation in a mixture, allyl alcohol was found to take up about 92 per cent of the hydrogen adsorbed. A change in the solvent was also observed to influence the degree of relative attack. In addition, a case of anomalous distribution of hydrogenation between methyl oleate and nitrobenzene in the presence of nickel has been observed by Green[2], who obtained, however, only a slow liquid-phase reduction of nitrobenzene alone, in opposition to its usual ease of hydrogenation.

f) *The Influence of Foreign Bodies.*

In certain cases, apart from the question of catalyst poisoning, small quantities of foreign constituents in the system hydrogenated have been found to exercise a farreaching effect on the speed and continuity of the hydrogenation.

Probably the most important effect of this class is the influence of traces of oxygen. Willstätter and Jacquet[3] found that the smooth hydrogenation of bodies such as the anhydrides of phthalic, naphthalic or maleic acids in the liquid phase with platinum was dependent on the continued presence of small quantities of oxygen in the system, since the reaction, after taking place normally for a short time, comes to a halt but can be re-started by admitting a trace of oxygen. The number of re-activations necessary for complete hydrogenation varied with the circumstances, usually about four or five being required; but, as an example of a case in which complete hydrogenation could only be effected after a large number of reactivations, about 20 g. of phthalic anhydride—dissolved in 75 c.c. of acetic acid and containing 5 g. of platinum black—absorbed 400 c.c. of hydrogen in the first instance and required about twenty reactivations with oxygen before the completion of the hydrogenation. In the final stages, more hydrogen could be introduced between the reactivations: thus, the next to the last activation allowed the absorption of over 1200 c.c., and the last activation 5600 c.c. of hydrogen.

While this phenomenon is shown actively only during the hydrogenation of certain types of compound, the hydrogenation of which leads especially intensively to the elimination of oxygen, it seems probable that this necessity for oxygen is not confined to bodies which show this effect, since the hydrogenation of, for instance, benzene comes to a similar stop if poison-free phthalic anhydride is added: further, Willstätter and Waldschmidt-Leitz[4] prepared, with great care, oxygen-free platinum and palladium by several methods and showed that these were inactive for hydrogenation in general. Thus, benzene, cyclohexene or limonene remained unhydrogenated provided that no oxygen was present; but if the hydrogen was removed from the shaking apparatus and

---

[1] J. Amer. chem. Soc. 51, 3418 (1929).

[2] J. Soc. chem. Ind. 55, 52 T (1933).

[3] Ber. dtsch. chem. Ges. 51, 761 (1918).

[4] Ber. dtsch. chem. Ges. 54, 113 (1920).

the catalyst treated with air, which was, finally, replaced by hydrogen, the hydrogenation then took place in the normal way.

A similar series of halts, which could, as before, be suppressed by periodical treatment with oxygen, was observed by CAROTHERS and ADAMS[1] and by KAUFMAN and ADAMS[2] in the hydrogenation of various aldehydes, including benzaldehyde, heptaldehyde and furfural, with platinum prepared from the oxide; and these workers made, further, the remarkable observation that the necessity for re-activation with air or oxygen could be avoided by adding to the system a trace of an *iron salt*, such as ferrous chloride. The addition of iron in this way not only, according to the quantity added, either eliminated the halts altogether or greatly increased the volume of hydrogen absorbable between subsequent activations, but also increased the velocity of hydrogenation generally; and, in most cases, smooth and rapid reduction to the corresponding alcohol took place. The use of relatively large concentrations of catalyst for the liquid-phase hydrogenation of aldehydes or ketones recommended by earlier authors[3] can accordingly be avoided by working in this way. The amount of iron salt required is very small; indeed, larger quantities than the optimum amount tend to reduce the reaction rate. As an example of the effect, 21 g. of benzaldehyde, dissolved in 50 c.c. of alcohol and containing 0.23 g. of platinum, required 22 hours treatment, with four reactivations of the catalyst with air, if no iron salt was present. If, however, about half a milligram of ferric chloride was added, the reaction proceeded in 7 hours without the necessity for reactivation with air.

5. The Poisoning of Hydrogenation Catalysts.

In view of the detailed treatment of catalyst poisoning in another section, the subject will here only be dealt with briefly and with special reference to its incidence in hydrogenation.

The common metallic hydrogenation catalysts—nickel, copper, cobalt, iron and the platinum metals generally—are all readily poisoned by the presence in the reacting system of traces of *sulphur*, *arsenic*, *phosphorus*, or certain of their compounds, which, even if present in small amounts, are preferentially adsorbed on the surface of the catalyst, in such a way that the surface elements in the catalyst lattice, by virtue of their obstructive occupation by the poison, are no longer free for normal adsorption or catalysis. In addition to these commoner toxic elements, many others, such as *mercury*, *lead*, *zinc* and *thallium*, may, if in a suitable form, act as hydrogenation poisons: further, the activity of these catalysts is also suppressed by a number of other toxic compounds, including the *cyanides* and *carbon monoxide*, in which the toxicity is inherent in the chemical grouping rather than in the presence of a poisonous element proper, the common property of all these poisons being their preferential and obstructive adsorption. The suppression of the activity of a catalyst may also take place mechanically, by the deposition of a cloaking film of, for instance, a colloidal or insoluble by-product or residue or, especially at high temperatures, by carbon deposition.

While the classical work of BREDIG and his collaborators on the action of poisons in the decomposition of hydrogen peroxide laid the foundation for the quantitative study of poisoning generally, the systematic quantitative investigation of this effect in catalytic hydrogenation may be regarded as beginning with the measurements of KELBER who, in 1916[4], studied in considerable detail the toxic

---

[1] J. Amer. chem. Soc. 45, 1071 (1923); 46, 1675 (1924).

[2] J. Amer. chem. Soc. 45, 3029 (1923).

[3] e. g. VAVON: C. R. hebd. Séances Acad. Sci. 154, 359 (1912).

[4] Ber. dtsch. chem. Ges. 49, 1868 (1916).

effect of a number of poisons, including hydrogen sulphide, carbon disulphide and potassium cyanide, on the activity of various forms of nickel in the hydrogenation of cinnamic acid. KELBER showed, among other results, that the sensitivity of the metal to poisoning depended on its surface-to-mass ratio: thus, a finely-divided nickel was, by reason of its greater relative surface, less sensitive than a relatively coarse nickel prepared by reduction from its oxide at a higher temperature; and the sensitivity could be still further decreased by employing a support, such as kieselguhr, which, by preventing sintering, maintained the finely-divided nature of the nickel even if this is exposed to a high temperature.

The quantitative variation of the activity of the catalyst with the poison content of the system was investigated by the author[1] in 1921. In general, the activity was found to vary linearly with the poison content until the greater part of the activity had been suppressed, when a region of inflexion occurred, accompanied by a more or less abrupt departure of the poisoning graph from its initial linear slope. This is shown, for the typical cases of the poisoning of platinum by sulphur and mercury, in the liquid-phase hydrogenation of oleic acid, in Fig. 6. Other poisons, for instance arsenic or zinc, behaved similarly; and the same type of variation was also observed for other catalytic reactions[2], including gas reactions. It was also found that the general kinetic form of the reaction remained undisturbed by partial poisoning, e. g. a zero-order reaction remained of zero order: accordingly, both from this standpoint and from that of rate of catalysis, the unobstructed fraction of the catalytic surface continues to work normally.

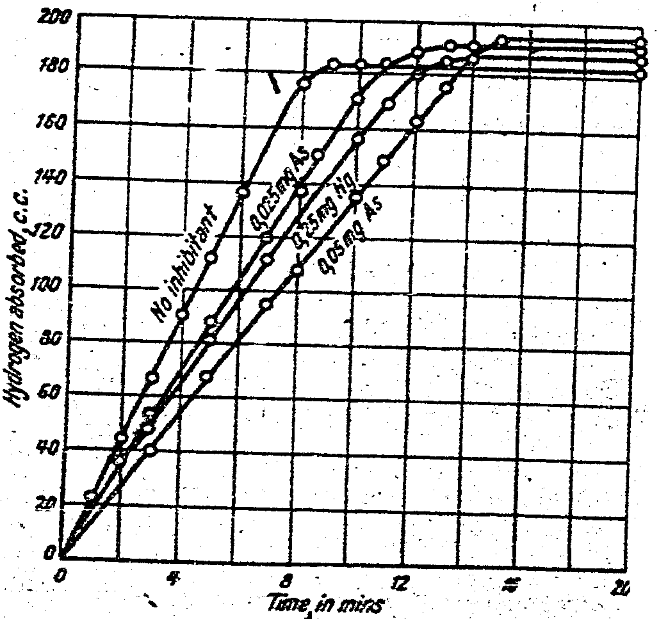


Fig. 6. Hydrogenation of oleic acid; poisoning graphs.

For the main portion of the poisoning graph, in which the activity falls linearly with the poison content, the influence of the poison on the activity may be represented[3] by an equation of the type:

$$k_c = k_0(1 - \alpha c)$$

in which k_c is the activity of the catalyst in the presence of a concentration, c, of the poison, k_0 is the original, unpoisoned activity and α is the poisoning coefficient. The value of α, under comparable conditions, constitutes a very convenient means of expressing the relative toxicity of individual poisons towards a given catalyst on a numerical toxicity scale.

The effective toxicity of a poison per g. mol. will, in general, be determined by factors of two types involving, firstly, the length of the adsorbed life on the catalytic surface and, secondly, the surface covered by each molecule adsorbed. Accordingly, for the general treatment of toxicity, we may write:

$$\text{Toxicity} = f(\tau), (s),$$

---

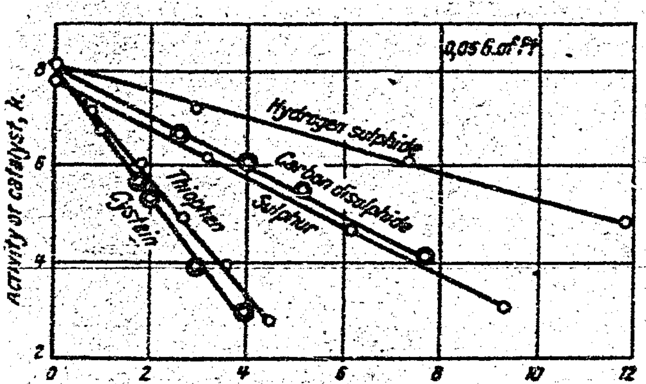
[1] MAXTED: J. chem. Soc. [London] 119, 225 (1921).

[2] J. chem. Soc. [London] 121, 1760 (1922). — MAXTED, DUNSBY: Ebenda 1928, 1600.

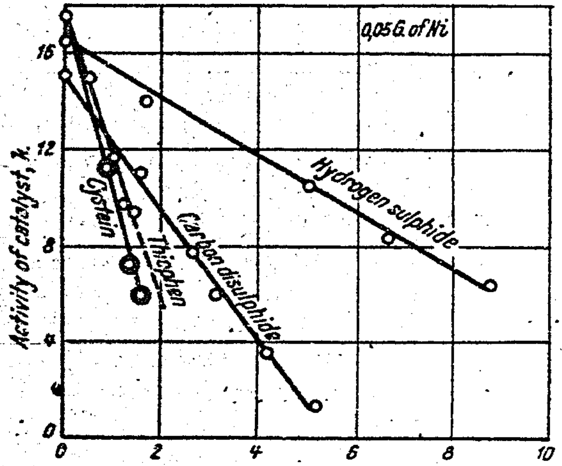
[3] MAXTED, STONE: J. chem. Soc. [London] 26, 672 (1934).

in which x is the mean adsorbed life of the poison and s is a size factor corresponding with the area of catalyst obstructed by each molecule of poison.

If, as is the case with strong poisons, the adsorbed life is relatively long, the effective toxicity should be determined principally by the molecular size of the inhibitant. That this is so is shown in Fig. 7 and 8 and in Table 12, which contains figures for the observed relative toxicities of a number of sulphur compounds towards a platinum and a nickel catalyst for the liquid-phase hydrogenation of crotonic acid[1].



Poison content, g.-atoms of sulphur × 10⁷.
Fig. 7. Hydrogenation of crotonic acid with a platin-catalyst.



Poison content, g.-atoms of sulphur × 10⁵.
Fig. 8. Hydrogenation of crotonic acid with a nickel catalyst.

Table 12.

Inhibitant	Mol. wt.	With Pt catalyst		With Ni catalyst	
		$\alpha \times 10^{-5}$	Relative toxicity per g. atom S	$\alpha \times 10^{-3}$	Relative toxicity per g. atom S
Hydrogen sulphide	34	3.4	1	7.5	1
Sulphur	$(32)_n$	6.4	1.9	—	—
Carbon disulphide	76	6.4	1.9	18.2	2.4
Thiophen	84	14.8	4.4	33.3	4.5
Cystein	121	16.7	5.0	40.0	5.4

The platinum catalyst employed was a relatively coarse-grained unsupported preparation, whereas the nickel was far more finely divided and supported on kieselguhr, the ratio of the sensitivities of the catalysts towards a given poison—as shown by the difference in the order of α, the poisoning coefficient, which can also be used as a measure of the sensitivity of a catalyst to poisoning—being of the order of fifty to one; but it is of interest to note that, in spite of the above wide difference in sensitivity, the relative toxicities of the various poisons, namely, the ratio of the toxicity of a given sulphur compound to that of another, was very similar for both metals. This similarity might be expected on grounds of the similarity in magnitude of the lattice constants of nickel and platinum (3.5 and 3.9 Å, respectively), each lattice being of the face-centred cubic type.

The effect of molecular size on the toxicity is seen more systematically by measurements within a homologous series of strong poisons such as the alkyl sulphides or thiols. Some relative toxicities in these two series of compounds —from methyl sulphide or thiol to cetyl sulphide or the corresponding thiol—

---

[1] Maxted, Evans: J. chem. Soc. [London] 1937, 603.

towards a platinum catalyst for the hydrogenation of crotonic acid[1] are summarised in Table 13.

Table 13.

Inhibitant	Mol. wt.	Chain Length. Å	Relative molecular toxicity
Hydrogen sulphide	34	—	1
Methyl sulphide	62	2.58	7.1
Ethyl sulphide	90	3.50	10.0
Butyl sulphide	146	6.08	15.1
Octyl sulphide	258	11.12	25.8
Cetyl sulphide	482	21.20	34.1
Ethyl mercaptan	62	3.50	3.9
Butyl mercaptan	90	6.08	6.0
Octyl mercaptan	146	11.12	10.1
Cetyl mercaptan	258	21.20	13.1

It will be seen that the molecular toxicity both in the thiol and in the sulphide series increases progressively with the chain length; further, that the sulphides, which contain two alkyl chains to each sulphur bead, are, as would be expected, more toxic for a given chain length than the corresponding single-chained thiol.

The increased toxicity per unit of sulphur brought about by the attachment of a normally non-toxic hydrocarbon chain or other structure to the sulphur atom is of considerable interest since long-chained molecules of the above types may be regarded as consisting of an anchor (i. e. the sulphur atom) attached more or less permanently to the surface and of a residual mobile chain, which—although of such a structure that, in the absence of the poisonous element, it would normally be freely alternatively adsorbed and evaporated—remains constrained in a preferential position for further attachment to the surface, compared with free molecules in the gas or liquid phase surrounding the catalyst. The effect of the permanent linkage at one point in causing a remaining, normally non-toxic, portion of the molecule to become effectively toxic has been called the anchor effect. Such molecules accordingly consist of two distinct portions, the hydrocarbon chain being probably mobile and comparable to a free gas or liquid molecule save for its constraint to the surface by the terminal anchor.

If the above view is correct, the effect of a second terminal sulphur atom—at the opposite end of the chain—should be to decrease the mobility and thus to restrict the surface potentially covered by an otherwise mobile chain of given length, with a consequent decrease in the molecular toxicity, an analogy being the restriction imposed over the area of drift of a boat if this is provided with two anchors in place of one; and it is a remarkable confirmation of the above conception that propylene dithiol, in spite of its possessing twice the sulphur content of the corresponding monothiol, has been found experimentally to be considerably less toxic than either this latter compound or than n-butyl thiol, which more nearly resembles propylene dithiol in chain length owing to the inclusion of the extra sulphur atom.

$$HS \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot SH \text{ (Propylene dithiol).} \quad (1)$$

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot SH \text{ (n-Propyl thiol).} \quad (2)$$

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot SH \text{ (n-Butyl thiol).} \quad (3)$$

On the other hand, if the two sulphur anchors are adjacent to one another, in place of being at opposite ends of the hydrocarbon chain, little effect on the

---

[1] Maxted, Evans: J. chem. Soc. [London] 1937, 1004.

toxicity is exerted by the second sulphur atom, an analogy being the ineffectiveness in a boat of two anchors at the same place—instead of at opposite ends—in restricting the area of circular drift.

The second factor in determining the toxicity of an inhibitant is, as already mentioned, the adsorbed life; for, irrespective of the molecular size, a body only acts as a poison by virtue of its possessing an abnormally long adsorbed life compared with that of normal reactants, the immediate consequence of this long adsorbed life being the obstructive occupation by the poison of catalytic surface which would otherwise be free for the adsorption and catalysis of the normal reacting species of the system catalysed. It should be noted that the partition of a poison between the adsorbed and the free gas or liquid phase is intimately connected with the length of the adsorbed life and can be used as a means of measuring this: further, a relatively long adsorbed life implies the substantially complete adsorption by the catalyst of all the poison present in the system—provided that this amount does not exceed the saturation limit for the catalyst present. For some poisons under certain conditions—particularly in gas-phase hydrogenation at low temperatures—this is approximately true; but, in most cases, a small but measurable residual concentration of the poison remains in the free phase; and, by studying the conditions of the distribution it is possible to introduce a correction for the non-adsorbed poison and thus to plot the activity of a catalyst against the concentration of poison actually adsorbed on its surface, in place of merely against the total poison present in the system. Graphs of this type are called true poisoning graphs, in contrast to effective poisoning graphs based on total, in place of on adsorbed, poison. The necessary correction for converting effective to true toxicity is usually not great for strong poisons with the catalyst concentrations usually used in practice: thus, Fig. 9 shows the effective and the true poisoning graphs for arsine in the liquid-phase hydrogenation of crotonic acid with a platinum catalyst in a system consisting of 10 c.c. of a N-solution of crotonic acid in acetic acid and 0.05 g. of platinum[1].

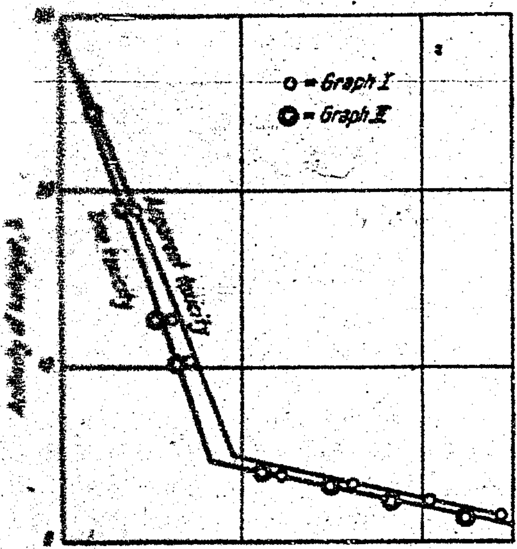


Fig. 9. Hydrogenation of crotonic acid with a platin catalyst. Effective and true poisoning graphs. Total AsH_3 present, g.-mols × 10^{-6} (graph I). AsH_3 absorbed, g.-mols × 10^{-6} (graph II).

Table 14.

Total KCN content (g. mols. × 10^{-4}) in 10 c.c.	KCN adsorbed (g. mols. × 10^{-4}) on 0.05 g. of catalyst	Distribution Ratio a KCN adsorbed to total KCN present	Distribution Ratio b KCN adsorbed to KCN free in 10 c.c. of solution
1.20	0.75	0.62	1.67
2.40	1.52	0.63	1.72
4.02	2.55	0.63	1.73
6.04	3.85	0.64	1.76
8.05	5.10	0.63	1.73
12.10	7.72	0.64	1.76
16.14	9.42	0.58	1.40

In order to determine true toxicities, it is accordingly necessary not only to measure the effective toxicity but also to determine the partition of the poison between the adsorbed and the free liquid or gas phase.

---

[1] Maxted, Evans: J. chem. Soc. [London] 1938, 2071.

In general—provided that the amount of poison present is not too great—the poison adsorbed on the catalyst varies linearly with the total amount of poison present and consequently, by a wellknown rule in proportion, also with the final concentration of poison in the free phase. This is shown in Table 14, which refers to the adsorption of cyanide ions (from potassium cyanide) by 0.05 g. of platinum black of average activity, the volume of the system being 10 c.c.

It will be seen that the cyanide, which is a poison of only medium toxicity in catalytic hydrogenation, is by no means completely adsorbed on this concentration of catalyst: further, the partition between the free and the adsorbed phase follows a linear course, as is shown by the constancy of the ratio in the last two columns of the table, provided that the total poison present is not ni excess of a concentration which falls slightly below 16×10^{-6} g.mol.

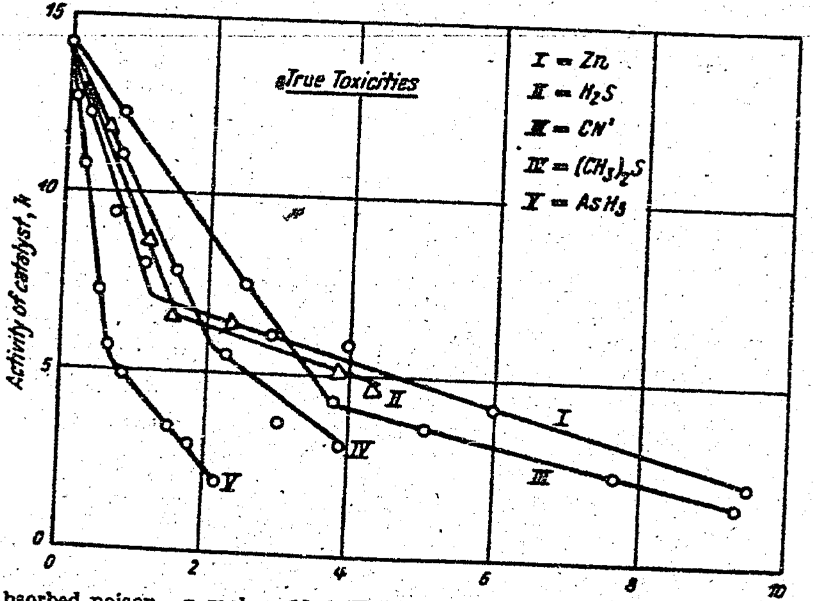


Fig. 10. Hydrogenation of crotonic acid with a platin catalyst. True toxicities of some poisons.

A course of similar form, namely, an initial linear portion followed by a more or less abrupt break from the initial slope as the poison content passes a critical concentration was given by a number of other molecularly simple poisons, the general form of the relationship being shown in Fig. 10.

Given a knowledge of the partition of the poison between the catalyst and the free gas or liquid phase, it becomes possible to draw true toxicity graphs in which the activity of the catalyst is plotted against the poison actually adsorbed on its surface. Some typical graphs of this nature, again for the hydrogenation of crotonic acid in the presence of 0.05 g. of platinum, are shown in Fig. 11[1].

It should be noted especially that the general form of the true poisoning graphs is of the flexed linear type also observed for the effective poisoning graphs. The most probable general significance of a linear relationship between the adsorbed poison content and the catalytic activity is the mutual equivalence of the catalysing surface elements concerned. While this point cannot, for reasons of space, be further discussed here, it should be pointed out that, by using poisons of known size as molecular measuring scales, it can be shown that the distance from active point to active point in the surface of catalysts such

---

[1] Maxted, Marsden: J. chem. Soc. [London] 1938, 839.

as platinum or nickel is probably the ordinary lattice distance. Accordingly, all surface elements are potentially active both for adsorption and for catalysis: further, true poisoning graphs of the type of Fig. 10 may be interpreted as evidence for the existence of at least two types or ranges of potential catalysing or adsorbing lattice-elements, all elements of a given type being apparently mutually equivalent. This is by no means incompatible with the adlineation theory of Schwab and Pietsch[1]; but it may, alternatively, be caused by the participation, in adsorption or catalysis, of a second or even of more deeply seated lattice layers in the catalyst—or catalysis or adsorption on an already adsorbed layer—both of which cases would give a secondary range of, within themselves mutually equivalent, catalysing or adsorbing points.

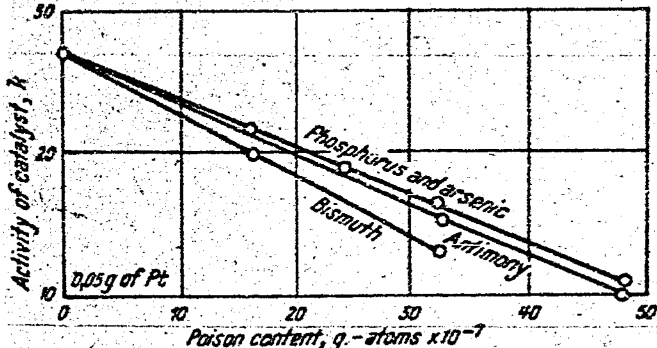


Fig. 11. Hydrogenation of crotonic acid with a platin catalyst. Activity of the catalyst plotted against the poison, actually absorbed on its surface.

6. Heat of Hydrogenation.

Hydrogenation is usually accompanied by a considerable evolution of heat, which, during the hydrogenation of substances on a large scale, may cause a very considerable rise in temperature if no provision for cooling is made.

In general, however, this heat of hydrogenation cannot be calculated with accuracy from combustion data, since it depends on differences in heats of combustion. Thus, H. v. Wartenberg and G. Krause[2] have pointed out that calculated heats of hydrogenation based on published values for the heats of combustion may, in some cases, vary by as much as 100 per cent, depending on the value accepted for the combustion heats. These workers determined the heat of hydrogenation of ethylene directly, by causing ethylene and hydrogen to react in a calorimeter in the presence of colloidal palladium. The results gave a value, for the reaction heat at constant pressure, of 30.6 kg. cals. per g. mol. of ethylene hydrogenated. In later work, however, a somewhat higher

Table 15.

Substance hydrogenated	Q, in cals. per g.-mol. (± 10—100 cals.) at 82°	Substance hydrogenated	Q, in cals. per g.-mol. (± 10—100 cals.) at 82°
Ethylene	32,824	Tetramethyl-ethylene	26,633
Propylene	30,115	Allene (+ $2H_2$)	71,280
n-Butylene	30,341	1,3-Butadiene (+ $2H_2$)	57,067
n-Heptene	30,137	1,4-Pentadiene (+ $2H_2$)	60,790
uns.-Methyl ethyl ethylene	28,491	1,5-Hexadiene (+ $2H_2$)	60,525
uns.-Methyl isopropyl ethylene	27,997	1,3-Cyclohexadiene (+ $2H_2$)	55,367
Cyclohexene	28,592	Cyclopentadiene (+ $2H_2$)	50,865
Trimethyl-ethylene	26,920	Benzene (+ $3H_2$)	49,802

---

[1] Pietsch, Kotowski, Berend: Z. physik. Chem., Abt. B 5, 1 (1929). — Schwab, Pietsch: Z. Elektrochem. angew. physik. Chem. 35, 135 (1929). — Schwab, Rudolph: Z. physik. Chem., Abt. B 12, 247 (1931).

[2] Z. physik. Chem., Abt. A 151, 105 (1930).

figure has been obtained; and F. D. Rossini[1], as a result of examination of available data, comes to the conclusion that the most trustworthy value is 32.64 ± 0.06 kg.-cals. per g. mol., based on hydrogenation data or 32.78 kg. cals. based on heats of combustion. Thus, in the case of ethylene, for which the combustion heats are known accurately, the indirect method gives a figure which is confirmed by the direct calorimetric determination of the reaction heat.

Probably the most systematic series of direct measurements of heats of hydrogenation are those of Kistiakowsky and his co-workers[2], whose results are summarised in Table 15.

For a discussion of the regularities, reference should be made to the original papers.

7. Hydrogenation with some Unusual Catalysts.

While, in the large majority of cases, hydrogenation is carried out in practice with catalysts either of the nickel group, including copper or with platinum metals, or, in certain cases, with catalysts of oxide or sulphide type, (e. g. chromium oxide, copper chromite or molybdenum oxide or sulphide) various other bodies have also been used, although their use is rare and, in some instances, restricted to reactions of special types.

In connection with catalytic hydrogenation with metals, it is of special interest that, in addition to metals which form chemisorptive adsorption complexes with hydrogen, a number of elements, the association of which with hydrogen may involve the formation of a hydride, also act catalytically. Thus, in the first periodic group, hydrogenation may be carried out by means of definitely hydride-forming elements such as *caesium*, which is able to bring about the union of ethylene and hydrogen, or the interaction of carbon monoxide and hydrogen, in each case even at room temperature[3]. It should be noted, however, that the presence of hydride on the caesium inhibited the reaction, the best results being obtained with freshly distilled caesium. On substituting sodium for caesium, hydride formation was again found to obstruct the catalytic activity completely (see, however, later).

The alkaline earth metals act somewhat similarly[4] and may be employed in the form of turnings, which are washed with ether to remove a film of grease and sealed into the glass reaction bulb. The reaction of ethylene with hydrogen takes place on *calcium* at room temperature and was also examined by Pease and Stewart at 100° and at 200°. From the standpoint of the possible intermediate formation of calcium hydride, it may be noted that while a calcium catalyst was found to be considerably more active after previous saturation with hydrogen, the interaction of ethylene with calcium hydride was relatively very slow. The formation of a surface hydride in which the hydrogen molecules are converted into negative hydrogen ions—which is the form in which hydrogen is present in calcium hydride—would thus appear not to be confirmed by this work; and, in the opinion of Pease and Stewart, it seems probable that even with catalysts such as calcium an action of the contact type is involved, in that these authors consider that no evidence is forthcoming that the hydride-forming property of the catalyst is responsible for its catalytic activity.

---

[1] J. Res. nat. Bur. Standards 17, 629 (1936).

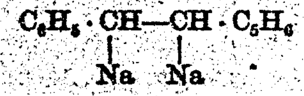
[2] G. B. Kistiakowsky, H. Romeyn, J. R. Ruhoff, H. A. Smith, W. E. Vaughan: J. Amer. chem. Soc. 57, 65, 876 (1935); 58, 137, 146 (1936).

[3] D. G. Hill, G. B. Kistiakowsky: J. Amer. chem. Soc. 52, 892 (1930). — O. Schmidt: Ber. dtsch. chem. Ges. 68, 1098 (1935).

[4] R. N. Pease, L. Stewart: J. Amer. chem. Soc. 47, 2763 (1925). — O. Schmidt: Z. physik. Chem. 165, 209 (1933); Ber. dtsch. chem. Ges. 68, 1098 (1935).

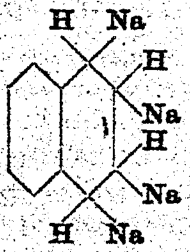
Sodium hydride may, however, be used as a hydrogenation catalyst at high hydrogen pressures (> 25 atm.) for the special case of the conversion of polycyclic hydrocarbons, such as naphthalene, anthracene, phenanthrene and stilbene, into reduced derivates. Thus, naphthalene gives practically pure tetralin and stilbene passes into dibenzyl. Sodium hydride cannot, on the other hand, be used for the reduction of olefines or of benzene or toluene, or for hydrocarbons such as diphenyl ethane[1].

According to HUGEL and GIDALY[2] the necessary condition for rendering a hydrocarbon susceptible to hydrogenation in this way is the power of forming addition compounds with sodium. Thus, with stilbene, it is known that a sodium addition product of the composition:

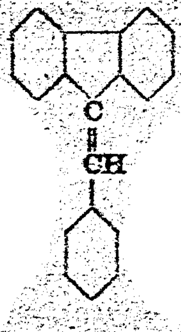


$$\underset{\displaystyle\mathrm{Na}}{\mathrm{C_6H_5\cdot CH}}\mathrm{-}\underset{\displaystyle\mathrm{Na}}{\mathrm{CH\cdot C_6H_5}}$$

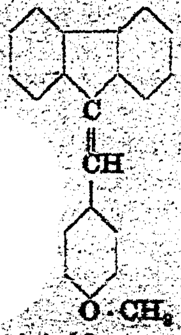
may be formed, which does not hydrogenate further than $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, since this product no longer combines with sodium. Naphthalene, however, forms a tetra-sodium derivate:



which then undergoes hydrogenation. Other bodies which form sodium addition compounds and can accordingly be hydrogenated, in addition to those already given, are benzalfluorene, anisal-fluorene and diphenyl-butadiene.



Benzal-fluorene.



Anisal-fluorene.

$C_6H_5 \cdot CH{=}CH \cdot CH{=}CH \cdot C_6H_5$

Diphenyl-butadiene.

The catalytic action of sodium is perhaps reflected in the combined hydrogenation and dehydrogenation observed by G. CUSMANO[3] with sodium derivatives of thymol, this taking place in a similar manner to the simultaneous dehydrogenation and hydrogenation frequently obtained with nickel or platinum.

Of other uncommon hydrogenating elements, *zinc* is a catalyst of fair activity and instances of its use will be found in connection with the hydrogenation of ethylene. *Lead and thallium* have been used for the catalytic reduction of nitrobenzene, under which further details are given: further, *manganese* and *chromium* apparently possess activity for general hydrogenation, including the reduction of ethylene[4].

The use of *rhenium* has been investigated by H. TROPSCH and R. KASSLER[5], who found that ethylene was to some extent hydrogenated to ethane in the presence of rhenium at 200—300°, and carbon monoxide could, in a similar

---

[1] G. HUGEL, FRIESS: Bull. Soc. chim. France (4) 49, 1042 (1931)
[2] Bull. Soc. chim. France 51, 639 (1933).
[3] Gazz. chim. ital. 60, 105 (1930).
[4] O. SCHMIDT: Ber. dtsch. chem. Ges. 68, 1098 (1935).
[5] Ber. dtsch. chem. Ges. 63, 2149 (1930).

way, be reduced at 350—400° to methane; but decomposition also occurred in each case. The activity of rhenium was confirmed by O. SCHMIDT[1].

In the work of M. S. PLATONOW, S. B. ANISSIMOW and W. M. KRASCHENINNIKOWA[2], metallic rhenium was found to possess only a very low activity at room temperature for the hydrogenation of maleic acid in aqueous solution and for cyclohexene in alcoholic solution. The results at higher temperatures in the gas phase were complicated by decomposition. Nitrobenzene, at 250—300°, gave some aniline, cyclohexene underwent partial hydrogenation to cyclohexane, but benzene decomposed without sensible hydrogenation.

Somewhat more satisfactory results were obtained on using rhenium supported on a carrier as a *dehydrogenation* catalyst for ethyl alcohol, an 11 to 12 per cent yield of acetaldehyde being given by one passage over the catalyst at 300°, and 14 per cent at 600°. With isopropyl alcohol[3] yields of acetone up to 85 per cent were obtained, the optimum temperature being 400°.

B. General Hydrogenation technique.

The present chapter is designed to deal with laboratory pratice in connection with catalytic hydrogenation. The first essential for successful hydrogenation, with ordinary metallic catalysts, is the availability of the substance to be hydrogenated in a state reasonably free from catalyst poisons, otherwise either the reaction will fail to take place or an inordinately large proportion of catalyst will be necessary, the greater part of which will be acting as an adsorbent for the poison rather than as a catalyst proper. However, by far the greater number of substances are, in their ordinary pure commercial form, sufficiently free from inhibitants to be hydrogenated without difficulty; and the necessity for special purification—save for the ordinary methods of re-distillation, re-crystallisation, or treatment with adsorbent carbon or fuller's earth—is relatively rare and, in practice, almost exclusively confined to substances, such as benzene or naphthalene, which contain sulphur compounds (e. g. thiophene or thionaphthenes) not removable by distillation. In such cases, a general method of purification consists in pre-treatment with a preliminary charge of the catalyst, or with a related catalyst; or it is in many instances possible to break up the poison and to transform it into a more easily absorbable form in which it can then be removed by adsorption. Elaborate purification in this way is, however, as already stated, in most cases unnecessary, unless specially purified standard substances, for instance, for kinetic studies or for comparison of hydrogenation speeds, are required.

Commercial electrolytic hydrogen, which contains as impurity only a trace of oxygen, constitutes the most satisfactory practical source of this gas. It is usually sufficiently pure to be used directly from the cylinders in which it is supplied; but if it is desired to remove the trace of oxygen this can be done by passing the gas through a gently heated tube containing palladium or platinum or—at a higher temperature—copper; or the removal of oxygen may be effected very conveniently by passage through a bulb containing an electrically heated platinum coil, the temperature of which is adjusted to a dull red, the gas being in each case subsequently dried, for instance with soda-lime or calcium chloride, to remove the water formed. Again, however, this purification

---

[1] Ber. dtsch. chem. Ges. 68, 1098 (1935).
[2] Ber. dtsch. chem. Ges. 68, 761 (1935).
[3] Ber. dtsch. chem. Ges. 69, 1050 (1936).

of commercial electrolytic hydrogen is seldom necessary. Hydrogen made from zinc, for instance in a generator of Kipp type, is by no means so suitable as electrolytic hydrogen on account of its arsenic content and requires purification. Probably the most satisfactory method of purification consists in sorption of the hydrogen by palladium maintained at room temperature, the gas being subsequently pumped off at a higher temperature; but the method is, in practice, only suitable for the preparation of small quantities of the gas, even when a fair amount of palladium is available. Hydrogen containing a trace of carbon monoxide, such as is obtained from most of the processes starting with fuel, is also less suitable than electrolytic hydrogen. The small quantity of carbon monoxide may be removed by passage of the hydrogen through a heated tube containing active nickel, preferably on a granular support such as bauxite or pumice, or as nickel chromite or in the form of nickel turnings previously activated by anodic oxidation in sodium carbonate solution; but, for effective removal, pressure treatment with these catalysts is preferable and, in any case, the methane formed remains in the hydrogen as a diluent. Accordingly, from every aspect, electrolytic cylinder hydrogen constitutes the most practical source of the gas for general laboratory use in hydrogenation.

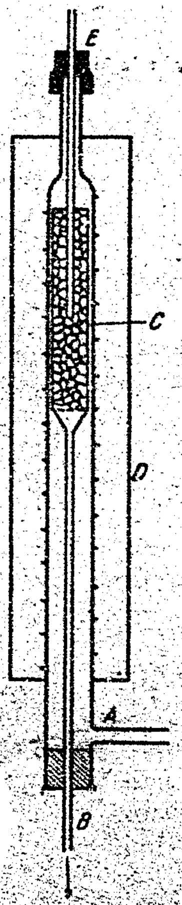


Fig. 12. Apparatus for the hydrogenation in the vapour state.

The most suitable apparatus will obviously depend on the form of the body to be hydrogenated and especially on whether the reaction is to be carried out in the liquid or in the gas or vapour phase. It will, accordingly, be convenient to consider gas-phase and liquid-phase apparatus separately.

1. Gas-phase Hydrogenation.

A convenient type of apparatus which is very suitable for general use either for the hydrogenation of gases or of liquids in the vapour state is illustrated in Fig. 12.

It consists of a pair of concentric tubes, *A* and *B*, of Pyrex or similar glass of the shape shown in the diagram, the catalyst, *C*, being contained in the upper portion of the inner tube. These tubes are inserted into a metal (e.g. iron or copper) furnace tube, *D*, of somewhat larger diameter, which is wound on a mica foundation with resistance wire or tape, the whole being covered with magnesia-asbestos sectional lagging. The measurement of temperature is carried out by a thermocouple inserted at *E*. It will be seen that the mixture of hydrogen and of the gas to be hydrogenated enters the larger of the glass tubes by way of the side piece, passes upwards through the annulus between the two tubes—which acts to some extent as a heat exchanger—the gas returning downwards through the catalyst to the exit at *B*. The catalyst, which should be of granular form (i.e. supported on a granular carrier such as bauxite, pumice or silica gel, or prepared in granules or in another compact form without such support) can, in this type of apparatus, be changed very easily by taking out the inner tube, *B*, on its supporting cork.

For the hydrogenation of liquids in a vapour form, a small washbottle, maintained at a suitable temperature by immersion in a bath, is fused on to *A*, condensation being prevented, if necessary, by a few turns of electrical winding on the connection (which should be made as short as possible) between the bubbling vessel and the tube *A*. Alternatively, the liquid may be dropped from a burette or dropping funnel into a small silica or pyrex vapourising chamber attached to *A* in place of the washbottle, hydrogen being passed through this heated vapourising chamber; but, for small-scale working, a bubbling carburettor in which the vapour content of the hydrogen is maintained by suitable temperature adjustment, usually constitutes a more easily regulated method of addition. With either method of adding the vapour, a condenser, with appropriate cooling, should be attached to the exit tube, *B*, for the condensation and recovery of the product.

Where it is not desired to set up a special apparatus, hydrogenation may be carried out in apparatus of simpler type, without electrical heating, by employing a large U-tube, immersed in an oil-bath, as the catalyst chamber; or even two pyrex distilling flasks, as in Fig. 13, may be used. In this latter arrangement, the smaller flask acts as the carburettor while the larger flask contains the catalyst, the temperature of these being adjusted by suitable baths. It should be noted that rubber stoppers cannot be used in places in which these become hot, on account of the danger of poisoning from the sulphur contained in these.

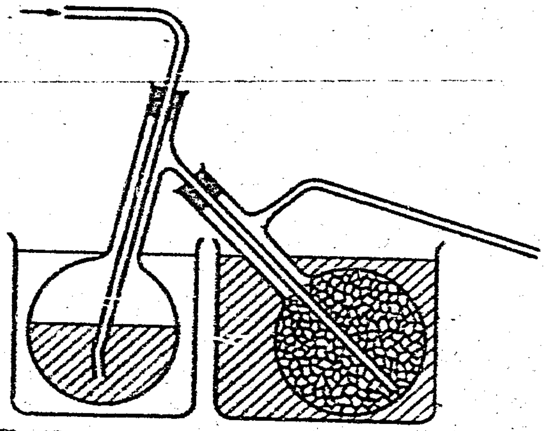


Fig. 13. Simple apparatus for the hydrogenation in the vapour state.

In most cases, whatever may be the type of apparatus used, the rate of flow of the mixture through the catalyst is adjusted to a value such that substantially complete hydrogenation occurs in one passage through the catalyst; but, should the reaction—for instance, by virtue of an abnormally low temperature or for any other reason—be abnormally slow, it may be necessary, as an alternative to using a larger catalyst chamber or more than one chamber in series, to circulate the gas or vapour mixture through the catalyst; and in any case, if the excess of hydrogen is to be recovered and re-used, some form of circulation is necessary. While circulation on a large scale, in which mechanical pumps can be used, is relatively easy, it is not common in laboratory practice to recover the excess of hydrogen, which is conveniently burnt at the exit of the apparatus. In cases, however, in which for any reason circulation of a gas mixture on a laboratory scale is desirable, this may be carried out very simply, without the use of a special pump, by means of an arrangement which has been successfully used by Schwab and his co-workers[1] for gaseous reactions such as the hydrogenation of ethylene and which might probably also be used for mixtures of hydrogen with a vapour of a liquid body. In this apparatus, which is illustrated diagrammatically in Fig. 14, the circulation depends on the convection caused by a temperature difference between the reaction vessel and a circuit connecting the upper with the lower end of this vessel. In the diagram, *RI* is the reaction vessel, containing the catalyst, and *B* is the cooled portion of the circuit. For further details reference should be made to Schwab and Zorn's paper. It is obvious that, with such an arrangement, the rate of circulation is not known; but the principle has much to recommend it, from the standpoint of simplicity, in avoiding the necessity for a positively acting circulation pump.

In Sabatier and Senderens' early work on gas-phase hydrogenation, finely-divided metallic powders, prepared by the reduction of nickel or other oxides,

---

[1] G. M. Schwab, H. H. v. Baumbach: Z. physik. Chem., Abt. B 21, 65 (1933). — Schwab, Staeger: Ebenda 25, 418 (1934). — G. M. Schwab, H. Zorn: Ebenda 32, 175 (1936).

were employed. These were distributed in a more or less even layer along a horizontal tube through which the mixture of hydrogen and the vapour of the substance to be hydrogenated was passed, the liquid being usually vapourised from a drop feed in the tube itself. An apparatus of this type is shown in Fig. 15;

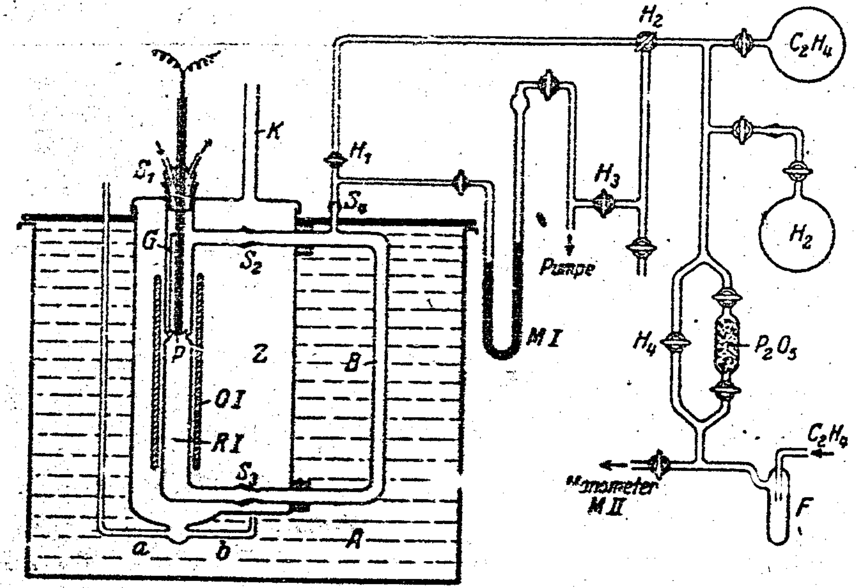


Fig. 14. Apparatus of SCHWAB and ZORN for gas-phase hydrogenation.

and, as is evident from the large amount of work which was carried out with this simple arrangement, it forms quite an effective method of hydrogenation.

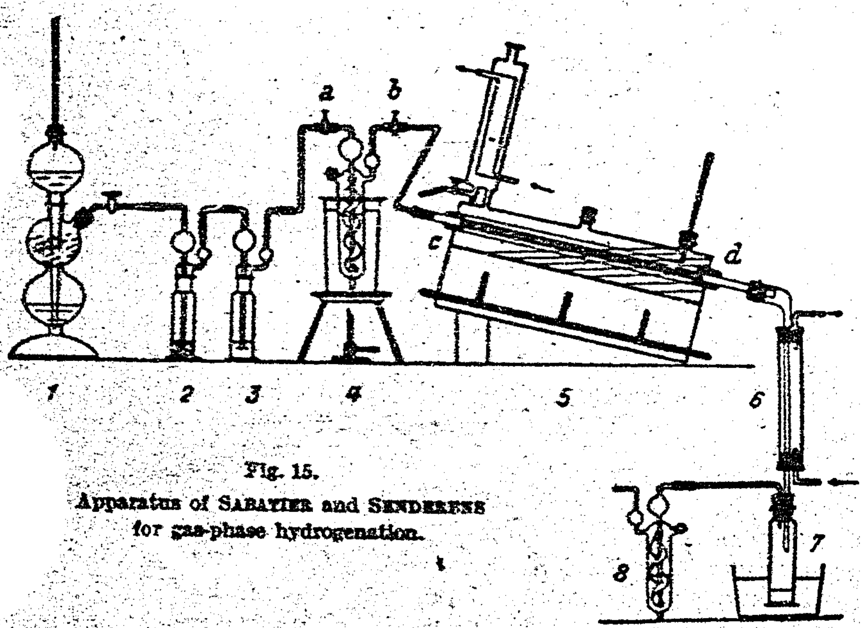


Fig. 15.
Apparatus of SABATIER and SENDERENS for gas-phase hydrogenation.

In all the methods of gas-phase hydrogenation, the reduction of the catalyst is best effected in the apparatus itself, preferably immediately before the catalyst is required for hydrogenation, the temperature being changed from that required for reduction to that used for the reaction. It is usual to employ a considerable excess of hydrogen, the rate of flow of the gas being measured either by passage through a meter or by means of a flow gauge of the orifice type.

2. Liquid-phase Hydrogenation.

By far the greater number of hydrogenations are, in practice, carried out in the liquid phase, using finely divided catalysts in suspension in the liquid. The method allows the use of low and easily controllable temperatures, and thus avoids to a large degree the formation of decomposition products due to excessive or irregular temperatures, smooth and complete conversion to a single product being a common feature of liquid-phase working.

With catalysts of the platinum group, the reaction is often carried out at room temperature. The body to be hydrogenated is usually dissolved in a solvent, e.g. in water, acetic acid, alcohol, ether or cyclohexane, although in the case of substances which are liquid at room temperature the use of a solvent is not necessary. The proportion of catalyst varies with the conditions and with the body hydrogenated; but, as a guide, 0.05 to 0.1 g. of platinum black to 10 c.c. of solution is usually sufficient if the linkage to be hydrogenated is not too difficult, and far less catalyst is often used. Catalysts of the nickel class, although they possess slight activity even at room temperature[1] are usually used at higher temperatures, for instance, at 120—180°, without a solvent, the body hydrogenated being in a liquid state in any case by virtue of the high temperature. It may, however, be noted that nickel and other catalysts which are specially suitable for low-temperature working may be made by leaching suitable nickel alloys according to the method developed by Raney, details of which are given elsewhere. Apart from this special form, finely-divided nickel or other similar catalysts are usually supported on a kieselguhr or other carrier; and a larger ratio of catalyst to unsaturated substance than that given above for platinum is usually employed. For laboratory working, one per cent of nickel in the body hydrogenated may be taken as an average figure for this; but far smaller proportions are used in technical work in which economy of nickel is important.

In most cases of laboratory hydrogenation, both in the liquid and in the gas phase, the use of an increased pressure is not necessary, above all for ethylenic linkages: accordingly, a description of pressure apparatus, which is of special use for the rapid liquid-phase hydrogenation of aromatic or heterocyclic rings or of ketonic groups, with a low concentration of catalyst, will be deferred until a later section.

Reaction velocity in liquid-phase hydrogenation is very largely dependent on an intimate degree of contact between the gaseous hydrogen, on the one hand, and the liquid system on the other. While the hydrogenation, particularly of a non-volatile liquid, may be carried out merely by passing a rapid current of hydrogen through the liquid containing the catalyst in suspension, for instance, in a distilling flask, this bubbling method, in which the hydrogen also acts as the means of agitation, is wasteful from the standpoint of gas consumption, since, for rapid reaction, a very rapid stream of hydrogen has to be used. It does, however, constitute a rather primitive means of hydrogenating a substance such as a glyceride, the excess of hydrogen being usually burnt as it leaves the side arm of the distilling flask.

In practice, the simplest method of inducing intimate contact between the liquid and the hydrogen consists in using some form of mechanical shaker by means of which the liquid is shaken with the gas. In an apparatus of this type, the hydrogen absorbed can readily be measured by connection with a gas burette and the progress of the hydrogenation followed.

---

[1] Kelber: Ber. dtsch. chem. Ges. 49, 55, 1868 (1916); 50, 305 (1917); 54, 1701 (1921).

An apparatus of this type, which has been used by the author continuously for over 20 years[1] with only minor modifications is shown diagrammatically in Fig. 16.

The charge to be hydrogenated is introduced, by means of the stoppered side tube, into the shaking pipette, *A*, which is immersed in a bath provided with an electric heater controlled by a thermostat, the reaction pipette being mounted in a light detachable metal block which is shaken vertically by means of an eccentric drive actuated by a constant speed motor. For smooth running, the vertical driving rod, on which the connecting rod is clamped, must be properly guided to give an accurately vertical motion; and, to avoid splashing, the length of the vertical stroke should be such that the bulb of the glass pipette does not emerge from the water in the thermostat at the highest part of the stroke; nor, similarly, should the metal connecting block break the surface of the water at its lowest position. A suitable shaking speed is 400—500 double strokes per minute.

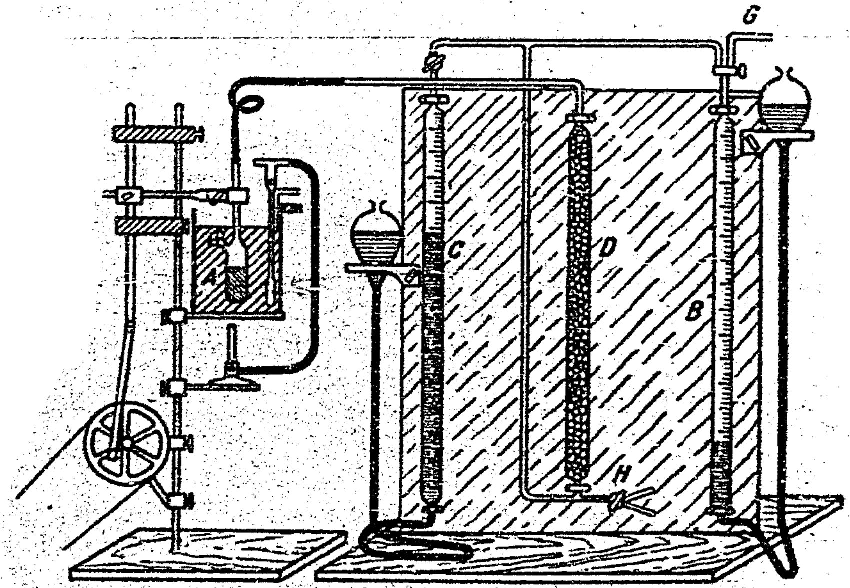


Fig. 16. Apparatus for hydrogenation in the liquid state.

The reaction pipette is connected, by means of a short piece of rubber pressure tubing, to the gas measuring system, which consists of a main burette, *B*, a reserve burette, *C*, and a drying tube, *D*, containing granular soda-lime or calcium chloride. The main hydrogen supply enters the apparatus at *G*, *H* being a 3-way stopcock with alternative connection to vacuum and to the hydrogen supply.

To use the apparatus, *A* is detached from its rubber connection, also, by loosening the thumbscrews, from the vertical driving rod. It is usually convenient to keep the connecting block permanently on the thick-walled, small-bored stem of the pipette, this stem being shielded from breakage from the points of the thumbscrews on the right of the block by packing the hole in the block with rubber faced with metal next to the screw points. The charge to be hydrogenated, together with the catalyst, is next introduced into the pipette by way of the side tube, the stopper of which is lubricated, after charging, by a trace of pure olive oil and fastened in its place by a rubber band attached to glass thorns. The burettes, *B* and *C*, are the completely filled with water by raising the attached cups and the taps at their upper ends closed, following which the pipette is re-inserted in its rubber connection and the whole apparatus, including the pipette, is several times alternately evacuated and filled with hydrogen by slowly rotating the three-way stopcock, *H*. During this evacuation and subsequent filling with gas, it is advisable to keep the pipette cool and not

---

[1] Trans. Faraday Soc. 13, 36 (1917).

1264

to immerse it in the bath (by re-clamping the metal block on the vertical rod of the shaker) until the final filling with hydrogen. Finally, hydrogen is introduced into the burettes by opening the stopcocks at the top, that at *C*, also the stopcock at *B*, being then closed. The volume in *B* is then read off, the shaker is started, and the course of the hydrogenation followed by the disappearance of the gas in *B*. It will be seen that, when this volume is exhausted, a reserve volume can be obtained from *C* and that there is also provision for refilling *C* as required, the connecting tube between *C* and the hydrogen supply having been previously swept out with hydrogen. For hydrogenation on a small scale, *A* may have a capacity of 25 c.c., and contain an actual charge of about 10 c.c., *C* and *B* being ordinary 100 c.c. Hempel burettes; but the size can, of course, be increased proportionately as required.

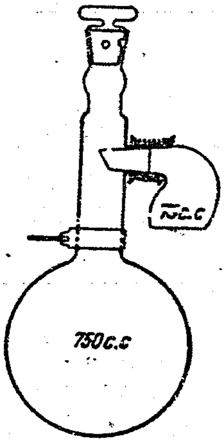


Fig. 17. Shaking flask of H. O. L. FISCHER and E. BAER.

While, in an apparatus of the above type, the hydrogenation does not usually begin with any substantial speed before the shaker is started, it may be necessary, in some circumstances, not to add the catalyst until the phase of preliminary evacuation and filling has been completed. A design of shaking flask which permits this, in which the catalyst is contained in a side-piece (see Fig. 17), attached by a ground-in joint and capable of rotation, has been described by H. O. L. FISCHER and E. BAER[1]. After evacuation of air and replacement by hydrogen in the usual way, the catalyst is added to the main charge by turning the side-piece.

For the hydrogenation of larger volumes of liquids, the shaking apparatus together with the gas-measuring system will need modification in order to be adapted to the greater weight of liquid to be shaken. Particularly for reactions at room temperature, a horizontally moving shaker carriage is very suitable, the shaking vessel itself being mounted at a suitable inclination on the moving carriage and connected to a gasholder of hydrogen. It is simpler, in such cases, not to immerse the shaking vessel in a liquid bath, but to employ electrical heating, together with an internal thermometer or thermocouple if a temperature higher than that of the room is required. It is obviously also possible, by employing a hydrogen reservoir in place of an ordinary gas-holder, to work at an increased pressure without special apparatus provided that this pressure is not too high; but for pressures above about 2 atmospheres, particularly if the volume to be hydrogenated is appreciable, properly constructed steel apparatus should, on grounds of safety, be used.

Many alternative forms of apparatus for liquid-phase hydrogenation other than those of shaker type have been described in the literature. Thus, especially for the hydrogenation of small volumes, a magnetically operated internal agitator may be used. A small apparatus embodying this form of agitation has been described by A. CASTILLE[2] and is illustrated diagrammatically in Fig. 18.

The agitator *A*, is constructed of platinum or platinum-iridium and consists of a series of perforated discs, the bottom plate being bellshaped and without perforations. The axial wire bearing this agitator terminates at its upper end in a small softiron cylinder, *B*. *M* is an electromagnet of adjustable height, provided with a mechanical current interruptor; and, on making and breaking the current, the agitator rises and falls. The remainder of the apparatus is conveniently made of pyrex or similar glass. It consists of a reaction vessel, *C*, of the shape shown, connected with a gas burette, *D*, which can also be used as a manometer, and with a

---

[1] Ber. dtsch. chem. Ges. 65, 343 (1932).

[2] Bull. Soc. chim. Belgique 46, 5 (1937).

stopcock, *E*, for evacuation and filling with hydrogen. It will be seen that, by working in this way, the necessity for a rubber or tubular metal spring connection to a shaking vessel is eliminated. In CASTILLE's work with this apparatus, the current was interrupted about once a second, by means of a pendulum, and mercury was employed in the gas burette. For working at pressures higher than atmospheric, the reaction vessel could be fastened in its place by means of screws. A further and somewhat similar magnetically operated apparatus has also been employed by B. FORESTI[1].

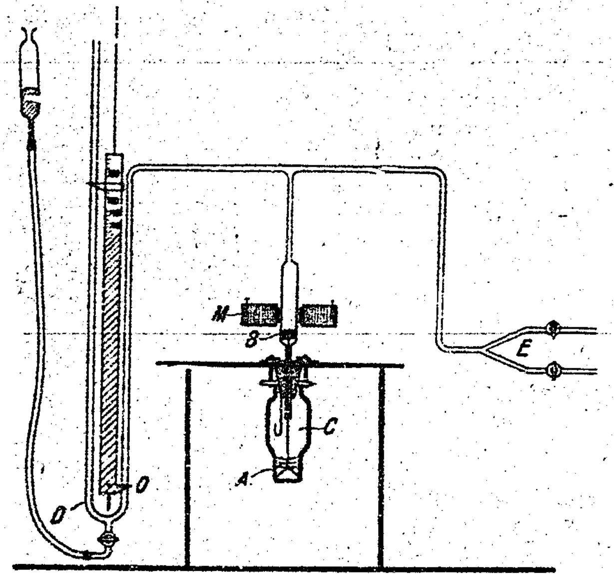


Fig. 18. Apparatus of CASTILLE for liquid phase hydrogenation.

3. Hydrogenation under Pressure.

While it is unnecessary in most cases of catalytic hydrogenation to use a high pressure, this may be necessary in special circumstances, particularly, as already mentioned, in the liquid-phase hydrogenation of ring compounds with nickel or the liquid-phase hydrogenation of ketonic groups with this catalyst or with copper, including related catalysts such as copper chromite.

The use of pressure in gas-phase hydrogenation is rare: thus, benzene, naphthalene, heterocyclic rings and ketones all hydrogenate well in vapour form with, for instance, nickel; although, under these conditions, more decomposition usually takes place than if the hydrogenation were carried out on the liquid substance. On account of the rarity of high-pressure gas-phase hydrogenation, no account of apparatus for this will be given; but, if this is required, reference should be made to high-pressure apparatus of the type used for the synthesis of ammonia. Such apparatus has, for instance, been successfully used for the hydrogenation of carbon monoxide to methyl alcohol, in which the high pressure is required for the displacement of the reaction equilibrium in the direction of methyl alcohol.

For liquid-phase high-pressure hydrogenation an autoclave provided with externally operated agitating gear may be used—and has been successfully employed, for instance, by SCHROETER[2] for reactions such as the hydrogenation of naphthalene at moderate pressures—but, for really high-pressure work, it is simpler to avoid the glands which are necessary with externally driven agitators by moving the reaction vessel as a whole, this vessel being usually given an oscillating or rocking motion, in view of the weight of high-pressure apparatus, rather than the vertical motion which is employed with small and light glass vessels. On the whole, on account of the greater solubility of hydrogen at high pressures, a far less intensive agitation is necessary than at low pressures. The connection with the high-pressure hydrogen supply is made by means of capillary metal tubing; and the progress of the hydrogenation is usually followed by the drop in pressure.

Rocking autoclaves of this type have been described by a number of workers[3].

---

[1] Ann. Chim. applicata 26, 207 (1936).

[2] Liebigs Ann. Chem. 426, 1 (1922).

[3] F. N. PETERS, O. C. STANGER: Ind. Engng. Chem. 20, 74 (1928). — L. PALFRAY: Bull. Soc. chim. France (5) 3, 508 (1936).

In **Peters** and **Stanger**'s apparatus (Fig. 19), the liquid to be hydrogenated is placed in a horizontal glass reaction tube, *A*, which is closed at both ends but has a small hole at the top side. This reaction tube is contained in the electrically heated high-pressure tube, *W*, which can be rocked about its central point by a rod and excenter. The capillary metallic connection for highpressure hydrogen is wound around the oxis. The permissible degree of agitation is not great; but, at pressures of the order of 100 to 300 atm., only moderate agitation is, as already mentioned, required.

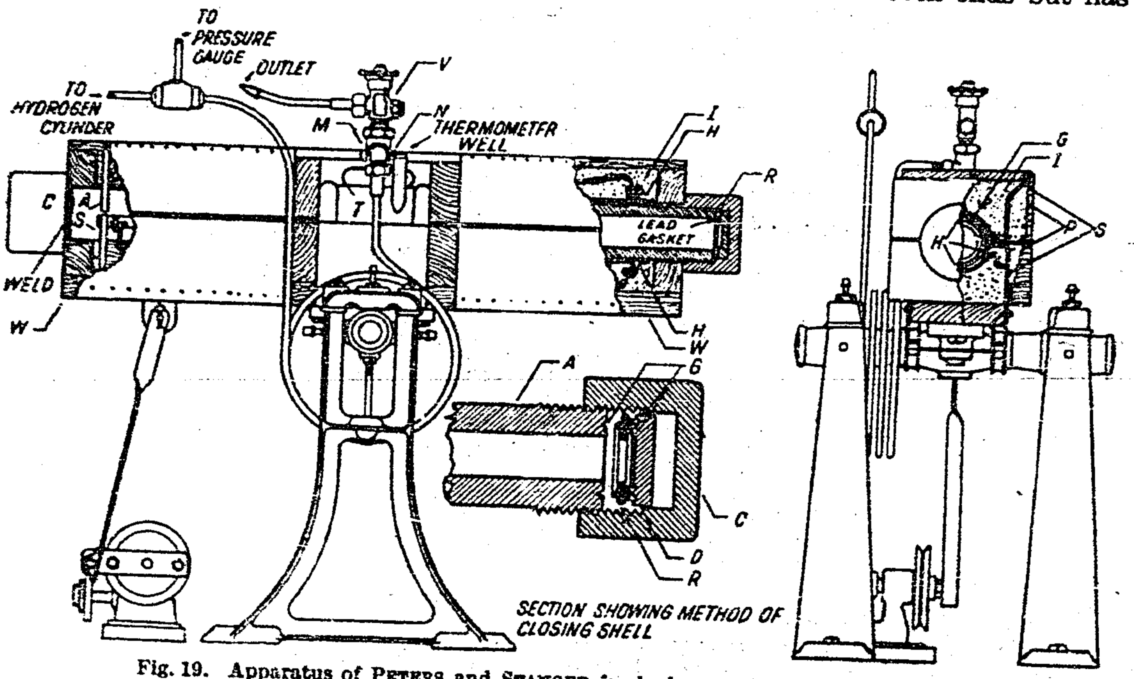


Fig. 19. Apparatus of **Peters** and **Stanger** for hydrogenation under pressure.

An alternative type of apparatus, which can be rocked or shaken according to its size or weight, is shown in Fig. 20[1]. This is most suitably attached to the high-pressure hydrogen supply, as before, by a small-bore coiled metal tube.

In the figure, *A* is the connection for this supply, which terminates within the vessel in a bent tube, of the form shown, in order to prevent the splashing of the hydrogenation liquid into the gas line, and *B* is a thermocouple pocket drilled in the wall. The outside and inside diameters in **Adkins**' apparatus, which was relatively small, were 5.4 and 1.9 cm. respectively, the external and internal lengths being 16.3 and 14.9 cm.; and the apparatus could be used for up to 80 c.c. of liquid, with pressures up to 300 atm. The bomb was provided with shaking gear in the usual way: a suitable temperature was obtained by electrical winding; and a pressure gauge and needle valve were fitted either immediately on the bomb or at the other end of the flexible tubing. An apparatus of this type can obviously be used either with or without a glass liner—or an internal glass reaction vessel of any suitable form—and it possesses the advantage of having only one closure. A larger vessel would preferably be mounted at a small angle to the horizontal, in place of being used vertically, and rocked in place of being shaken.

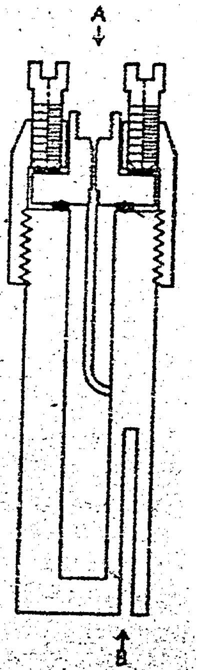


Fig. 20. Apparatus of **Adkins** for high-pressure hydrogenation.

In the above descriptions, engineering details have purposely been omitted, for reasons of space; and, for further information as to suitable material, wall

---

[1] H. **Adkins**: J. Amer. chem. Soc. 55, 4272 (1933).

thickness and the various types of high-pressure closure, reference should be made to any standard textbook dealing with the subject (e.g. to that of TONGUE[1]). Details relative to some of these points are also contained in ADKINS' paper[2], and in a paper by the author[3]. In making closures, it should be borne in mind that jointing material containing sulphur (such as vulcanised fibre) cannot be used in hydrogenation apparatus with ordinary catalysts, at any rate in parts which come into contact with liquid or which are exposed to a high temperature: further, for the sake of safety, it is absolutely essential that all apparatus should be properly constructed and periodically tested in strict accordance with high-pressure practice. For hydrogenation on a larger scale, internal agitators are employed in place of moving the apparatus as a whole; or agitation may be obtained very effectively by a circulation pump in conjunction with baffles in the reaction vessel.

C. Hydrogenation Catalysts.

Hydrogenation catalysts may for convenience be divided into two types, namely into the classical metallic catalysts such as platinum or nickel and into a second, more recently introduced, class containing various catalytically active oxides or sulphides such as chromium oxide, or molybdenum oxide or sulphide, or composite catalysts related to these. This second class is usually of more limited application, but its members are in many cases tolerant towards sulphur and other normal poisons.

The present section deals mainly with special methods of preparation of some of the more important hydrogenation catalysts of these types, principally from the standpoint of standard laboratory technique. Accordingly, no attempt has been made to deal with catalysts which are not in common use.

I. Metallic Catalysts.

Into this class fall the elements of the transition groups—nickel, cobalt, iron and the platinum metals—and, outside the group, copper. Other metals, in addition, possess sufficient activity for specially easy reductions, such as the conversion of nitrobenzene to aniline, but are not sufficiently active for general hydrogenation, although in some cases, e. g. with zinc, an activity comparable with that of the normal hydrogenating metals may be shown.

With catalysts of this group, activity is dependent on the strict observance of definite preparative technique, including the absence of catalyst poisons and the avoidance of temperatures high enough to cause sintering. The form in which the catalyst is used will depend on whether it is to be suitable for liquid phase hydrogenation or for the treatment of gases or vapours: further, the effective area of the metal is often raised to a high value either by methods of preparation which lead to relatively finely divided or—especially with the platinum metals—even to colloidal forms, or by the use of porous supports, which also prevent the reduction of catalytic surface at high temperatures by sintering. It is usual to regard the platinum metals as being especially suitable for hydrogenation in liquid media at low temperatures, while catalysts of the nickel group are used at relatively high temperatures; but this generalisation is perhaps hardly justified, since even ordinary nickel catalysts—apart from special catalysts of the so-called alloy-skeleton type—may, if suitably prepared, show appreciable

---

[1] The Design and Construction of High-Pressure Chemical Plant. London: Chapman and Hall, 1934. [2] Loc. cit. [3] Chim. et Ind. 45, 366 (1926).

activity at room temperature, while metals of the platinum group are used both for hydrogenation and for dehydrogenation, in some circumstances, in the temperature range usually reserved for the nickel group. Within each group, moreover, there is a definite gradation of properties in that, for instance, copper is, in general, a milder hydrogenating catalyst than nickel and is less likely to cause decomposition; but earlier statements that a given metal is incapable of acting in a given reaction have, with increasing knowledge of their preparation and use, in many cases, had to be revised. Thus copper, which was at one time thought to be incapable of hydrogenating a benzenoid bond, has, in later work, been shown to be active both for benzene and for aromatic bodies generally.

It will be convenient to consider, firstly, the preparation of catalysts of the platinum group, which are usually easily reduced from their compounds, in solution or in liquid suspension and, secondly, the preparation of base metal catalysts which require higher reduction temperatures.

1. Metals of the Platinum Group. Pt, Pd, (Rh, Ru, Os, Ir).

a) *Ordinary Platinum Catalysts.*

From the standpoint of practical hydrogenation, only platinum and palladium are of importance, although the remaining metals all possess catalytic activity and have in rarer instances been used for hydrogenation. The same general method of preparation may be employed for each of these metals, save in the few cases where the relatively small difference in chemical properties within the group renders a particular preparative method unsuitable for metals other than the one for which it is described. The platinum metals are, in general, employed for liquidphase hydrogenation, in the form of finely divided suspensions: in some cases they have been used in a colloidal state. They have, to a lesser degree, been applied to hydrogenation in the gas or vapour phase, and they are good vapour-phase dehydrogenation catalysts, with which frequently less by-product formation is obtained than, for instance, with nickel.

For the preparation of platinum catalysts in a finely-divided, non-colloidal form, an aqueous solution of chloroplatinic acid (technical platinum chloride) may be reduced with an alkaline formate or with alkaline formaldehyde. Mond, Ramsay and Shields[1] recommend the following procedure for reduction with an *alkaline formate*.

25 g. of chloroplatinic acid are dissolved in about 500 c.c. of water and boiled. After neutralising with sodium carbonate, the boiling solution is slowly poured into a boiling solution of about 25 g. of sodium formate in 500—600 c.c. of water. Violent effervescence, accompanied by the precipitation of the platinum, takes place; and, in order to avoid the possibility of loss, it is, in practice, found advisable to have ready a large clean basin (the author uses a large circular pneumatic trough) in which the beaker can be placed if excessive frothing occurs. The reduction is rather capricious and, in some cases, the mixture needs to be maintained for some time at the boiling point before the precipitation—which may occur suddenly and violently—takes place. It is, however, a reliable and convenient way of obtaining active platinum in good yield. After precipitation, the platinum is washed with distilled water many (for instance, twenty) times by decantation. It usually settles reasonably quickly at first, so long as traces of electrolytes are present; but, during later stages of washing, it may be necessary to allow it to remain for several hours, or even overnight, before once more decanting, and it may even be advantageous to centrifuge, in order to reduce the time of settling, although this latter course has, in the author's experience, only been required in one or two instances spread

---

[1] Philos. Trans. Roy. Soc. London, Ser. A 186, 661 (1895).

over many years' working with the method. Finally, the washed platinum is dried at 100—110° in air, and ground in an agate mortar to break up any lumps and to obtain a homogeneous preparation.

Reduction with *formaldehyde* yields an equally good product.

According to the directions given by O. Loew[1], 50 g. of platinum chloride are dissolved in a small quantity (up to 50—60 c.c.) of distilled water, then mixed with 70 c.c. of 40—45 per cent formaldehyde. 50 g. of sodium hydroxide, dissolved in an equal weight of water, are added, with good cooling. The greater part of the metal is precipitated at once. R. Willstätter and D. Hatt[2] recommend that the alkaline mixture should, after this initial precipitation, be raised to 50° for about a quarter of an hour. The washing is usually carried out by decantation, and there is some tendency to the formation of a yellow solution still containing a little platinum (some of which is precipitated on boiling); further, the platinum may in later stages of washing become highly dispersed, and settle only with difficulty, as before. R. Feulgen[3] has stated that this tendency may be overcome by shaking the platinum with distilled water containing a little acetic acid. It is stated that vigorous shaking, coupled with the presence of the acetic acid as an electrolyte, prevents the platinum from going over into a colloidal condition.

The direct reduction of platinum or palladium from their chlorides or oxides may also be carried out with hydrogen. Dry reduction does not, in general, lead to an active catalyst, on account of sintering effects: further, in the case of the chlorides, platinum chloride is less easy to handle, on account of its deliquescent character, than palladium chloride. Probably the quickest method of all for the preparation of a palladium catalyst of reasonably high activity consists in suspending finely ground palladium chloride in an organic solvent, such as cyclohexane or decalin, through which a stream of hydrogen is passed. The hydrogen chloride produced during the reduction is partly removed with the gas stream; but sodium carbonate may be added to neutralise this. As a still simpler alternative, palladium chloride may be added as such to the solution of the substance to be hydrogenated, in almost any solvent and with or without the addition of sodium carbonate, reduction being effected, for instance, by shaking with hydrogen. The reduction, as suspensions in liquids, of platinum or palladium *oxides* is still more satisfactory, and may even, if required, be carried out in water. Platinum oxide is, however, not easy to prepare in good yield by the action of sodium carbonate or hydroxide on platinum salts, on account of the formation of soluble alkaline platinum compounds; but precipitated platinum oxide (e. g. PtO_2) or palladium oxide, by whatever method they are made, reduces easily and gives a very active catalyst. The temperature of reduction of platinum oxide depends on the method of preparation and on its previous history. It usually reduces, with hydrogen and in a liquid suspension, well below 100°; but it is sometimes capricious and for this reason care should be taken in employing low-boiling liquids such as cyclohexane or water as the suspending medium. In practice, the temperature is gradually raised, with passage of hydrogen through the suspension, until reduction, which is accompanied by blackening, occurs.

Probably the most effective way of making platinum oxide or palladium oxide consists in the fusion method, which has been developed by Adams and his co-workers, the platinum or palladium chloride being fused with an alkali nitrate. As a result of the treatment, easily reducible oxides are obtained,

---

[1] Ber. dtsch. chem. Ges. 23, 289 (1890).
[2] Ber. dtsch. chem. Ges. 45, 1472 (1912).
[3] Ber. dtsch. chem. Ges. 54, 360 (1921).

which can be added directly to the system to be hydrogenated, in that they readily pass into metals in the presence of hydrogen.

For the preparation of *platinum oxide*, V. Voorhees and R. Adams[1] give the following directions.

20 g. of sodium nitrate are mixed, in a 150 c.c. porcelain casserole, with platinum chloride, corresponding with 1 g. of platinum, previously dissolved in 5 c.c. of water. The mixture is heated gently and stirred with a glass rod until water has been expelled, when the temperature is raised to fusion. After the brown oxides of nitrogen cease to be evolved, the mass is allowed to cool and treated with 50 c.c. of water. The brown precipitate is washed by decantation and finally on a filter until the filtrate no longer shows the nitrate reaction. It is, however, difficult to obtain a completely alkali-free product, the usual alkali content of the washed product being about 2 per cent for a fusion temperature of 400—500°, and rising for higher fusion temperatures.

The most suitable fusion temperature[2] is 400—500°, the variation with temperature of fusion in the activity of the resulting catalyst for the reduction, under standard conditions, of maleic acid being summarised in Table 16. The same temperature (400—500°) is also conducive to the production of an oxide which is most easily reduced by hydrogen.

Table 16.

Maximum temperature of fusion °C.	Time, in mins., required for reduction of maleic acid
390—400	10
490—500	11
590—600	19
650	17
700	16

Fusion may, if desired, be carried out in other nitrates, but the resulting catalyst is apparently not so active as when sodium nitrate is employed. Adams and Shriner's results with other fusion media are summarised in Table 17. It will be noted that the temperature given by Adams and Shriner (500—530°) for the fusion of the platinum chloride with calcium nitrate is lower than the normal melting point of the latter salt, but probably this was depressed by the platinum salt—possibly by some water still present.

Table 17.

Fusion medium	M. P. °C.	Temperature of fusion °C.	Time, in mins., required for reduction of benzaldehyde by resulting platinum
$LiNO_3$	253	490—500	12
$NaNO_3$	312	490—500	10
KNO_3	337	490—500	25
$Ca(NO_3)_2$	561	500—530	80
$Ba(NO_3)_2$	575	600—630	135
$Sr(NO_3)_2$	645	630—640	No reduction

The above fusion method is a general one which can be applied also to other metals of the platinum group. Thus R. L. Shriner and R. Adams[3] give the following directions for preparing *palladium oxide*.

50 g. of sodium nitrate and a solution of palladous chloride corresponding with 2 g. of Pd are thoroughly mixed in a 150 c.c. casserole, then evaporated to dryness and further heated until fused. At 350°—370°, a vigorous evolution of nitrogen oxides occurs, with some foaming. After this evolution, the temperature is raised rapidly and maintained between 575° and 600° for five minutes. It is then cooled, dissolved in 200 c.c. of distilled water, and the palladous oxide filtered off. This cannot be washed with pure water, since it tends to become colloidal; a dilute (1%) solution of sodium nitrate was used for washing. It is finally dried in a vacuum over sulphuric acid.

Before considering the methods of preparation of colloidal catalysts, a few words may be said with reference to the use of *supports* in liquid-phase hydro-

---

[1] J. Amer. chem. Soc. 44, 1397 (1922).

[2] R. Adams, R. L. Shriner: J. Amer. chem. Soc. 45, 2173 (1923).

[3] J. Amer. chem. Soc. 46, 1683 (1924).

genation with catalysts of the platinum group. The employment of a support (kieselguhr, magnesia, calcium carbonate, active carbon, barium sulphate, etc.) in general increases considerably the catalytic effectiveness per unit weight of platinum, although a support is not necessary in liquid media to prevent surface reduction by sintering on account of the low hydrogenation temperatures employed: further, a support may to some degree render more difficult the subsequent recovery of platinum for re-use, by simple solution of the spent catalyst in aqua regia. If a supported catalyst is desired, the reduction of platinum chloride solutions, especially by the alkali formate or formaldehyde method, can readily be carried out in the presence of the carrier; or platinum or palladium oxide may be precipitated on to kieselguhr, carbon, or barium sulphate etc. A quick method, which has been used by the author, for the production of supported platinum consists in evaporating a solution of the chloride on to kieselguhr, which after thorough drying in an oven at 100—150° is quickly (to avoid deliquescence) ground under decalin. The suspension is reduced, at the lowest temperature at which reduction occurs, by passage of hydrogen through the suspension, after which it is washed on a filter with alcohol to remove the decalin and subsequently, very thoroughly, with water. It must not, during the washing, be allowed to dry, otherwise it may glow and lose activity. This tendency is also observed, in general, with all methods of preparation in which platinum is prepared in the presence of organic solvents or in which it is liable to contain adsorbed hydrogen or carbon monoxide. It is particularly dangerous with all such preparations of platinum to employ a vacuum desiccator for drying or storage, in that, on sudden admission of air, a rise of temperature and loss of activity may occur. This applies very widely both to supported and to unsupported platinum, and should be noted as a general caution in dealing with all forms of platinum or related metals. A properly prepared platinum stock, whether on a support or not, may, however, be stored in stoppered bottles for many months without appreciable change in activity.

In a systematic study of the variation of the activity of a supported palladium catalyst with the particular support used, T. Sabalitschka and W. Moses[1] found that the effectiveness in the series of carriers: blood charcoal, bone charcoal, sugar charcoal, barium sulphate, kieselguhr, diminished in the order given, save that barium sulphate and kieselguhr were approximately equal. The catalysts were prepared, for instance, by immersing the support in a palladium chloride solution in air, which was replaced by hydrogen for reduction after adsorption had taken place. Supports such as calcium carbonate are very suitable where the platinum or palladium is present, before reduction, as a chloride, since they also neutralise the hydrochloric acid produced on passing hydrogen.

b) *Colloidal Platinum Metals.*

The preparation and use, for hydrogenation, of platinum metals in a stable colloidal form is largely due to the work of Paal, Skita, Kelber, and their collaborators, who developed precipitation methods in the presence of suitable protective colloids, since colloidal metals, prepared for instance by Bredig's immersed arc technique, are not by themselves very suitable for hydrogenation work. The colloidal condition is, however, by no means essential in ordinary hydrogenation.

Protective colloids for stabilising colloidal platinum were made by Paal[2] by treating egg albumen with aqueous sodium hydroxide under conditions for

---

[1] Ber. dtsch. chem. Ges. 60, 786 (1927). — T. Sabalitschka, K. Zimmermann: Ebenda 63, 375 (1930). — [2] Ber. dtsch. chem. Ges. 35, 2195 (1902).

details of which reference should be made to the original paper. The degradation products are, after addition, for instance, of acetic acid, divided into two groups, namely into so-called protalbic acid, which is thrown down as a precipitate, and into so-called lysalbic acid, which remains in solution. Both classes of colloid are purified by dialysis before use.

In order to prepare *colloidal platinum* protected by *sodium lysalbate*, C. **Paal** and C. **Amberger**[1] add 2 g. of chloroplatinic acid, dissolved in a little water, to a solution of 1 g. of sodium lysalbate in about 30 c.c. of water containing additional sodium hydroxide in quantity sufficient to combine with the chlorine contained in the platinum salt. Hydrazine hydrate is added in slight excess, whereupon the clear dark-brown solution darkens, the process being accompanied by foaming and by the evolution of gas. After reduction has taken place, the solution is dialysed against water, filtered, cautiously concentrated on a water bath, and finally brought to dryness in a vacuum desiccator. It is obtained in the form of black, very lustrous, brittle lamellae, which are easily and completely dispersed in water.

Sodium protalbate may be employed similarly. Thus, **Paal** and **Amberger** took 2 g. of sodium protalbate in 30 c.c. of water, and in the presence of soda, as before, added 3.6 g. of platinum chloride. After completion of the reduction with hydrazine, which took 5 hours, the colloidal platinum was dialysed as before.

For the preparation of *colloidal palladium*, 1.6 g. of palladium chloride (= 1 g. Pd) was dissolved in 25 c.c. of water and added to 2 g. of sodium protalbate containing soda in slight excess. The reddish-brown solution was then treated with hydrazine hydrate, as for platinum, and the colloidal palladium was purified by dialysis, concentrated at 60—70° and dried in vacuo. Colloidal iridium could be obtained similarly.

As an alternative method of reduction, *hydrogen* may be used. In an example given by **Paal** and **Amberger**[2] a solution of 2.5 g. of palladium chloride (= 1.5 g. Pd) in water acidified with a very little hydrochloric acid was added to 50 c.c. of water containing 1.5 g. of sodium protalbate and slightly more soda than was necessary for reaction with the chlorine of the palladium chloride. The clear, dark-brown solution was heated to 60° on a water bath and hydrogen was passed through for two hours. The solution became black and, as far as could be seen, no separation of non-colloidal palladium took place: however, if, for instance in a partially filled flask, the gas current splashes some of the liquid on to the heated glass, the metal produced in these splashes is non-colloidal. Purification by dialysis was carried out as before.

Gum arabic was introduced as a protective colloid for platinum metal catalysts by A. **Skita**[3], who observed that palladium was precipitated in a stable colloidal form on treating with hydrogen an aqueous-alcoholic solution of palladium chloride, containing gum arabic as a protective colloid, provided that a body such as an unsaturated aldehyde or ketone is present. The colloidal state can also be induced, even in the absence of an unsaturated ketone, by inoculating the solution with a little colloidal palladium prior to the passage of hydrogen; or a colloidal preparation may occur spontaneously in the presence of gum arabic without special precautions being taken at all. The above remarks apply also to the preparation of colloidal platinum[4]. The colloidal preparations are purified by dialysis and are dried with the usual precautions.

For the production of colloidal platinum metals which remain *effective in acetic acid solution*, C. **Kelber** and A. **Schwarz**[5] recommend degraded gluten as the protective colloid.

---

[1] Ber. dtsch. chem. Ges. 37, 124 (1904).
[2] Ber. dtsch. chem. Ges. 38, 1398 (1905).
[3] Ber. dtsch. chem. Ges. 42, 1627 (1909).
[4] A. **Skita**, W. A. **Meyer**: Ber. dtsch. chem. Ges. 45, 3579 (1912).
[5] Ber. dtsch. chem. Ges. 45, 1950 (1912).

Thus, 4 g. of palladium chloride, dissolved in a little water, are added to 16 g. of a solution prepared by heating gluten with acetic acid and containing 50 per cent of the degraded gluten. The clear, dark brown solution is made slightly ammoniacal, and hydrazine hydrate is added drop by drop. After the completion of the reduction, which is accompanied by foaming and by the evolution of gas, the solution is dialysed against water and carefully evaporated, as in the other methods. The black scales are easily dispersed both in water and in acetic acid, and are also not readily coagulated even by mineral acids. The above proportion of protective colloid to palladium leads to a preparation containing 20 per cent of palladium.

c) *Platinum Metal Catalysts for Gas-Phase Use.*

A few remarks may, finally, be made with regard to platinum and other catalysts for gas phase working. Finely divided preparations are, in general, not suitable for use in this way, since the mixture of hydrogen with the gas or vapour to be hydrogenated can only be passed over the surface of such catalysts; and, although metallic powders have in some cases been used both for gaseous hydrogenation and dehydrogenation, it is preferable to use a granular support, or to make up a mixture of finely divided platinum with a finely divided support into granules by means of a pelleting machine, and thus to produce a catalyst which permits, without undue obstruction, the passage of a gas mixture through its mass. Probably the simplest method of making a catalyst of this nature consists in impregnating asbestos, pumice, silica gel, bauxite, or other fibrous or granular carriers with platinum or palladium chloride, or, in the case of osmium, with osmic acid; but the activity of the resulting catalyst will depend largely on the conditions of the reduction. If dry reduction is employed, some checking of the sintering effect which leads to an inactive catalyst and which is due largely to rapid uncontrolled reduction, can be obtained by using hydrogen in conjunction with a large excess of an inert gas, such as nitrogen, the percentage of hydrogen being increased as the reduction proceeds; but a more satisfactory way is to reduce the palladised or platinised granules in a liquid medium, which controls the temperature and from which the granules can afterwards be removed. An especially suitable method consists in reduction by hydrogen in a liquid in which the platinum or palladium compound is insoluble, e. g. in decalin. As an alternative to the use of granular supports, pelleted catalysts which are stable at reasonably high temperatures, can be made by passing finely divided platinum on a finely divided support (for instance, a catalyst consisting of 80 per cent of kieselguhr and 20 per cent of platinum) through a pelleting machine, the lubricant and binder depending on the substance to be hydrogenated.

2. Metals of the Nickel Group: Ni, Co, Fe, Cu.

The metals of this group are reduced from their compounds with greater difficulty than the platinum metals and, consequently, require other methods of preparation, the most usual method being the reduction of the oxide with hydrogen at a temperature which is, in general, maintained as low as possible in order to avoid loss of activity by sintering. In view of the relatively high reduction temperature which these metals require, the use of a refractory support is in almost all cases of considerable advantage, in that the reduction can, in this way, be carried out at temperatures which would not be permissible in the absence of the carrier; and the resulting catalysts are more stable towards temperature in use, and are also, by virtue of their greater effective surface, more resistant to poisoning. A further method of producing nickel and other catalysts possessing a relatively large surface and consequently a high activity, consists in leaching certain alloys, such as aluminium- or siliconnickel, with aqueous alkalies, whereby the metal is left in a highly porous, almost sponge-like state. Such catalysts are of high activity at low temperatures, but collapse on being heated beyond a certain temperature range.

a) *Preparation by the Reduction of Oxides etc.*

The reduction of oxides or of various salts such as the basic carbonate, the formate, or others, which in many cases pass through the oxide as an intermediate stage, constitutes the commonest method of making catalysts of this group. The activity of the resulting catalyst depends, as is usual, both on the reducibility of the oxide from which the metal is produced and on the temperature of the reduction. For general liquid-phase hydrogenation, in which a catalyst of high activity is required, this activity is obtained by the careful following of the methods of preparation which have been shown by experience to give the most active catalysts, above all avoiding the exposure of the materials both to high temperatures and to conditions which give a less reducible oxide.

Nickel may be made very conveniently, and in a highly active form, by the reduction of the basic carbonate either as such or after conversion of this to the black oxide, Ni_2O_3.

In order to prepare the carbonate, 112 g. of purest nickel sulphate and a slight excess (120—130 g.) of the calculated weight of sodium carbonate crystals are dissolved separately in water and poured simultaneously, at room temperature and with vigorous stirring, into a third beaker containing the support (e. g. 71 g. of kieselguhr, made into a thin paste) if one is used. The above proportion of support gives a catalyst which, after reduction, contains about 25 per cent of nickel. The ratio of the support to the nickel can of course be increased: in some commercial catalysts the ratio is as high as 10 to 1. After precipitation, the nickel carbonate is filtered on a Büchner funnel and thoroughly washed with cold water. Since a basic carbonate of not very constant composition is produced, the amount of soda required for the precipitation of a given weight of nickel sulphate varies somewhat with the conditions, but it is essential that the soda should have been in excess, as will be shown by the absence of green colour in the first filtrate. There appears to be little advantage in substituting nickel nitrate for the sulphate, the catalyst made from either salt possessing about the same activity. Similarly, sodium hydroxide may, if desired, be substituted for sodium carbonate, with precipitation of nickel hydroxide; but, again, no advantage is obtained. Indeed, nickel hydroxide is usually more difficult to filter and wash and, in practice, the carbonate is almost always used.

During the drying of the washed filter cake, this should not be exposed to temperatures higher than about 50°, otherwise a bright-green, less easily reducible oxide may be formed. In small quantities it is most easily dried either on a porous plate in a current of warm air or in a vacuum desiccator; or, on a larger scale, it may be broken up and stacked in a shallow layer on wooden slats in a drying box through which warm air is passed. Drying is best carried out slowly and may take from a few hours to several days, according to the amount to be treated. Above all, it must not be dried by heat alone.

The thoroughly dried nickel carbonate, after being ground to a fine powder in a mortar or mill, is reduced directly; or it may be previously converted into the black oxide, Ni_2O_3. This intermediate step is not essential, but it certainly gives a highly active catalyst. If this is done, a not too large quantity of the powdered carbonate is placed in a porcelain dish and heated, with constant stirring, until it has been converted into a velvety-black, very finely divided powder, the conversion being accompanied by the evolution of carbon dioxide from small conical craters which form in the mass and by the absorption of oxygen from the air, whereby the degree of oxidation of the nickel is raised. It is advisable, in order to avoid overheating, not to heat the basin with a flame directly, but to place it on a shallow circular air-bath, for instance on a shallow tin box, which is heated in turn by a Bunsen flame. General hydrogenation experience has shown that this black oxide of nickel gives a more active catalyst than most specimens of the green oxide; but it is doubtful whether it has any real advantage over a carefully prepared basic carbonate reduced as such.

Nickel oxide may also be made by the ignition of the nitrate, which, either alone or mixed with a support such as kieselguhr, is placed in a porcelain dish and heated, with stirring, on an air-bath, as described above, until the evolution of oxides of nitrogen has ceased. The method avoids the rather long washing and drying operations which are necessarily associated with precipitated oxides or carbonates, but it does not, in general, lead to catalysts of such high activity. A lower activity—especially in certain gas-phase hydrogenations or dehydrogenations, in which a too vigorous catalyst may lead to excessive decomposition at high temperatures or to a product more highly hydrogenated than is desired—is, in some cases, actually advantageous. Further, in place of using an oxide, good nickel catalysts may also be made by the direct reduction with hydrogen of a number of organic nickel salts, for instance, nickel formate, solutions of these being used, as before, to impregnate a porous carrier.

The general effectiveness of individual *supports* varies somewhat with the particular specimen taken, but A. KAILAN and O. STÜBER[1] obtained the following results for the various carriers given in Table 18.

Table 18.

Carrier	Relative activity per unit of nickel	Carrier	Relative activity per unit of nickel
Animal charcoal	1.0	Ceria	2.6
Lime charcoal	1.4	Alumina	5.6
Talc	1.7	Kieselguhr	7.7

It will be seen that kieselguhr was the most efficient of the carriers examined; but the lesser efficiency of supports of the carbon type is not in conformity with the results of other workers and may be due to the use by KAILAN and STÜBER of relatively low-surfaced specimens. As a further and very effective method of incorporating a carrier, co-precipitation may be employed. Thus, hydroxides or carbonates of metals such as nickel or copper may be co-precipitated with, for instance, magnesium hydroxide[2].

The *reduction of nickel oxide,* or its equivalent, to metal is the final stage in all the above methods of preparation; and the temperature at which this reduction is effected, in addition to its speed and duration, are of paramount importance in determining the activity of the nickel produced. With unsupported nickel catalysts, the influence of this temperature is especially marked and optimum activity may be induced by not pushing the reduction to completeness, namely to such a stage that sintering begins or that the reduced nickel is no longer supported on some unreduced nickel oxide. A suitable reduction temperature is about 300°; but supported nickel catalysts may be reduced at far higher temperatures (e. g. even up to 450°) without excessive loss of activity.

The *reduction operation,* on a laboratory scale, is most conveniently carried out in a pyrex distilling flask, which is immersed in a bath containing a fused mixture of sodium and potassium nitrates, from which it can be removed periodically in order to follow the progress of the reduction. The flask is provided with a leading-in tube, which passes through a cork in its neck and reaches to its bottom; and the

---

[1] Mh. Chem. 62, 90 (1933).

[2] H. S. TAYLOR, G. G. JORIS: Bull. Soc. chim. Belgique 46, 241 (1937).

hydrogen, after passage through the flask, may be burnt at the sidearm or at a jet attached to the side-arm by rubber tubing. The contents of the flask may, if desired, be shaken periodically to assist the uniformity of the reduction. In general, no advantage is obtained by previously drying the hydrogen. Reduction may, of course, also be carried out in an electrically heated furnace; but the use of a fused-salt bath constitutes a very effective method of temperature control and enables the change in colour (blackening) on reduction to be readily seen. A mixture of about equal parts of sodium and potassium nitrates melts at about 220° and may be readily melted by a simple Bunsen burner in a small metal saucepan, or even in a large enamelled iron mug. It is advisable, when re-melting the bath from the cold, to allow the bunsen flame to play on its side, rather than on the bottom alone, in order to avoid what may be dangerous spurting of the molten salt during early stages in its melting, due to the development of pressure by the expansion of an enclosed liquid layer at the bottom without free access to the surface.

Precipitated nickel oxide begins to reduce in hydrogen at a temperature which may vary between 210° and 230°[1]. The optimum reduction temperature has been the subject of considerable work. Thus, G.-M. SCHWAB and L. RUDOLPH[2] give the following relative figures for an unsupported nickel catalyst (Table 19).

From these, the optimum temperature would seem to be about 350°. This is somewhat higher than that obtained by earlier workers: thus, SABATIER and SENDERENS recommended 300—350°, the lower limit of these temperatures giving the higher activity; but the best reduction temperature varies, as has already been stated, widely with the history of the nickel oxide (in that ignited oxides reduce at higher temperatures and give less active catalysts than those prepared at low temperatures), as well as with the size of the batch reduced, and with the time and rate of passage of the hydrogen. The reduction time also varies but, in a flask reduction, for instance with not more than 50 c.c. of catalyst contained in a 200 c.c. distilling flask, 1—1½ hours should be sufficient, provided that the hydrogen current is reasonably rapid.

Table 19.

Reduction temperature °C.	Relative activity of reduced nickel
306	1.00
356	1.15
406	0.35
456	0.20
556	0.17

With *supported* nickel catalysts, higher reduction temperatures still may be employed. Thus, C. KELBER[3] found that a support such as kieselguhr prevented diminution of effective surface by sintering even at 450°, and A. KAILAN and F. HARTEL[4] observed that a kieselguhr-supported nickel catalyst increased continuously in activity as the reduction temperature was raised from 345° to 550°. This is supported by the previous results of A. KAILAN and H. C. HARDT[5] which are summarised in Table 20. The use of such high reduction temperatures would, from the standpoint of practical technique, make necessary reduction in an electrically heated vessel in place of a flask heated in a molten nitre bath.

Table 20.

Reduction temperature °C.	Relative activity of resulting nickel
250	1.0
320	2.9
400	4.2
500	4.45
550	4.55

The resulting metal is, of course, *pyrophoric*, and cannot be exposed to air. It is best preserved by covering either with the liquid to be hydrogenated or with a suitable hydrogenation solvent; or, especially in the case of supported

---

[1] MÜLLER: Pogg. Ann. 136, 51 (1869). — J. B. SENDERENS, J. ABOULENC: Bull. Soc. chim. France (4) 11, 641 (1912).

[2] Z. physik. Chem., Abt. B 12, 427 (1931).

[3] Ber. dtsch. chem. Ges. 49, 55 (1916).

[4] Mh. Chem. 70, 347 (1937).

[5] Mh. Chem. 58, 307 (1931).

nickel, it may be handled in air for a short time without losing activity or becoming hot provided that it is quite cold and that the hydrogen has previously been removed as far as possible by passage of nitrogen or carbon dioxide through the reduction vessel. The inert gas apparently forms a temporary protective covering, which is sufficiently persistent to permit the transfer of the catalyst from a reduction flask to the reaction vessel in which it is to be used; but it may in certain cases be advantageous to reduce in the reaction vessel itself, especially immediately before the nickel is actually required, and thus to avoid the necessity for transference, with the attendant possibility of loss of activity; although the risk of this is not great if proper precautions are taken.

In the foregoing directions, attention has been paid principally to nickel catalysts. *Copper*, *cobalt*, and *iron catalysts* are made in similar ways, the principal preparative difference lying in the temperature required for the reduction with hydrogen of the oxide to metal. The reducibility of copper oxide varies greatly with its method of preparation; but, in general, a reduction temperature of just below 200° gives a satisfactory catalyst if the copper hydroxide or carbonate is unsupported[1]; but supported copper catalysts may, as with nickel, be reduced at higher temperatures. Similarly, a temperature of about 400° has been recommended for cobalt oxide and about 450° for iron oxide.

The course of the reduction by hydrogen of all the above oxides is autocatalytic, in that it is catalysed, at the oxide-metal interface, by metallic nuclei. The velocity thus begins slowly, then rises to a maximum and subsequently decreases. The autocatalytic reduction of nickel oxide has been investigated by A. Benton and P. H. Emmett[2] and the corresponding reduction of copper oxide by C. R. A. Wright, A. P. Luff and E. H. Rennie[3] and by R. N. Pease and H. S. Taylor[4].

b) *Reduction in Liquids.*

Before leaving catalysts made by the reduction of oxides, a few remarks may be made with regard to wet reduction. If the oxide or other compound reduces below 300°, reduction may also be carried out by leading a current of hydrogen through a suspension of the oxide in a suitable organic liquid. Overheating during reduction is very effectively prevented and under suitable conditions very active catalysts are obtained. The method was used at one time in the hydrogenation of glyceride oils, the nickel catalyst being produced in situ merely by suspending nickel oxide or carbonate in the oil and passing hydrogen at 250—260°; but, on account of the water produced, its use for substances which are easily hydrolysed, such as a glyceride, is not entirely satisfactory, owing to the possibility of forming decomposition products. Better results are obtained by reducing nickel carbonate or copper carbonate in a high-boiling hydrocarbon. Liquid reduction of oxides of this class is, however, not very usual, in view of the simplicity of the dry reduction method.

c) *Nickel and related catalysts for gas-phase hydrogenation.*

Sabatier and Senderens, in their original work on hydrogenation in the gas phase, used finely divided metal powders which were employed as a layer along a heated horizontal tube through which the mixture to be hydrogenated was passed. It is probably preferable to employ granular catalysts in, for in-

---

[1] P. Sabatier, J. B. Senderens: C. R. hebd. Séances Acad. Sci. 130, 1760 (1900); 133, 321 (1901). [2] J. Amer. chem. Soc. 46, 2728 (1924).

[3] J. chem. Soc. [London] 33, 1 (1878); 35, 475 (1879).

[4] J. Amer. chem. Soc. 43, 2179 (1921).

stance, a vertical reaction tube of the type illustrated in Fig. 12. The catalysts may be made by impregnating granules of pumice, bauxite or other porous materials with suitable soluble nickel, copper, cobalt, or iron salts such as the nitrate or formate, the granules being subsequently reduced with hydrogen in the ordinary way; but better results are usually obtained with pelleted catalysts made by passing finely divided supported catalysts through a pelleting machine. Thus, nickel carbonate or oxide on the usual kieselguhr base may be thoroughly dried in air, then finely ground and incorporated with a small percentage of a suitable lubricant and binder (e. g. a metallic soap). It is then rubbed through a fine sieve and fed into the hopper of the pelleting machine, the dies of which are set to give pellets of suitable size. This machine automatically delivers an approximately constant charge into the die, compresses it by means of a steel punch and ejects the pellet, the operation being repeated continuously.

An entirely different type of catalyst which is also very suitable for gas-phase hydrogenation is made by anodically oxidising nickel turnings in an electrolyte consisting of aqueous sodium carbonate[1]. A black nickel oxide is produced, and the turnings, which are usually contained in nickel cages, are, after thorough washing with water, placed in a cylindrical reaction vessel and reduced with hydrogen immediately before the passage of the mixture to be hydrogenated. This catalyst may also, if required, be used for liquid-phase hydrogenation by allowing a film of the liquid to flow over the nickel in a hydrogen atmosphere.

d) *Alloy-skeleton hydrogenation catalysts*[2].

Highly active nickel and other catalysts, which are especially suitable for hydrogenation at temperatures lower than those usually employed with metals of the nickel group, may be prepared by dissolving out the aluminium component of a nickel-aluminium alloy by means of aqueous sodium hydroxide[3]. Nickel-silicon alloys may also be used and the method may also be applied to copper and to other metals.

The alloys themselves, in the case of nickel-aluminium, may be made by aluminothermic methods or by dissolving nickel in molten aluminium[4]. The nickel should in the fusion method be used in the form of compact ingots since the finely-divided metal oxidises superficially and does not readily alloy with the aluminium. The activity of the resulting nickel does not vary greatly with the composition of the initial alloy, a suitable composition corresponding to 40—50 per cent of nickel. Since the alloy has subsequently to be broken up and powdered for the soda treatment, friability is of some importance. A friable alloy of the approximate composition $NiAl_3$ (containing 42 per cent of nickel) is especially easy to prepare, the calculated quantity of nickel being added to molten aluminium at 1200°, when the temperature rises to about 1500°. After being cooled, the alloy is powdered in a steel mortar and passed through a fine sieve.

The interaction of the alloy with soda occurs with considerable violence. L. W. Covert and H. Adkins[5] give the following directions for this stage of the preparation:

---

[1] E. J. Lush: E. P. 203218.

[2] Compare: Schröter: Z. angew. Chem. 54, 229 (1941).

[3] M. Raney: Amer. P. 1628190.

[4] C. Dupont: Bull. Soc. chim. France (5) 3, 1022 (1936). — R. Paul: Ebenda 1506. — G.-M. Schwab, H. Zorn: Z. physik. Chem., Abt. B 32, 172 (1936).

[5] J. Amer. chem. Soc. 54, 4116 (1932).

300 g. of the finely ground alloy are added slowly (in two to three hours) to a solution of 300 g. of sodium hydroxide in 1200 c. c. of distilled water contained in a 4-litre beaker and surrounded by ice. The mixture is then heated on a hot plate for four hours, with occasional stirring, at 115—120°. A further 400 c.c. of an approximately 20 per cent solution of sodium hydroxide is then added, and the mixture kept at 115—120° for about three hours, or until hydrogen is no longer evolved, after which it is diluted to a volume of 3 litres. The nickel is washed six times by decantation, and then alternatively on a Büchner funnel and by decantation until the filtrate is neutral to litmus. The nickel is then washed three times with 95 per cent alcohol and kept under alcohol. It may also be stored under water; but it is strongly pyrophoric when dry. As a slight modification of the above procedure, it is convenient, in order to avoid undue violence during the first stage of the leaching, to cover the alloy with water and to add to this the sodium hydroxide solution in small quantities[1], the reaction vessel being, as before, cooled in ice. As soon as the first violent action is over, the vessel can be placed on a water-bath and the leaching continued, with about three changes of 20—30 per cent soda in the ordinary way. Throughout the preparation, it is necessary to bear in mind the easily oxidisable and pyrophoric nature of the nickel, which is produced in a heavy, easily washed state. Particularly, on replacing the water by alcohol, it is necessary to avoid the drying of part of the nickel on the sides of the vessel, which should be washed down with an alcohol wash-bottle.

In place of storage under a liquid, it may, for convenience in weighing out, (since it cannot be weighed in air without protection) be stored in a solid such as stearin, any trace of alcohol which adheres to the metal—which, of course, cannot be dried—being removed by passage of hydrogen through the stearin-nickel suspension at a temperature slightly above the melting point of stearin. The stearin is now allowed to solidify with vigorous mechanical stirring in an atmosphere of nitrogen or hydrogen, in order to ensure a uniform dispersion of nickel throughout the solidified mass. When cold, it can be cut into small pieces for weighing; but it is found to be inadvisable to powder the suspension, since in that case some diminution in activity occurred on storage. In its final form, the nickel can be stored for at least several weeks in a closed bottle without appreciable change in activity by oxidation; but it is convenient to seal up in an evacuated vessel any stock not required immediately. In opening stock sealed up in this way, nitrogen is admitted; but this precaution may not be necessary.

The special feature of alloy-skeleton catalysts is their abnormal activity at low temperatures. Thus COVERT and ADKINS (loc. cit.) state that, whereas acetone, in the presence of a supported nickel catalyst, could not be hydrogenated much below 100°, complete hydrogenation was obtained with alloy-skeleton nickel at 23°, at a hydrogen pressure of 2—3 atm.; and G. DUPONT[2], who examined the reduction of a large number of substances with alloy-skeleton nickel at room temperature, obtained a hydrogen absorption which in some cases exceeded 100 c.c. per minute in a reaction system containing about 15 g. of the body to be hydrogenated and 10 g. of nickel suspended in 20 g. of absolute alcohol. Among the bodies hydrogenated were allyl alcohol, n-heptene, undecylenic acid, acrolein, phenyl ethylene, and a large number of terpenes. Ethylene itself was also hydrogenated readily at room temperature.

The high activity of this type of catalyst at low temperatures has been ascribed by F. FISCHER and K. MEYER[3] to the presence of relatively large numbers of extra-lattice atoms; and G.-M. SCHWAB and H. ZORN[4] found, as the result of X-ray studies by G. WAGNER, that the activity increased with the

---

[1] E. B. MAXTED, R. A. TITT: J. Soc. chem. Ind. 57, 197 (1938).

[2] Bull. Soc. chim. France (5) 3, 1021, 1030 (1936).

[3] Ber. dtsch. chem. Ges. 67, 253 (1934).

[4] Z. physik. Chem., Abt. B 32, 159 (1936).

content of röntgenographically amorphous material in the catalyst, but that the most active preparations contained the largest nickel crystallites. This latter observation would seem to show that the activity due to crystallographically amorphous particles is sufficiently high to outweigh the activity of atoms in the normal lattice. In any case, activity due to extra-lattice atoms, or even to a highly-surfaced, sponge-like structure, such as would be expected in catalysts prepared by a leaching process, should be relatively easily destroyed on exposure to heat, in that labile extra-lattice material will tend to become rearranged in normal lattice form, and any sponge-like structure will tend to collapse. This relatively rapid loss of activity during use is observed even at 150°, whereas ordinary, and especially supported nickel catalysts continue to work even at higher temperatures without such diminution in effectiveness. Alloy-skeleton metals are thus essentially low-temperature catalysts although, as has already been stated, ordinary kieselguhr-supported nickel may also be prepared so as to be active at room temperature[1]. Alloy-skeleton catalysts are usually used in practice in relatively high proportions per unit weight of unsaturated body treated. They are especially useful in selective hydrogenation (q.v.) in which, according to G. Dupont (loc. cit.), distributions of hydrogenation are obtainable which are impossible with, for instance, platinum black; and they will also, in some cases, very conveniently permit the arrest of an acetylenic hydrogenation at the ethylenic stage.

On account of the different optimum temperatures of use of alloy-skeleton and of ordinary supported nickel catalysts, it is difficult to compare the catalytic effectiveness, per unit weight of nickel, of typical catalysts of the two types; but, if 140—160° is taken as the temperature of maximum activity of supported nickel in liquid-phase hydrogenation and if 110—120° is regarded as the highest permissible temperature with alloy-skeleton nickel, on account of its collapse at higher temperatures, it was, in the case of the hydrogenation of an oil[2], found that, as a very rough figure, an average kieselguhr-supported nickel has about twice the catalytic effectiveness, per unit weight of nickel, of the alloy-skeleton. The variation of the initial activity of alloy-skeleton nickel with the working temperature was also determined and compared with the activity of an equivalent weight of nickel in its ordinary supported form at 160°. The results are summarised in Table 21. On account of the solidification of the hardened oil on the catalyst, temperatures below 45° could not be employed. The alloy-skeleton catalyst, on account of its high surface factor was, moreover, found to be less easily poisoned than the supported nickel, which in turn is less susceptible to poisoning than reduced nickel in the absence of a support.

Table 21.

Temperature °C.	Relative initial activity of alloyskeleton nickel	Relative initial activity, compared with that of an equal weight of nickel in ordinary kieselguhr-supported form
45	1.0	0.03
67	2.4	0.075
86	4.65	0.15
113	7.3	0.23
150	10.8	0.34

For the production of aluminium alloys containing *silicon*, G.-M. Schwab and H. Zorn[3] recommend heating granulated nickel with technical, large-grained silicon for 25 minutes at 1600°. The product is then powdered and added in small portions to a 30 per cent caustic soda solution cooled, as before, in ice and containing about three times the calculated quantity of soda. It is then refluxed with the soda for 20 hours and afterwards washed twice with fresh dilute soda and about six times with water.

---

[1] Compare, for instance, Kelber: Ber. dtsch. chem. Ges. 49, 55 (1916).
[2] Maxted, Titt: loc. cit. [3] Z. physik. Chem., Abt. B 32, 172 (1936).

The friability of the alloy and the activity of the nickel vary with the ratio of nickel to silicon. Schwab and Zorn give the following figures, in which the activity of nickel from the silicon alloy was also compared with that obtained with aluminium. It will be seen that the aluminium alloy, in this case at any rate, gave the more active catalyst; but the activities were compared at 150°, for the hydrogenation of ethylene.

Table 22.

Nickel catalyst from:	Nature of alloy	Relative catalytic activity at 150°
$NiSi_2$	Friable	3
$NiSi$	Difficult to powder	1
$NiAl_3$	Friable	6

Alloy-skeleton hydrogenation catalysts containing metals other than nickel have also been described. Thus, the corresponding *iron* alloy-skeleton catalysts have been prepared, in a very similar way to nickel, by R. Paul and G. Hilly[1] by treating an iron-aluminium alloy with alkalies; and copper and cobalt catalysts of this type have been studied by L. Foucounau[2]. *Copper* is most easily made from copper-zinc-aluminium alloys, since alloys of copper and aluminium alone are only slowly attacked by soda.

Thus, Devarda's alloy (50 per cent Al, 45 per cent Cu, 5 per cent Zn), which may be bought in finely powdered form, is added to a 30 per cent solution of sodium hydroxyde, cooled in ice as for nickel. When the first action is complete, for instance after 10—11 hours, the solution is heated gently until no more hydrogen is evolved. It is retreated with soda twice (i. e. three times in all), and washed and preserved under alcohol.

The resulting copper possesses an activity only approximately equal to that made by reduction in the ordinary way; and it can also be made by leaching the alloy with hydrochloric acid, in which case the catalyst is less active. Foucounau applied it to many of the standard reactions for which copper is specially suitable, e. g. for the dehydrogenation, at 170—270°, of ethyl alcohol to aldehyde and of benzyl alcohol to benzaldehyde, and for the reverse reaction, namely for the hydrogenation of aldehydes and ketones to alcohols at 125—150° at hydrogen pressures up to 100 atm. Aromatic rings were, however, not attacked. It will be noticed that in this work, the catalyst was used only at relatively high temperatures.

In the case of *cobalt*, cobalt-aluminium alloys were made aluminothermally (L. Foucounau, loc. cit.) by allowing 20 g. of aluminium to react with 150 g. of Co_3O_4. The ingot was powdered in a steel mortar and passed through a fine sieve. The method of preparation of the catalyst is, as with copper, very similar to that of nickel. It is added in small portions to well-cooled, 30 per cent sodium hydroxide, which, after about 12 hours, is heated not higher than 60° until hydrogen is no longer given off. The re-treatment (twice) with soda and subsequent washing are as for nickel; but there is a tendency for the alkaline liquid to become blue owing to the solution of part of the cobalt.

The cobalt prepared in this way was used by Foucounau, at 175—250°, for the dehydrogenation of ethyl and other alcohols and for various hydrogenation reactions under pressure, at 100—200°. Unlike copper, it readily hydrogenates the benzene nucleus; but a temperature of 175—200° is usually necessary for this. Its activity at, for instance, room temperature, which is of special interest from the standpoint of its similarity to alloy-skeleton nickel, does not, however, appear to have been studied.

---

[1] C. R. hebd. Séance Acad. Sci. 206, 608 (1938).

[2] Bull. Soc. chim. France (5) 4, 58, 63 (1937).

II. Hydrogenation Catalysts of Oxide and Sulphide Types.

Hydrogenation catalysts of this type, especially molybdenum oxide or sulphide or tungsten oxide or sulphide, differ from catalytically active metals firstly in being less susceptible to or even completely indifferent to the presence of ordinary catalyst poisons and, secondly, in being, in some cases, capable of carrying out reactions which cannot be smoothly accomplished by metals; indeed, outside those reactions for which they are specially adapted, their use is rather restricted, all the more since molybdenum or tungsten catalysts only become active at relatively high temperatures. Thus, while they very readily bring about the reduction of, for instance, a carbonyl group to an alcohol or the elimination of hydroxyl, their useful application for the simple hydrogenation of ethylenic or other unsaturated carbon—carbon linkages is by no means as wide as the metals, save in cases in which the oxide catalyst (e. g. nickel chromite or copper chromite) itself probably partly passes into metal in the presence of hydrogen at the temperature employed for the reaction. Oxide hydrogenation catalysts may be divided into two classes, namely, those of the chromium oxide or chromite type, including chromium oxide itself and other simple oxides, and into a second class of oxides, containing molybdenum oxide and tungsten oxide. Hydrogenation catalysts of the sulphide type may be divided somewhat similarly into classes represented, for instance, by nickel sulphide and by molybdenum sulphide.

1. Catalysts of the Chromite Type[1].

Most of these catalysts contain chromium oxide or its equivalent, in conjunction with a second component; but chromium oxide without such addition is active at, for instance, 400° both for the general hydrogenation of ethylenic and other bonds and for the dehydrogenation of cyclohexane[2]. It may be prepared by precipitating chromium nitrate with ammonium hydroxide at room temperature, a suitable strength of chromium nitrate solution being 0.04 molar. The precipitate is washed 5—10 times by decantation, dried at 110° and broken into granules of suitable size. The catalyst becomes active for catalytic hydrogenation at 350—370°. Chromium oxide may also be made by the very gentle ignition of ammonium bichromate in a vacuum; but **Lazier** and **Vaughen** report that the ignition of chromium nitrate or oxalate led to inactive catalysts. Amorphous chromium oxide, on being heated, in some cases suddenly glows and becomes transformed into a light green modification, this glowing being accompanied by the loss of its activity. A further method, which has been used by **H. S. Taylor** and **L. M. Yeddanapalli**[3] for preparing chromium oxide catalysts for the dehydrogenation of cyclohexane, consists in boiling a solution of chromic nitrate with ammonium acetate, then cooling, adding ammonia, and again boiling. After being washed, the precipitate is dried at 100—140° and heated to 400° in hydrogen. More usually, however, chromium oxide is employed in conjunction with *nickel*, *copper* or *zinc*. These catalysts may under the conditions of use, undergo partial reduction and may therefore be regarded as nickel or other metal catalysts containing chromium oxide as an internal support, the chromium oxide being thus somewhat analogous to alumina in alumina-iron ammonia catalysts, although, in the case of chromium-oxide supported metals or oxides, activated adsorption of hydrogen also takes place on the support; and, as with mixed catalysts, **G.-M. Schwab** and

---

[1] Compare: **Ch. Grundmann**: Angew. Chem. 54, 469 (1941).

[2] **W. A. Lazier**, **J. V. Vaughen**: J. Amer. chem. Soc. 54, 3080 (1932).

[3] Bull. Soc. chim. Belgique 47, 162 (1938).

R. Staeger[1] have shown that abnormal mutual activation (or, in some cases, abnormal deactivation) only takes place in composite oxide systems in which X-ray examination gives evidence for some form of chemical combination or of inter-lattice penetration.

H. Adkins and R. Connor[2] give the following directions for the preparation of *copper chromite*:

Ammonium hydroxyde (about 150 c.c. in an exemple given) is added to a solution of 126 g. (0.5 g. mol.) of ammonium dichromate in 500 c.c. of water until the formation of ammonium chromate is complete, this being indicated by a change in colour from orange to yellow. After allowing the solution to cool, 241.6 g. (1 g. mol.) of cupric nitrate crystals (+ $3H_2O$) in 300 c.c. of water are added with stirring. The reddish brown precipitate is filtered off, dried at 100—110°, then finely powdered and decomposed by heating gently in a porcelain casserole over a bunsen flame. After the decomposition has begun, the heat of reaction is almost sufficient in itself to complete the decomposition; and, as soon as the spontaneous reaction is at an end, the casserole is heated further until fumes cease to be evolved and the contents are converted to a black powder which is so finely divided as to be almost like a liquid. The heating must be carried out cautiously by movement of the flame and stirring, in order to avoid local over-heating. The product is allowed to cool, suspended in 200 c.c. of a 10 per cent solution of acetic acid, filtered, washed thoroughly with water, dried for 12 hours at 100—110°, and finely powdered. The yield of copper chromite from the above quantities of materials should be about 113 g. No special reduction before use is necessary since this occurs under the conditions in which the catalyst is used.

J. C. W. Frazer and C. B. Jackson[3] propose a slight modification in making an analogous *nickel* compound:

One g.mol. (290 g.) of nickel nitrate crystals (+ $6H_2O$) and one g.mol. (100 g.) of chromic acid are dissolved in 250 c.c. of water, and to the solution 3 g.mols. of ammonium hydroxide are added all at once with rapid stirring. The yellowish red precipitate is filtered off on an suction funnel and washed once with about 50 c.c. of water to remove the mother liquor. After drying at 110°, a sample of the precipitate has the composition, $Ni_2O \cdot (NH_4)_2 \cdot (CrO_4)_2$. This is decomposed by heat in the manner described above for copper chromite. The decomposed material corresponds to $2NiO \cdot Cr_2O_3$.

The catalyst is reduced before use with hydrogen in the usual way. Frazer and Jackson recommend that the temperature should be raised at the rate of about 120° an hour until 350° is reached, this temperature being then maintained for at least 4 hours. The temperature is subsequently still further raised—at the rate of 90° per hour—to 540°. After being maintained at this temperature for half an hour, the reduced pyrophoric catalyst is cooled in carbon dioxide or nitrogen and introduced into the liquid to be hydrogenated.

With catalysts prepared by the ignition of copper ammonium chromate, both the yield of catalyst and its activity are found to vary with the quantity of ammonium hydroxide used for its precipitation; and it is found advantageous to incorporate barium, calcium, or magnesium, which apparently stabilise the catalysts against excessive reduction and increase their activity[4].

Thus, 900 c.c. of a solution containing 2[illegible]1 g. of hydrated copper nitrate and 31.3 g. of barium nitrate at 80° were added to 900 c.c. of a solution containing 151.2 g. of ammonium dichromate and 225 c.c. of 28 per cent ammonium hydroxide at 25—30° C. The precipitate was filtered, pressed with a spatula, and drained as far as possible. It was next dried overnight at 7[illegible] and decomposed in three por-

---

[1] Z. physik. Chem., Abt. B 27, 439 (1934).

[2] J. Amer. chem. Soc. 54, 10[illegible] (1931).

[3] [illegible] Amer. chem. Soc. 58, 950 (1936).

[4] R. Connor, K. Folkers, H. Adkins: J. Amer. chem. Soc. 54, 1138 (1932).

tions, with stirring, in a casserole as above, using a free flame, which was removed when the decomposition had begun. After continuing the stirring, there was a sudden evolution of gas and the mass became black. The product was leached with 10 per cent acetic acid (600 c.c.) for 30 minutes, filtered, further washed with 600 c.c. of water in six portions, dried overnight at 125° and powdered. The yield was 170 g.

Catalysts containing magnesium, calcium, or strontium may be prepared in the same way as that given in the preceding paragraph. In preparations on onethird the above scale, 10 g. of $MgNO_3 \cdot 6H_2O$, 6.6 g. of calcium nitrate or 8.5 g. of strontium nitrate was substituted for the barium nitrate, the yields being 34, 38, and 36 g. of catalyst respectively. The catalyst containing calcium was particularly active.

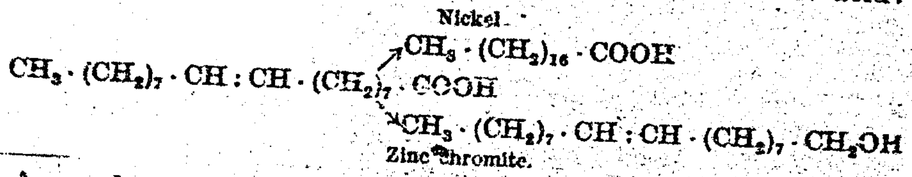
Mixed oxide catalysts of similar composition are also made by the decomposition of oxalates, nitrates, carbonates, or even by mechanically mixing copper oxide and chromium oxides. CONNOR, FOLKERS and ADKINS recommend the following procedure for the preparation of a catalyst from a mixture of carbonates:

5.4 g. of barium nitrate were dissolved in 50 c.c. of boiling water, 77.2 g. of hydrated chromium nitrate $[Cr_2(NO_3)_6 15H_2O]$, separately, in 450 c.c. of warm water, and 100 g. of hydrated copper nitrate $[Cu(NO_3)_2 3H_2O]$ in 150 c.c. of water. The three solutions were mixed at 35°, and 94.4 g. of ammonium carbonate $[(NH_4)_2CO_3 \cdot H_2O]$ in 535 c.c. of water were added, when a voluminous precipitate formed, accompanied by effervescence. The precipitate was filtered off on a suction funnel, washed twice with 50 c.c. portions of water, dried at 110—120°, powdered and decomposed, in two portions, by ignition, as before, at 190—230°. The product was suspended in 100 c.c. of 10 per cent acetic acid, filtered, washed twice each time with 75 c.c. of water, and dried at 110—120°. Yield, 57 g.

Zinc chromite is made by methods similar to those used for nickel on copper. J. SAUER and H. ADKINS[1] recommend dissolving 250 g. (1 g. mol.) of ammonium dichromate in 600 c.c. of water, concentrated ammonium hydroxide being added until the colour of the liquid has changed from orange to yellow. This should require about 400 c.c. of ammonia. 379 g. (2 g. mols.) of zinc nitrate, dissolved in 800 c.c. of water are now added; and the yellow precipitate is filtered, washed and dried overnight in an oven at 85°. The zinc chromate thus produced may be decomposed to chromite by gentle heating, as before.

According to another method of preparation[2], 200 g. of zinc oxide were mixed with 22 g. of chromic acid and enough water added to form a thick paste. 100 g. of 4—8 mesh pumice was mixed with the paste and the mixture dried at 150°. It could, of course, also have been pelleted or extruded either alone or with a finely-divided support such as kieselguhr or clay.

Zinc chromite is of special interest in that it does not readily hydrogenate simple unsaturated carbon-carbon linkages but very easily reduces a carbonyl group or even a carboxyl group. It accordingly does not hydrogenate ethylene[3], but is a good catalyst for the reduction of acetone to isopropyl alcohol; and, with bodies containing both an unsaturated linkage and a carboxyl group (as such, or in the form of an ester), the latter may be reduced while the double bond remains unattached (J. SAUER and H. ADKINS, loc. cit.). In this it differs fundamentally from the metals such as nickel. Thus, with oleic acid:



$$CH_3\cdot(CH_2)_7\cdot CH:CH\cdot(CH_2)_7\cdot COOH \begin{array}{l}\xrightarrow{\text{Nickel}} CH_3\cdot(CH_2)_{16}\cdot COOH\\ \xrightarrow[\text{Zinc chromite}]{} CH_3\cdot(CH_2)_7\cdot CH:CH\cdot(CH_2)_7\cdot CH_2OH\end{array}$$

---

[1] J. Amer. chem. Soc. 59, 1 (1937).

[2] H. H. STORCH: J. physik. Chem. 32, 1744 (1928).

[3] VAUGHEN: J. Amer. chem. Soc. 58, 3719 (1932).

Nickel chromite, on the other hand, has very nearly the same hydrogenating properties as metallic nickel, *copper chromite* occupying an intermediate position according to the temperature at which it is used. The action of these catalysts is discussed in greater detail later. They are employed at temperatures varying from about 250° to 350°.

2. Molybdenum Oxide and Tungsten Oxide.

Catalysts of this type differ from the chromite class of hydrogenating catalysts in the temperature at which they become active and in the scope of their application. They usually require a working temperature of at least 350°, and in many cases are used at 450—500°. Accordingly, like their sulphur counterparts molybdenum sulphide or tungsten sulphide, their use is restricted to the hydrogenation (usually under pressure) of substances, such as naphthalene, which are stable at these high temperatures, or for the reverse process of dehydrogenation; and they are also good catalysts for the reduction of phenols to hydrocarbons. They are unaffected by the presence of sulphur: indeed, sulphur may raise the activity.

In their simplest form they need little special preparation. Porous granular supports such as bauxite or active charcoal may be impregnated with aqueous ammonium molybdate or tungstate, the molybdate solution being, for instance, evaporated to dryness in a porcelain dish in the presence of the support; and the granules, after being dried, are heated, preferably in the hydrogenation vessel itself and in a current of hydrogen, to remove ammonia by the conversion of the ammonium molybdate to molybdenum oxide. As an alternative, a paste made from ammonium molybdate or from molybdic acid, together with a finely divided carrier, is dried and pelleted in the usual way.

Molybdenum oxide catalysts have also been prepared[1] by adding powdered molybdic acid to colloidal silica, the paste being warmed and stirred until the silica coagulates and a uniform mixture is obtained which can be dried without any tendency to separate. It is then re-moistened to form a paste and extruded in threads from a press. The intermediate drying process was adopted to exclude the possibility of an increased silica concentration in the first part of the thread, which usually has a higher water content. China clay (4 : 1) may be mixed to the above catalyst as a filler; and alumina may be used in place of silica[2]. The extruded thread, which may for laboratory work conveniently have a diameter of about 0.1 inch, is dried in an oven and broken up into small lengths.

The ratio of support to catalyst was found to have a considerable influence on the activity, and the effect of the inclusion of various promoters was also investigated. Molybdenum oxide catalysts containing phosphorus, and made by heating ammonium phosphomolybdate, have been described by F. E. T. KINGMAN[3].

3. Sulphide Catalysts.

The principal catalytic use of sulphides such as *nickel sulphide* or *cobalt sulphide* is for the catalytic decomposition of organic sulphur compounds; but they may also be used as true hydrogenation catalysts,—for instance, in the case of nickel sulphide, for the hydrogenation of carbon disulphide to methyl thiol[4]. A suitable nickel sulphide may be made by the action of carbon disul-

---

[1] R. H. GRIFFITH, J. H. G. PLANT: Proc. Roy. Soc. [London], Ser. A 148, 191 (1935). — H. HOLLINGS, R. N. BRUCE, R. H. GRIFFITH: Ebenda 186.

[2] R. H. GRIFFITH: Trans. Faraday Soc. 33, 405 (1937).

[3] Trans. Faraday Soc. 33, 784 (1937).

[4] SABATIER, ESPIL: Bull. Soc. chim. France (4) 15, 228 (1914). — B. CRAWLEY, R. H. GRIFFITH: J. chem. Soc. [London] 1938, 720. — R. H. GRIFFITH, S. G. HILL: ibidem 717.

phide vapour, diluted with nitrogen, on an ordinary supported nickel catalyst at 350°. The probable composition of the active sulphide is stated to be Ni_3S_2.

The second type of sulphide catalyst, which is represented by *molybdenum sulphide* or *tungsten sulphide*, is used widely as a sulphur-tolerant hydrogenation catalyst for the hydrogenation of phenols to hydrocarbons, for the hydrogenation of aromatic hydrocarbons such as naphthalene without the necessity for the prior removal of impurities, and for the corresponding dehydrogenation process. They are, accordingly, important commercial catalysts for the treatment of tars as well as for the so-called hydrogenation-cracking of fuel products generally, especially where this treatment is carried out in the vapour phase.

They may be prepared by the action of hydrogen sulphide or carbon disulphide on molybdenum or tungsten sulphides; or they may be prepared directly by evaporating ammonium thiomolybdate or thiotungstate on to a granular support such as bauxite, pumice, or active carbon, the product being subsequently heated in a porcelain basin to remove the ammonia. The solution of ammonium thiomolybdate is conveniently made by passing hydrogen sulphide for several hours through a solution of ammonium molybdate. Alternatively, they may also be made in a pelleted or extruded form. Thus, F. E. T. KINGMAN (loc. cit.) precipitated molybdenum sulphide from aqueous ammonium thiomolybdate with sulphuric acid and compressed this into small pellets. A filler such as kieselguhr can, of course, be added; and KINGMAN found, as for molybdenum oxide, that the activity was markedly increased by the coprecipitation, with the molybdenum sulphide, of ammonium phosphomolybdate. The trisulphide, MoS_3, probably becomes converted to MoS_2 under the conditions of its use.

D. The applications of Hydrogenation.

The general plan followed in the present section, in which the application of catalytic hydrogenation is dealt with more systematically, is to group the bodies hydrogenated according to the nature of the unsaturated linkage and to consider in the first place principally parent substances, especially in the parts dealing with the hydrogenation of ring compounds.

The literature necessary for a systematic survey is still incomplete, since only certain substances possess sufficient representative or intrinsic interest for their hydrogenation to have been studied; but the existing gaps can, to a large degree, be filled up by analogy; and, in any case, the number of substances with regard to the hydrogenation of which published information exists, is now very great.

The unsaturated linkages which can be hydrogenated catalytically include, firstly, the three main types of carbon-carbon linkings, represented respectively by ethylenic, acetylenic, and benzenoid bonds; secondly, various chain or cyclic links in which one partner only is carbon—for instance, the carbon-nitrogen or carbon-oxygen linkings in rings such as pyrrol or furane, or ketonic, or nitrile groups—and, thirdly, unsaturated bonds not involving carbon at all, e.g. the azo, —N : N—, link.

In addition to reactions involving saturation only, catalytic reduction with hydrogen may result in the elimination of elements such as oxygen or a halogen—with consequent separation of water or of a halogen acid. This process frequently constitutes a more advanced stage: thus, aldehydes or ketones may pass, by saturation, to an alcohol and subsequently—by reduction—to a hydrocarbon. It is not possible, in many cases, to keep these two types of process separate; but the reactions dealt with first are mainly those in which the simple saturation of an unsaturated linkage occurs.

It may be noted that maximum catalytic activity is by no means always desirable, especially in cases in which it is desired to isolate an intermediate reduction product. Thus, in the reduction of bodies containing an ethylenic linkage in a side-chain attached to a benzene ring, the selective hydrogenation of the chain can often be carried out without appreciable hydrogenation of the nucleus by employing a catalyst of relatively low activity. Further, even when there is no question of selective attack, the use of a very active catalyst, especially in gas-phase hydrogenation at high temperatures, may lead to more extensive decomposition than with a catalyst of lower activity.

An interesting example of the raising of the yield of an intermediate product by adjusting the activity of a catalyst has been observed by Rosenmund and Zetsche[1] in connection with the liquid-phase hydrogenation of benzoyl and other acid chlorides, it being found possible to arrest the process:

$$R \cdot COCl \rightarrow R \cdot CHO \rightarrow R \cdot CH_2OH \rightarrow R \cdot CH_3$$

almost entirely at the aldehyde stage by partially poisoning the palladium catalyst used.

I. Hydrocarbons and Fundamental Cyclic Bodies.

1. Hydrogenation of Alkenes.

In the classical work of Sabatier and Senderens[2] ethylene and the other simple alkenes were hydrogenated by passage, together with hydrogen, over a layer of reduced nickel, cobalt or copper contained in a horizontal tube at a temperature of 100—160° with nickel, or 180—250° with copper. Iron and platinum were also used, but were observed to lose activity rapidly owing to carbon deposition.

The reaction is, however, more efficiently carried out in one of the vertical types of apparatus for gas phase hydrogenation illustrated in Chapter *B* (e.g. Fig. 12), and with a pelleted or supported granular catalyst, preferably employing an excess of hydrogen; and, if the catalyst is carefully prepared, reaction may occur even at low temperatures. Thus, R. N. Pease and L. Stewart[3], who used metals supported on small fragments of diatomite brick, found that nickel and cobalt caused the interaction of hydrogen and ethylene to take place fairly rapidly even at —20°, while iron became moderately active at 0°, copper at 50°, and silver at 100°. However, the reaction velocity, as has already been discussed, rises to a maximum, as the hydrogenation temperature is increased, and subsequently decreases. V. N. Morris and L. H. Reyerson[4] give 240° as the temperature of maximum activity for a nickel catalyst supported on silica gel, the corresponding temperature for

Table 23.

Catalyst	Temperature °C.	Rate of flow of gas. C.cs. per g. of catalyst per min.	Percentage hydrogenation
Cu-silica	240	69	26.2
		26	43.8
		6	74.8
Pt-silica	60	171	72.1
		78	78.6
		49	83.4
		30	92.5
		16	97.2
Pd-silica	80	91	92.6
		57	94.5
		37	97.4
		14	99.8

---

[1] Ber. dtsch. chem. Ges. 54, 425 (1921).

[2] C. R. hebd. Séances Acad. Sci. 124, 616 (1897); 130, 1761; 131, 40 (1900); 134, 1137 (1902).

[3] J. Amer. chem. Soc. 49, 2783 (1927).

[4] J. physic. Chem. 31, 1220 (1927).

palladium—and probably also for platinum—being of the order of 60°. These authors also give the following figures for the rate of conversion, at these optimum temperatures, with catalysts of this type, the gas mixture used containing two volumes of hydrogen to one of ethylene (Table 23).

The far higher activity of platinum and palladium, especially the latter, compared with that of copper, is well shown; but the corresponding relative rate of working of nickel, which is considerably more active than copper, is not included in MORRIS and REYERSON's figures. Some account of the working of a semi-industrial plant employing nickel has, however, been given by C. SPRENT[1]. Ethylene, which had been made by the dehydration of alcohol with alumina, was mixed with a slight excess of hydrogen and passed, at a pressure of 30 to 40 atm., over nickel on pumice at a temperature of 200°. When working in this way, it was found advisable—in order to avoid an undue rise of temperature, owing to the exothermic nature of the process—not to pass the undiluted ethylene-hydrogen mixture by itself over the catalyst but to employ a mixture containing 80 per cent of ethane, 10 per cent of ethylene and 10 per cent of hydrogen. This can readily be done by using a closed circulation system, in which the fresh hydrogen-ethylene mixture is added to the required proportion at a point in the circuit before the reaction chamber, while the ethane produced (except that required for re-cycling) is condensed as a liquid after the passage of the mixture through the catalyst. At the ordinary pressure, the reaction was far slower; and SPRENT considers the use of an increased pressure advisable if the process is to be operated on an industrial scale. It is stated that quite a small unit successfully made 25 kg. of liquid ethane a day and that it ran continuously, save for the occasional blowing off of the excess of hydrogen.

Before leaving the subject of the rate of working of various catalysts for ethylene hydrogenation, some figures, due to O. SCHMIDT[2], for the relative activity of nickel and other catalysts at low temperatures may be given. In SCHMIDT's measurements, an ethylene-hydrogen mixture was allowed to flow at atmospheric pressure through a small reaction vessel containing an unsupported metal catalyst, usually prepared by the reduction of the carbonate or hydroxide with hydrogen. The percentage conversion to ethane obtained at various temperatures and rates of flow are summarised in Table 24.

Table 24.

Catalyst	Wt. of catalyst taken g.	Gas rate, in c.c. per min.	Hydrogenation temperature °C.	Percentage conversion to ethane
Nickel	0.34	3.0	20	100
		22.0	20	97.6
Cobalt	1.0	2.9	22	98
		17.0	22	94
Iron	1.1	3.4	21	1.9
		3.5	100	15.0
Copper	1.0	0.6	100	57
		3.4	20	4.8
		3.5	100	92
Silver	1.0	13.5	100	77
		3.3	20	2—3

The results emphasise the high activity both of nickel and cobalt at the ordinary temperature, and show well the degree of increase in the activity of copper as the reaction temperature is raised from 20° to 100°. Other work on

---

[1] J. Soc. chem. Ind. 32, 171 (1913). [2] Z. physik. Chem. 118, 103 (1925).

the hydrogenation of ethylene with copper at low temperatures (0—40°) has been carried out by H. S. TAYLOR and G. G. JORIS[1]. In this case, a catalyst supported, by co-precipitation, on magnesia was employed. Other studies of the same reaction on copper have been made by G. HARKER[2]; and the subject has also been investigated, principally, however, from the standpoint of reaction kinetics, by a large number of other workers, e. g. CONSTABLE and PALMER, to whom reference is made in another section.

The union of ethylene and hydrogen also takes place readily in the presence of a number of less common hydrogenation catalysts. Thus, O. SCHMIDT (loc. cit.) studied the activity of **zinc**, which he prepared by the action of magnesium on an alcoholic solution of zinc chloride in the absence of air. Under the same conditions as in Table 24, i. e. with about 1 g. of catalyst, an ethylene conversion of 84 per cent was obtained at 80° with a gas rate of 1.2 c.c. per minute, and 64 per cent conversion at 17° with about the same rate of flow. Further, R. N. PEASE and L. STEWART have measured at 25° and at 100° the rate of interaction of ethylene and hydrogen in the presence of **calcium**. The catalyst, which consisted of calcium turnings which had been washed with ether, was more active after it had previously been saturated with hydrogen; but the rate of interaction between calcium hydride and ethylene (as distinct from the catalytic action of calcium hydride on a mixture of ethylene and hydrogen) was too slow to make it probable that calcium hydride itself is formed as an intermediate product in the catalytic form of the reaction. The hydrogenation of ethylene may also be carried out with oxide catalysts, for instance, with **chromium oxide**, which has been successfully applied[3] also for ethylene homologues, e. g. for propylene and octylene.

The hydrogenation of these *higher olefines* takes place very similarly to that of ethylene. Thus[4], they may be hydrogenated in the vapour phase by SABATIER and SENDERENS' method or by any of the modifications of this already described under ethylene. C. SCHUSTER[5] states that the rate of hydrogenation, in the presence of a **nickel catalyst**, decreases with an increase in chain length, in that butylene hydrogenates more slowly than propylene and this, in turn, than ethylene. SCHUSTER gives the following figures for the half-life period, at room temperature, of various olefines adsorbed on his catalyst (nickel supported on active charcoal) and submitted in the adsorbed state to the action of hydrogen under comparable conditions.

Table 25.

Olefine	Half-life period Mins.
Ethylene	8
Propylene	104
α-Butylene	228
β-Butylene	485
iso-Butylene	1100

Olefines can, of course, also be hydrogenated in the liquid phase. Thus, PAAL and SCHWARZ[6] hydrogenated ethylene by shaking a mixture of this gas and hydrogen with a solution containing **colloidal platinum**; and olefines higher than C_4 are themselves liquids at room temperature.

2. Hydrogenation of Acetylene.

The hydrogenation of acetylene and its derivatives is in many cases complicated by polymerisation. In general, they are, however, very easily hydro-

---

[1] Bull. Soc. chim. Belgique 46, 241 (1937). [2] J. Soc. chem. Ind 51, 314 T (1932).

[3] W. A. LAZIER, J. V. VAUGHEN: J. Amer. chem. Soc. 54, 3080 (1932).

[4] C. R. hebd. Séances Acad. Sci. 134, 1137 (1902).

[5] Trans. Faraday Soc. 28, 406 (1932); Z. Elektrochem. angew. physik Chem. 38, 614 (1932). [6] Ber. dtsch. chem. Ges. 48, 994 (1915).

genated; and it is usually possible, at any rate to some degree, to arrest the hydrogenation at a stage corresponding with the production of an ethylenic body. De Wilde[1], as long ago as 1874, hydrogenated acetylene with **platinum black** and observed that, if hydrogen is present in sufficient excess, the reaction proceeds smoothly to ethane. **Nickel, copper, cobalt** and **iron** catalysts were used by Sabatier and Senderens[2], with various complications due both to partial polymerisation and to the deposition of carbon. With nickel, the reaction began in the cold; and side reactions could to a large degree be avoided by using a large excess of hydrogen. The reaction, with copper, was less energetic and began at 130—180°, according to the activity of the catalyst.

More recently, the hydrogenation of acetylene in the presence of **platinum, palladium** or **copper**, supported on silica gel, has been investigated by V. N. Morris and L. H. Reyerson[3], who found that a considerable proportion of ethylene was contained in the product (the main constituent of which was, of course, ethane), even when hydrogen is present in excess. The platinum catalyst worked well at 100°, palladium at 50° or over, and copper at 200°; but polymerisation of the acetylene also occurred.

Acetylene is also very easily hydrogenated in the liquid phase. Thus, stepwise reduction, with production of ethylene as an intermediate product, has been carried out with colloidal platinum metals[4]. For instance, on circulating, at room temperature and in a closed system, a mixture of equal parts of acetylene and hydrogen through a solution containing **colloidal palladium** until the volume of the gas had been reduced to one half, Paal and Hohenegger obtained a product containing 71 per cent of ethylene and 10 per cent of ethane, the remainder being unchanged acetylene and hydrogen. The use of **palladium** of relatively low activity was found to be conducive to good yields of the intermediate product. **Colloidal platinum** may be substituted for palladium[5]; and the prior conversion of acetylenic into ethylenic linkings before the latter are further attacked is apparently general, since it has also been observed with **palladium, copper**, alloy-skeleton **nickel**, and alloy-skeleton **iron**[6], both for acetylene itself and for its derivatives. The reasonably sharp separation of the intermediate stage is, as already mentioned, usually more easily obtained with relatively inactive catalysts: thus, it occurs more distinctly with copper than with nickel; indeed, in some cases, with catalysts of low activity such as iron, or even copper, the reaction may apparently come to a halt at the formation of the double linkage. This is illustrated in Sabatier and Senderens' work on the hydrogenation of *n-amylacetylene*[7] with nickel, which gave principally ethane, and with copper, with which the product was mainly ethylene; but the ease of stoppage can be changed, even with the same metal, by decreasing the activity of the catalyst.

Other homologues, and substituted acetylenes generally, can be reduced in a similar manner. Thus, C. Kelber and A. Schwarz[8], who worked with colloidal

---

[1] Ber. dtsch. chem. Ges. **7**, 353 (1874).

[2] C. R. hebd. Séances Acad. Sci. **124**, 616 (1897); **128**, 1173 (1899); **130**, 250, 1559, 1628; **131**, 187, 267 (1900).

[3] J. physic. Chem. **31**, 1337 (1927).

[4] C. Paal, C. Hohenegger: Ber. dtsch. chem. Ges. **48**. 275 (1915).

[5] C. Paal, A. Schwarz: Ber. dtsch. chem. Ges. **48**, 1202 (1915).

[6] M. Bourguel, R. Courtel, V. Gredy: Bull. Soc. chim. France (4) **51**, 253 (1932). — G. Dupont: Ebenda (5) **3**, 1030 (1936). — R. Paul, G. Hilly: C. R. hebd. Séances Acad. Sci. **206**, 608 (1938).

[7] C. R. hebd. Séances Acad. Sci. **135**, 87 (1902).

[8] Ber. dtsch. chem. Ges. **45**, 1946 (1912).

palladium in acetic acid solution, were able to arrest the reduction of *phenyl acetylene* and of *tolane* (diphenyl acetylene) by interrupting the absorption of hydrogen at the appropriate stage, the intermediate products being styrene and stilbene respectively.

$$\underset{\text{Phenyl acetylene.}}{Ph\cdot C\vdots CH} \rightarrow \underset{\text{Styrene.}}{Ph\cdot CH:CH_2} \rightarrow \underset{\text{Phenyl ethylene.}}{Ph\cdot CH_2\cdot CH_3.} \qquad (1)$$

$$\underset{\text{Tolane.}}{Ph\cdot C\vdots C\cdot Ph} \rightarrow \underset{\text{Stilbene.}}{Ph\cdot CH:CH\cdot Ph} \rightarrow \underset{\text{Dibenzyl.}}{Ph\cdot CH_2\cdot CH_2\cdot Ph.} \qquad (2)$$

The hydrogenation of *diphenyl-di-acetylene* was also studied and found to proceed analogously, namely, to give the corresponding butadiene, which, on further reduction, passed into diphenyl-butane:

$$\underset{\text{Diphenil diacetylene.}}{Ph\cdot C\vdots C\cdot C\vdots C\cdot Ph} \rightarrow \underset{\text{Diphenyl-butadiene.}}{Ph\cdot CH:CH\cdot CH:CH\cdot Ph} \rightarrow \underset{\text{Diphenyl butane.}}{Ph\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot Ph.}$$

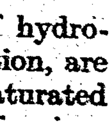
3. Hydrogenation of Hydrocarbon Rings.

a) *General.*

While all unsaturated hydrocarbon rings can be hydrogenated by methods similar to those used for unsaturated linkages in chains, the hydrogenation of the benzene nucleus occupies a special position, not only on account of the importance of benzene derivatives generally, but also by reason of the reversibility of the reaction and because of the relatively slow rate at which the hydrogenation of benzenoid bonds occurs, compared with that of ethylenic linkings. The benzene nucleus is extremely difficult to reduce non-catalytically: it is, for instance, not attacked by nascent hydrogen; and, certainly, one of the most important results of **Sabatier** and **Senderens'** original work on the activity of nickel was the immediate possibility of preparing, in bulk and reasonably easily, both cyclohexane and a very large number of other hydro-aromatic bodies which had up to then only been obtainable with difficulty and in low yields by reduction of their parent bodies with, for instance, hydrogen iodide.

The special properties of the benzene ring, from the standpoint of hydrogenation, namely the reversibility and the relative slowness of the reaction, are shared by certain heterocyclic rings, e. g. by pyridine, but not by unsaturated carbocyclic rings other than benzene: indeed, these other carbocyclic rings may, in agreement with their general chemical properties, be regarded as cyclic olefines. Their hydrogenation, partly on account of their lesser importance and partly by reason of difficulties in the preparation of individual members, has been far less systematically studied than is the case with benzene derivatives; but it is possible, in most instances, to give some account of the hydrogenation of typical examples of each class; and in the following treatment, these cyclic bodies are arranged according to the number of carbon atoms contained in them.

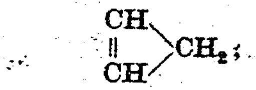
It has been found convenient, for ease in writing, to retain the **Kekulé** double bond method of expressing benzenoid structure when giving the structural formulae of bodies containing aromatic rings, in place of employing a notation of the type:



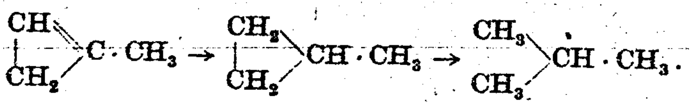
which more accurately represents the modern conception of the structure of benzene.

b) Hydrogenation of 3-, 4- and 5-Carbon Rings.

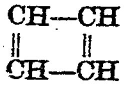
The simplest unsaturated hydrocarbon of this series, *cyclopropene*,



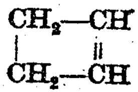
has been described by M. P. **Freundler**[1]; but there appears to be some doubt as to its existence, and its hydrogenation has not been studied. The hydrogenation of *methyl cyclopropene* has, however, been carried out by B. K. **Mereshkovski**[2] in the presence either of **palladium**, at about 80°, or of **nickel**, at 180°. The product is methyl-cyclopropane which passes, by ring fissure, to isobutane.



Of the two possible unsaturated 4-carbon rings:

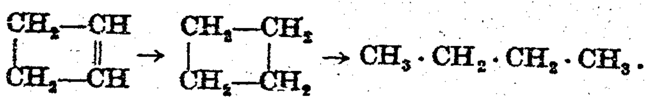


Cyclo-butadiene.



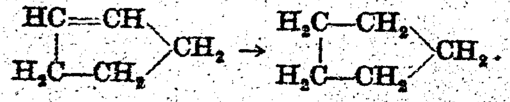
Cyclobutene.

the hydrogenation of *cyclobutene* has been studied by R. **Willstätter** and J. **Bruce**[3], by passage with hydrogen over **nickel**. With simple rings of this type, the reaction is, as was seen with methyl cyclopropane, complicated by the tendency of the cyclomethylene produced to pass into a straight-chain hydrocarbon by ring fissure in such a way as to give n-butane in addition to cyclobutane.

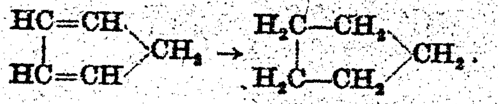


The corresponding simple 3-carbon polymethylene, *trimethylene*, opens to form n-propane more readily than the above 4-membered ring[4]; but, in view of the lesser strain, no corresponding decyclisation is obtained with cylcopentane, cyclohexane, cycloheptane or cyclo-octane, although, as will be mentioned later, cyclic hydrocarbons containing more than six carbon atoms in the ring may re-arrange themselves in such a way as to form benzene derivatives.

Cyclopentene has been hydrogenated by M. **Godchot** and F. **Taboury**[5] by passage, with hydrogen, over reduced **nickel** at 125°. The normal product, cyclopentane, was obtained.



The corresponding diene, *cyclopentadiene*, also hydrogenates smoothly. The reaction was examined by J. F. **Eijkman**[6]; and as with cyclopentene, cyclopentane was produced on gas-phase hydrogenation with **nickel**.



---

[1] Bull. Soc. chim. France (3) 17, 614 (1897).

[2] J. russ. physik.-chem. Soc. 46, 97 (1914).

[3] Ber. dtsch. chem. Ges. 40, 3979 (1907).

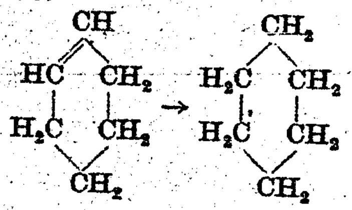
[4] **Willstätter**, **Bruce**: Ber. dtsch. chem. Ges. 40, 1480 (1907).

[5] Ann. Chim. et Physique (8) 26, 47 (1912).

[6] Chem. Weekbl. 1, 7 (1903).

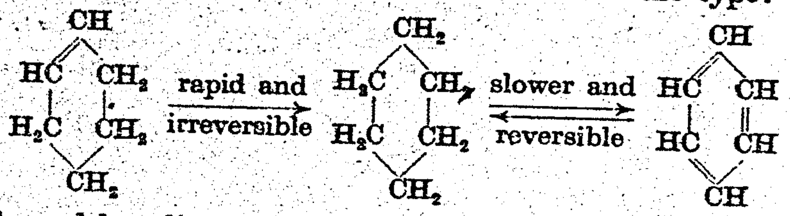
c) *Hydrogenation of 6-Carbon Rings.*

The hydrogenation of *cyclohexene* to cyclohexane occurs normally with platinum at room temperature.



At higher temperatures, apparent *dehydrogenation* to benzene also occurs. Thus, J. Böeseken and K. H. A. Sillevis[1] obtained a product containing about 60 per cent of cyclohexane and 40 per cent of benzene, together with small quantities of unchanged cyclohexene, by passing cyclohexene, in a current of an inert gas, over finely-divided nickel at 180°; and a similar apparent dehydrogenation was observed by P. Sabatier and G. Gaudion[2] to occur at 350—360° even in the presence of hydrogen.

This dehydrogenation of cyclohexene, which from its structure, general properties and easy and rapid hydrogenation, contains an ethylenic rather than a benzenoid bond, is probably apparent only, since, if hydrogen is either originally present or if even traces of this are formed by decomposition, cyclohexane will be produced, which will pass, by loss of hydrogen, into benzene. Certainly, no cyclohexene or other intermediate product is isolated during the hydrogenation of benzene or the dehydrogenation of cyclohexane, or on bringing a mixture of benzene and cyclohexane into contact with nickel; and the apparent dehydrogenation of cyclohexene probably involves a reaction of the type:



Two possible *cyclohexadienes* exist, namely,

cyclohexadiene-(1:3)

and

cyclohexadiene-(1:4)

of which the first, 1:3, compound is best known[3]. In the presence of platinum at room temperature, this rapidly absorbs hydrogen and passes into cyclohexane[4]. At high temperatures, e. g. with nickel at 180°, even in the absence of hydrogen, passage into benzene and cyclohexane, according to the generation reaction:

$$3C_6H_8 \rightarrow C_6H_{12} + 2C_6H_6$$

has been observed by J. Böeseken, M. de Groot and W. van Lookeren Campagne[5]; but, as with cyclohexene, this may not entail the direct dehydrogenation of cyclohexadiene.

---

[1] Proc. Kon. Akad. Wetensch. Amsterdam 16, 499 (1913).

[2] C. R. hebd. Séances Acad. Sci. 168, 670 (1919).

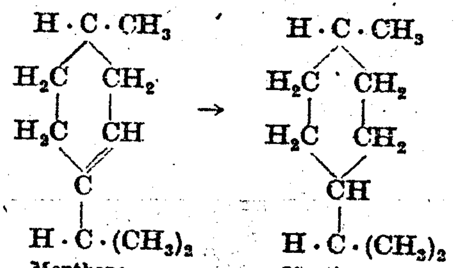
[3] A. v. Baeyer: Liebigs Ann. Chem. 278, 108 (1893). — Crossley: J. chem. Soc. [London] 85, 1403 (1904). — Zelinsky, Gorsky: Ber. dtsch. chem. Ges. 41, 2479 (1908). — C. Harries: Ebenda 45, 809 (1912).

[4] R. Willstätter, D. Hatt: Ber. dtsch. chem. Ges. 45, 1469 (1912).

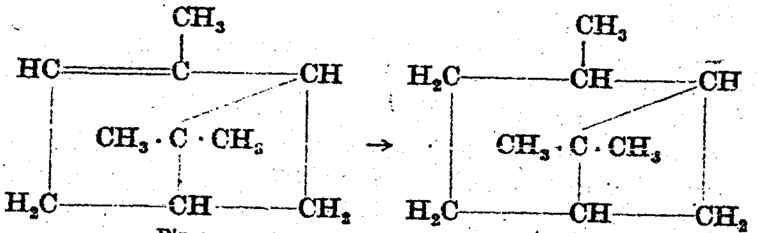
[5] Recueil Trav. chim. Pays-Bas 37, 255 (1918).

Of the alkyl-substituted cyclohexene hydrocarbons, special interest is, from the standpoint of terpene chemistry, attached to menthene and to corresponding bridged-ring derivates, such as pinene.

Menthene, on being hydrogenated either in the vapour phase over nickel[1] or, as a liquid, with platinum or with nickel, preferably under a slight hydrogen pressure, passes rapidly into menthane.

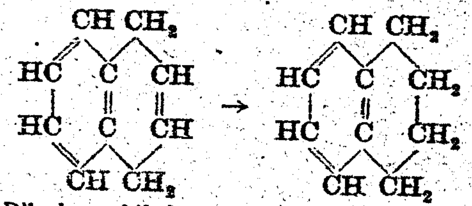

Menthene. Menthane.

Pinene reacts similarly, i. e.


Pinene.

Other substituted cyclohexenes also hydrogenate very easily to give normal reduction products. Thus, **Murat**[2] has hydrogenated *1,2-methyl-ethyl cyclohexene*. Bodies such as *phenyl cyclohexene*, which contain an easily reduced cyclohexene ring attached to an aromatic nucleus, pass quickly into phenyl cyclohexane[3], which is then more slowly transformed into cyclohexyl-cyclohexane.

The same ease of hydrogenation was, moreover, found by **Willstätter** and **King**[4] for the naphthalene analogue of phenyl-cyclohexene, *dihydronaphthalene*, which passes, in the presence of platinum, into tetrahydro-naphthalene at a speed comparable with that observed, for instance, in the hydrogenation of styrene: indeed, the hexene ring in this type of compound behaves almost as a closed ethylenic chain.


Dihydronaphthalene.

The subsequent addition of hydrogen occurs, of course, at a far lower rate.

d) The Hydrogenation of Benzene.

Benzene was first hydrogenated catalytically by **Sabatier** and **Senderens** in 1901[5] by passing a mixture of benzene and hydrogen over a layer of reduced

---

[1] **Sabatier, Senderens**: C. R. hebd. Séances Acad. Sci. 132, 1256 (1901).
[2] Bull. Soc. chim. France (4) 1, 774 (1907).
[3] **Sabatier, Murat**: C. R. hebd. Séances Acad. Sci. 154, 1390 (1912).
[4] Ber. dtsch. chem. Ges. 46, 527 (1913).
[5] C. R. hebd. Séances Acad. Sci. 132, 210, 566, 1254 (1901).

nickel in a heated glass tube in accordance with their standard vapourphase technique. Hydrogenation, in a similar manner, of homologues of benzene and of condensed ring bodies such as naphthalene followed; and, in view of the wide applicability of the method, this discovery by **Sabatier** and **Senderens** of the hydrogen-activating properties of nickel for the reduction of the benzene nucleus quickly paved the way to the easy preparation of hydro-aromatic bodies of the most varied nature. **Sabatier** and **Senderens** found that the reaction between benzene and hydrogen began, with nickel, at about 70°, a suitable working temperature being however about 180°. Other metals, e. g. cobalt or platinum, were stated to be less suitable; but this statement, especially in the case of the platinum metals, has had later to be revised, since **Zelinsky** and his co-workers have successfully used platinum metals both for the vapour-phase hydrogenation of benzene and for dehydrogenation: further, copper, which was found by **Sabatier** and **Senderens** to be inactive for benzene hydrogenation, has been shown by **Pease** and **Purdum**[1] to act also for this reaction; and most of the early ambiguities as to the activity of various metals for the hydrogenation of benzene are due to the relative slowness of the reaction compared with that of olefines—which renders necessary the use of active and well-prepared catalysts—as well as to the thiophene content of commercial benzene. As a rough guide to the permissible rate of passage, it may be mentioned that **Sabatier** and **Senderens**, who used a layer of unsupported nickel about 2 ft. in length in a heated combustion tube, were able to hydrogenate up to 10 c.c. of benzene an hour.

In practice, if vapour-phase hydrogenation is desired, this is conveniently carried out in an apparatus of the type illustrated in Fig. 12, using a granular or pelleted nickel or platinum-metal catalyst, i. e. nickel or a platinum metal supported on granular bauxite, pumice, silica gel etc., or these metals supported on, for instance, finely divided kieselgur and compressed into pellets, as already described. Nickel turnings, the surface of which has been activated by anodic oxidation (see the section dealing with the preparation of nickel catalysts) may also be used. With all forms of nickel a slight pressure—for instance, 5—10 atm.—is conducive to a higher speed of reaction, but is not necessary; and, if overheating is guarded against, the reaction, even with nickel, proceeds without much carbon deposition or other side reactions and, if the benzene is reasonably pure, the activity of the catalyst persists for a considerable time, often under commercial conditions for several weeks. It should be remembered, especially when working on a larger scale, that the hydrogenation of benzene is an exothermic process and that lack of proper temperature control may lead to local overheating and decomposition, accompanied by deposition of carbon on the catalyst, and that an excess of hydrogen (which can be circulated) is desirable.

Zelinsky and **M. Turowa-Pollak**[2], as already mentioned, found that all the platinum metals could be used for the vapour-phase hydrogenation of benzene, the reaction being especially smooth with palladium or osmium, although probably platinum itself would give equally good results. They employed, for instance, osmium supported on asbestos, the catalyst—which contained one part of osmium to three parts of the support—being made by reducing asbestos, previously impregnated with aqueous osmic acid, by means of alkaline formaldehyde solution.

Catalysts such as nickel chromite also hydrogenate benzene; but the use of sulphur-tolerant catalysts of the molybdenum sulphide type—which is of special

---

[1] J. Amer. chem. Soc. 47, 1435 (1925).

[2] Ber. dtsch. chem. Ges. 58, 1298 (1925); 62, 2865 (1929).

interest in view of the thiophene content of ordinary benzene—is complicated, both from the standpoint of equilibrium and from that of decomposition, by the high temperature (400—450°) at which this class of catalyst becomes active; and, although some hydrogenation, especially under pressure, results, satisfactory yields of cyclohexane are not obtained. These catalysts have, however, been used extensively for the hydrogenation-cracking of technical products containing naphthalene or phenols.

As an alternative to vapour-phase treatment, benzene may be readily hydrogenated in the *liquid phase*, either as such or dissolved in a solvent. Thus, R. WILLSTÄTTER and D. HATT[1] found that cyclohexane was produced without side reactions on shaking a solution of benzene in acetic acid with hydrogen at room temperature. The reaction is not a rapid one, even when the benzene is previously carefully purified from sulphur and other poisons: for instance, in comparative measurements with other unsaturated bodies, it was found[2] that benzene, when hydrogenated in this way, with platinum black at 40°, absorbed hydrogen at about a quarter the rate of oleic acid or about one sixth the rate of crotonic acid. A reaction system containing about 1 g. of benzene, in 10 c.c. of acetic acid, and 0.04 g. of platinum black, absorbed hydrogen, at 40°, at an initial rate of 5—6 c.c. per minute, approximately the same rate being obtained on substituting benzoic acid for benzene.

Liquid-phase hydrogenation *under pressure*[3], if suitable apparatus is available, constitutes probably the most efficient method of making cyclohexane in bulk, since reaction temperatures at which nickel catalysts can be used can be attained with maintenance of the liquid phase, without the use of a solvent. Thus, G. F. SCHOOREL, A. J. TULLENERS and H. I. WATERMAN[4] used nickel supported on kieselgur at 190°, at an initial hydrogen pressure of 100 atm., and obtained with ease a substantially complete conversion of benzene into cyclohexane. The method has also been investigated by S. KOMATSU, K. SUGINO and M. HAGIWARA[5], who observed that hydrogenation even with copper became easier at high pressures. The influence of pressure on the rate of hydrogenation of benzene with nickel, in the liquid phase at 120°, has been followed quantitatively by H. ADKINS, H. I. CRAMER and R. CONNOR[6]. The pressure was, however, not maintained at a constant value throughout the run; but the figures of Table 26 summarise the main effect. The charge consisted of 0.16 g. mol. (12.5 g.) of benzene and 1 g. of catalyst. The times were taken from that corresponding with the attainment of the temperature and pressure required.

Table 26.

Time hrs.	Percentage hydrogenation at		
	30 ± 17 atm.	169 ± 19 atm.	323 ± 17 atm.
0	17	29	34
0.5	40	68	75
1.0	61	90	93
1.5	76	98	100
2.0	87	100	—
2.5	96	—	—
3.0	100	—	—

All ordinary catalysts require the use of carefully purified benzene. In addition to the methods of purification already described (see p. 649), the last traces of impurity may be removed on a small scale, previous to hydrogenation, by treating the benzene at room temperature with platinum black—or with active nickel—the poisons being adsorbed by the metal, from which the

---

[1] Ber. dtsch. chem. Ges. 45, 1471 (1912).
[2] MAXTED, STONE: J. chem. Soc. [London] 1934, 672.
[3] For early work, see IPATIEW: Ber. dtsch. chem. Ges. 40, 1281 (1907).
[4] J. Instn. Petrol. Technologists 18, 179 (1932).
[5] Proc. Imp. Acad. [Tokyo] 6, 194 (1930).
[6] J. Amer. chem. Soc. 53, 1402 (1931).

purified benzene is preferably separated by decantation rather than by distillation. It appears advantageous, especially with nickel, to carry out also this preliminary purification process in a hydrogen atmosphere.

Of the naturally occurring poisons, sulphur, whether present as thiophene, as carbon disulphide or even the free element, is strongly toxic; and, as already mentioned, failure to hydrogenate benzene at a reasonable rate is usually due to the presence of difficultly removable sulphur compounds. Some figures for the observed effective toxicity of carbon disulphide in benzene hydrogenation, in a system containing about 1 g. of benzene, dissolved in 10 c.c. of acetic acid, and 0.0085 g. of platinum black, are given in Table 27[1]. The comparison was carried out at 40°, at atmospheric pressure.

Table 27.

Carbon disulphide content mg.	Rate of hydrogenation (c.c. H_2 per minute)
0	4.5
0.01	3.9
0.03	3.2
0.06	2.2
0.10	1.3
0.15	1.2

Thiophene, in a somewhat similar system, was found to have approximately the same effective toxicity towards platinum as carbon disulphide, their effective toxicities per g. atom of sulphur being in the ratio of 4.4 (thiophene) to 1.9 (carbon disulphide) on a toxicity scale in which the effective toxicity of hydrogen sulphide is taken as unity[2]. The difference between effective and real toxicity has already been dealt with in an earlier section (see pp. 640 to 646); and, in any case, the observed toxicity may vary widely with the fineness of division, i. e. the ratio of surface to mass, of the particular catalyst employed: thus, in some typical measurements, the sensitivity towards poisoning of a finely-divided nickel catalyst on a kieselguhr support was found to be only of the order of one-fiftieth that of a relatively coarse-grained platinum black.

The influence of a number of other possible inhibitants which may occur naturally in benzene hydrogenation has been studied by G. Dougherty and H. S. Taylor[3]. With a nickel catalyst, water vapour up to 2 per cent of the hydrogen used had only a slight retarding effect; but *carbon monoxide* was markedly poisonous, especially at reaction temperatures of 100° or less. As the reaction temperature was raised, the poisoning was less noticeable; but large quantities of carbon monoxide stopped the reaction even at 180°. Cyclohexane also has a depressing effect on the velocity at low temperatures, but this effect diappears at 180°. The temperature coefficient of the reaction between 80° and 90° C. was found to be approximately 1.65 for the 10° rise.

Little needs to be said with regard to the hydrogenation of the simpler *homologues* of benzene, since these undergo hydrogenation in a way very similar to benzene itself. Thus, R. Willstätter and D. Hatt[4] described the hydrogenation of *toluene, xylene* and *durene* with **platinum** in acetic acid solution; and the hydrogenation of these bodies with **nickel** in the vapour phase was studied by Sabatier and Senderens. Under the latter conditions, some decomposition of long side chains may occur.

Bodies such as *diphenyl, diphenyl methane, triphenyl methane,* or *dibenzyl* (s-diphenyl ethane) are also hydrogenated normally[5]; and it is, in most cases,

---

[1] Maxted, Stone: loc. cit.

[2] Maxted, Evans: J. chem. Soc. [London] 1937, 603.

[3] J. physic. Chem. 27, 533 (1923).

[4] Ber. dtsch. chem. Ges. 45, 1464 (1912).

[5] Sabatier, Murat: C. R. hebd. Séances Acad. Sci. 154, 1390 (1912). — J. F. Eijkman: Chem. Weekbl. 1, 7 (1903). — M. Godchot: C. R. hebd. Séances Acad. Sci. 147, 1057 (1908).

possible to obtain an intermediate reduction product in which one ring only has been reduced. Thus, with diphenyl:

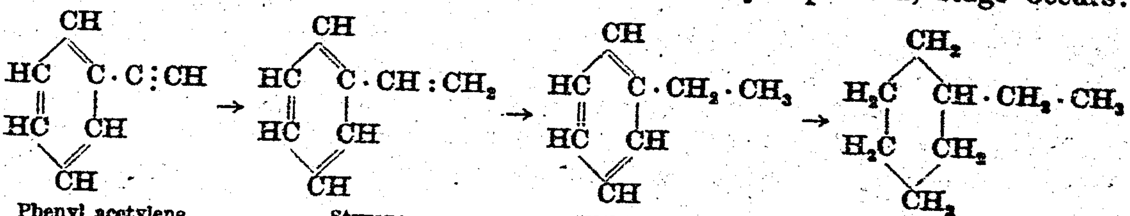
$$C_6H_5 \cdot C_6H_5 \rightarrow C_6H_5 \cdot C_6H_{11} \rightarrow C_6H_{11} \cdot C_6H_{11}.$$

If the hydrogenation is carried out in the vapour phase at a high temperature, there is in many cases a tendency to some form of cyclic *re-arrangement*, for instance, with the formation—by ring closure—of a more stable system, as discussed in greater detail later. Diphenyl methane, in this way, gives fluorene, and dibenzyl passes into phenanthrene.

The possibility of hydrogenation *in stages* also exists with substances which contain benzene rings in addition to an unsaturated aliphatic chain. The most important compounds of this type are *styrene*, $C_6H_5 \cdot CH:CH_2$, *stilbene*, $C_6H_5 \cdot CH:CH \cdot C_6H_5$, *phenyl-acetylene*, $C_6H_5 \cdot C:CH$, and *tolane* (diphenyl acetylene), $C_6H_5 \cdot C:C \cdot C_6H_5$.

Styrene (phenyl-ethylene) is easily hydrogenated to ethyl benzene either in the vapour or liquid phase; but the ethyl benzene then undergoes further hydrogenation only slowly, and, by using a catalyst of low activity the process may be arrested at the intermediate stage. SABATIER and SENDERENS, when using a **copper** catalyst—or even a **nickel** catalyst of low activity—obtained ethyl benzene only[1], whereas, with more active conversion, the ethyl cyclohexane was produced. The rapid absorption of the first molecule of hydrogen compared with that of the succeeding three molecules was also noticed by R. WILLSTÄTTER and V. L. KING[2] during hydrogenation in the liquid phase in the presence of **platinum**, the final product being ethyl cyclohexane, as in SABATIER and SENDERENS' vapour phase method. *Stilbene* reacts very similarly.

With the *phenyl acetylenes* a further, also easily separated, stage occurs:



Phenyl acetylene. Styrene. Ethyl benzene. Ethyl cyclohexane.

This hydrogenation has been studied by KELBER and SCHWARZ[3] with **palladium**, and by SABATIER and SENDERENS for gas phase hydrogenation. In the latter case, a **copper** catalyst only reduced phenyl acetylene as far as ethyl benzene; but ethyl cyclohexane was obtained on using **nickel**. KELBER and SCHWARZ also observed a similar reduction in stages on hydrogenating the corresponding diphenyl acetylene, tolane.

e) *The Benzene-Cyclohexane Equilibrium.*

Where benzene is hydrogenated in the vapour phase at a high temperature, the degree of possible completeness of hydrogenation will depend on the conditions of equilibrium at the temperature and pressure used.

G. DOUGHERTY and H. S. TAYLOR[4] give in Table 28 the calculated values, on the basis of the NERNST approximation formula, for the equilibrium constant:

$$K = \frac{(C_6H_6) \times (H_2)^3}{(C_6H_{12})}$$

at temperatures up to 800° abs.

---

[1] C. R. hebd. Séances Acad. Sci. 132, 1254 (1901).

[2] Ber. dtsch. chem. Ges. 46, 535 (1913).

[3] Ber. dtsch. chem. Ges. 45, 1946 (1912).

[4] J. physic. Chem. 27, 533 (1923).

Experimental determinations were made by G. H. BURROWS and C. LUCARINI[1], using a platinum catalyst, which is more satisfactory than nickel on account of the relative absence of side reactions and decomposition. From this work, K_p is 0.183 at 266—267° C. and 0.617 at 280°. These experimental values agree fairly well with those calculated by the NERNST approximation:

$$\log_{10} K_p = -\frac{Q}{4.57\,T} + 3(1.75\log_{10} T) + 3(1.6),$$

if Q is taken as —51,600 cals.

Table 28.

Temperature °C.	log K_p
0	—16.91
27	—13.85
200	— 1.21
227	— 0.03
527	8.17

The benzene-cyclohexane equilibrium has also been followed experimentally by N. D. ZELINSKY and N. PAVLOV[2] from the dehydrogenation side, using platinum metal catalysts. The observed equilibrium mixtures, i. e. the limit conversions possible with a stoichiometric mixture of benzene and hydrogen at a total absolute pressure of 1 atm., are summarised in Table 29, in which have also been inserted the values calculated as above on the basis of the NERNST equation. The value of Q, which is required for this calculation, cannot be derived from thermochemical data with great accuracy (see direct measurements of heats of hydrogenation) and has in this case been taken as —49,600 cals. It may be noted that the value of Q obtained by KISTIAKOWSKY and his collaborators[3] is —49,800 cals.

Table 29. *Benzene-cyclohexane equilibrium* (Stoichiometric mixture at 1 atm. total pressure).

Temperature °C.	Limiting percentage conversion of benzene to cyclohexane	
	Observed (ZELINSKY and TAYLOR)	Calculated
264	53.2	63
281	30.0	31
300	16.0	14.3
310	9.6	7.6
332	2.2	1.4
407	1.7	0.1

The agreement between the observed and the roughly calculated figures is fairly good, save at the higher temperatures, considering that the heat of hydrogenation was not accurately known. From the nature of the process:

$$C_6H_6 + 3\,H_2 = C_6H_{12},$$

the equilibrium can be displaced towards cyclohexane both by using an excess of hydrogen over the stoichiometric amount and by employing increased pressure: indeed, calculation shows that the reaction is very susceptible to displacement by pressure. Thus, at a temperature at which K_p has a value of 100 (probably just below 400° C), the influence of pressure on the limiting conversion, with a stoichiometric mixture of benzene and hydrogen, is given in Table 30.

Table 30. *Benzene-cyclohexane equilibrium* ($K_p = 100$)

Pressure atm.	Limiting percentage conversion of benzene to cyclohexane
1	0.4
3	10.4
5	28.2
10	61.0
50	91.5
100	95.4
200	97.5

In practice, however, at such high temperatures, very considerable decomposition occurs; and, while considerable quantities of, for instance, hydrogenated naphthalene are formed during the hydrogenation of naphthalene with high-temperature catalysts such as molybdenum sulphide, if the operation is carried out at a high pressure, the similar treatment of benzene does not, as already mentioned, lead to a good yield of cyclohexane.

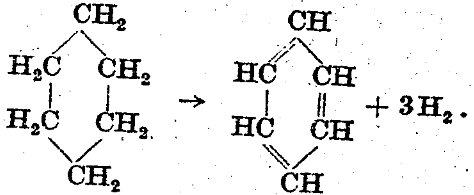
---

[1] J. Amer. chem. Soc. 49, 1157 (1927).

[2] Ber. dtsch. chem. Ges. 56, 1249 (1923).

[3] J. Amer. chem. Soc. 57, 65, 876 (1935); 58, 137, 146 (1936).

Dehydrogenation of Cyclohexane. The reversal of the benzene hydrogenation process at high temperatures was discovered by SABATIER and SENDERENS[1], in that cyclohexane, on being led over active **nickel**, was observed to become resolved into benzene and hydrogen according to the reversed process:

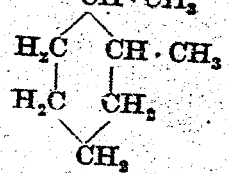


A suitable reaction temperature[2] was found to be about 280°; but the degree of conversion will obviously depend on the equilibrium discussed in the preceding section; and under the conditions used, considerable decomposition with production of methane or of free carbon also occurred. It has been stated by ZELINSKY and KOMMAREWSKI[3] that dehydrogenation with less decomposition may be obtained if the nickel is used in conjunction with alumina, preferably in granular form on a clay support.

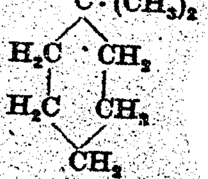
Dehydrogenation with still less by-product formation is obtainable by using the platinum metals, all of which are active for the reaction; and much of the work on dehydrogenation catalysts of this type is due to ZELINSKY and his collaborators. The reaction temperatures imposed by equilibrium conditions are necessarily high, although, if necessary, the equilibrium may be displaced towards the benzene side by working at a reduced pressure or by using an inert gas as a diluent. ZELINSKY[4] recommends, with **palladium**, a reaction temperature of about 300°. As a rough guide to the reaction velocity, it may be mentioned that a 40 per cent conversion of cyclohexane to benzene was obtained on passing, at 300°, cyclohexane at the rate of about 2.5 c.c. per hour per gram of palladium, whereas over 80 per cent conversion was observed with a rate of passage of cyclohexane of 0.3—0.5 c.c. per g. Pd. Cyclohexane may also be dehydrogenated by **oxides of chromium or of vanadium**, a suitable temperature being 385—400° [5]; and **molybdenum oxide or sulphide** has also been used.

As with cyclohexane, a suitable apparatus for carrying out the dehydrogenation is of the type illustrated in Fig. 12, in conjunction with a pelleted or granular palladium catalyst, e.g. palladium supported on granular bauxite. The dehydrogenation of methyl-cyclohexane and of other homologues of cyclohexane may be carried out in very much the same way as that of cyclohexane itself.

In general, the capacity for undergoing simple hydrogenation is—as far as carbocyclic rings are concerned—a property peculiar to true *hydro-aromatic* derivatives only. This may be shown, for instance, by the varying behaviour of the two di-substituted bodies:



1, 2-Dimethyl-cyclohexane
(Easily dehydrogenated).



1, 1-Dimethyl-cyclohexane
(Not dehydrogenated).

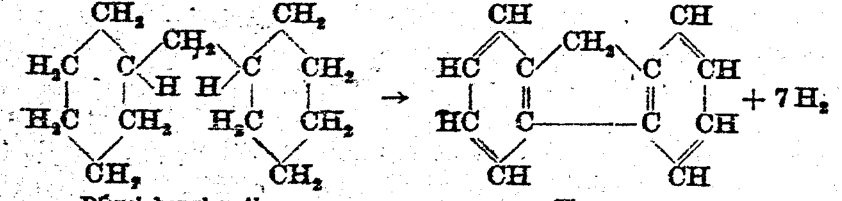
---

[1] C. R. hebd. Séances Acad. Sci. 132, 566 (1901).
[2] SABATIER, MAILHE: C. R. hebd. Séances Acad. Sci. 137, 240 (1903).
[3] Ber. dtsch. chem. Ges. 57, 667 (1924).
[4] Ber. dtsch. chem. Ges. 44, 3121 (1911).
[5] H. S. TAYLOR, L. M. YEDDANAPALLI: Bull. Soc. chim. Belgique 47, 162 (1938).

the first of which undergoes dehydrogenation normally to o-xylene in the presence of platinum, while the derivative having the two methyl groups at the same carbon atom is not susceptible to dehydrogenation, since it is not a true hydroaromatic body in that no corresponding benzene compound is possible[1]. Susceptibility to dehydrogenation is, further, not only peculiar to true 6-carbon hydro-aromatic bodies but is also common to all bodies which fall into this class. Accordingly, not only can all dimethyl cyclohexanes having the methyl groups attached to different carbon atoms be readily dehydrogenated, but also all poly-alkyl cyclohexanes of this type, in addition, for instance, to condensed rings such as are contained in hydrogenated naphthalenes.

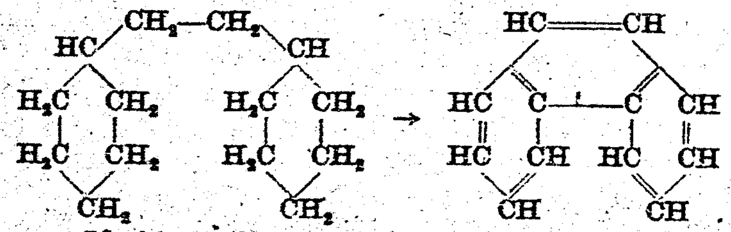
However, while only 6-membered ring can, in general, be dehydrogenated, certain rare exceptions to this rule appear to exist. Thus, Zelinsky has shown that the dehydrogenation of a pentamethylene ring attached to a 6-membered hydro-aromatic ring may involve the cyclopentane ring also, in that *cyclohexyl-cyclopentane* has been stated to undergo dehydrogenation in both rings,—while *phenyl-cyclopentane* or *cyclopentane* itself[2] cannot be dehydrogenated.

In many cases, Zelinsky and his co-workers[3] have shown that dehydrogenation is accompanied by the formation of a more stable ring system. Two examples of this, in which the more stable system is formed by ring closure, are given by the dehydrogenation of *dicyclohexyl-methane* which, on passage over platinum at 300°, passes into fluorene:



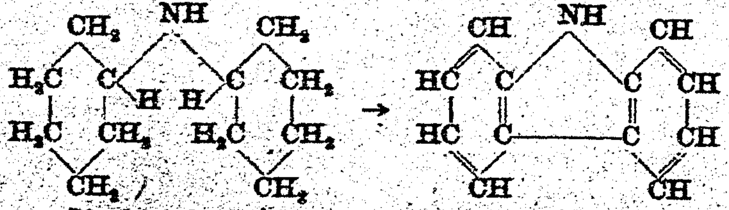
Dicyclohexyl-methane Fluorene

and by *dicyclohexyl-ethane*, which gives phenanthrene:



Dicyclohexyl-ethane. Phenanthrene.

While the general dehydrogenation of heterocyclic bodies is treated more particularly in a later section, it may be mentioned that nitrogen-containing rings can be formed similarly to the above. Thus, *dicyclohexylamine* passes into carbazole:



Dicyclohexylamine. Carbazole.

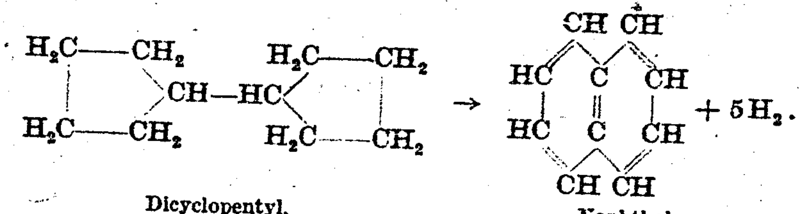
---

[1] Zelinsky, Delzowa: Ber. dtsch. chem. Ges. 56, 1716 (1923).

[2] Zelinsky, Levina: Ber. dtsch. chem. Ges. 66, 477 (1933).

[3] N. D. Zelinsky, I. Titz, L. Fatejew: Ber. dtsch. chem. Ges. 59, 2580 (1926). — Zelinsky, Titz, Gaverdowskaja: ibidem 2590. — Zelinsky, Titz: ibidem 62, 2869 (1929).

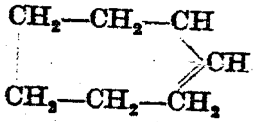
Finally, an instance may be given of a case in which the dehydrogenation of a 5-membered ring is made possible by the formation of a more stable 6-carbon ring system. If *dicyclopentyl* is passed over platinum at 300°, dehydrogenation occurs very readily with production of naphthalene, according to the rearrangement:

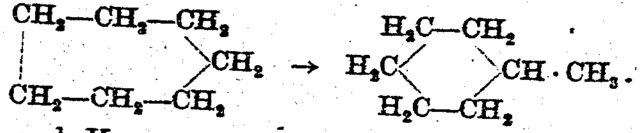


Dicyclopentyl. Naphthalene.

The dehydrogenation of condensed hydro-aromatic rings such as that in decahydronaphthalene is treated later in conjunction with the hydrogenation of the respective hydrocarbon.

f) Hydrogenation of 7- and 8-carbon Rings.

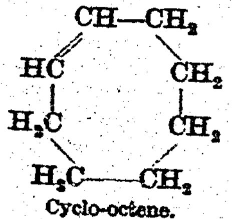
Cycloheptene, , may be hydrogenated with nickel to give a normal product, cycloheptane[1] and probably this reaction would take place more smoothly with platinum-metal catalysts at room temperature, since R. Willstätter and T. Kametaka[2] have shown that cycloheptane, at high temperatures, readily undergoes re-arrangement to methyl-cyclohexane, with formation of the more stable 6-carbon ring.



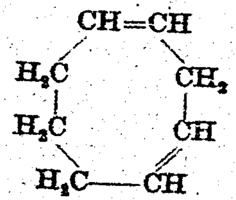
Willstätter and Kametaka have also examined the hydrogenation of $\Delta^{1,3}$-cycloheptadiene which, like cycloheptene, gives cycloheptane.

Much of the work in the field of 8-carbon rings is due to Willstätter and his collaborators[3].

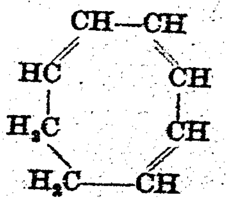
The hydrocarbons which have been investigated include:



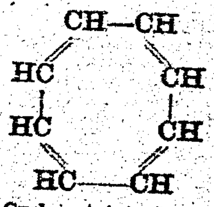
Cyclo-octene.



Cyclo-octadiene (1-4).



Cyclo-octatriene (1-3-5).



Cyclo-octatetraëne (1-3-5-7).

All these hydrocarbons are readily hydrogenated to cyclo-octane by platinum or other catalysts. The cyclooctatetraëne studied is of special interest, since it is the 8-carbon counterpart of benzene. It shows, however, olefinic rather than benzenoid properties. Thus, it adds eight hydrogen atoms quickly in the pre-

---

[1] N. A. Rosanow: J. russ. physik.-chem. Soc. 48, 309 (1916).

[2] Ber. dtsch. chem. Ges. 41, 1480 (1908).

[3] R. Willstätter, H. Veraguth: Ber. dtsch. chem. Ges. 38, 1975 (1905); 40, 957 (1907). — Willstätter, T. Kametaka: Ebenda 41, 1480 (1908). — Willstätter, E. Waser: Ebenda 43, 1176 (1910); 44, 3423 (1911). — Willstätter, M. Heidelberger: Ebenda 46, 517 (1913).

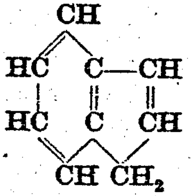
sence of platinum in contrast to the relatively slow addition of hydrogen to benzene: further, it is not readily nitrated, it adds bromine immediately and it reacts violently with potassium permanganate.

On treating *cyclo-octane* with **nickel** at a high temperature, no dehydrogenation occurs; but the hydrocarbon, as was the case with cycloheptane, undergoes a cyclic re-arrangement to form a 6-carbon ring, dimethyl-cyclohexane being produced:

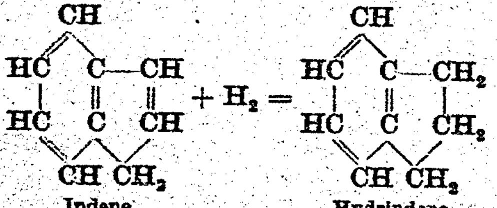
$$C_8H_{16} \rightarrow C_6H_{10} \cdot (CH_3)_2 .$$

g) *Hydrogenation of condensed carbocyclic rings.*

The hydrogenation of condensed benzene rings is very similar to that of benzene itself, in that these bodies are hydrogenated by the same general methods. The reaction, further, is reversible, the equilibrium between the hydrogenated bodies and their parent condensed aromatic hydrocarbon being analogous to that between cyclohexane and benzene. The chief point of difference lies in the frequently observed greater ease of reduction of one or more of the component rings compared with others. Thus, naphthalene is relatively easily and quickly reduced to the tetra-hydro derivate, in which one ring only becomes saturated. The reduction of the second ring then proceeds, if the hydrogenation is continued, considerably more slowly and with greater difficulty.



Indene, which is the simplest of the common condensed ring hydrocarbons, contains one aromatic and one five-membered ring, the latter being far more easily hydrogenated. Consequently, the most easily made reduction product is dihydroindene: indeed, reduction to this stage occurs with sufficient ease to be effected with nascent hydrogen; and in this the bond hydrogenated resembles a very reducible ethylenic linkage. J. v. Braun, Z. Arkuszewski and Z. Köhler[1] carried out the reduction catalytically, with **palladium** in methyl alcohol solution, and obtained a quantitative yield of dihydroindene (hydrindene) in place of the far lower yield usually obtained by reduction with nascent hydrogen, e. g. with sodium in absolute alcohol[2]. The bond hydrogenated is shown in the equation:



Indene. Hydrindene.

Hydrindene is more readily made in large quantities by hydrogenation in a liquid state in the presence of **nickel**. J. v. Braun and G. Kirschbaum[3] employed an autoclave provided with a rotating agitator and, with a reaction temperature of 200°, were able to reduce 500 g. of indene to hydrindene in 2 hours with a hydrogen pressure of 10—15 atm.

---

[1] Ber. dtsch. chem. Ges. 51, 282 (1918).

[2] Gattermann: Liebigs Ann. Chem. 347, 382 (1906).

[3] Ber. dtsch. chem. Ges. 55, 1680 (1922).

The hydrogenation to this stage is, of course, not reversible, since the benzene ring is not saturated; but complete reduction, involving also the benzene ring, has been obtained by J. F. Eijkman[1] by passage of hydrindene vapour and hydrogen over **nickel.**

Naphthalene is undoubtedly the most important hydrocarbon of the condensed class, both from the standpoint of its availability in relatively large quantities and from the very large amounts of tetrahydro- and decahydronaphthalene (tetralin and decalin) which are now made technically.

It may be hydrogenated in the vapour phase, in solution, or in a liquid state without a solvent, the first and last of these methods being the more important. In the early work of Sabatier and Senderens[2], naphthalene and hydrogen were passed over finely divided **nickel** at 175—200°, both tetrahydro- and decahydronaphthalene being produced according to the condition employed.

The hydrogenation of naphthalene by Sabatier and Senderens' method has also been studied by H. Leroux, who led the mixture of naphthalene and hydrogen over pumice-supported nickel contained in a tube which was maintained at reaction temperature by insertion through a heated metal block[3]. The naphthalene-hydrogen mixture was obtained by bubbling hydrogen through a heated wash-bottle containing melted naphthalene. Reduction to tetrahydronaphthalene took place easily at a working temperature of 200°, a convenient temperature for the naphthalene wash-bottle being 150°; and the decahydro derivative could be obtained either from naphthalene or, more easily, from tetrahydronaphthalene by slow passage at 160° over very active nickel, prepared by reduction at 250°. If the working temperature rose above 170°, Leroux observed evidence of dehydrogenation.

An alternative procedure in vapour-phase hydrogenation involves the use, as the catalyst, of compact nickel turnings, the surface of which has been previously activated by anodic oxidation. E. J. Lush[4], working with a catalyst of this type, found that substantially pure tetrahydronaphthalene could be obtained at 160—200° with a moderate hydrogen pressure. Further conversion to the decahydro compound was only obtained to any degree if the conditions were changed so that naphthalene or tetrahydronaphthalene flowed over the nickel turnings in liquid form.

As with benzene, much of the early work on the hydrogenation of naphthalene with platinum metals was done in solution: for instance, Willstätter and Hatt[5] hydrogenated naphthalene in ether or acetic acid in the presence of **platinum,** the reaction taking place more rapidly in the latter solvent. The principal difficulty encountered in hydrogenating naphthalene under these conditions, in which a small and limited amount of catalyst is used, is to be found in the natural sulphur content of all ordinary specimens of naphthalene. These sulphur compounds, which are principally cyclic, are removed technically by special methods. They may, on a small scale, be removed by previous adsorption with platinum black or nickel as described for benzene. Willstätter and Hatt purified their naphthalene in some cases by recrystallisation from a solvent and in other cases by conversion into derivatives which could be separated from the sulphur compounds.

The reaction, as in high-temperature hydrogenation, usually went first of all to *tetrahydro-naphthalene*, and the occurrence in the hydrogenation of dissolved naphthalene with platinum at room temperature, in some cases, of tetrahydro-

---

[1] Chem. Weekbl. 1, 7 (1903). [2] C. R. hebd. Séances Acad. Sci. **132**, 1254 (1901).
[3] Ann. Chim. physique (8) **21**, 458 (1910).
[4] J. Soc. chem. Ind. **46**, 454 (1927). [5] Ber. dtsch. chem. Ges. **45**, 1471 (1912).

naphthalene as a very definite intermediate product—whereas, in other cases, only *decahydronaphthalene*, together with unchanged naphthalene is obtained on interrupting the hydrogenation—has been studied by R. Willstätter and F. Seitz[1], who found that the presence or absence of *oxygen* in the platinum black influences the production either of the tetra- or of the decahydro body. In general, tetrahydronaphthalene was obtained with platinum blacks of relatively high or relatively low oxygen content, while decahydronaphthalene was produced in the presence of intermediate concentrations of oxygen. Willstätter and Seitz postulated two distinct reaction courses leading, on the one hand, to decahydronaphthalene by way of the tetrahydro compound and, on the other, to decahydronaphthalene, possibly by intermediate stages involving dihydro compounds, for details of which the original paper should be consulted.

The hydrogenation of *molten* naphthalene on a larger scale has been described by G. Schroeter[2], who employed an autoclave provided with rotating agitators at hydrogen pressures up to 40 atm. Provision was made for the removal of the hydrogenated product—by distilling off under diminshed pressure—or for the addition of fresh charges of naphthalene; and Schroeter states that many hydrogenations (e. g. 25—40) can in this way be carried out without opening the autoclave or renewing the catalyst. In order that this may be possible, the naphthalene used must, of course, previously be carefully freed from catalyst poisons, for instance, by treating the raw naphthalene, in a molten state, with finely-divided or easily fusible metals. In contradistinction to the behaviour of naphthalene in Willstätter's work with platinum at low temperatures, in which no very definite dividing line between the formation of tetralin and decalin was observed, the hydrogenation proceeds only very slowly after tetrahydronaphthalene has been formed.

Schroeter gives the following directions for the preparation of tetralin. 512 g. (4 g. mol.) of so-called "hot-pressed" naphthalene, which had been previously purified by treatment with metals, as above, was placed in a 4-litre autoclave together with 15—20 g. of the nickel catalyst. After the naphthalene had been melted, the cover of the autoclave, carrying the rotating agitator, valves, manometer etc. was placed in position and hydrogen at 12—15 atm. admitted, the temperature being raised, with agitation, to 180—200° by gas heating or in an oil bath. At this reaction temperature, the pressure usually fell about 1 atmosphere in 45—60 seconds, and it was the practice to raise this again to 12—15 atm. as soon as the pressure had fallen to 5—8 atm., the operation being continued until the calculated volume of hydrogen for conversion to tetralin (178 l. at 0° and 760 mm.) had been absorbed. Working in this way, it was found possible to complete the reduction in 1—$1^{1}/_{4}$ hours. The tetralin obtained had a density of 0.974—0.976 at 20°, melted at —27 to —30°, and boiled at 206—208°.

The further conversion of tetralin to decalin could best be effected by transferring the tetralin to another autoclave in which it was re-hydrogenated in the presence of fresh nickel under similar conditions to those already given. A reaction time of about 4 hours, at 12—15 atm., was required.

While the most usual non-platinum catalyst is nickel, copper chromite[3] also catalyses the reaction satisfactorily at, for instance, 200° and at a pressure of 100—200 atm., tetralin being produced. Further hydrogenation of this to decalin was not observed under these conditions: however, S. Komatsu, K. Sugino, and M. Hagiwara[4] have reported the production both of decalin and of tetralin

---

[1] Ber. dtsch. chem. Ges. 56, 1388 (1923).

[2] Liebigs Ann. Chem. 426, 1 (1922).

[3] D. M. Musser, H. Adkins: J. Amer. chem. Soc. 60, 664 (1938).

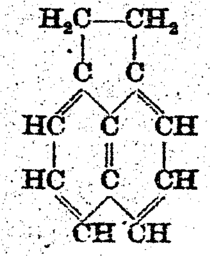
[4] Proc. Imp. Acad. [Tokyo] 6, 194 (1930).

by the hydrogenation of naphthalene with copper at high temperatures and pressures. The use of copper for the hydrogenation of aromatic rings is thus apparently facilitated by a high pressure.

It may also be mentioned that increasing quantities of hydrogenated naphthalenes are being produced by pressure hydrogenation with catalysts of the **molybdenum sulphide** type. The special interest in the use of these sulphur-tolerant catalysts lies in the fact that crude naphthalene, or even naphthalene-containing oils, can be used without purification. The temperature usually employed is about 400⁰, or even slightly above this, the pressure being, for instance, 200 atm.

An entirely different method which has been described for the hydrogenation of naphthalene consists in employing, as the catalyst, **sodium hydride** under a high hydrogen pressure[1]. Naphthalene is treated, at 320⁰ and in the presence of, for instance, 1 g. mol. of sodium hydride to 3 g. mols. of naphthalene, with hydrogen at a pressure of 100—150 atm. in an autoclave provided with suitable agitators. The resulting product is substantially pure tetralin, and the catalyst may be used for further charges. In order to prepare the sodium hydride, sodium is agitated with hydrogen under pressure and at a temperature of 380⁰.

Reverting to the general hydrogenation of naphthalene in the presence of ordinary catalysts such as nickel or platinum, the process is, as with all true hydro-aromatic rings, *reversible* at high temperatures, naphthalene being obtained on distilling either tetrahydro- or decahydronaphthalene over nickel or a platinum metal at, for instance, 300⁰. There appears to be some ambiguity, however, as to whether tetrahydronaphthalene is produced as an intermediate product in the dehydrogenation of the decahydro compound; and probably the latter body first undergoes dehydrogenation to naphthalene which in the presence of the hydrogen produced, may, if the catalyst is a suitable one, then be hydrogenated to some extent to tetralin. Thus, ZELINSKY[2] led decahydronaphthalene over **palladium** at 300⁰ and obtained naphthalene exclusively, while SABATIER[3] states that, in the presence of **nickel** at 200⁰, dehydrogenation of the decahydro to the tetrahydro derivative occurs and that this tetrahydride then passes into naphthalene if the temperature is raised to 300⁰. The difference may, however, be due to the different catalysts, since ZELINSKY found that **platinum** hydrogenated naphthalene, apparently directly, to the decahydro derivative.



Acenaphthene contains two fused benzene rings joined to a pentamethylene residue and, from its structure greatly resembles naphthalene; indeed, it can be regarded as a closed ethyl naphthalene, in which each end of the ethyl chain has become joined to a benzene ring in the manner shown in the structural formula.

It is hydrogenated, like naphthalene, very easily to a tetrahydro derivate, in which one benzene ring still remains unattacked, and, more slowly, to deca-

---

[1] G. HUGEL, FRIESS: Bull. Soc. chim. France (4) 49, 1042 (1931).

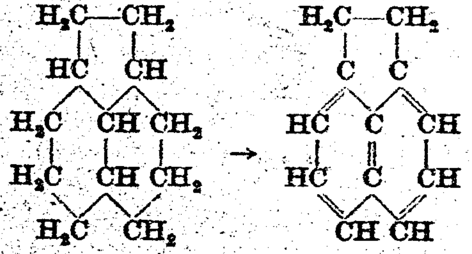
[2] Ber. dtsch. chem. Ges. 56, 1723 (1923).

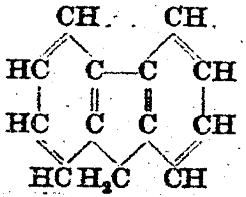
[3] Catalysis in Organic Chemistry, D. van Nostrand Co., p. 230. New York 1922.

hydroacenaphthene. This reaction was carried out with nickel, in the vapour phase at 200—250°, by **Sabatier** and **Senderens**[1] and by M. **Godchot**[2].

Acenaphthene may also very conveniently be hydrogenated in a fused condition. It was reduced in this way with nickel under pressure, both to tetra- and to decahydro-acenaphthene by **Ipatiew**[3]; and J. v. **Braun** and G. **Kirschbaum**[4] found that a quantitative yield of tetrahydroacenaphthene was obtained, also with nickel at a high pressure, by employing the general technique described by **Schroeter** (loc. cit.) for the hydrogenation of naphthalene. According to v. **Braun** and **Kirschbaum**, commercial acenaphthene may be sufficiently purified by one crystallisation from alcohol to be hydrogenated without difficulty. In addition to tetrahydro-acenaphthene, the completely hydrogenated decahydro-acenaphthane has been obtained by **Ipatiew**[5] by working with nickel at a higher pressure; but here again the tetrahydro body was formed as an intermediate product.

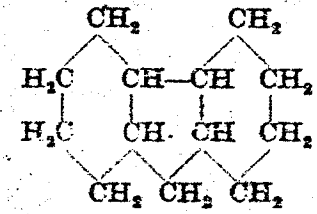
It may be noted that hydrogenated acenaphthenes may be *dehydrogenated* normally in spite of their containing a 5-carbon ring[6], since this latter ring is only partly involved:





Fluorene resembles acenaphthene in containing two 6-carbon and one 5-carbon ring, the method of ring fusion being, however, different.

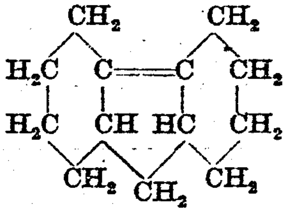
J. **Schmidt** and R. **Mezger**[7] state that the hydrogenation of this body does not take place very easily; but, using **Sabatier** and **Senderens**' method, they report the production of a decahydro derivative, both benzene rings being hydrogenated simultaneously. The formation of decahydrofluorene was apparently confirmed by **Ipatiew**[8] by hydrogenating fluorene with nickel at 290° and 120 atm.; and by repeating the hydrogenation, the product was further converted into the completely saturated compound, dodecahydrofluorene:



It may be noted that, while the above authors agree in reporting the intermediate production of the decahydro compound, this would probably not be expected, and further work on this point would be of interest. The formulation of this body, as an intermediate hydrogenation stage, presents difficulties. **Schmidt** and **Mezger** propose the structure:

---

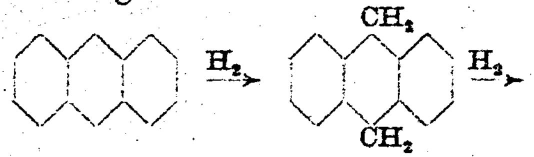
[1] C. R. hebd. Séances Acad. Sci. 182, 1257 (1901).
[2] Bull. Soc. chim. France (4) 3, 329 (1908).
[3] Ber. dtsch. chem. Ges. 42, 2094 (1909).
[4] Ber. dtsch. chem. Ges. 55, 1662 (1922).
[5] Ber. dtsch. chem. Ges. 42, 2094 (1909).
[6] J. v. **Braun**, E. **Hahn**, J. **Seemann**: Ber. dtsch. chem. Ges. 55, 1687 (1922).
[7] Ber. dtsch. chem. Ges. 40, 4560 (1907). [8] Ber. dtsch. chem. Ges. 42, 2092 (1909).



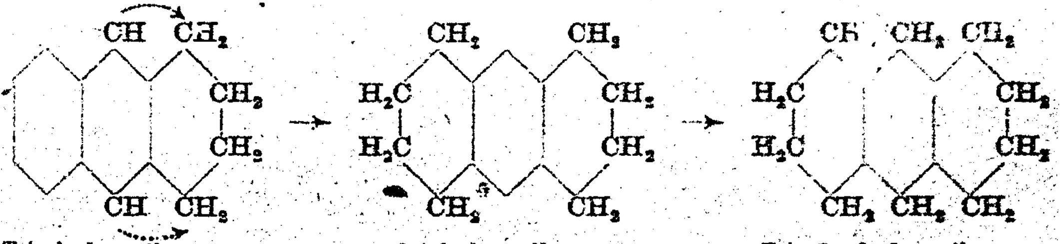
but a residual unsaturated bond of this type should be very readily hydrogenated, in place of remaining unattacked.

M. Godchot[1], who hydrogenated *anthracene* by Sabatier's method in the vapour phase with **nickel**, obtained three main products, namely a tetrahydro, an octahydro- and a fully hydrogenated tetradecahydro-anthracene. The first of these was stated to be the main product at a temperature of 260°: octahydro-anthracene was obtained by slow passage at 200—205°; and the saturated hydride was prepared by further hydrogenating the octahydride at 175—180° slowly and with very active nickel oxide. The hydrogenation of anthracene in stages has also been carried out by W. Ipatiew, W. Jakolew and L. Ratikin[2], who observed the same three reduction products. The reaction was carried out with nickel at 260—270°, at a hydrogen pressure of 100—125 atm. Anthracene, from its structure, will obviously also be capable of hydrogenation in *solution* by means of **platinum** or **palladium.** Probably, however, the most suitable method consists in treating *molten* anthracene, in the presence of supported finely-divided nickel, with hydrogen under pressure in an autoclave provided with an agitating system, as in Schroeter's work on hydrogenation of naphthalene.

The course followed in the progressive hydrogenation of anthracene is of considerable interest. As has been shown by G. Schroeter[3], the first hydrogenation product is the meso-dihydro derivative identical with that obtained non-catalytically, e. g. by the action of sodium in alcoholic solution. On further hydrogenation, however, this undergoes a remarkable change involving the displacement to an outside ring of the hydrogen previously added to the meso ring, a tetrahydro-anthracene, of the structure given below, being formed. The structure of this body was confirmed by its synthesis in other ways, for instance, by its synthesis from tetrahydro-naphthalene (see also J. v. Braun and O. Bayer[4]). The next stage in the hydrogenation is the production of the symmetrical octahydro body which, finally, passes into the fully saturated tetradecahydro-anthracene. The successive stages are thus



Anthracene. Dihydro-anthracene.



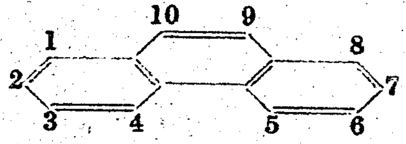
Tetrahydro-anthracene. Octahydro-anthracene. Tetradecahydro-anthracene.

---

[1] C. R. hebd. Séances Acad. Sci. 139, 604 (1904); Ann. Chim. et Physique (8) [illegible], 468 (1907).
[2] Ber. dtsch. chem. Ges. 41, 996 (1908).
[3] Ber. dtsch. chem. Ges. 57, 2063 (1924).
[4] Ber. dtsch. chem. Ges. 58, 2667 (1925).

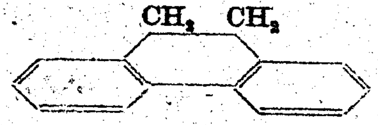
The *de-hydrogenation* of hydrogenated anthracenes takes place normally on passing these over **palladium** at 300°. **Nickel** acts similarly but is apt to give decomposition products in addition to anthracene: further, with nickel, the product may also contain tetrahydro-anthracene.

Phenanthrene, from its structure,



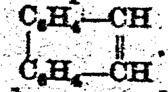
presents the possibility of a large number of hydrogenated products.

Of these, 9,10-hydro-phenanthrene is easily made either by Sabatier and Senderens' method with **nickel**[1] or more conveniently by hydrogenation in the liquid phase in the presence of **platinum**[2]. According to Schmidt and Fischer's procedure, 5 g. of phenanthrene were dissolved in 100 c.c. of ether and 3 g. of platinum black added. The mixture was boiled under a reflux condenser and a rapid current of hydrogen led through the boiling solution. The hydrogenation occupied 6—8 hours (during which additional ether was added to replace that lost in the gas stream) and led to pure 9,10-hydro-phenanthrene:



without the formation of higher hydrogenated products; indeed, both Schmidt and Mezger and Schmidt and Fischer were unable to obtain these by direct hydrogenation. Hydrogenation to the completely reduced hydrocarbon, $C_{10}H_{24}$, was, however, effected by W. Ipatiew, W. Jakolew and L. Ratikin[3] by repeated treatment under pressure in the presence of **nickel**, and intermediate hydrogenation stages were probably also obtained.

The ease of hydrogenation of the 9 : 10 bond is probably due, in spite of the completely cyclic structure of phenanthrene, to the almost purely ethylenic nature of this particular bond, since phenanthrene can be regarded as diphenylene ethylene,



$$\begin{array}{l} C_6H_4\text{—}CH \\ | \qquad\quad \| \\ C_6H_4\text{—}CH \end{array}$$

. From this standpoint, J. R. Durland and H. Adkins[4] have used **copper chromite**—which is characterised by a far greater activity towards ethylenic than towards benzenoid linkings—for the production of pure dihydrophenanthrene. If the temperature is too high, some octahydrophenanthrene is also produced; and the conditions vary somewhat with the activity of the catalyst and with the purity of the phenanthrene. Thus, these authors recommend a temperature of 150° at a pressure of 150—200 atm., under which conditions an 87 per cent yield of the dihydro compound was obtained. At 220°, the main product was an octohydrophenanthrene in which the two outside rings had been saturated. On the other hand, Burger and Mosettig[5], using a less pure sample of phenanthrene, obtained at 200° principally the dihydride. Alloy-skeleton **nickel** may also be used and is especially satisfactory for the production of higher hydrogenation products. Thus, on hydrogenating

---

[1] Ann. Chim. et Physique (4) 8, 319 (1905). — J. Schmidt, R. Mezger: Ber. dtsch. chem. Ges. 40, 4240 (1907).

[2] J. Schmidt, Ernst Fischer: Ber. dtsch. chem. Ges. 41, 4225 (1908).

[3] Ber. dtsch. chem. Ges. 41, 996 (1908).

[4] J. Amer. chem. Soc. 59, 135 (1937).

[5] J. Amer. chem. Soc. 57, 2731 (1935); 58, 1857 (1936).

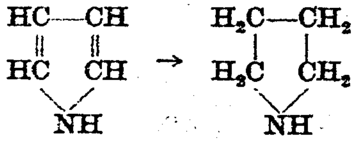
phenanthrene or dihydrophenanthrene dissolved in methyl cyclohexane with this catalyst at 150°, octahydrophenanthrene was produced and, at about 200°, complete hydrogenation to tetradecahydrophenanthracene was obtained.

Of the derivates of phenanthrene, retene (l-methyl-4-isopropyl phenanthrene) has been hydrogenated by Ipatiew, the saturated derivate, $C_{18}H_{32}$, being ultimately produced.

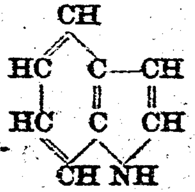
4. Hydrogenation of Heterocyclic Rings.

a) Hydrogenation of Rings Containing Nitrogen.

Pyrrol, which is the simplest common substance of this type, has been hydrogenated normally, by Sabatier and Senderens' method[1] and by means of **platinum** metals at low temperatures[2], pyrrolidine being formed:

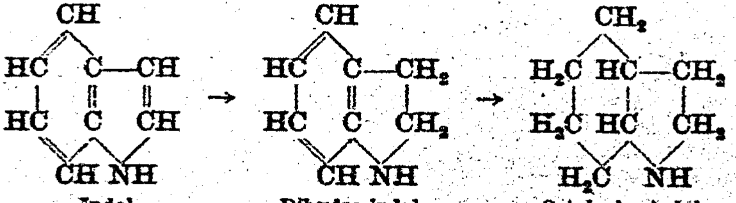

Pyrrol. Pyrrolidine.

Experimental details of the reduction have been given by L. M. Craig and R. M. Hixon[3]. The mixture taken for hydrogenation consisted of 10 c.c. of pyrrol, a slight excess of hydrochloric acid (6 c.c.), 0.2 g. of **platinum oxide** catalyst and 100 c.c. of absolute alcohol. The reduction, which was carried out in a shaker at 4 atm., was complete in about 6 hours. The pyrrol should be re-distilled immediately before use.



Indol, reacts similarly, save that there is here, as with naphthalene, the possibility of hydrogenation in stages; and, if the reaction is carried out in the vapour phase at a high temperature with **nickel**, much decomposition occurs[4].

The hydrogenation of indol in the *liquid phase* with nickel has been studied by J. v. Braun, O. Bayer and G. Blessing[5]. The indol, which was hydrogenated in decalin solution at 225°, gave octahydroindol, with dihydro-indol as the intermediate product:


Indol. Dihydro-indol. Octahydro-indol.

The next higher condensed ring body of the pyrrol group is *carbazol*, which is produced by the addition of another benzene ring to indol. The hydrogenation of this body was examined by M. Padoa and C. Chiavis[6] by distillation over **nickel** at 200° and at a pressure of 10 atm. Under these conditions considerable decomposition was observed with formation of indol derivatives. Hydrogenation

---

[1] M. Padoa: Atti R. Accad. Lincei (1) 15, 29 (1906); Gazz. chim. ital. 36 (2), 317 (1906).

[2] Willstätter, Hatt: Ber. dtsch. chem. Ges. 45, 1477 (1912).

[3] J. Amer. chem. Soc. 52, 806 (1930).

[4] M. Padoa, O. Carrusco: Atti R. Accad. Lincei (1) 15, 699 (1906).

[5] Ber. dtsch. chem. Ges. 57, 392 (1924).

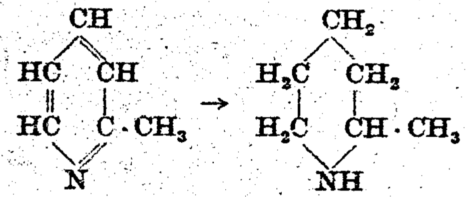
[6] Atti R. Accad. Lincei (5) 16 (2), 762 (1907).

in the *liquid phase* with nickel, also under pressure, was more successful[1]. Thus, N-methyl-carbazol gave a tetrahydro and an octahydro derivative. Reduction to the saturated dodecahydro-N-methyl carbazol was not obtained.

The hydrogenation of *pyridine*, which is the nitrogen analogue of benzene, is of considerable importance. Early work on this subject includes the conversion by Skita and Meyer[2] of pyridine to piperidine by hydrogenation with colloidal **platinum metals** and investigations by Sabatier and Mailhe[3] of the gas-phase hydrogenation of pyridine with **nickel**, in the course of which much decomposition was observed.

Later work has shown that pyridine may be hydrogenated by any of the ordinary hydrogenation methods, even in the vapour phase with nickel if care is taken to avoid overheating. The process is, however, rather slow even with pure pyridine.

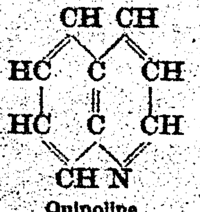
Homologues of pyridine undergo hydrogenation similarly. Thus, the hydrogenation of α-picoline, α,γ-lutidine and 2,4,5-collidine in the liquid phase with platinum at a slight pressure (2—3 atm.) has been examined by A. Skita and W. Brunner[4], normal reaction products being obtained, e. g. with α-picoline:



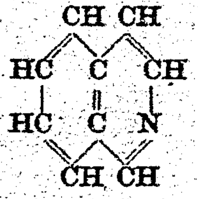
A very suitable method of hydrogenation is with a kieselguhr-supported nickel catalyst in the *liquid phase* at a high hydrogen pressure in an autoclave fitted with suitable agitating gear or, on a smaller scale, in a high-pressure shaker. Thus, Adkins and Cramer[5], who used this type of technique, obtained substantially complete hydrogenation after about 10 hours treatment at 200°, with a hydrogen pressure of 25 to 175 atmospheres. Catalysts such as **nickel chromite** or **nickel molybdite** may also be used.

The process, like the hydrogenation of benzene, is reversible; and the *dehydrogenation* of piperidine in the presence of **platinum** and of **palladium** has been examined by N. Zelinsky and G. Pawlow[6]. These authors give figures for the percentage dehydrogenation obtained at various temperatures, but the equilibrium conditions were not measured. Palladium, as in other dehydrogenations, was a better catalyst than platinum.

Quinoline and *isoquinoline*



Quinoline.



Isoquinoline.

are each very easily hydrogenated to the tetrahydro derivative and, far more slowly, to the fully saturated decahydro compound, the reduction being thus

---

[1] J. v. Braun, H. Ritter: Ber. dtsch. chem. Ges. 55, 3792 (1922).
[2] Ber. dtsch. chem. Ges. 45, 3579 (1912).
[3] C. R. hebd. Séances Acad. Sci. 144, 784 (1907).
[4] Ber. dtsch. chem. Ges. 49, 1597 (1916).
[5] J. Amer. chem. Soc. 52, 4349 (1930).
[6] Ber. dtsch. chem. Ges. 57, 669 (1924).

very similar to that of naphthalene. In this process the heterocyclic ring is reduced first.

In the case of quinoline, hydrogenation with **colloidal platinum** at room temperature has been described by A. Skita and W. A. Meyer[1]. In acetic acid solution. complete reduction to decahydroquinoline was obtained with a hydrogen pressure of 3 atm.; and the reaction could be stopped at the tetrahydro compound by interrupting the absorption after the required volume of hydrogen had been taken up. At atmospheric pressure, with a platinum catalyst, the reaction may stop at the tetrahydro stage. Quinoline was also hydrogenated by W. Ipatiew[2] with **nickel** at a high pressure, both the deca- and the tetra-hydride being obtained.

The hydrogenation of quinoline and its homologues in the liquid phase with nickel under pressure has, further, been studied in considerable detail by J. v. Braun, A. Petzold and J. Seemann[3]. As a method of purification, the quinoline was recrystallised from alcohol in the form of its difficultly soluble sulphate. It then hydrogenated at 200—215°, the reaction proceeding rapidly (in 60—70 mins.) to tetrahydro-quinoline at which stage the absorption of hydrogen suddenly stopped. The yield was quantitative; and homologues of quinoline—e. g. methyl, ethyl, phenyl and other quinolines—could be reduced to tetrahydro derivatives similarly. On raising the temperature to 250°, some decahydroquinoline was formed. W. S. Ssadikow and A. K. Michailow[4] have used an **osmium-ceria catalyst** for this reaction, tetra-and decahydroquinoline being obtained.

The hydrogenation of *isoquinoline* occurs very similarly. Tetrahydro-isoquinoline, in which the nitrogen ring is hydrogenated, was made by Skita[5] by liquid-phase hydrogenation with **platinum**; and the reduction, as with quinoline, could be pushed to completion by using a higher pressure, e. g. 3 atm.[6]

The reduction of isoquinoline has also been studied by J. Raneldo and A. Vidal[7] who, on hydrogenating with **platinum oxide**, obtained principally the tetrahydro compound if the reaction was carried out at room temperature and decahydroisoquinoline if the temperature was raised to 100°.

The hydrogenation process, both with quinoline and isoquinoline, is reversible, as would be expected from the nature of the rings involved. The *dehydrogenation* of tetrahydroquinoline in the presence of **nickel** at 190° was investigated by M. Padoa and G. Scagliarini[8], who observed, however, considerable decomposition and the formation of skatol.

Acridine, which is the nitrogen analogue of anthracene, should be capable of hydrogenation by stages in a smilar way. In the vapour phase, in the presence of **nickel** at 270°, decomposition to dimethyl quinoline was, however, obtained by Padoa and Fabris[9].

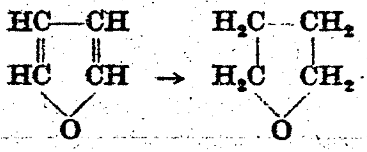
b) *Hydrogenation of Rings Containing Oxygen.*

The most important fundamental substance of this type if *furfurane*, the hydrogenation of which was studied by A. Bourgnignon[10] by passing a mixture

---

[1] Ber. dtsch. chem. Ges. 45, 3593 (1912).
[2] Ber. dtsch. chem. Ges. 41, 991 (1908).
[3] Ber. dtsch. chem. Ges. 55, 3779 (1922).
[4] Ber. dtsch. chem. Ges. 61, 1800 (1928).
[5] Chemiker-Ztg. 38, 605 (1914).
[6] A. Skita: Ber. dtsch. chem. Ges. 57, 1977 (1924).
[7] An. fisic. Quim. 28, 76 (1930). [8] Atti R. Accad. Lincei 17 (1), 728 (1908).
[9] Atti R. Accad. Lincei 16 (1), 921 (1907).
[10] Bull. Soc. chim. Belgique 22, 87 (1908).

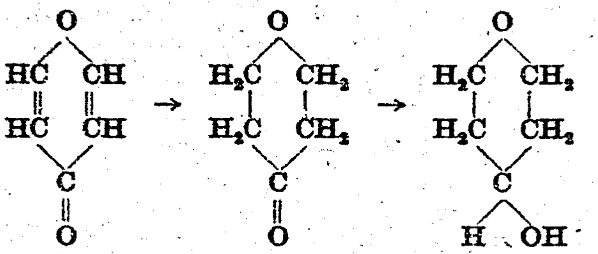
of hydrogen and furfurane over nickel at 170°, tetrahydrofurfurane being formed:



Under these conditions, however, decomposition products were also obtained.

Of furfurane derivatives, the aldehyde, furfural, is of special interest by reason of its availability on a large scale. Its hydrogenation will be dealt with in a later section.

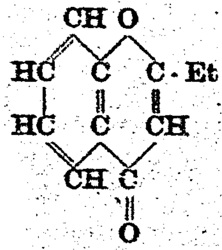
The hydrogenation of *pyrones* may lead to at least two types of product, according to whether the ring alone, or the extra-cyclic oxygen atom, in addition to the nucleus, is attacked. Thus, from γ-pyrone, simple tetrahydropyrone or γ-hydroxytetrahydropyran are obtained.



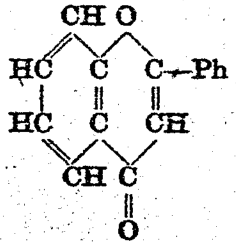
γ-Pyrone. Tetrahydropyrone. γ-Hydroxytetrahydropyran.

R. Monzingo and H. Adkins[1] recommend, in order to obtain a relatively simple product, the carrying out of the reduction as quickly and at as low a temperature as is compatible with the catalyst employed. Thus, with copper chromite at 120—135°, a 50 per cent yield of the hydroxytetrahydropyran, together with 23 per cent of tetrahydropyrone, was obtained. The hydrogenation was, as is usual with copper chromite, carried out under pressure, the pyrone being dissolved in ethyl alcohol. Raney nickel may also be used at, of course, a lower temperature.

Similar alternative products are formed during the hydrogenation of other bodies of pyrone type, for instance, *chromones* or *flavones*:



2-Ethylchromone.



Flavone (2-Phenylchromone).

II. Various Derivatives.

In the first part of this systematic survey, particular attention has been paid to the hydrogenation of hydrocarbons and of fundamental ring systems generally. It is now proposed to deal with various derivatives of these basic structures, these derivatives being classified for convenience according to their chemical nature.

In some cases, the hydrogenation of a derivative differs little from that of its parent body: thus, the reduction of benzoic acid or of oleic acid, so long as only the ethylenic double bond or the benzene ring is hydrogenated, closely

---

[1] J. Amer. chem. Soc. 60, 669 (1938).

resembles the reduction of the parent hydrocarbon. If, however, the special group contained in the particular class of derivates—in this instance, the carboxyl group—itself undergoes reduction, the reaction involved is fundamentally different. For example, oleic acid may be reduced to the corresponding unsaturated alcohol, to the saturated alcohol, or even to the hydrocarbon, the process being thus not merely one of simple saturation, in that the replacement of oxygen by hydrogen and the splitting off of water may occur.

It will be convenient to deal first of all with the reduction of alcohols and ketonic bodies, then with other oxygen-containing derivatives and, finally, with derivatives containing elements such as nitrogen or the halogens.

1. Hydrogenation of Alcohols and Phenols.

The hydrogenation of an unsaturated alcohol takes place in much the same way as the reduction of the corresponding hydrocarbon, save that, particularly if a high reaction temperature is employed, the process may also involve the elimination of the hydroxyl group and the formation of a hydrocarbon by the splitting off of water. Thus, with *allyl alcohol*:

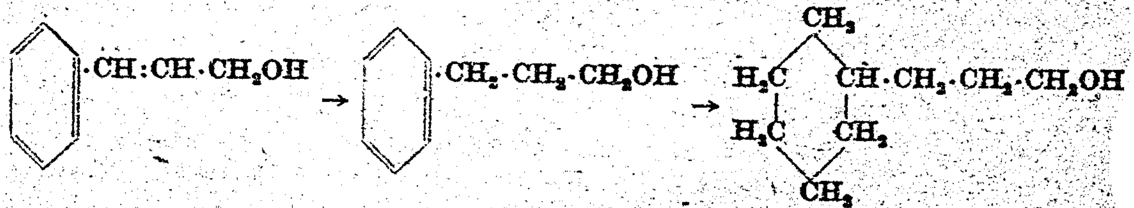
$$\underset{\text{Allyl alcohol.}}{CH_2:CH\cdot CH_2OH} \rightarrow \underset{\text{n-Propyl alcohol.}}{CH_3\cdot CH_2\cdot CH_2\cdot OH} \rightarrow \underset{\text{n-Propane.}}{CH_3\cdot CH_2\cdot CH_3}.$$

Under ordinary conditions, only the first of these processes occurs. For instance, SABATIER[1] hydrogenated allyl alcohol by the vapour method over **nickel** at temperatures up to 170° and obtained propyl alcohol without appreciable production of propane. The easiest way of hydrogenating allyl alcohol is in the liquid phase in a shaker in the presence of **platinum** or **palladium.** The hydrogen is absorbed at a normal velocity for an ethylenic bond, some typical rates for which are given later in connection with the hydrogenation of ethylenic acids.

Higher ethylenic alcohols may be hydrogenated similarly. Many of these, which were previously not very accessible, have been made available by the reduction of the carboxyl group of the corresponding unsaturated acid or its esters without attacking the double bond. For instance, by hydrogenation in the presence of **zinc chromite**, oleic acid passes into *octadecenol*:

$$\underset{\text{Oleic acid.}}{CH_3\cdot(CH_2)_7\cdot CH:CH\cdot(CH_2)_7\cdot COOH} \rightarrow \underset{\text{Octadecenol.}}{CH_3\cdot(CH_2)_7\cdot CH:CH\cdot(CH_2)_7\cdot CH_2OH}.$$

which can, if required, be readily hydrogenated to the saturated alcohol by any of the standard methods. This easy hydrogenation also applies to bodies such as *cinnamyl alcohol*, which is conveniently hydrogenated with **platinum black** in a shaker, in acetic acid solution. The first, rapidly occurring stage is the saturation of the chain, followed far more slowly by that of the nucleus.



It may be noted that allyl alcohol, in addition to being hydrogenated, may, like all alcohols, also be *dehydrogenated*. Thus, on passage over **copper**[2], it

---

[1] C. R. hebd. Séances Acad. Sci. 144, 879 (1907).

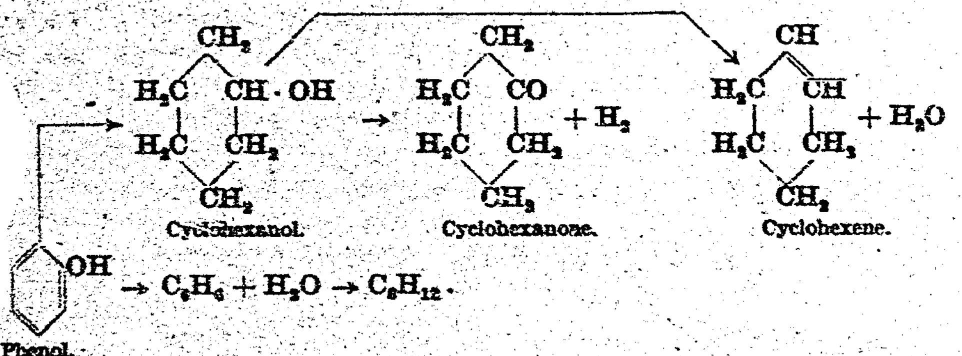
[2] SABATIER, SENDERENS: C. R. hebd. Séances Acad. Sci. 136, 983 (1905). F. H. CONSTABLE: Proc. Roy. Soc. [London], Ser. A 113, 254 (1927).

passes into acrolein, which in virtue of its ethylenic nature takes up hydrogen with formation of *propionaldehyde*.

$$\underset{\text{Allyl alcohol.}}{CH_2:CH\cdot CH_2OH} = \underset{\text{Acrolein.}}{CH_2:CH\cdot CHO} + H_2 = \underset{\text{Propionaldehyde.}}{CH_3CH_2\cdot CHO}.$$

Sabatier and Senderens obtained in this way a yield of over 50 per cent of propionaldehyde containing only a little acrolein; and Constable, who regards the production of propionaldehyde as an isomerisation alternative to rehydrogenation, has examined the relative velocity of these two processes on copper over the temperature range 245—280°. While the dehydrogenation of alcohols generally will be treated in connection with its reverse reaction (hydrogenation of aldehydes and ketones), it may be noted here that the rate of dehydrogenation of allyl alcohol over copper was found by Constable to be approximately equal to that of ethyl alcohol.

The hydrogenation of *phenol* was studied by Sabatier and Senderens[1] by passing this body with hydrogen over **nickel** at 200° or over. The temperature used by Sabatier is somewhat higher than that employed by later workers. Under these conditions cyclohexanol is formed by saturation of the nucleus. This latter body, particularly when passed by itself over a catalyst such as **nickel** or **copper** in the absence of hydrogen, is dehydrogenated to cyclohexanone, or, by loss of water, passes to cyclohexene; but the formation of cyclohexanone may also occur to some degree during hydrogenation. In addition, elimination of hydroxyl may occur with production of benzene or of cyclohexane. The following products are therefore possible:



The latter type of reaction, involving the removal of the hydroxyl group and passage of the phenol into hydrocarbon is usually carried out with a catalyst of the **molybdenum sulphide** type and will be dealt with in a later section.

The influence of various factors in the catalytic reduction of liquid phenol and its homologues to cyclohexanol and corresponding derivatives has been examined in considerable detail by A. Brochet[2] and by G. L. Juchnovski and I. I. Sorokin[3]. **Nickel**, prepared in the ordinary way from the carbonate, has an appreciable activity for the hydrogenation of phenol even at 50°; and this activity was found by Brochet to increase progressively with the temperature up to about 130°, at which it had a value about 10 times that at 55°. For reasonably rapid reaction, an increased pressure was necessary, for instance 10 to 15 atm. at 100—150°, under which conditions the product is stated to be free from cyclohexanone and cyclohexene. The time required for hydrogenation depends, of course, on the temperature and pressure and on the amount of

---

[1] C. R. hebd. Séances Acad. Sci. 137, 1025 (1903).
[2] Bull. Soc. chim. France (4) 31, 1270 (1922).
[3] Ukrainian chem. J. 6 (Tech.), 159 (1931); ex Brit. chem. Abstr., B 1932, 493.

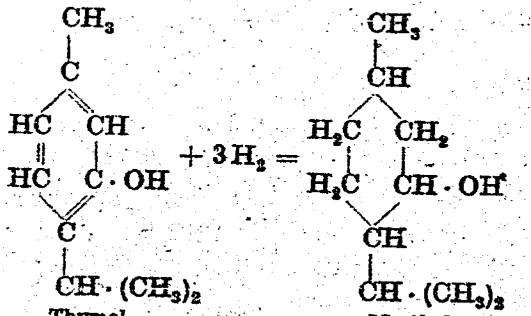
catalyst employed. Thus, Brochet, using 200 g. of phenol with 20 g. of nickel, was able to complete the process in about one hour at 200° at a pressure of 15—25 atm., whereas, in another run, 700 g. of phenol with 7 g. of catalyst were hydrogenated at 150—160° in 20 hours or, with 40 g. of catalyst, 10 hours.

Ortho-, *meta-* and *para-cresol* were found to hydrogenate at about the same rate as phenol itself, the corresponding methylcyclohexanol being produced. In each case the nickel could be used for more than one operation, the average wastage of nickel being stated to be about 1 g. per 150 g. of phenol hydrogenated. Juchnovski and Sorokin's results were very similar and extended also to o-, m- and p-cresol.

Phenol can also be hydrogenated with the platinum metals either in the liquid or in the dissolved state. Thus, Willstätter and Hatt[1] reduced phenol in acetic acid solution with **platinum** and obtained both cyclohexanol and, by further reduction, cyclohexane.

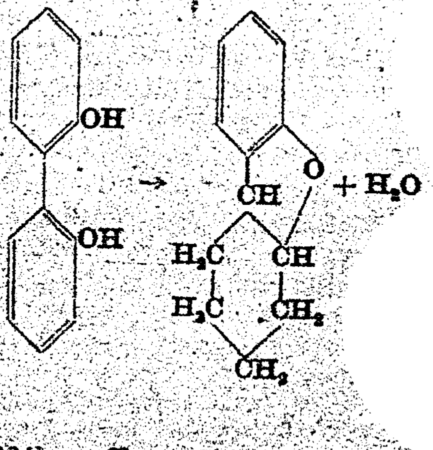
The hydrogenation of phenol and of its simpler homologues—the cresols and xylenols—is of some technical interest, since the corresponding cyclohexanols, and to some extent the cyclohexanones which are obtained from these by dehydrogenation, are now made commercially for use as solvents and for other purposes.

Thymol (3-methyl-6-isopropyl-phenol) is a further homologue the hydrogenation of which is important technically, since, on reduction, it passes into menthol.


Thymol. Menthol.

This reaction is usually carried out in practice by means of **nickel**, with liquid thymol and with a moderate hydrogen pressure, a suitable hydrogenation temperature being 100—150°. Saturation of the ring takes place at the normal rate for reactions of this type and, if the temperature is not too high, little formation of hydrocarbon occurs. Menthol exists in several stereoisomeric forms, which are not of equal physiological activity. The hydrogenation of thymol can, if required, be effected in the vapour phase; but, in this case, reduction to menthane also occurs to a considerable degree[2].

The reduction of certain di-phenols is of interest in view of the manner in which water is eliminated. Thus, J. v. Braun[3], on hydrogenating *o-diphenol* with **nickel** under pressure, obtained principally a semi-reduced diphenylene oxide:



---

[1] Ber. dtsch. chem. Ges. 45, 1475 (1912).

[2] M. Dominikiewicz: Roczniki Farmacji 2, 28 (1924); ex Chem. Zbl. 1924 II, 327.

[3] Ber. dtsch. chem. Ges. 55, 3761 (1922).

With di- and tri-hydroxy phenols, reduction both of the hydroxyl groups and of the ring takes place. Sabatier and Senderens[1] examined the hydrogenation of *pyrocatechin*, *resorcinol* and *hydroquinone* in the vapour phase with **nickel** at 250°. The first product was phenol which, by loss of a further hydroxyl group, passed into benzene.

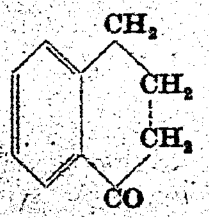
K. Packendorff[2] has *hydrogenated* these bodies with **platinum**. With, for instance, resorcinol, rapid reduction to cyclohexane and cyclohexanol occurred at room temperature. The hydroxyl group is not protected by alkylation.

Of trihydroxyphenols, *pyrogallol* has been reduced by Sabatier and Mailhe[3], the principal product with **nickel** at a relatively low temperature being hexahydropyrogallol in which the hydroxyl groups remain unreduced.

The naphthols are hydrogenated very similarly to the phenols. H. Leroux[4] hydrogenated both α- and *β-naphthol* in the gas phase with **nickel** and obtained the corresponding tetrahydro and, more slowly, the decahydronaphthol. A working temperature of 135° is recommended for the α-compound and 150° for β-naphthol.

The hydrogenation of the naphthols in the *liquid* state has been examined by A. Brochet and R. Cornubert[5]. In a typical run, 200 g. of α-naphthol, containing 20 g. of nickel, were hydrogenated at 130° and at a pressure of 15 atm. The absorption of hydrogen took place fairly rapidly (in two or three hours) to 95 per cent of the volume corresponding with the tetrahydro naphthol, after which the absorption became slow. The reduction of β-naphthol, also to the tetrahydro derivative, proceeded similarly; but the decahydro body could not be obtained easily.

According to G. Schroeter[6], while the reduction of β-naphthol in the liquid phase by hydrogen at moderate pressures, using a nickel catalyst at about 200°, gives a normal product consisting principally of tetrahydro-β-naphthol, the method is, however, not recommended for the preparation of the corresponding α-compound, since the hydrogenation of α-naphthol under these conditions led to a product containing only 25—30 per cent of tetrahydro-α-naphthol, the remainder being tetralin together with about 10 per cent of a ketone, α-ketotetrahydronaphthalene:



It is to be noted that these complications do not occur with the β-compound.

In the case of bodies such as the naphthols, a variety of intermediate products are possible according to whether prior hydrogenation of the oxygen-containing or of the non-substituted ring occurs, or whether oxygen is eliminated, the end-product being of course in every case decahydronaphthalene. The subject has been investigated in some detail by D. M. Musser and H. Adkins[7] with special reference to the difference in the effect produced with **Raney nickel** and with **copper chromite**.

---

[1] Ann. Chim. et Physique (8) **4**, 428 (1905).
[2] Ber. dtsch. chem. Ges. **68**, 1251 (1935).
[3] C. R. hebd. Séances Acad. Sci. **146**, 1193 (1908).
[4] C. R. hebd. Séances Acad. Sci. **141**, 953 (1905); Ann. chim. et Physique (8) **21**, 484 (1910). [5] Bull. Soc. chim. France (4) **31**, 1280 (1922).
[6] Liebigs Ann. Chem. **426**, 68 (1922). [7] J. Amer. chem. Soc. **60**, 664 (1938).

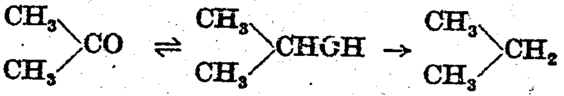
2. Hydrogenation of Aldehydes and Ketones.

The hydrogenation of aldehydic and ketonic groups does not, in general, take place as rapidly as would be expected from the ease with which the reaction can be carried out, even with catalysts of relatively low hydrogenating power, such as copper zinc chromite, or even non-catalytically with nascent hydrogen.

a) *Aliphatic aldehydes and ketones.*

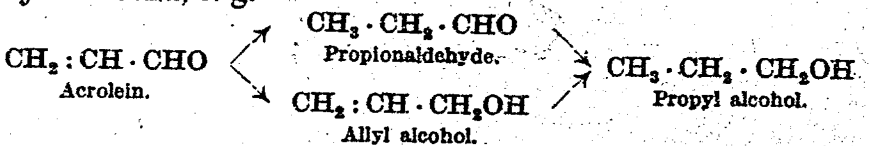
The reduction process, which leads to a primary alcohol in the case of an aldehyde and to a secondary alcohol with ketones, is, moreover, reversible; and may, if the hydrogenation temperature is high, proceed further to the irreversible production of a hydrocarbon by the elimination of oxygen as water. Thus, in the typical cases of acetaldehyde and acetone:

$$CH_3\cdot CHO \rightleftharpoons CH_3\cdot CH_2OH \rightarrow CH_3\cdot CH_3$$



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO \rightleftharpoons \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH_2$$

In addition, unsaturated aldehydes or ketones will also undergo saturation f their ethylenic bond, e. g.



$$CH_2:CH\cdot CHO \rightarrow CH_3\cdot CH_2\cdot CHO \text{ or } CH_2:CH\cdot CH_2OH \rightarrow CH_3\cdot CH_2\cdot CH_2OH$$

The earlier work on the catalytic reduction of aldehydes and ketones generally was carried out by SABATIER and SENDERENS in the vapour phase: they are, however, sometimes more satisfactorily hydrogenated in the liquid state, for instance under pressure in the presence of **nickel**, or, especially if the bodies are volatile, with **platinum**, in which latter case, however, there may be a tendency for the reaction to proceed as far as the hydrocarbon.

The hydrogenation in the vapour phase of *formaldehyde*, *acetaldehyde* and some of the lower homologous aldehydes was studied by SABATIER and SENDERENS in 1903[1]. All gave the corresponding alcohol smoothly and without the formation of by-products when passed with hydrogen over **nickel** at 100 to 140°; and, with these low-boiling bodies, hydrogenation in the gas phase is probably the most suitable method. *Acetone* was reduced in a similar way to isopropyl alcohol without any formation of pinacone. *Methyl-ethyl-ketone*, *dimethyl-ketone* and higher ketones behaved similarly.

For the reverse reaction, namely, the production of aldehydes or ketones by the *dehydrogenation* of primary or secondary alcohols, SABATIER and SENDERENS[2] recommend **copper** in place of nickel, since the latter metal, at the high temperatures required for effective dehydrogenation, is apt to cause decomposition.

The hydrogenation of aldehydes and ketones in the liquid or dissolved state, in the presence of **platinum black**, was examined by G. VAVON[3]. The reaction is somewhat slow. Thus, 40 g. of *acetaldehyde*, diluted with 100 c.c. of water and containing 15 g. of platinum prepared by LOEW's method, absorbed 20 l. of hydrogen after 24 hours shaking at room temperature, the reduction to ethyl alcohol being complete. Other aldehydes hydrogenated by VAVON in the same

---

[1] C. R. hebd. Séances Acad. Sci. 137, 301 (1903); Ann. Chim. et Physique (8) 4, 395 (1905). [2] C. R. hebd. Séances Acad. Sci. 136, 738, 921, 983 (1903).

[3] Ann. Chimie (9) 1, 167 (1914).

way include *isovaleric aldehyde*, $(CH_3)_2 \cdot CH \cdot CH_2 \cdot CHO$, *oenanthic aldehyde*, $CH_3 \cdot (CH_2)_5 \cdot CHO$, and the important terpenic aldehyde, *citral*. Aliphatic ketones were hydrogenated similarly; but, unless these were diluted with water, the reduction went to a large extent as far as the hydrocarbon. As with the aldehydes, the reaction is slow; for instance 60 g. of acetone, diluted with 60 c.c. of water, required to be shaken with 15 g. of platinum for 15 hours at room temperature before the reaction was complete; but the product consisted of substantially pure isopropyl alcohol containing no pinacone. It is to be noted that catalytic hydrogenation both of aldehydes and of ketones differs from reduction with nascent hydrogen (sodium amalgam etc.) not only in giving a resultant free from secondary condensation products but also in leading to a substantially quantitative yield, the yields with nascent hydrogen being often very low. Other simple ketones hydrogenated by VAVON were *methyl-ethyl-ketone* (18 g. of which, in 30 g. of acetic acid, with 10 g. of platinum, required 3 hours for complete reduction to methyl-ethly-carbinol), *diethyl ketone*, and *methyl-propyl-ketone*.

The carbonyl group is, further, easily reduced by catalysts other than those of the classical metallic type. Thus, acetone[1] was readily hydrogenated to isopropyl alcohol by a **zinc chromite** catalyst at 370°, at a pressure of 150 atm., the use of the high pressure being necessitated by equilibrium conditions at the temperature employed. The zinc chromite was inactive for the hydrogenation of ethylenic bonds between carbon atoms.

Catalysts of the sulphide type have also been used. N. A. ORLOV, S. A. GLINSKICH and N. A. IGNATOVITSCH[2] obtained an approximately 60 per cent yield of n-heptane by reducing *di-propyl ketone* in the presence of a **molybdenum-sulphide-cobalt-oxide** catalyst, at a temperature of 345° and with a hydrogen pressure of 100—120 atm. It will be seen that under these conditions the hydrocarbon rather than the alcohol is produced.

b) *Aldehyde-alcohol and Ketone-alcohol Equilibria.*

In the typical cases of acetaldehyde and acetone, the equilibria between these bodies and the corresponding alcohols have been studied quantitatively by E. K. RIDEAL[3].

The reaction heat, Q, in the equation:

$$CH_3CHO + H_2 = CH_3 \cdot CH_2OH + Q,$$

is too indefinite, when derived from heats of combustion to allow the accurate calculation of the equilibrium constant:

$$K_p = \frac{P_{H_2} \times P_{CH_3 \cdot CHO}}{P_{C_2H_5OH}}$$

by means of an expression of the usual type

$$\log_{10} K_p = -\frac{Q}{4.571\,T} + 1.75\,\Sigma\nu \log_{10} T - \frac{\beta\,T}{4.571} + \Sigma\nu\,C$$

or

$$\log_{10} K_p = -\frac{Q}{4.571\,T} + 1.75 \log_{10} T - 3.75 \times 10^{-4}\,T + 2.2$$

n which the chemical constants and the variation with temperature of the specific heats of the aldehyde and alcohol are assumed respectively to be equal

---

[1] J. V. VAUGHEN, W. A. LAZIER: J. Amer. chem. Soc. 53, 3719 (1931).

[2] J. Chim. appl. (russ.) 8, 1170 (1935).

[3] Proc. Roy. Soc. [London], Ser. A 99, 153 (1921).

and to compensate for one another, the chemical constant of hydrogen being taken as 2.2, and β, the temperature coefficient of the specific heat of hydrogen, as 0.001714. This indefiniteness is also true for acetone, for which RIDEAL points out that a discrepancy of 1 per cent in the determination of the heats of combustion would make Q indefinite between the values 12,000 and 21,000 cals.

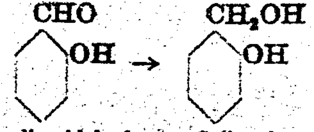
Experimental measurements were carried out by a static method in the presence of copper. The variation of the equilibrium with the temperature was very large, as would be expected on the basis of the calculated values. The percentage decomposition, for ethyl and for isopropyl alcohol observed at various temperatures, is summarised in Table 31.

Table 31.

Substance	Temperature °C	K_p	Percentage decomposition at 1 atm.
Ethyl alcohol	105	6.44×10^{-4}	2.5
	150	1.60×10^{-3}	3.9
	175	4.77×10^{-3}	6.7
	200	1.21×10^{-2}	10.6
	225	4.52×10^{-2}	19.5
	250	2.32×10^{-1}	38.0
	275	0.91	60.2
Isopropyl alcohol	105	2.82×10^{-3}	5.3
	150	2.04×10^{-2}	13.6
	175	0.177	29.0
	200	0.523	51.1
	225	1.35	66.9
	250	4.82	85.0
	275	12.0	92.8

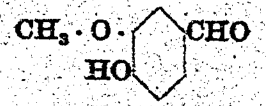
c) *Aromatic Aldehydes.*

The reduction of the simple aromatic aldehydes by SABATIER and SENDERENS' method with nickel leads principally to the hydrocarbon[1]; but they are readily reduced to the corresponding alcohol by liquid phase hydrogenation and, in general, react more rapidly than aliphatic aldehydes: for instance, VAVON (loc. cit., p. 709), working as already described for aliphatic aldehydes, was able to reduce 106 g. of *benzaldehyde* to benzyl alcohol in $2^1/_2$ hours, with 8 g. of platinum black, the aldehyde being diluted with an equal weight of ethyl alcohol as a solvent. *Salicylic aldehyde* passed equally rapidly into saligenin, the yield being quantitative:

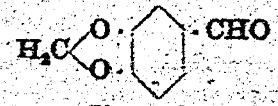


Salicylic aldehyde. Saligenin.

Reduction in the liquid phase with platinum has also been applied to various other aromatic aldehydes; and the reaction is a general one, being also applicable to bodies such as *vanillin* and *piperonal.*



Vanillin.



Piperonal.

It will be noted that in all the above hydrogenations, the aldehydic group is attacked before the benzene nucleus.

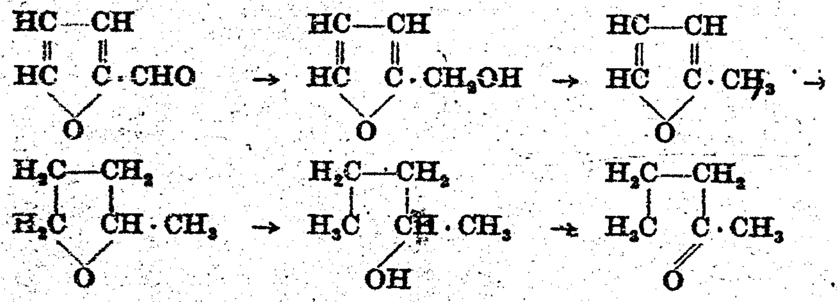
d) *Hydrogenation of Furfural.*

Of cyclic aldehydes other than aromatic aldehydes, furfural, in which the aldehydic group is attached to an oxygen-containing ring, is of special interest on account of its large-scale availability. The hydrogenation of furfural was

---

[1] C. R. hebd. Séances Acad. Sci. 137, 301 (1903).

carried out by the vapour method, with **nickel**, by M. Padoa and U. Ponti[1]. The primary product was furfuryl alcohol, but nuclear hydrogenation also occurred and there was, subsequently, some ring fission with the production of methyl butyl alcohol and of methyl propyl ketone:



Some furane was also formed by the splitting off of the chain without ring fissure.

The hydrogenation of furfural takes place somewhat more smoothly at lower temperatures in the liquid phase; but, if hydrogenation is allowed to proceed to completion, some decomposition products appear always to be formed. Thus, furfural has been hydrogenated in the presence of **platinum**, which may be introduced as **platinum oxide**[2]. Reduction as far as furfuryl alcohol occurred quantitatively and without complication; but, on continuing the hydrogenation beyond this stage, tetrahydrofurfuryl alcohol, pentane-diol-1,2, pentane-diol-1,5 and n-amyl alcohol were produced. The reduction comes to a standstill unless the catalyst is periodically oxygenated; and the platinum was also found to be activated by small quantities of **ferrous chloride**. The best results were obtained by the use of 50 g. of furfural, 150 c.c. of alcohol, 1 g. of catalyst and 1.2 c.c. of 0.1 M ferrous chloride. In the shaker used by Kaufmann and Adams, and with a hydrogen pressure of 1—2 atmospheres, about four molecular equivalents of hydrogen were absorbed in four hours, during which period three activations with oxygen were necessary.

e) *Aromatic Ketones.*

The hydrogenation of aromatic ketones may be carried out by methods very similar to those already given for aliphatic ketones; but with **nickel** at high temperatures, there is a tendency towards the formation of hydrocarbon and even to the saturation of the nucleus. For instance, Sabatier and Murat[3] obtained, from *benzophenone*, diphenyl methane or dicyclohexyl methane according to the temperature and the activity of the nickel:

$$\underset{\text{Benzophenone.}}{C_6H_5 \cdot CO \cdot C_6H_5} \rightarrow \underset{\text{Diphenyl methane.}}{C_6H_5 \cdot CH_2 \cdot C_6H_5} \rightarrow \underset{\text{Dicyclohexyl methane.}}{C_6H_{11} \cdot CH_2 \cdot C_6H_{11}} .$$

Analogous results, namely reduction to hydrocarbon, were also obtained with mixed aromatic-aliphatic ketones such as *acetophenone*, $C_6H_5 \cdot CO \cdot CH_3$, which was reduced to ethyl benzene. Hydrocarbons are also obtained at high temperatures in the vapour phase with **copper**.

The reduction of aromatic ketones to *alcohols* was carried out, with **platinum black** at room temperature, by Vavon (loc. cit., p. 709). The reduction of these bodies does not take place very quickly and requires the use of relatively active platinum. As an example, 18 g. of *benzophenone*, dissolved in 40 g. of ether,

---

[1] Atti R. Accad. Lincei (5) 15 (2), 610 (1906); Gazz. chim. ital. 37 (2), 105 (1907). [2] W. E. Kaufman, R. Adams: J. Amer. chem. Soc. 45, 3029 (1923).
[3] Ann. Chim. et Physique (9) 4, 264 (1915).

together with 8 g. of platinum black, required 3 hours' treatment in a shaker at room temperature for conversion into diphenyl carbinol.

$$C_6H_5 \cdot CO \cdot C_6H_5 \rightarrow C_6H_5 \cdot CH(OH) \cdot C_6H_5.$$

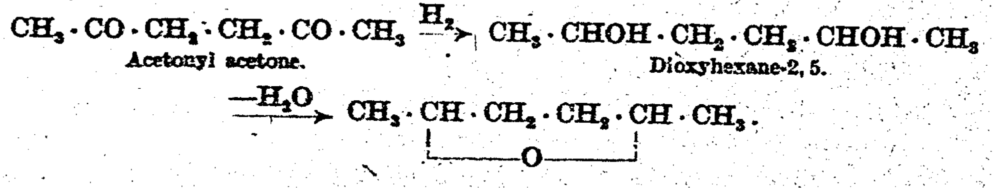
With *acetophenone* dissolved in acetic acid the most readily produced derivative, even with platinum at low temperatures, was the hydrocarbon, ethyl benzene; but some alcohol could be isolated from the product if the reaction was interrupted after the absorption of one g. mol. of hydrogen.

f) *Hydrogenation of diketones.*

Diketones, whether aliphatic or containing aromatic nuclei attached to a ketonic chain, are reduced in the vapour or liquid state by methods very similar to those used for the mono-ketones. Thus, SABATIER and SENDERENS[1] hydrogenated a number of typical α-, β-, and γ-diketones in the vapour phase with nickel at 140—150°. Normal products were obtained with the α- and γ-diketones examined, e. g.

$$\underset{\text{Di-acetyl.}}{CH_3 \cdot CO \cdot CO \cdot CH_3} \rightarrow \underset{\text{Butanolone-2, 3.}}{CH_3 \cdot CHOH \cdot CO \cdot CH_3} \rightarrow \underset{\text{Butanediol-2, 3.}}{CH_3 \cdot CHOH \cdot CHOH \cdot CH_3},$$

but the β-diketone examined (acetyl acetone) underwent considerable decomposition under the conditions employed. With acetonyl acetone dehydration of the diol occurred:

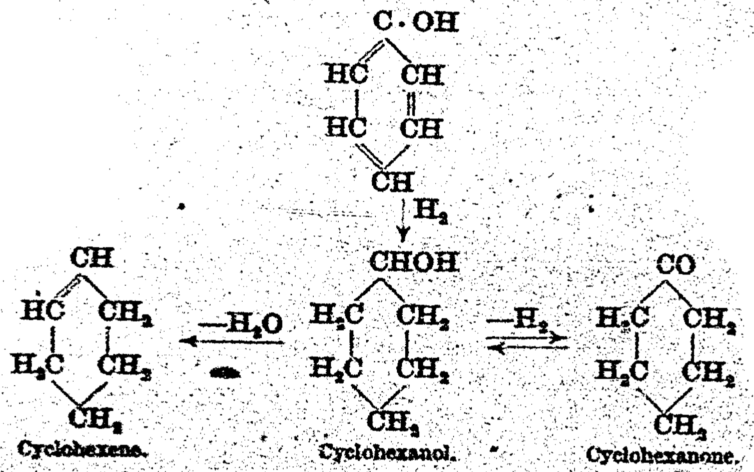


$$\underset{\text{Acetonyl acetone.}}{CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3} \xrightarrow{H_2} \underset{\text{Dioxyhexane-2, 5.}}{CH_3 \cdot CHOH \cdot CH_2 \cdot CH_2 \cdot CHOH \cdot CH_3}$$
$$\xrightarrow{-H_2O} CH_3 \cdot \underbrace{CH \cdot CH_2 \cdot CH_2 \cdot CH}_{O} \cdot CH_3.$$

Diketones are also hydrogenated in the *liquid* phase, either with platinum or, preferably under pressure, with nickel. In this case the reaction proceeds smoothly, without the formation of by-products as at high temperatures.

g) *Hydrogenation of Cyclic Ketones.*

A further class of ketones exists in which the oxygen of the carbonyl group is actually attached to a ring. The most important of these is *cyclohexanone*, which is reversibly hydrogenated to cyclohexanol by nickel. SABATIER and



---

[1] C. R. hebd. Séances Acad. Sci. 144, 1086 (1907).

SENDERENS[1] recommend for the hydrogenation a temperature of 160—175°, with a large excess of hydrogen.

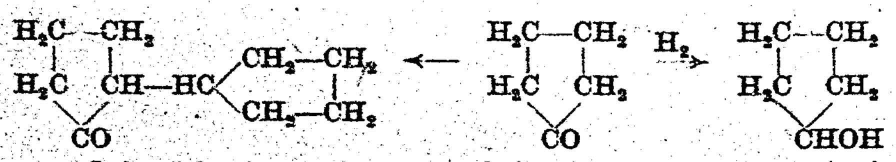
The reverse reaction, namely, the *dehydrogenation* of cyclohexanol, which is easily made by the hydrogenation of phenol, is of special interest. The principal product is cyclohexanone, but small quantities of cyclohexene and even of benzene are also obtained, the latter particularly if the dehydrogenation catalyst is nickel.

To prepare cyclohexanone from its alcohol, cyclohexanol, the latter may be passed, without hydrogen, over a **copper catalyst** at 300—330°, the cyclohexanone being obtained almost pure. Copper is not, however, as suitable as nickel for the reaction in the hydrogenation direction—namely, for the reduction of cyclohexanone to cyclohexanol—on account of its lower activity and consequent slowness of the reaction. On the other hand, nickel can also be used for the dehydrogenation, provided that the temperature and the activity of the catalyst are carefully controlled in order to avoid decomposition and nuclear dehydrogenation in addition to the loss of hydrogen by the alcoholic group.

The hydrogenation of cyclohexanone in the *liquid* phase with **platinum black** was studied by VAVON[2]. Reduction took place rapidly, substantially pure cyclohexanol being produced. As an index to the speed, 27 g. of cyclohexanone, dissolved in an equal weight of ether, with 8 g. of platinum black underwent complete hydrogenation in 75 minutes in a shaker at room temperature and pressure.

The three *methyl cyclohexanols*, prepared by the hydrogenation of o-, m- or p-cresol are *dehydrogenated*[3] to the corresponding methyl cyclohexanone—or, conversely, the methyl cyclohexanone may be hydrogenated to the methyl cyclohexanol—by methods similar to those used for the parent bodies. SABATIER and SENDERENS, however, observed some nuclear dehydrogenation back to the cresol even in the presence of **copper**. Reasonably pure methyl cyclohexanone, accompanied by a little methyl-cyclohexene and a little cresol, was, however, obtained with this catalyst at 300° [4].

A further cyclic ketone, the hydrogenation of which has been studied by GODCHOT and TABOURY[5], is *cyclopentanone*. This, on hydrogenation over **nickel** in the vapour phase, gave, in addition to the normal products cyclopentanol and cyclopentane, considerable quantities (e. g. 40 per cent) of a condensation product, α-cyclopentyl-pentanone:



Cyclopentyl-pentanone. Cyclopentanone. Cyclopentanol.

The formation of this product, which is apparently produced by the hydrogenation of a condensation product a between two molecules of cyclopentanone, may be avoided by carrying out the hydrogenation at a low temperature. VAVON found, on hydrogenating cyclopentanone dissolved in ether, with **platinum** at room temperature, that only cyclopentanol was produced. 30 g. of the pentanone, in 100 g. of ether, were reduced completely on being shaken at room temperature with 8 g. of platinum black for 4 hours.

---

[1] Ann. Chim. et Physique (8) 4, 401 (1905); C. R. hebd. Séances Acad. Sci. 137, 1026 (1903). [2] Ann. Chimie 1, 187 (1914).

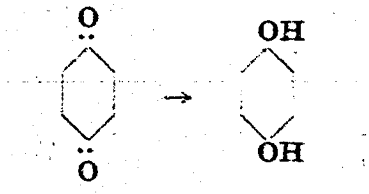
[3] SABATIER, SENDERENS: Ann. Chim. et Physique (8) 4, 466 (1905).

[4] SABATIER, SENDERENS: C. R. hebd. Séances Acad. Sci. 140, 350 (1905).

[5] Ann. Chim. et Physique (8) 25, 41 (1911).

h) *Hydrogenation of Quinones.*

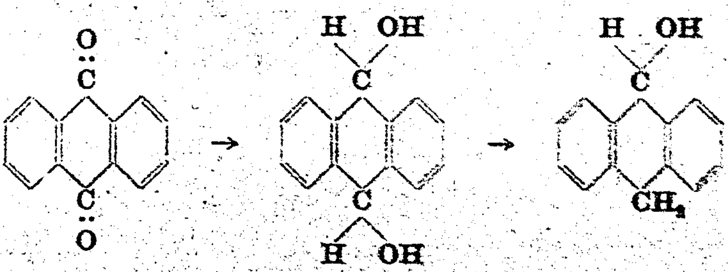
Quinones, which may be regarded as cyclic diketones, are usually very easily reduced. They were originally hydrogenated in the vapour phase by **Sabatier** and **Senderens**[1], who were able to obtain a substantially quantitative yield of hydroquinone by passing a mixture of *quinone* and hydrogen over nickel at 190°. At substantially higher temperatures, the mono-phenol and, subsequently, benzene are formed. The reaction was also successfully applied to *toluquinone*, *p-xyloquinone* and *thymoquinone*, the corresponding hydroquinone being formed if the temperature is not too high.



p-Benzoquinone. Hydroquinone.

Hydroquinone is also formed very easily and smoothly by hydrogenating quinone in solution at room temperature with, for instance, platinum: indeed, the reduction takes place sufficiently easily to be carried out effectively by reducing agents such as sulphurous acid in the absence of catalysts.

The catalytic hydrogenation of a number of condensed quinones, including anthraquinone and phenanthraquinone with nickel under pressure, has been examined by J. v. **Braun** and O. **Bayer**[2]. With, for instance, *anthraquinone*, alternative progressive hydrogenation of the ring system or the reduction of the oxygen atoms to hydroxyl is possible; further, the hydroxyl groups may themselves be reduced. Thus, the first stages of the hydrogenation under the conditions employed, i. e. with a reaction temperature of 160—170° and a hydrogen pressure of 4 atm., involve the following steps:



Anthraquinone. Dihydro-anthrahydroquinone. Dihydro-anthranol.

It will be noted that, in virtue of the rapid formation of the meso-dihydro body (see the hydrogenation of anthracene), the first product which could be isolated was the corresponding dihydro-anthrahydroquinone, although the formation of anthrahydroquinone might itself have been the first step in the hydrogenation. The reduction of the hydroxyl groups then begins, either before or together with the progressive hydrogenation of the rings. On the other hand, A. **Skita**[3] who worked with platinum at a low temperature, observed under these conditions a rapid absorption of 5 molecules of hydrogen with production

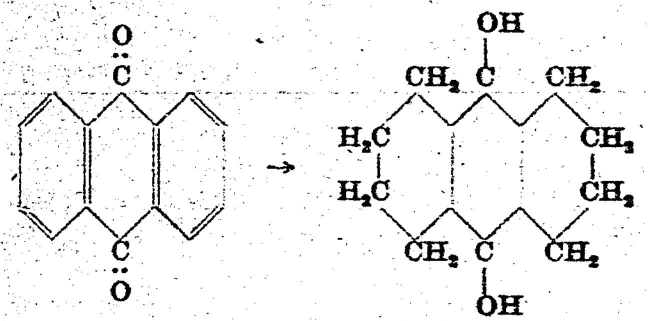
---

[1] C. R. hebd. Séances Acad. Sci. 146, 457 (1908).

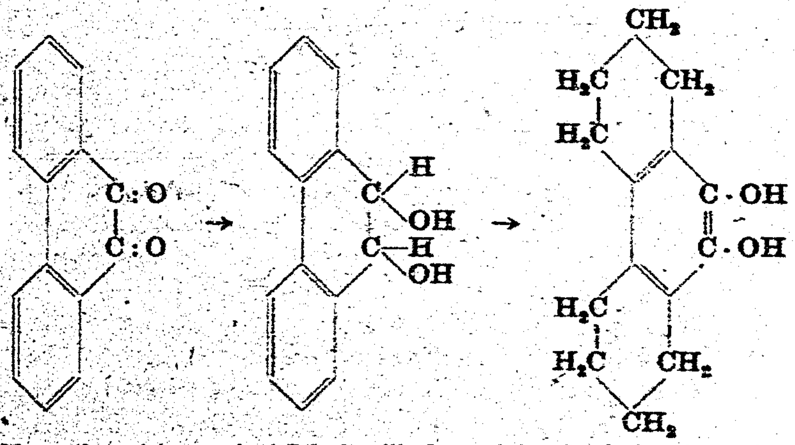
[2] Ber. dtsch. chem. Ges. 58, 2667 (1925).

[3] Ber. dtsch. chem. Ges. 58, 2685 (1925).

of octahydroanthrahydroquinone, which may possibly be produced by way of a meso dihydro derivative.


Anthraquinone. s-Octahydro-anthrahydroquinone.

A very similar reaction was obtained with *phenanthraquinone*, but in this case a dihydro-dihydroxy body was isolated as an intermediate product.


Phenanthraquinone. 9, 10-Dihydro-dihydroxy-anthracene. s-Octahydro-phenanthrahydroquinone.

For evidence of the probable constitution of the octahydro-phenanthrahydroquinone, the formation of which involves a transposition of two hydrogen atoms from the centre ring, reference should be made to the work of Schroeter in the hydrogenation of anthracene itself[1].

3. The Reduction of Carboxylic Acids.

As already discussed, the reduction of a carboxylic acid or ester may involve two distinct types of process according to whether the point of attack is an unsaturated chain or ring attached to the carboxyl group or whether the reduction of this group itself takes place. Processes of the first of these types do not differ essentially from reactions which have been treated in earlier sections; but the catalytic hydrogenation of the higher ethylenic fatty acids, usually in the form of their glycerides, is of great technical importance in connection with the so-called *hardening of oils*, namely, the artificial production of solid fats from liquid glycerides.

a) Ethylenic Acids.

The lower ethylenic acids are relatively easily reduced, even by nascent hydrogen; but, as the chain length increases they are no longer attacked by nascent hydrogen and their catalytic hydrogenation also becomes slower. As a

---

[1] Ber. dtsch. chem. Ges. 57, 2003 (1924).

class, however, they are more rapidly hydrogenated than, for instance, aromatic acids. Thus, the following experimental figures[1] may be taken as illustrative of the relative speeds of saturation under similar conditions of a short and of a relatively long chain olefinic acid compared with that of an aromatic acid. In this case, the hydrogenation was carried out with **platinum** at 40°, the unsaturated acid being dissolved in acetic acid; but the same sequence will be followed also under other conditions (Table 32).

Table 32.

Substance hydrogenated	Relative rate of hydrogenation
Crotonic acid, $CH_3 \cdot CH : CH \cdot COOH$	1.0
Oleic acid, $CH_3 \cdot (CH_2)_7 \cdot CH : CH \cdot (CH_2)_7 \cdot COOH$	0.7
Benzoic acid, $C_6H_5 \cdot COOH$	0.05

The hydrogenation of these and other unsaturated acids, also of their esters where these are readily volatile, may be carried out in the vapour phase as well as in the liquid or dissolved state. For vapour treatment, **nickel** is probably the most suitable catalyst, and it is usually preferable to employ an ester rather than the acid itself since this may attack the metal catalyst. G. DARZENS[2] found that *ethyl acrylate* was rapidly hydrogenated to ethyl propionate on passage with hydrogen over nickel at 180°.

$$CH_2 : CH \cdot COOEt + H_2 = CH_3 \cdot CH_2 \cdot COOEt.$$

Ethyl crotonate and esters of higher ethylenic acids are reduced similarly. Copper is by far not so active as nickel. The vapour-phase method can also be applied to esters of aromatic acids containing unsaturated side chains, such as *cinnamic acid*, in which case the aliphatic chain is hydrogenated far more rapidly than the nucleus; but their relatively low volatility renders them more readily reduced in a liquid state. This also applies to higher ethylenic acids such as *oleic acid*, all the more since a more suitable reaction temperature for all these acids for hydrogenation with nickel is somewhat lower than that used by DARZENS, for instance, 130—150°.

In practice, however, unsaturated acids are almost always hydrogenated either as liquids, either with or without a solvent. If **platinum** or **palladium** (or other metals of the same group) are used, the acids themselves can be taken; but with a **nickel** catalyst it is preferable, as in vapour-phase working, to use an ester. Hydrogenation is usually carried out in a shaker or similar apparatus, but it may, in the case of non-volatile acids or their esters, also be effected very simply by bubbling a brisk current of hydrogen through a suspension of the catalyst in the acid or ester, as described in a previous section.

As examples of the practical hydrogenation of small quantities of these acids under laboratory conditions, 1 g. of *crotonic acid*, dissolved for instance in 10 c.c. of acetic acid, should, in the presence of 0.05 to 0.[illegible] g. of **platinum black**, absorb hydrogen at a rate between 10 and 25 c.c. per minute on being shaken with this gas at room temperature, the course of the reaction being almost linear until a stage approaching saturation is reached. A higher olefinic acid, under the same conditions, will absorb hydrogen somewhat more slowly and an aromatic acid much more slowly, in accordance with the typical relative rates already given. In general, the hydrogenation rate rises progressively with the temperature up to about 80° and subsequently decreases.

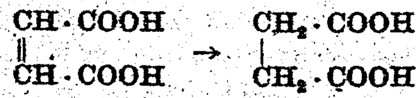
---

[1] MAXTED, STONE: J. chem. Soc. [London] 1934, 26.

[2] C. R. hebd. Séances Acad. Sci. 144, 328 (1907).

For hydrogenation with **nickel**, on a somewhat larger laboratory scale, 100 g. of an unsaturated ester, e. g. ethyl crotonate, ethyl oleate or a natural glyceride such as olive oil, may be mixed with, for instance, 1—2 g. of kieselguhr-supported nickel, and agitated in a shaker in a hydrogen atmosphere at 125 to 140°. The rate of the reaction depends on the activity of the catalyst and on the speed of shaking; and usually several hours will be required for substantially complete saturation, if the hydrogenation is carried out at atmospheric pressure. On a technical scale, a higher pressure is almost always employed; and the ratio of nickel to ester is considerably less. Further details are given in the section devoted to the technical hydrogenation of oils. The hydrogenation of an unsaturated ester may also be carried out, at relatively low temperatures by a catalyst of the alloy-skeleton type. Thus, 10 c.c. of olive oil was found[1] to absorb hydrogen in a shaker at an initial rate of about 11 c.c. per minute at 86° in the presence of 0.2 g. of **Raney nickel.**

Dibasic ethylenic acids, such as maleic or fumaric acids or their esters, readily undergo hydrogenation in solution in the presence of **platinum** or **palladium.** Thus, the author found that a system consisting of 0.6 g. of *maleic acid*, dissolved in 10 c.c. of acetic acid, and 0.05 g. of platinum black absorbed hydrogen in a shaker at room temperature, or slightly above, at a rate comparable with, but somewhat lower than, crotonic acid (see above). The hydrogenation of these acids and of the next higher group of isomers—*mesaconic*, *citraconic* and *itaconic* acids—was studied by S. FOKIN[2]. Reduction takes place normally, e. g. succinic acid is formed from maleic acid:



$$\begin{array}{c}CH\cdot COOH\\ \Vert\\ CH\cdot COOH\end{array} \rightarrow \begin{array}{c}CH_2\cdot COOH\\ |\\ CH_2\cdot COOH\end{array}$$

b) *Reduction of Hydroxy-Olefinic Acids.*

The only common member of this class is *ricinoleic acid*,

$$CH_3\cdot(CH_2)_5\cdot CH(OH)\cdot CH_2\cdot CH : CH\cdot(CH_2)_7\cdot COOH,$$

which occurs in large quantities as a constituent of castor oil. When castor oil is hydrogenated technically with **nickel** at a high temperature, considerable reduction of the hydroxyl group of this acid, in addition to the saturation of its double bond, takes place, with production of stearic acid. It is, however, easily possible, either by using a low temperature with nickel or, better, by employing **platinum**, to saturate the ethylenic linkage without attacking the hydroxyl and thus to produce a hydroxystearic acid.

c) *Ethylenic Acids containing more than one Double Bond.*

The lower acids of this type, such as butadiene carboxylic acid, $CH_2 : CH\cdot CH : CH\cdot COOH$, are not of special interest from the standpoint of hydrogenation, save perhaps that they should add hydrogen in two stages. The next higher homologue, *sorbic acid*, has been hydrogenated by FOKIN (loc. cit.) with **platinum**, the normal staturated product being obtained.

$$\underset{\text{Sorbic acid.}}{CH_3\cdot CH : CH\cdot CH : CH\cdot COOH} + 2H_2 = \underset{\text{Caproic acid.}}{CH_3\cdot(CH_2)_4\cdot COOH.}$$

Certain higher members of this class are, on the other hand, of very great importance in connection with the technical hydrogenation of oils, since they

---

[1] MAXTED, TITT: J. Soc. chem. Ind. 57, 197 (1938).

[2] J. russ. physik.-chem. Soc. 40, 276 (1908).

occur in very large quantities as glyceryl esters in the natural glycerides. The most important of these poly-ethylenic long-chain fatty acids are *linoleic acid*, which is a C_{18} acid containing two double bonds, and the corresponding three double bond acid, *linolenic acid*. Both of these are widely distributed, linolenic acid being found in linseed oil. *Clupanodonic acid* is a third and equally important acid, which is characteristic of whale and fish oils and contains five ethylenic linkages; but, whereas linoleic and linolenic acids (like the hydroxy acid, ricinoleic acid, already discussed) are derived from oleic or stearic acid, clupanodonic acid is a C_{22} acid derived from behenic acid. The constitution of these bodies and their relationship to their parent acids are shown below.

Stearic acid, $CH_3 \cdot (CH_2)_{16} \cdot COOH$.

Oleic acid, $CH_3 \cdot (CH_2)_7 \cdot CH:CH \cdot (CH_2)_7 \cdot COOH$.

Linoleic acid, $CH_3 \cdot (CH_2)_4 \cdot CH:CH \cdot CH_2 \cdot CH:CH \cdot (CH_2)_7 \cdot COOH$.

Linolenic acid, $CH_3 \cdot CH_2 \cdot CH:CH \cdot CH_2 \cdot CH:CH \cdot CH_2 \cdot CH:CH \cdot (CH_2)_7 \cdot COOH$.

Behenic acid, $CH_3 \cdot (CH_2)_{20} \cdot COOH$.

Clupanodonic acid,

$$\left.\begin{array}{l} CH_3 \cdot CH_2 \cdot (CH:CH \cdot CH_2 \cdot CH_2)_3 \cdot (CH:CH \cdot CH_2)_2 \cdot CH_2 \cdot COOH. \\ \text{or possibly} \\ CH_3 \cdot CH_2 \cdot (CH:CH \cdot CH_2 \cdot CH_2)_2 \cdot CH:CH \cdot CH_2 \cdot (CH:CH \cdot CH_2 \cdot CH_2)_2 \cdot COOH. \end{array}\right\}$$

In the course of the hydrogenation of these acids in the technical *hardening of oils*, step-wise saturation of the various double linkages occurs; and, since the order in which the double bonds are filled with hydrogen varies somewhat with the conditions under which the hydrogenation is carried out, a hardened fat which has been reduced to a given iodine value will not necessarily in every case possess the same melting point. This melting point and other physical properties will, of course, also vary with the nature of the oil, i. e. with the particular unsaturated acids and their distribution as mixed glycerides, even if the oil is, as before, reduced to a given iodine value. For further details, reference should be made to a work on oil hardening. It may be noted, however, that, in view of the indefinite melting point of mixed glycerides, it is usual technically to determine the melting point of the fatty acids, (the so-called titre), in place of the glycerides themselves.

d) *The Hydrogenation of Oils.*

The hydrogenation, or so-called hardening, of glyceride oils constitutes an industrial reaction which is of great importance as a method of transforming liquid oils into solid fats. Save for the scale on which it is applied, the reaction is in essence the same as the hydrogenation of the corresponding unsaturated fatty acids; but the process will be described in somewhat greater detail as a convenient example of procedure in large-scale hydrogenation.

The liquid oils which are usually hydrogenated consist of glycerides of various unsaturated acids, namely, of oleic, linoleic, linolenic and other acids, the constitution of which has already been given, the hardening operation consisting in the saturation with hydrogen of the ethylenic bonds in these acids, which are treated in the glyceride form. The commonly hydrogenated oils include whale oil, including fish and marine animal oils generally, cotton-seed, linseed and arachis oils, also castor oil (which contains an unsaturated hydroxy-acid, ricinoleic acid) and many others. The universally used catalyst is nickel.

All these oils, in their crude state, usually contain albuminoid and other impurities which, unless removed, tend to poison or cloak the catalyst and thus to make necessary the use of an unnecessarily large quantity of nickel. The first stage in the treatment accordingly consists in *refining* the crude oil. The nature and sequence of the refining operations vary with the oil treated; but, in almost all cases, these will include washing with soda, to remove free fatty acids, and treatment with fuller's earth to remove colouring matter and albuminoid impurities. The oil is subsequently dried in vacuum pans without exposure to an excessively high temperature. In addition, particularly with whale and fish oils, it may be necessary, before the above methods of refining, to wash with sulphuric acid, which helps to free the oil from entrained water and albuminoids, partly by coagulation and partly by charring. All these processes are normal operations in oil refining; and, for further details, reference should be made to any textbook dealing with the oil industry. In most cases, any good pale commercial oil can be hydrogenated without difficulty; but, for economic reasons, hydrogenation has frequently to be applied to low-grade fish and other oils. It is desirable that the oil, after refinement, shall be reasonably free from water, which causes frothing in the hydrogenation tanks and tends to split the oil into glycerine and free fatty acid, which may, in the presence of traces of oxygen in the hydrogen used, also attack the nickel catalyst and cause an unnecessary diminution in its activity.

The most commonly used form of nickel consists of the finely divided metal supported on kieselguhr. This is made by the general method already described in the chapter dealing with the preparation of catalysts.

Thus, 1 cwt. of nickel sulphate crystals and a slight excess of sodium carbonate (120—130 lbs. of soda crystals, since the nickel carbonate produced is basic) may be dissolved separately in two tanks, mounted over a third tank containing 96 lbs. of kieselguhr made into a smooth paste with water. These solutions are run simultaneously, at room temperature, into the kieselguhr tank, which is provided with a rotating agitator, by means of which the nickel carbonate formed is evenly precipitated on to the kieselguhr. After precipitation, the sludge is filtered through a filter press and washed thoroughly in the press in the ordinary way. The runnings from the press should be colourless from the start: if they are slightly green, too little soda has been used in the precipitation. For the washing, ordinary tap water is quite satisfactory, there being no necessity to use distilled water.

The next stage is the *drying* of the catalyst. This must be done without exposure to a high temperature, otherwise a bright green carbonate is formed which is less easy to reduce and gives a less active nickel. It will be noticed that, in the directions given in the preceding paragraph, the precipitation also was carried out in the cold rather than from boiling solutions. The most effective way of drying the filter cake in such a way as to obtain an easily reduced carbonate consists in stacking this on wooden or nickel gratings in a drying cabinet through which air at a temperature not higher than 50° is passed (a cabinet containing a closed steam or hot water coil in its base and provided with adjustable ventilating doors is very suitable); or a continuous dryer may be used. In such a cabinet, the drying takes place slowly and may occupy several days; but, for an active catalyst, the drying operation should not be hurried. The dried cake, which may, especially if the heating is uneven, be blackened in places owing to formation of the black sesquioxide, should be friable enough to be powdered between the fingers without any suspicion of adhesion or clogging. It is then ground, for instance in a vertical rotary grinding mill, and charged into the reducer.

In its simplest form, this reducer consists of a rotating container mounted in a gasfired brickwork enclosure. This revolving type of reducer leads to a very even heat distribution and to thorough mixing of the catalyst during reduction; but a stationary vessel with internal agitating gear—or a continuous reducing plant, through which the catalyst is fed continuously, as an alternative to batch treatment—can, of course, be used. After charging, the temperature is slowly brought up to about 300° usually, in the batch type of reducer, first of all without passing hydrogen. During this period which, with a moderate sized reducer, may last about two hours, carbon dioxide and some water vapour are evolved. As the evolution of these slackens, hydrogen is introduced, and reduction is carried out in a reasonably rapid stream of hydrogen until a stage is reached at which the whole of the charge possesses a uniform black colour, as seen by samples removed through a small sampling tube. If the reduction is pushed too far, a less active catalyst will result; and the optimum stage of reduction is (apart from measuring the water evolved) usually judged by experience. Under ordinary conditions of working, an average time of reduction will be about five hours, with a temperature of 300—350° in the case of a kieselguhr supported-catalyst; but small charges reduce more quickly than this, and the temperature should be kept as low as is consistent with a not too slow reduction. The reduced metal is of course pyrophoric: however, samples for inspection of the progress of the reduction can usually be removed without trouble in a closed sampling tube which is cooled before being opened; and, after the reduction has been completed, the reducer, together with the charge, is allowed to become thoroughly cold, and the hydrogen replaced by an inert gas (carbon dioxide or nitrogen). With these precautions, the catalyst can be removed from the reducer safely and without loss of activity, and may be discharged into an open tank of cold oil, brought under the discharging door of the reducer, without the necessity for an air-tight seal. It is thoroughly mixed with the oil; and the concentrated mixture of oil and catalyst thus obtained is stored in an air-tight container and added, as a source of catalyst, to the main charges of oil to be hydrogenated.

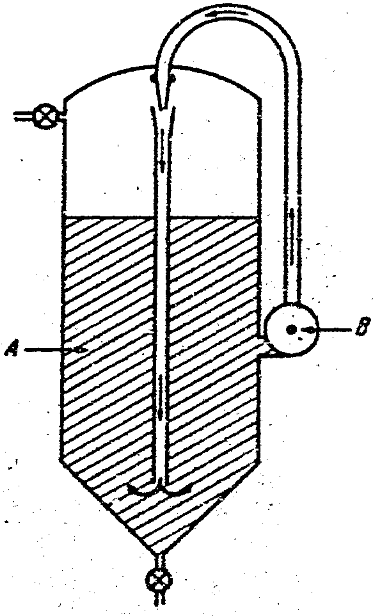


Fig. 21. Vessel for the hydrogenation of oils.

The hydrogenation operation itself is carried out in tall cylindrical reaction tanks heated to the required temperature (120—160°) by means of a closed steam coil or jacket or by a liquid-fed heating system. The speed of the reaction depends to a high degree on the intimacy of contact between the hydrogen and the oil, and, for this reason, apparatus of special design is often employed. Apart, however, from such special devices for dispersing the hydrogen through the oil, the general construction of a typical hydrogenation vessel is shown diagrammatically in Fig. 21, in which *A* is the vessel itself and *B* is a high-speed circulating pump, by means of which hydrogen is passed through the oil contained in the vessel, fresh hydrogen being added to the gas circuit to compensate for that absorbed by the oil. It is usual to preheat the oil and to dry this thoroughly by vacuum treatment before admitting the charge to the hydrogenation vessel; and this evacuation may also be repeated after adding the catalyst and before admitting hydrogen. The amount of nickel required varies greatly with the quality of the oil and with the general conditions. As a rough guide, this may, for instance, be 0.2 per cent of the oil treated; but lower concentrations are frequently used in modern practice. The hydrogenation is usually carried out at an increased pressure, which may for ordinary working conveniently be of the order of 10 atmospheres, with an initial temperature of 120—130°, which tends to rise as the hydrogenation proceeds, owing to the exothermic nature of the reaction, the temperature at the end being frequently 150—160°. As an alternative method of working, the operation may be started at 150—160°, which is approximately the temperature of maximum velocity, and the charge maintained at this temperature throughout by suitable cooling. The time required varies within wide limits, according to the amount of catalyst used and the general conditions; but, under ordinary conditions of working, the operation usually takes several hours. In the above description, no attempt has, for reasons of space, been made to describe particular types of hydrogenation vessels[1].

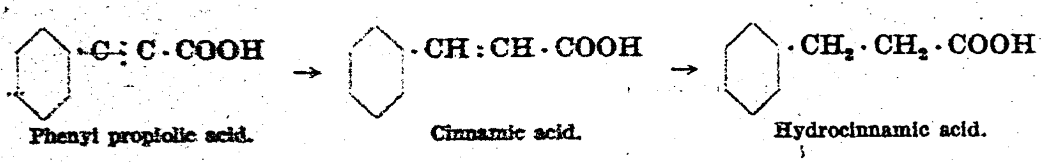
The progress of the hydrogenation is followed by measuring the volume of hydrogen adsorbed or by taking samples and observing the change in the refractive index of these, after filtration to remove the catalyst; or the hardness may be judged by allowing small samples to solidify. The hardened oil is usually subsequently graded in the ordinary way on the basis of its iodine value, but this test requires too long a time to be applied during the hydrogenation itself.

After hydrogenation is completed, the oil is discharged into a receiver, cooled somewhat, and filtered in filter presses to remove the catalyst, which may be sufficiently active for re-use. These hydrogenated oils are used in very large quantities in the soap and edible fat industries.

e) *Hydrogenation of Acetylenic Acids.*

The acetylenic acids are not very important. *Propiolic acid*, $CH \vdots C \cdot COOH$, or its esters, are easily hydrogenated in the liquid phase; and, as was the case with acetylene itself, the reaction may be arrested at an intermediate stage in such a way as to allow the isolation of the corresponding ethylenic acid.

This was studied by C. PAAL and W. HARTMANN[2] with *phenyl propiolic acid* which, on being hydrogenated (as the sodium salt) in a shaker in the presence of **colloidal palladium**, gave a maleinoid form of cinnamic acid if the reduction was interrupted after the required volume of hydrogen had been absorbed. Further hydrogenation led to hydrocinnamic acid.



f) *Hydrogenation of Aromatic Acids.*

All ordinary aromatic acids may be hydrogenated in the nucleus by methods very similar to those used for the parent hydrocarbons; but the reaction does not, in general, go well in the vapour phase at high temperatures on account of decomposition. This decomposition is less if esters are hydrogenated in place of the acids: thus, SABATIER and MURAT[3] obtained fair yields of methyl and other hexahydrobenzoates by hydrogenating the corresponding benzoic ester over **nickel** at relatively low temperatures.

Benzoic acid was hydrogenated in the liquid phase by WILLSTÄTTER and HATT[4]. For instance, 2 g. of benzoic acid in 20 c.c. of acetic acid, in the presence of 0.7 g. of platinum, absorbed in a shaker at 16° the theoretical volume of hydrogen for conversion into hexahydrobenzoic acid in 75 minutes, the operation being carried out at normal pressure.

Naphthoic acid and other condensed aromatic acids may be hydrogenated in the same way. The reaction is, as has already been stated, far slower than for aliphatic acids; and it is usually advantageous to use an increased pressure. As with benzoic acid itself, **nickel** may be used in place of platinum, save that it is usually desirable, with catalysts other than those of the platinum group, to

---

[1] For details of these, reference may be made to the author's book: "Catalysis and its Industrial Applications" (London: J. and A. Churchill 1933), or to ELLIS: "Hydrogenation of Oils" (New York: Van Nostrand Co.).

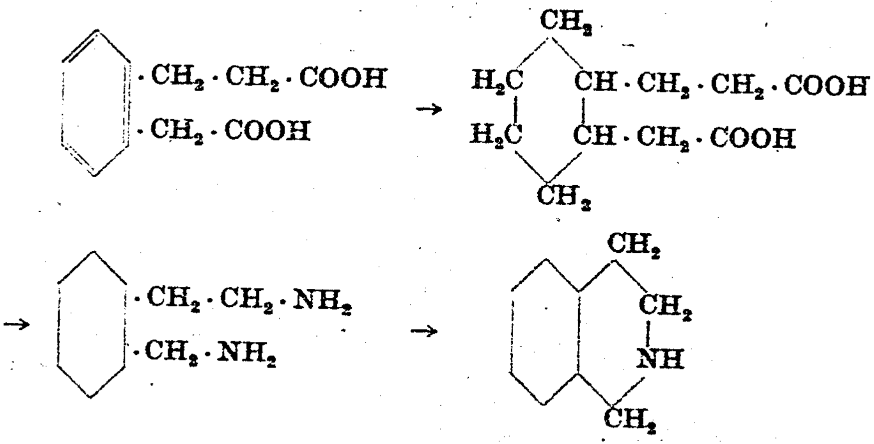
[2] Ber. dtsch. chem. Ges. 42, 3930 (1909).

[3] C. R. hebd. Séances Acad. Sci. 154, 924 (1912).

[4] Ber. dtsch. chem. Ges. 45, 1476 (1912).

employ an ester in place of an acid, which tends to attack a nickel catalyst. However, IPATIEW[1] was able to hydrogenate both α- and β-naphthoic acids with nickel at a high pressure, both tetrahydro and decahydro derivatives being obtained.

Dibasic acids like phthalic acid are reduced similarly[2]. This also applies to more complicated dicarboxylic acids such as phenylene-acetic-propionic acid, which was hydrogenated by L. HELFER[3] as a step towards the synthesis of hexahydro-isoquinoline:

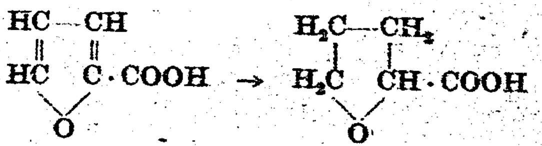


According to SKITA[4], the hydrogenation reaction is most easily carried out with **colloidal platinum** protected by gum arabic, in acetic acid solution, especially in the presence of hydrochloric acid.

Hydroxy acids, such as salicylic acid, are easily hydrogenated by **platinum black** in aqueous solution or suspension[5]; indeed, the use of water as a hydrogenation liquid gave in these cases better results than acetic acid. Hydrogenation with platinum at room temperature took place in the nucleus only, the hydroxyl group remaining intact.

g) *Heterocyclic Acids.*

Carboxylic acids containing an unsaturated heterocyclic ring undergo hydrogenation in much the same way as their parent bodies. Thus, pyromucic acid was reduced by H. WIENHAUS and H. SORGE[6] by hydrogenation in a shaker with **colloidal platinum**, protected by gum arabic, in aqueous solution.



Pyromucic acid. Tetrahydro pyromucic acid.

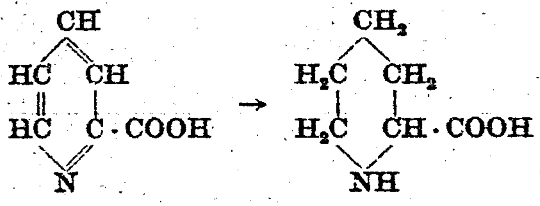
The same hydrogenation has also been carried out by KAUFMAN and ROGERS with ethyl pyromucate, using platinum derived from its oxide.

Other heterocyclic acids may also be reduced by standard hydrogenation methods. For instance, picolinic acid on hydrogenation in a solvent with

---

[1] Ber. dtsch. chem. Ges. 42, 2100 (1909).
[2] IPATIEW, O. PHILIPOW: Ber. dtsch. chem. Ges. 41, 1001 (1908).
[3] Helv. chim. Acta 6, 785 (1923).
[4] Ber. dtsch. chem. Ges. 57, 1977 (1924).
[5] J. HOUBEN, A. PFAU: Ber. dtsch. chem. Ges. 49, 2294 (1916).
[6] Ber. dtsch. chem. Ges. 46, 1927 (1913).

platinum, passes into the corresponding piperidine carboxylic acid; but the rate of reaction is slow.



4. Hydrogenation of the Carboxyl Group.

The catalytic hydrogenation of the carboxyl group of an organic acid, with production of an alcohol or of a hydrocarbon, according to the general course:

$$R \cdot COOH \rightarrow R \cdot CH_2OH \rightarrow R \cdot CH_3$$

does not take place very readily and requires treatment at temperatures somewhat higher than those normally employed in hydrogenation. For these reasons the possibility of reducing the group catalytically has only recently been recognised. It can, however, be carried out with most of the ordinary hydrogenation catalysts—such as metallic nickel or catalysts of the copper chromite, nickel chromite or zinc chromite type—provided that the temperature is sufficiently high; and, while a high pressure is usually used, this latter condition does not appear to be necessary. The production of an alcohol or of a hydrocarbon depends, as would be expected, partly on the catalyst and partly on the temperature and duration of the treatment; and esters may be employed in place of the acids themselves, in which case two alcohols, derived respectively by the regeneration of the ester alcohol and by the reduction of the acid, are produced, e. g.

$$R \cdot COOEt \rightarrow R \cdot CH_2OH + Et \cdot OH.$$

The process is thus a catalytic alternative to the non-catalytic reduction of esters introduced by Bouveault and Blanc[1], but differs from this in giving relatively high yields and in freedom from side reactions.

The catalytic hydrogenation of a number of esters in the liquid phase to alcohols with **copper chromite** was studied by H. Adkins and K. Folkers[2]. In general, a working temperature of 250° and a pressure of 220 atm. were used. Some typical results are summarised in Table 33.

Table 33.

Ester	Product	Yield
Ethyl valerate	n-Amyl alcohol	94
Ethyl laurate	Lauryl alcohol	97
Ethyl myristate	Myristyl alcohol	98
Ethyl cinnamate	Phenylpropyl alcohol	83
Ethyl trimethyl acetate	Tert.-Butyl carbinol	88
Ethyl succinate	Tetramethylene glycol	80

It will be seen that good yields of the corresponding alcohol are in each case obtained.

The reduction of some higher fatty acids and their esters both to alcohols and to hydrocarbons was investigated by W. Schrauth, O. Schenck and K. Stickdorn[3]. Thus, 40 g. of stearic acid gave a yield of 31 g. of octadecyl

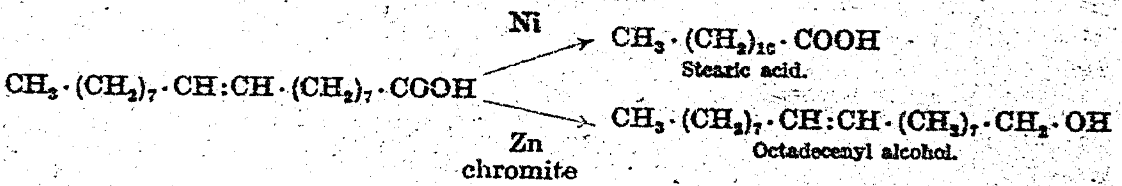
---

[1] Bull. Soc. chim. France (3) 31, 666 (1904).
[2] J. Amer. chem. Soc. 53, 1095 (1931).
[3] Ber. dtsch. chem. Ges. 64, 1314 (1931).

alcohol when shaken with hydrogen, at 325° and 280 atm., in the presence of 4 g. of **zinc-copper-chromite**. Very similar results were, however, also obtained with an ordinary kieselguhr-supported **copper** catalyst: for instance, caprylic acid was reduced to octyl alcohol, and methyl caproate to decyl alcohol. The use of **nickel** tended to give a hydrocarbon. Methyl laurate, when hydrogenated with this catalyst at 390° and 280 atm., gave dodecane, which was also obtained from lauric acid with copper on kieselguhr. The time required for the reaction, even with copper, is relatively short. Thus, 40 g. of lauric acid, with 4 g. of a copper-kieselguhr catalyst, underwent reduction in 60 minutes in a high-pressure shaker at 270 atm. and at a temperature up to 390°. The production of alcohol or of hydrocarbon is, as already mentioned, partly a function of the catalyst and partly of the temperature and other conditions of hydrogenation; and it will be noted that the temperatures used by SCHRAUTH, SCHENCK and STICKDORN are considerably higher than those employed by ADKINS and FOLKERS. Other work on the reaction of esters to alcohols with nickel has been carried out by PALFRAY and SABATAY[1], who converted ethyl laurate into a mixture of the corresponding alcohol (dodecanol) and hydrocarbon (dodecane) by hydrogenation in the liquid phase at 260°, with a hydrogen pressure of 150 kg./cm.^{2}. With ethyl phenyl acetate—$C_6H_5 \cdot CH_2 \cdot COOEt$—the reaction product contained both $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot OH$ and $C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot OH$, in addition to the corresponding hydrocarbons.

The use of a high pressure appears not to be essential. O. SCHMIDT[2] was able to reduce esters such as ethyl oleate very simply by passing a mixture of the vapour of the ester and hydrogen through a **copper chromite** catalyst, supported on silica gel, at 270—280° and at atmospheric pressure. The product contained 80—90 per cent of octadecyl alcohol, which was obtained as a white crystalline deposit in the receiver.

In the case of an acid containing both an unsaturated linkage and a carboxyl group, it is possible to hydrogenate preferentially either the one position or the other according to the catalyst and conditions of hydrogenation chosen. Thus, while ordinary catalysts, especially at low temperatures, hydrogenate the double bond exclusively, catalysts containing zinc, such as **zinc chromite**, tend to attack the carboxyl group to the exclusion of the double bond, the alternative course of the reduction, for instance with oleic acid, being:



$$CH_3 \cdot (CH_2)_7 \cdot CH{:}CH \cdot (CH_2)_7 \cdot COOH \begin{array}{l} \xrightarrow{\text{Ni}} \underset{\text{Stearic acid.}}{CH_3 \cdot (CH_2)_{16} \cdot COOH} \\ \xrightarrow[\text{Zn chromite}]{} \underset{\text{Octadecenyl alcohol.}}{CH_3 \cdot (CH_2)_7 \cdot CH{:}CH \cdot (CH_2)_7 \cdot CH_2 \cdot OH} \end{array}$$

The method therefore allows the easy production of unsaturated alcohols, most of which are otherwise difficult of access. Work in this field has been carried out by J. SAUER and H. ADKINS[3], who used both zinc chromite and other related catalysts and reduced esters rather than the acids themselves. In the results tabulated below, it will be noticed that catalysts containing zinc did not attack the double bond, whereas those in which copper was present as a component gave a saturated acid or alcohol, rather than an unsaturated alcohol (Table 34).

---

[1] Bull. Soc. chim. France (5) 3, 682 (1936).
[2] Ber. dtsch. chem. Ges. 64, 2051 (1931).
[3] J. Amer. chem. Soc. 59, 1 (1937).

Table 34.

Ester hydrogenated	Catalyst	Temperature °C	Product	Yield
Ethyl oleate	**Zinc chromite**	300	Octadecenol	50—60
Butyl oleate	**Zinc chromite**	300	Octadecenol	65
Butyl erucate	**Zinc chromite**	295	Docosenol	68
Butyl oleate	**Copper chromite**	250	Octadecanol	86
Ethyl oleate	**Copper molybdite**	250	Ethyl stearate	70

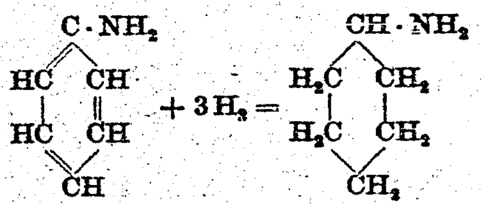
The catalytic preparation of these long-chain alcohols, both of the saturated and of the ethylenic class has become of considerable technical importance.

It may, further, be noted that the hydrogenation of optically active esters to alcohols gives a product which possesses the same type of optical activity as the starting material. Bowden and Adkins[1] hydrogenated a number of bodies of this class with **copper chromite**, the reduction being in general carried out in the liquid phase at 250° under a pressure of 150—200 atm.

5. Hydrogenation of Aromatic Amino Derivatives.

The hydrogenation of aniline and similar bodies does not differ greatly from the nuclear saturation of other aromatic bodies, save that the splitting off of ammonia, with formation of secondary and tertiary amines, may occur.

Sabatier and Senderens[2] found that, on passing a mixture of aniline and hydrogen over reduced **nickel** at 190°, cyclohexylamine was produced:



At the same time, dicylohexylamine, $(C_6H_{11})_2 \cdot NH$, cyclohexylaniline, $C_6H_5 \cdot NH \cdot C_6H_{11}$, and other products were obtained. Substituted anilines, such as methyl or ethyl aniline, dimethyl aniline etc. behaved similarly; but, with benzylamine, ammonia was split off with formation of toluene:

$$C_6H_5 \cdot CH_2 \cdot NH_2 + H_2 = C_6H_5 \cdot CH_3 + NH_3.$$

Aniline was hydrogenated in the liquid phase by Willstätter and Hatt[3] with **platinum**. The product contained only a small percentage of the primary amine.

A. Skita and W. Berend[4] made the important observation that the percentage of primary amine in the product, in addition to being dependent on the temperature, could be changed by the addition of *hydrochloric acid*, in such a way as to give pure primary or pure secondary cyclohexylamine at will. These authors, who used **colloidal platinum**—in the presence of gum arabic as a protective colloid stable towards acids—give the following directions for the preparation of pure cyclohexylamine. The charge taken for hydrogenation consisted of 240 c.c. of the colloidal platinum solution (containing 110 c.c. of acetic acid and 1.5 g. of platinum), 10 c.c. of 36 per cent hydrochloric acid and 8.4 g. of aniline. This, on being shaken at 21° with hydrogen at a pressure of 3 atm., absorbed the theoretical quantity of hydrogen in $2^1/_2$ hours. Only

---

[1] J. Amer. chem. Soc. 56, 689 (1934).

[2] C. R. hebd. Séances Acad. Sci. 138, 457 (1904); Ann. Chim. et Physique (8) 4, 376 (1905).

[3] Ber. dtsch. chem. Ges. 45, 1476 (1912).

[4] Ber. dtsch. chem. Ges. 52, 1519 (1919).

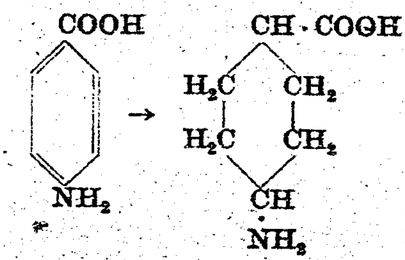
cyclohexylamine (yield, 8 g.) was found in the product. If, on the other hand, the hydrochloric acid was omitted, the product consisted of about 40 per cent or primary and 60 per cent of secondary amine.

For the preparation of almost pure secondary amine the reaction is carried out at 55—60°, in place of at room temperature, and the hydrochloric acid is not added. A typical product obtained under these conditions contained about 80 per cent of dicyclohexylamine and 20 per cent of cyclohexylamine. Very similar results were given by toluidine.

The hydrogenation of aryl-substituted aliphatic amines, such as benzylamine of β-phenyl-ethylamine, takes place only very slowly under ordinary conditions of liquid phase hydrogenation. It can, however, be effectively carried out by using colloidal platinum, particularly in the presence of acetic and hydrochloric acids in a similar way[1] to that described for aniline. With *benzylamine*, $C_6H_5 \cdot CH_2 \cdot NH_2$, the addition of hydrochloric acid is apparently unnecessary, since 10 g. of commercial benzylamine, in 30 c.c. of acetic acid, absorbed slightly more than the theoretical volume of hydrogen in 8 hours at 50—60°, with a hydrogen pressure at 3 atm., the catalyst consisting of about 1.5 g. of colloidal platinum prepared by SKITA's inoculation method in the presence of gum arabic.

With *β-phenyl-ethylamine*, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot NH_2$, however, hydrochloric acid was used. The charge hydrogenated (at 50—60° and at 3 atm.) consisted of 10 g. of the amine in 35 c.c. of acetic acid, 10 c.c. of concentrated hydrochloric acid and 140 c.c. of a **colloidal platinum** solution containing 1 g. of platinum and 6 g. of gum arabic. The conversion was finished in $5^1/_2$ hours.

Amino-acids, such as *anthranilic acid* and *p-aminobenzoic acid* are stated not to hydrogenate well in acetic acid, but to react smoothly in the form of a water solution or suspension[2]. Thus, 1 g. of p-amino-benzoic acid together with 0.3 g. of **platinum black** absorbed approximately the required volume of hydrogen for the hydrogenation of the ring after shaking, with water, in a hydrogen atmosphere for $9^1/_2$ hours, whereas, in acetic acid, hydrogenation was incomplete.



6. The Reduction of Miscellaneous Linkages Containing Nitrogen.

The hydrogenation of certain cyclic nitrogen compounds, such as pyridine, has—by reason of the close similarity of the process to the reduction of purely carbocyclic rings—already been treated in a previous section immediately after the hydrogenation of benzene. With these exceptions, the remaining nitrogen-containing linkages are now, for covenience, considered together.

These groups involve in some cases a carbon-nitrogen linkage such as is present in the cyanides and isocyanides: in other classes, the unsaturated bond lies between nitrogen atoms only, e. g. in the azo, —N : N—, group; or the linkage may involve oxygen groupings of various types, as in the nitro compounds, in nitrous esters, or in bodies such as azoxybenzene. In the hydrogen-

---

[1] A. SKITA: Ber. dtsch. chem. Ges. 57, 1977 (1924).

[2] J. HOUBEN, A. PFAU: Ber. dtsch. chem. Ges. 49, 2294 (1916).

ation of these latter groups, the reduction usually involves the elimination of oxygen as water.

Catalytic hydrogenation of the above bodies is, in many cases, only an alternative method of carrying out a reaction which can also be effected non-catalytically by means of nascent hydrogen. Catalytic reduction, however, frequently gives higher yields of the simple reduction product, and may, in addition, greatly simplify the manipulation required.

a) *Hydrogenation of Nitriles and Isonitriles.*

The catalytic hydrogenation of nitriles in the vapour phase was examined by Sabatier and Senderens[1]. In the typical case of methyl cyanide, this was led, together with hydrogen, over reduced nickel at 180—200°, the product being condensed by means of ice and salt. This product was found to consist of the three corresponding amines:

$$CH_3\cdot CN \begin{array}{l} \nearrow CH_3\cdot CH_2\cdot NH_2 \text{ (Primary ethylamine)} \\ \rightarrow (CH_3\cdot CH_2)_2\cdot NH \text{ (Secundary ethylamine)} \\ \searrow (CH_3\cdot CH_2)_3N \text{ (Tertiary ethylamine)} \end{array}$$

of which the secondary amine was the most abundant. Higher aliphatic cyanides reacted similarly: thus, ethyl cyanide gave mono-, di-, and tri-propylamine. Aromatic cyanides, under Sabatier and Senderens' conditions, split off ammonia. For instance, with phenyl cyanide:

$$C_6H_5CN + 3H_2 = C_6H_5\cdot CH_3 + NH_3.$$

Isonitriles undergo hydrogenation similarly; but, as would be expected from their structure, give products differing from those obtained from the nitriles. Sabatier and Mailhe[2] hydrogenated methyl isocyanide with **nickel** in the vapour phase at 160—180° and obtained, as the principal product, dimethylamine. A small quantity of ethylamine was also produced, due probably to the isomerisation of part of the isonitrile to nitrile:

$$\underset{\text{Methyl isocyanide.}}{CH_3\cdot NC} + 2H_2 = CH_3\cdot NH\cdot CH_3$$

$$\underset{\text{Methyl cyanide.}}{CH_3\cdot CN} + 2H_2 = CH_3\cdot CH_2\cdot NH_2.$$

Ethyl isocyanide behaved similarly, giving secondary methylethylamine, $C_2H_5\cdot NH\cdot CH_3$, in place of propylamine as obtained from ethyl cyanide. Copper could be substituted for nickel but was far less active.

The hydrogenation of nitriles to amines is a reversible process, in that the *dehydrogenation* of an amine to a nitrile occurs readily on passage over a metallic catalyst at a high temperature, according to the general equation:

$$R\cdot CH_2\cdot NH_2 = 2H_2 + R\cdot CN.$$

P. Sabatier and G. Gaudion[3] found that *benzylamine*, when passed over **nickel** at 300—350° in the absence of hydrogen, gave benzonitrile; but some splitting off of ammonia occurred, part of the nitrile being further reduced to toluene. Aliphatic amines react similarly: thus, isoamylamine gave isovaleric nitrile.

In the liquid phase, the reduction of nitriles to amines was carried out with **palladium** by Paal and Gerum[4], who obtained benzylamine from phenyl cyanide.

---

[1] Ann. physic. Chim. (8) 4, 403 (1905); C. R. hebd. Séances Acad. Sci. 140, 482 (1905). [2] Bull. Soc. chim. France (4) 1, 612 (1907).

[3] C. R. hebd. Séances Acad. Sci. 165, 224 (1917).

[4] Ber. dtsch. chem. Ges. 42, 1553 (190

The subject was investigated in greater detail by H. Rupe and K. Glenz[1]. In this work, **nickel** was employed as the catalyst. Thus, 10 g. of amyl cyanide, dissolved in a mixed solvent containing 50 c.c. of alcohol, 50 c.c. of water and 40 c.c. of ethyl acetate, were shaken with hydrogen in the presence of 20 g. nickel catalyst at room temperature. The volume of hydrogen required for the conversion of the cyanide into an amine was absorbed in 24 hours. Benzyl cyanide, $C_6H_5 \cdot CH_2 \cdot CN$, and phenyl propyl cyanide, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CN$, reacted similarly. The principal product is usually the secondary amine. The mechanism of the reaction was further studied by H. Rupe and E. Hodel[2]. It may be noted that whereas Rupe and his collaborators, when working in solutions containing aqueous alcohol, obtained secondary amines, K. W. Rosenmund and E. Pfankuch[3] obtained primary amines by working in acetic acid solution. Thus, with a **palladium** catalyst, both phenyl cyanide and benzyl cyanide gave good yields, respectively, of benzylamine and phenyl-ethylamine, $Ph \cdot CH_2 \cdot CH_2 \cdot NH_2$.

According to W. H. Carothers and G. A. Jones[4], reduction in acetic anhydride solution, using a **platinum** catalyst, leads to the pure primary amine. Accordingly, benzonitrile (phenyl cyanide), benzyl cyanide, and o- and p-tolunitrile were smoothly reduced in this way, secondary amines being absent in the product. It was noted further that, while the reduction proceeded at a practicable rate in glacial acetic acid, acetic anhydride and alcohol, it took place only very slowly in ether. In solvents other than acetic anhydride, a mixture of primary and secondary amines was produced. On the whole, the production of a pure primary amine appears to depend on the fixation of this by employing an acid reduction medium: thus, W. H. Hartung[5] obtained the pure primary product in a solution of absolute alcohol containing hydrogen chloride. Further[6], it may be noted that primary amines are transformed into secondary amines on being heated in a neutral solvent (xylene) in the presence of platinum and hydrogen.

Paal and Gerum[7] assume, in the reduction of nitriles, the intermediate formation of an aldimine, e. g. with benzonitrile:

$$C_6H_5 \cdot C \vdots N + H_2 = C_8H_5 \cdot CH : NH.$$

Benzaldimine.

These bodies have been prepared by V. Grignard and R. Escourrou[8] by hydrogenating nitriles under reduced pressure with **nickel** or **platinum**. Aldimines are also produced in the vapour-phase reduction of nitriles with a **copper** catalyst at 150°[9], their production being favoured by a high rate of passage over the catalyst. No aldimine was obtained from aliphatic nitriles such as acetonitrile or iso-valeronitrile.

b) Reduction of Isocyanates.

Sabatier and Senderens[10] have studied the catalytic reduction of aliphatic and aromatic isocyanates by passing these in vapour form over **nickel** at 180

---

[1] Helv. chim. Acta 5, 937 (1922).
[2] Helv. chim. Acta 6, 865 (1923).
[3] Ber. dtsch. chem. Ges. 56, 2258 (1923).
[4] J. Amer. chem. Soc. 47, 3051 (1925).
[5] J. Amer. chem. Soc. 50, 3370 (1928).
[6] K. W. Rosenmund, G. Jordan: Ber. dtsch. chem. Ges. 58, 51 (1925).
[7] Loc. cit.; see also Rupe, Hodel: loc. cit.
[8] C. R. hebd. Séances Acad. Sci. 180, 1883 (1925).
[9] S. Komatsu, S. Ishida: Mem. Coll. Sci., Kyoto Imp. Univ. 1927, 331.
[10] Bull. Soc. chim. France (4) 1, 615 (1907).

to 190°. In general, the reduction takes place normally, with formation of amines and elimination of the oxygen as water:

$$\underset{\text{Ethyl isocyanate.}}{C_2H_5 \cdot N : CO} + 3H_2 = \underset{\text{sec. ethylmethylamine.}}{C_2H_5 \cdot NH \cdot CH_3} + H_2O \quad \cdots$$

$$\underset{\text{Phenyl isocyanate.}}{C_6H_5 \cdot N : CO} + 3H_2 = \underset{\text{Phenyl methylethylamine.}}{C_6H_5 \cdot NH \cdot CH_3} + H_2O \quad \cdots$$

but secondary reactions also occur. Thus, with phenyl isocyanate, the water produced reacts with unchanged isocyanate with production of diphenyl urea:

$$2C_6H_5 \cdot N : CO + H_2O = (C_6H_5NH)_2CO + CO_2.$$

c) *Diazo, Triazo, and Allied Compounds.*

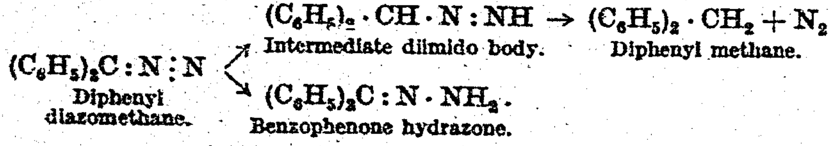
The hydrogenation of many bodies of this class, even at low temperatures, is complicated by their instability and by the ease with which nitrogen is eliminated. Thus, *ethyl diazoacetate*, on being shaken with hydrogen in the presence of palladium[1] loses nitrogen and passes into ethyl acetate:

$$N_2 : CH \cdot COOEt + H_2 = CH_3 \cdot COOEt + N_2.$$

It may, however, be noted that *diazomalonic ester* was successfully hydrogenated without elimination of nitrogen, the product being the hydrazone of the oxomalonic ester:

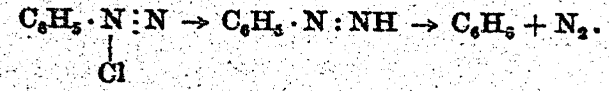
$$\underset{\text{Ethyl diazomalonate.}}{N_2C(COOEt)_2} + H_2 = \underset{\text{Hydrazone of ethyl oxomalonate.}}{H_2N \cdot N : C(COOEt)_2}.$$

A very similar reaction occurs with bodies of the type of *diphenyl diazomethane*, which is reduced principally to diphenyl methane together with a little benzophenone hydrazone. STAUDINGER postulates the intermediate formation of a di-imido reduction compound as a prior stage in the formation of diphenyl methane, the course of the reaction being thus:



$$\underset{\substack{\text{Diphenyl}\\\text{diazomethane.}}}{(C_6H_5)_2C : N \vdots N} \begin{array}{l} \nearrow \underset{\text{Intermediate diimido body.}}{(C_6H_5)_2 \cdot CH \cdot N : NH} \rightarrow \underset{\text{Diphenyl methane.}}{(C_6H_5)_2 \cdot CH_2} + N_2 \\ \searrow \underset{\text{Benzophenone hydrazone.}}{(C_6H_5)_2C : N \cdot NH_2}. \end{array}$$

This course may be compared with the formation of hydrocarbons in the reduction of aromatic diazo bodies on reduction with, for instance, alkaline stannous salts:



$$C_6H_5 \cdot \underset{\substack{|\\Cl}}{N} \vdots N \rightarrow C_6H_5 \cdot N : NH \rightarrow C_6H_6 + N_2.$$

Triazo compounds also lose nitrogen on hydrogenation. Thus, *hydrazoic acid* on reduction passes into ammonia, together possibly with some hydrazine; and its salts, on being shaken in solution with platinum and hydrogen, give amides, which in the presence of water are hydrolysed to hydroxides.

$$\begin{aligned} Na \cdot N_3 + H_2 &= NaNH_2 + N_2 \\ NaNH_2 + H_2O &= NaOH + NH_3. \end{aligned}$$

In the case of organic azides, the reaction can be arrested at the amino stage. In this way[2], *triazo-methane* or *triazo-benzene* readily gives methylamine and

---

[1] H. STAUDINGER, A. GAULE, J. SIEGWART: Ber. dtsch. chem. Ges. 49, 1896 (1916); Helv. chim. Acta 4, 212 (1921). — H. WIENHAUS, H. ZIEHL: Ber. dtsch. chem. Ges. 65, 1461 (1932). [2] WIENHAUS, ZIEHL: loc. cit.

aniline, respectively, on being shaken with hydrogen in the presence of palladium at 0°.

$$\underset{\text{Triazo-methane.}}{CH_3 \cdot N_3} + H_2 = CH_3NH_2 + N_2.$$

d) *Reduction of Azobenzene.*

The hydrogenation of azobenzene with **colloidal palladium** was carried out by A. SKITA[1]. Reduction as far as hydrazobenzene took place relatively rapidly and this was followed by further reduction to aniline.

$$\underset{\text{Azobenzene.}}{C_6H_5 \cdot N : N \cdot C_6H_5} + H_2 = \underset{\text{Hydrazobenzene.}}{C_6H_5 \cdot NH \cdot NH \cdot C_6H_5}. \qquad (1)$$

$$C_6H_5 \cdot NH \cdot NH \cdot C_6H_5 + H_2 = 2C_6H_5 \cdot NH_2. \qquad (2)$$

The first of these two stages, with a system consisting of 9 g. of azobenzene in 250 c.c. of alcohol and 0.03 g. of colloidal palladium protected by gum arabic, was complete in 5 minutes, using a shaker supplied with hydrogen at an excess pressure of 1 atm., whereas the conversion to aniline required over 4 hours.

Azobenzene was also reduced by SABATIER and SENDERENS[2] in the vapour phase with a **nickel** catalyst at 290°, the product under these conditions being aniline containing a little cyclohexylamine.

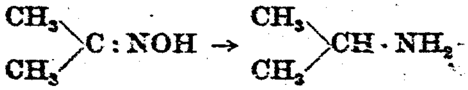
e) *Hydrogenation of Oximes.*

Both aldoximes and ketoximes may readily be reduced catalytically to amines containing the same number of carbon atoms.

The hydrogenation of a number of oximes in the vapour phase, by means of **nickel** at 150—180°, was studied by MAILHE and MURAT[3]. From the oxime derived from acetaldehyde, ethylamine was obtained:

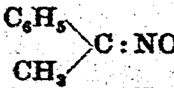
$$CH_3 \cdot CH : NOH \rightarrow CH_3 \cdot CH_2 \cdot NH_2.$$

The oxime of acetone gave isopropylamine:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C:NOH \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH \cdot NH_2$$

the primary amine being accompanied by secondary and tertiary amines. Oximes of higher ketones, including those of mixed ketones, behaved similarly; and **copper** may be used as the catalyst in place of nickel.

Mixed aromatic and aliphatic oximes of the type:  $\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>C:NOH$, (derived from acetophenone), also benzophenone oxime, $(C_6H_5)_2 \cdot C : NOH$, and oximes of cyclic ketones such as cyclohexanone and menthone could be reduced to amines in the same way. The method accordingly forms an easy way of preparnig certain amines which are otherwise difficult of access.

Oximes may advantageously be reduced in the dissolved state. Thus, ROSENMUND and PFANKUCH[4] obtained a 91 per cent yield of benzylamine by hydrogenating benzaldoxime with **platinum** in acetic acid solution.

f) *Reduction of Amides.*

Acid amides are hydrogenated to amines according to the general course

$$R \cdot CO \cdot NH_2 + 2H_2 = R \cdot CH_2 \cdot NH_2 + H_2O.$$

---

[1] Ber. dtsch. chem. Ges. 45, 3312 (1912).

[2] Bull. Soc. chim. France (3) 35, 259 (1906).

[3] Bull. Soc. chim. France (3) 33, 962 (1905); (4) 9, 464 (1911). — AMOUROUX: Ebenda 214.

[4] Ber. dtsch. chem. Ges. 56, 2258 (1923).

Mailhe[1], who employed Sabatier and Senderens' method, found that acetamide was converted into ethylamine by passage over **nickel** at 230°, a similar reaction being obtained with propionamide. The secondary amine was formed in addition to the primary body. **Copper** could be employed in place of nickel.

The use of **copper chromite** catalysts for this reaction in the liquid phase has been investigated by Wojcik and Adkins[2]. The solvent employed was found to exert a considerable influence on the nature of the product. Thus, in ethyl alcohol, in place of the normal reaction, the principal product was an alcohol, presumably according to the course:

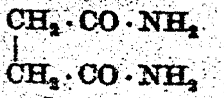
$$R\cdot CONH_2 + Et\cdot OH = R\cdot COOEt + NH_3 \qquad (a)$$
$$R\cdot COOEt + 2H_2 = R\cdot CH_2OH + EtOH, \qquad (b)$$

and a suitable solvent for the simple hydrogenation to an amine is stated to be dioxane. In general, the reaction was carried out at 250°, under a hydrogen pressure of 200—300 atm., using 350—400 c.c. of dioxane as the solvent for each g. mol. of amide, or twice this quantity per g. mol. of diamides such as succinamide. Some typical results are contained in Table 35.

Table 35.

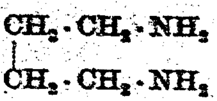
Amide hydrogenated	Percentage of copper chromite used, calc. on amide	Time of Hydrogenation Hrs.	Product
Heptamide	22	7.5	Heptylamine
Lauramide	20	0.8	Duodecylamine
Succinamide	27	5.5	Pyrrolidine

It will be seen that, under the conditions employed by Wojcik and Adkins, the reaction product may undergo ring closure with loss of a molecule of ammonia.



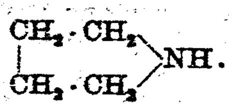
$$\begin{array}{l} CH_2\cdot CO\cdot NH_2 \\ | \\ CH_2\cdot CO\cdot NH_2 \end{array}$$

Succinamide.



$$\begin{array}{l} CH_2\cdot CH_2\cdot NH_2 \\ | \\ CH_2\cdot CH_2\cdot NH_2 \end{array}$$

1, 4-Butane diamine.



Pyrrolidine.

7. Reduction of Nitrogen-Oxygen-Compounds.

a) *Oxides of nitrogen.*

The reduction of oxides of nitrogen to ammonia was noticed by Kuhlmann in 1838[3], and was first examined systematically by Sabatier and Senderens, principally with **nickel** or **copper** catalysts.

Nitrous oxide differs from the remaining oxides in giving no ammonia. Sabatier and Senderens[4] found that reduced nickel exerted no decomposing action on nitrous oxide at room temperature; but, if hydrogen is present, reaction takes place with a spontaneous rise in temperature and the nitrous oxide is reduced to nitrogen:

$$N_2O + H_2 = N_2 + H_2O.$$

Copper did not catalyse the reaction at room temperature; but, above 180°, the process proceeds as with nickel. The replacement of hydrogen by an equal volume of nitrogen was also observed by H. Wienhaus and H. Ziehl[5] on

---

[1] Bull. Soc. chim. France (3) 35, 614 (1906).
[2] J. Amer. chem. Soc. 56, 2419 (1934).
[3] C. R. hebd. Séances Acad. Sci. 7, 1107 (1838).
[4] Ann. Chim. et physique (8) 4, 406 (1905).
[5] Ber. dtsch. chem. Ges. 65, 1461 (1932).

hydrogenating nitrous oxide in a shaker with an aqueous suspension of colloidal palladium at room temperature. As at higher temperatures, no ammonia or hydrazine was obtained.

Nitric oxide and the higher oxides of nitrogen, on the other hand, all give ammonia on reduction. SABATIER and SENDERENS[1], on passing a mixture of nitric oxide and hydrogen over nickel or copper at temperatures above 180°, obtained a mixture of ammonia and nitrogen, the formation of nitrogen being, as would be expected, favoured by high temperatures.

With *nitrogen peroxide*, interesting addition compounds (nitro-nickel and nitro-copper) are formed[2] at low temperatures; but, at temperatures above about 180°, ammonia is produced. The reaction temperature may rise spontaneously in the latter case, both with nickel and copper; and, with ratios of nitrogen peroxide to hydrogen within the required limits, there may be danger of an explosion. Nitrogen pentoxide or nitric acid vapours are reduced similarly, with production of a mixture of ammonia and nitrogen.

b) *Reduction of Aliphatic Nitro Compounds.*

If a mixture of the vapour of *nitromethane* with an excess of hydrogen is passed over nickel at 150—180°, methylamine is produced[3]:

$$CH_3 \cdot NO_2 + 3H_2 = CH_3 \cdot NH_2 + 2H_2O,$$

but at high temperatures, the reaction leads to methane and ammonia. Copper may be substituted for nickel, but the reaction product is more complicated and contains an addition product of nitro-methane and methylamine, $CH_3 \cdot NO_2 \cdot NH_2 \cdot CH_3$, which was obtained in crystalline form.

Nitro-ethane was reduced by hydrogen in the presence of nickel at 200°, with formation of ethylamine, in a similar way to nitro-methane; and, even with copper, the reaction takes place without complication, save that the use of an excessively high temperature leads to the production of nitrogen.

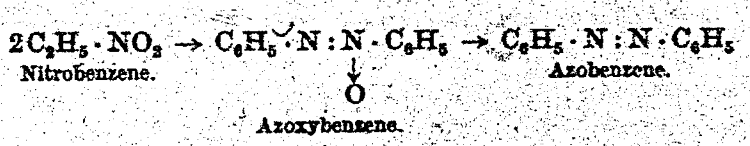
c) *Aromatic Nitro Compounds.*

These bodies are very easily reduced by all hydrogenation catalysts both in the vapour phase and in a dissolved or liquid state.

Normally the reduction product consists of the corresponding amine, e. g. nitrobenzene is reduced substantially quantitatively to aniline:

$$C_6H_5 \cdot NO_2 + 3H_2 = C_6H_5 \cdot NH_2 + 2H_2O,$$

but, by working in alkaline solution[4] it is possible to pass through a series of intermediate products similar to those obtained also in the non-catalytic reduction of nitrobenzene in alkaline media, the reaction course under these conditions being:



$$\underset{\text{Nitrobenzene.}}{2C_2H_5 \cdot NO_2} \rightarrow \underset{\text{Azoxybenzene.}}{C_6H_5 \cdot N : \underset{\overset{\downarrow}{O}}{N} \cdot C_6H_5} \rightarrow \underset{\text{Azobenzene.}}{C_6H_5 \cdot N : N \cdot C_6H_5}$$

$$\rightarrow \underset{\text{Hydrazobenzene.}}{C_6H_5 \cdot NH \cdot NH \cdot C_6H_5} \rightarrow \underset{\text{Aniline.}}{2C_6H_5 \cdot NH_2}.$$

---

[1] C. R. hebd. Séances Acad. Sci. 135, 278 (1902); Ann. Chim. et Physique: loc. cit., p. 407.

[2] SABATIER, SENDERENS: Ann. Chim. et Physique (7) 7, 413 (1895).

[3] SABATIER, SENDERENS: Ann. Chim. et Physique (8) 4, 410 (1905).

[4] A. BROCHET: Bull. Soc. chim. France (4) 15, 554 (1914).

The vapour-phase hydrogenation of *nitrobenzene* to aniline was investigated by Sabatier and Senderens[1]. **Nickel,** especially if highly active, was found not to be so suitable as **copper,** in that hydrogenation of the benzene nucleus also occurred with production of cyclohexylamine; and these authors recommend the employment of a copper catalyst at 300—400°; but other hydrogenating metals, including **iron, cobalt** and **platinum** were also successfully used.

The reaction has been studied in considerable detail in a series of papers by O. W. Brown and C. O. Henke[2]. For gas-phase hydrogenation, these authors consider that nickel may be a better commercial catalyst than copper, on account of its rapid action, even though copper gives higher percentage yields. The obtaining of a nickel catalyst of suitable activity—by choosing a suitable temperature for its reduction from the oxide, and, if the oxide is prepared by the ignition of the nitrate, by carrying out also this stage at a suitable temperature—has a fundamental effect on the yield of aniline obtained. Brown and Henke recommend a temperature of 450° for the ignition of the nickel nitrate to oxide, a temperature of 435—475° for the reduction of this oxide with hydrogen, and an actual hydrogenation temperature of 192°. Under these conditions, a yield of over 90 per cent of aniline could be obtained, with nitrobenzene and hydrogen at the rate, respectively, of 3.7 g. and 17 l. per hour, in the presence of nickel derived from 16 g. of oxide. With copper, the best results were obtained by igniting the nitrate at 414° and reducing the oxide at 314°. This catalyst gave yields of aniline up to 97.5 per cent on passing nitrobenzene and hydrogen, at 253° and at the same rates as those given above for nickel, over copper derived from 29 g. of the oxide. The permissible rate of passage is thus lower with copper. As has been found in other reactions, however, copper prepared by reducing a precipitated oxide is preferable to that made by an ignition method; and the effectiveness is further increased by mounting it on an asbestos or other support[3].

By reason of the ease of the reduction, the reaction may also be catalysed by a large number of metals which are usually not sufficiently active to be effective for hydrogenation generally. Thus, **silver,** prepared by the reduction of the carbonate at 280° gave yields of aniline up to over 98 per cent with similar rates of passage to those employed with copper and nickel, with a hydrogenation temperature of 300° and with silver derived from 20 g. of the basic carbonate. Silver is thus an even better catalyst than copper, since it combines a high yield with a relatively high rate of possible passage of the mixture of nitrobenzene and hydrogen. **Gold** may also be used. This is stated to have a high initial activity, which subsequently decreases.

Many other catalysts have been employed, with varying degrees of success. **Lead,** obtained by the reduction of the oxide at 270°, gives, at 270—290°, fair yields of aniline, together with some azobenzene (80—90 per cent of aniline and 10—20 per cent of azobenzene under the optimum conditions studied)[4]. The use of **tin** may be noted, in view of the employment of this metal as a very effective catalyst also in the hydrogenation-cracking of coal. From nitrobenzene, yields of aniline up to 98—99 per cent were given, at 275—300°, by a catalyst made by reducing tin oxide or tin oxalate with hydrogen at 294°.[5] The catalytic

---

[1] Ann. Chim. et Physique (8) **4**, 414 (1905); C. R. hebd. Séances Acad. Sci. **135**, 226 (1902).

[2] J. physic. Chem. **26**, 161, 272, 715 (1922).

[3] O. W. Brown, C. O. Henke: J. physic. Chem. **26**, 715 (1922).

[4] C. O. Henke, O. W. Brown: J. physic. Chem. **26**, 324 (1922).

[5] O. W. Brown, C. O. Henke: J. physic. Chem. **27**, 52 (1923).

reduction of nitrobenzene may also be carried out with **bismuth, antimony, manganese** or **chromium.**

Thallium, made by reducing thallic oxide at about 250°, is of special interest in that it induces the formation of azobenzene almost to the exclusion of aniline. Thus, Henke and Brown found that, on passing, at 260°, nitrobenzene at the rate of 4 g. per hour and hydrogen at 1.7 l. per hour (13 per cent excess) over a catalyst derived by the reduction of 21 g. of thallic oxide, a yield of 90 per cent of azobenzene and 4 per cent of aniline was obtained.

Of oxide catalysts, the use of **manganous oxide** by Sabatier and P. Fernandez[1] may be mentioned. These workers also used **zinc oxide;** but, under the conditions employed, this probably underwent reduction to the metal. In each case, however, the reaction product was complex: thus, on passing a mixture of nitrobenzene and hydrogen over manganous oxide at 300—600°, the product contained—in addition to aniline—di- and tri-phenylamine, benzene, ammonia and carbon dioxide. With **vanadium oxide**[2] yields of aniline up to 92 per cent were observed; but the product also contained a little diphenylamine. The best temperature with this catalyst was 403°, with a nitrobenzene feed of 4.9 g. per hour and a hydrogen flow of 14 l. per hour, in the presence of 15 g. of vanadium pentoxide.

Many *two-component catalysts* have also been proposed. Thus, Doyal and Brown obtained a 99 per cent yield of aniline with **copper chromite at 310°;** and Griffiths and Brown[3] report yields of the same order with **cobalt manganite** prepared by the reduction of cobalt permanganate. The optimum temperature in this latter case was 260°; but, with cobalt manganite, the yield is very sensitive to variations in temperature.

The hydrogenation of nitrobenzene in the vapour phase has been treated in considerable detail both on account of the extensive experimental details which are available in the published literature and by reason of the many, in some cases unusual, hydrogenation catalysts which have been employed. The reduction may, however, be equally well carried out in the liquid phase in which it possesses interest from the standpoint of its reaction velocity which would—in view of the ease of reduction—be expected to be high.

With **platinum,** or **palladium,** catalysts, the reduction, for instance, in alcoholic solution, takes place very easily[4], either at room temperature or at temperatures slightly above this. S. G. Green[5] states, however, that nitrobenzene is only slowly reduced in the liquid phase with nickel, but that the reaction velocity may be increased by introducing various long chain carbon compounds such as methyl palmitate, methyl oleate or a high-boiling paraffin. Green suggests that this action appears to be associated with some influence of the long-chain carbon compound on the state of dispersion of the nickel. However, commercial specimens of nitrobenzene may hydrogenate surprisingly slowly in the liquid phase even with platinum. In some work of the author and V. Stone[6] in which this slowness of hydrogenation was encountered, the reaction velocity for hydrogenation in the liquid phase with platinum was increased to a value no less than 150 times that given by the purest nitrobenzene which could be purchased, merely by careful purification from catalyst poisons. Since ordinary

---

[1] C. R. hebd. Séances Acad. Sci. 185, 241 (1927).

[2] H. A. Doyal, O. W. Brown: J. physic. Chem. 36, 1549 (1932).

[3] J. physic. Chem. 42, 107 (1938).

[4] C. Paal, C. Amberger: Ber. dtsch. chem. Ges. 38, 1406 (1905). — Paal, J. Gerum: Ebenda 40, 2209 (1907). — A. Skita, W. A. Meyer: Ebenda 45, 3579 (1912).

[5] J. Soc. chem. Ind. 52, 52 T, 172 T (1933). [6] J. chem. Soc. [London] 1934, 672.

nitrobenzene contains much of the thiophene and other sulphur compounds present in the benzene from which it is made—possibly as nitroderivatives—and may, in addition, contain traces of sulphonic acids derived from the mixture of nitric and sulphuric acids used in nitration, it is probable that some of the cases of slow hydrogenation in the liquid state in the presence of small and limited quantities of catalyst may be due to its poison content. This, however, does not explain the interesting observation of GREEN, quoted above, on the accelerative action of long-chain bodies.

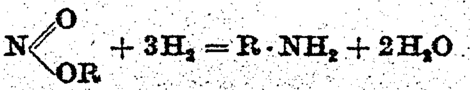
Nitrobenzene has also been reduced with hydrogen *under pressure*. Thus the high-pressure liquid-phase reduction of nitrobenzene and other nitro compounds has been studied by O. W. BROWN, G. ETZEL, and C. O. HENKE[1]. The reaction was carried out with a **nickel** catalyst at hydrogen pressures between 15 and $47^1/_2$ atmospheres. In a typical experiment, a quantitative yield of aniline was obtained, with nitrobenzene dissolved in benzene, at a hydrogenation temperature of 215°. It is apparently necessary, particularly in the larger scale hydrogenation of nitro bodies, to exercise caution. Thus, T. S. CARSWELL[2] has reported that a *violent explosion*, following the rapid absorption of hydrogen, resulted during the hydrogenation of nitro-anisole in an autoclave at 250° in the presence of nickel.

Other aromatic nitro compounds react in a way very similar to nitrobenzene, and their hydrogenation consequently needs little special description. Thus, SABATIER and SENDERENS[3] hydrogenated o- or m-*nitrotoluene* in the vapour phase with **copper** at 300—400° or with **nickel** at 200—250°, good yields of the corresponding toluidine being obtained. α-Nitronaphthalene was reduced similarly; and vapour-phase hydrogenation was also applied to dinitro bodies, e. g. dinitrobenzene or dinitrotoluene give a good yield of the corresponding diamine[4].

These reactions may, of course, also be carried out in the liquid phase. For reduction in this way in the presence of nickel, reference may be made to the work of O. W. BROWN, G. ETZEL and C. O. HENKE[1].

d) *Reduction of Esters of Nitrous Acid.*

Nitrous esters may be regarded as differing from nitro compounds by an oxygen linking between the alkyl group and nitrogen. Their reduction to amines by a reaction of the type:



$$\mathrm{N}{\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{OR}}} + 3\mathrm{H_2} = \mathrm{R \cdot NH_2} + 2\mathrm{H_2O} \qquad (1)$$

which is analogous to the corresponding reduction of a nitro compound:

$$\mathrm{R \cdot NO_2} + 3\mathrm{H_2} = \mathrm{R \cdot NH_2} + 2\mathrm{H_2O} \qquad (2)$$

cannot readily be carried out non-catalytically, for instance by zinc and acid or by sodium amalgam.

Reaction (1), however, occurs if a nitrite is passed, together with hydrogen, over **nickel**. Thus, G. GAUDION was able to hydrogenate methyl, ethyl, and higher alkyl nitrites by treatment with nickel at 180—200° or with copper at a somewhat higher temperature, the general technique being that of SABATIER

---

[1] J. physic. Chem. 32, 631 (1928).

[2] J. Amer. chem. Soc. 53, 2417 (1931).

[3] Ann. Chim. et Physique (8) 4, 417 (1905).

[4] G. MIGNONAC: Bull. Soc. chim. France (4) 7, 154, 823 (1910)

and SENDERENS. It is probable that prior isomerisation of the nitrite to a nitro-compound occurs, the course of the reaction being thus:

$$EtO \cdot NO \rightarrow Et \cdot NO_2 \rightarrow EtNH_2.$$

This isomerisation has been studied by P. NEOGI and T. CHOWDHURI[1], who found that the change occurred spontaneously on heating the alkyl nitrite to temperatures above 100°.

e) *Reduction of Nitrosamines.*

The reduction of aromatic nitrosamines follows a different course according to whether the reaction is carried out non-catalytically, for instance by means of zinc and acetic acid[2], or by shaking with hydrogen in the presence of palladium[3]. In the former case, the reduction leads to di-aryl hydrazines: in the latter, to di-aryl amines, with evolution of nitrogen.

$$(C_6H_5)_2N \cdot NO + 2H_2 = (C_6H_5)_2N \cdot NH_2 + H_2O \qquad (1)$$

$$2(C_6H_5)_2N \cdot NO + 3H_2 = 2(C_6H_5)_2NH + N_2 + 2H_2O. \qquad (2)$$

III. The Hydrogenation of Oxides and Sulfides of Carbon.

The reaction between hydrogen and carbon monoxide has become of very great importance on account of the possibility of varying the reaction product, by changing the catalyst and general conditions of the hydrogenation, in such a way as to give not only methane but also various alcohols or higher hydrocarbons.

Thus, with normal metallic catalysts such as **nickel** at high temperatures, simple reduction to methane occurs:

$$CO + 3H_2 = CH_4 + H_2O.$$

Under suitable conditions, however, catalysts containing **nickel** or **cobalt** in conjunction with other constituents may be made to synthesise higher hydrocarbons from mixtures of carbon monoxide and hydrogen. This is the so-called benzine synthesis of FISCHER and TROPSCH.

Thirdly, by using mild hydrogenating catalysts such as **zinc chromite** at high pressures, methyl alcohol is synthesised:

$$CO + 2H_2 = CH_3 \cdot OH.$$

Finally, the interaction of carbon monoxide and hydrogen may lead to the production either of higher alcohols or to complex mixtures of various oxygenated derivatives. Each of these processes is of the greatest industrial importance. The FISCHER-TROPSCH synthesis provides a means of manufacturing liquid hydrocarbons of almost every nature—including artificial petrol, heavy oils and lubricating oils—directly from every sort of fuel: the synthesis of methyl alcohol and, to a lesser degree, of higher alcohols has already attained the rank of an industrial process of considerable magnitude; and the conversion of carbon monoxide to methane is of interest in the gas industry as a means of providing gas of relatively high calorific value.

1. Hydrogenation of Carbon Suboxide.

The first oxide of carbon, in order of the degree of oxidation, is carbon suboxide, C_3O_2, which was first prepared by O. DIELS,

---

[1] J. chem. Soc. [London] 109, 701 (1916); 111, 899 (1917).
[2] E. FISCHER: Liebigs Ann. Chem. 190, 175 (1874).
[3] C. PAAL, W. N. YAO: Ber. dtsch. chem. Ges. 63, 57 (1930).

The hydrogenation of carbon suboxide in the gas phase with **nickel** or **platinum** supported on silica gel was studied by K. A. Kobe and L. H. Reyerson[1]. Under the conditions used, the principal product, at 200—300°, was propylene:

$$CO:C:CO + 5H_2 = CH_3 \cdot CH:CH_2 + 2H_2O.$$

This body, or the saturated hydrocarbon, propane, would be expected from the constitution. No reaction was obtained on liquid-phase hydrogenation with platinum.

2. Reduction of Carbon Monoxide and Dioxide.

a) Production of Methane.

The reduction of carbon monoxide or dioxide to methane was observed by Sabatier and Senderens in 1902[2]. With **nickel**, these authors found that the reaction began at 180—200° and took place easily at 230—250°, with production of methane and water. Above 250° some deposition of carbon occurred, according to the reaction:

$$2CO = CO_2 + C.$$

Cobalt, at 300°, could also be used; but copper was stated by Sabatier and Senderens not to be active for the reduction of carbon monoxide.

Carbon dioxide was hydrogenated very similarly. With **nickel**, the reaction:

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

began at 230° and took place readily at 300°; and, at temperatures below 400°, no deposition of carbon on the catalyst was observed. **Cobalt** began to be active at 300° and acted similarly to nickel; but **copper** only reduced carbon dioxide as far as the monoxide, a suitable reaction temperature for this being 420—440°.

Many attempts have been made to utilise the catalytic reduction of oxides of carbon, and especially of carbon monoxide, as a means for manufacturing a gas of high calorific value from water gas, by the conversion of its carbon monoxide into methane. The principal difficulty encountered lies in the deposition of carbon on the catalyst. This may be minimised by using a gas containing a large excess of hydrogen. Thus, Erdmann[3] has described tests on a small works scale in which water gas, after removal of part of its carbon monoxide by a preliminary low-temperature treatment, was passed over a **nickel** catalyst at 280—300°. The preliminary treatment in general raised the hydrogen content of the gas to over 80 per cent and decreased the carbon monoxide to less than 20 per cent. With gas of this composition, little or no deposition of carbon was observed. An alternative method of raising the hydrogen-carbon monoxide ratio is obviously by reaction with steam.

As a variation to the normal reduction course, Armstrong and Hilditch[4] find that a reaction approximating to:

$$2CO + 2H_2 = CH_4 + CO_2 \tag{1}$$

takes place on passing a mixture of equal parts of carbon monoxide and hydrogen over nickel at temperatures below 300°. A suitable temperature at atmospheric pressure is 280°; and the reaction proceeds at increased pressures more or less the same as at atmospheric pressure, except that, with nickel, the minimum temperature of interaction rises with increasing pressure, namely with increasing

---

[1] J. physic. Chem. 35, 3025 (1931).

[2] C. R. hebd. Séances Acad. Sci. 134, 514, 680 (1902); Ann. Chim. et Physique (8) 4, 418 (1905).

[3] J. Gasbeleucht. 54, 737 (1911).

[4] Proc. Roy. Soc. [London], Ser. A 103, 25 (1923).

stability of nickel carbonyl at any given temperature. With cobalt, the normal hydrogenation

$$2CO + 3H_2 = CH_4 + H_2O \qquad (2)$$

preponderates and the decomposition of carbon monoxide to carbon and carbon dioxide also takes place to a considerable extent. ARMSTRONG and HILDITCH consider that reaction (1) is due to interaction of carbon monoxide with water vapour (which is always present), with production of carbon dioxide and hydrogen, which latter then reduces a second molecule of carbon monoxide. The importance of the reaction lies in the possibility of using gas mixtures not containing a large excess of hydrogen; but the process involves the ultimate removal of carbon dioxide.

b) *Synthesis of Methanol.*

The equilibrium percentage of products in the reaction:

$$\underset{\text{1 vol.}}{CO} + \underset{\text{2 vols.}}{2H_2} = \underset{\text{1 vol.}}{CH_3 \cdot OH}$$

will obviously be influenced by pressure; and, by using mild hydrogenation catalysts such as **zinc** or even **copper** at high pressures, it is found possible to raise the production of methyl alcohol, compared with that of methane, until the alcohol becomes the principal product. Early work on this synthesis was done by PATART[1] and by AUDIBERT[2] the former of whom used **zinc oxide** as the catalyst at 400—420° and at a pressure of 150—200 atm.

The calculation of the equilibrium constant:

$$K_p = \frac{p_{CH_3OH}}{p_{CO} \times p^2_{H_2}}$$

and, consequently, of the equilibrium percentage of methyl alcohol at various temperatures and pressures is rendered difficult by the lack of sufficiently exact thermochemical data; but calculations of this figure have been made by a number of workers including KELLEY[3] and AUDIBERT and RAINEAU[4].

The equilibrium has been discussed critically by W. A. BONE[5], who emphasises the figures of D. M. NEWITT, B. J. BYRNE and H. W. STRONG[6], which were obtained experimentally both by static and flow methods in the presence of a reduced $3ZnO \cdot Cr_2O_3$ catalyst to which 0.5 per cent of **copper nitrate** had been added.

As a guide to the equilibrium percentages obtained experimentally at various temperatures between 280° and 338°, and at pressures of the order of 100 atm., some of NEWITT, BYRNE and STRONG's results are reproduced in Table 36.

Table 36.

Reaction temperature °C.	Reaction pressure Atm.	Partial pressure of methyl alcohol Atm.	K_p	Method of approach
280	84.6	16.9	5.0×10^{-4}	Decomposition
	91.9	16.3	4.0×10^{-4}	Synthesis
289	99.8	18.2	3.1×10^{-4}	Decomposition
	100.4	16.2	2.8×10^{-4}	Synthesis
306	98.4	10.2	1.4×10^{-4}	Decomposition
	95.8	7.2	1.2×10^{-4}	Synthesis
320	96.4	5.0	6.7×10^{-5}	Decomposition
	95.8	4.8	6.4×10^{-5}	Synthesis
338	99.1	3.8	4.3×10^{-5}	Decomposition
	88.4	2.6	4.6×10^{-5}	Synthesis

---

[1] Chim. et Ind. 13, 179 (1925). [2] Chim. et Ind. 13, 186 (1925).
[3] Ind. Engng. Chem. 18, 78 (1926); 21, 53 (1929).
[4] Ind. Engng. Chem. 20, 1105 (1928).
[5] Proc. Roy. Soc. [London], Ser. A 127, 251 (1930).
[6] Proc. Roy. Soc. [London] 123, 236 (1929).

On the whole, the free energy change could be represented, in close agreement with the experimental results, by the free energy equation:

$$\Delta F = 70.5\,T - 30{,}500\,.$$

This relationship enables the experimental results to be extrapolated over the entire temperature range at which it is practicable to utilise the reaction for the manufacture of methyl alcohol. The results of this extrapolation are summarised in Table 37.

Table 37.

Temperature °C.	K_p
260	1.2×10^{-3}
280	4.5×10^{-4}
300	1.6×10^{-4}
320	6.7×10^{-5}
340	2.9×10^{-5}
360	1.3×10^{-5}
380	6.3×10^{-6}

On this basis, the equilibrium mixture, at 327° and 200 atm., would contain about 18 per cent of methyl alcohol, 55 per cent of hydrogen and 27 per cent of carbon monoxide. These figures differ substantially from those calculated by Audibert and Raineau or those of Kelley, which, under the same conditions of temperature and pressure, correspond respectively with 41.5 and 84 per cent of methyl alcohol in the equilibrium mixture.

The original catalyst used by Patart was **zinc oxide**, at 400—420° and at a pressure of 150—250 atm.; but the activity of zinc oxide may be increased by the use of a second component such as **chromium oxide** or **copper oxide**. **Copper** itself may also be used; but its activity varies greatly with its method of preparation in such a way that some workers have found the activity of copper to be low, while others have reported a fair activity.

According to the results of Audibert and Raineau (loc. cit.), the activity of copper oxide is raised by the addition of small quantities of zinc oxide; but the catalyst is stated to be sensitive to deactivation by heat, and the most resistant catalysts were obtained by promoting copper with **beryllium oxide**. The effect of the addition of zinc oxide to copper oxide was followed quantitatively by P. K. Frolich, M. R. Fenske, P. S. Taylor, and C. A. Southwich[1], the effect of increasing quantities of zinc oxide under comparable conditions of operation being shown in Table 38. The temperature and pressure used were 320° and 204 atm.

Table 38.

Composition of catalyst in g. mols. per cent		Percentage of CO converted to CH_3OH
CuO	ZnO	
80	20	0.5
60	40	3.7
50	50	8.5
40	60	13.5
30	70	14.5
20	80	14.2
10	90	13.4
0	100	12.5

It is probable that the increased activity of many of these two-component catalysts is due to a high degree to internal support action, even if each component possesses individual activity. This, of course, also applies to catalysts containing more than two components. Metallic supports may also be used. Thus, W. K. Lewis and P. K. Frolich[2] worked with a catalyst which consisted, before reduction, of 36 per cent of zinc oxide, 44 per cent of copper oxide and 20 per cent of aluminium oxide, prepared by co-precipitation and supported on metallic copper, the ratio of catalyst to copper support being 1 to 3. The function of the copper is to give a catalyst of higher thermal conductivity and thus to bring about a more even heat distribution throughout the catalyst mass.

The promotion of zinc oxide with **chromium oxide** is of special interest, since catalysts of the zinc chromite type probably constitute the most suitable

---

[1] Ind. Engng. Chem. 20, 1327 (1928).

[2] Ind. Engng. Chem. 20, 285 (1928).

contact bodies for the synthesis, both on account of their high activity per unit of volume and of their resistance to deactivation by heat. R. L. Brown and A. E. Galloway[1] give the following figures for the rate of production of methyl alcohol in terms which make possible the derivation of the production per unit volume and per unit weight of zinc oxide and of reduced zinc chromate. It will be noted that although the yield per volume from reduced zinc chromate is higher than from zinc oxide alone, the yield per unit of weight—by reason of the greater density of reduced zinc chromate—is less. The tests were carried out at 400° and 180 atm (Table 39).

Table 39.

Catalyst	Volume of catalyst	Weight of catalyst	Methyl alcohol produced			
			S.V. = 7500		S.V = 16,200	
	c.c.	Grams	g./hr.	%	g./hr.	%
Zinc oxide	250	60	68	8.2	87	4.5
Basic zinc chromate .	250	165	—	—	137.5	7.4
Normal zinc chromate	250	242	130	16.8	184	9.6

With lower space velocities, a higher percentage of methyl alcohol per passage was obtained; but, as is necessarily the case in such reactions, this corresponded with a lower space-time yield on account of the slowness of passage. Thus, under the above conditions, at a space velocity of 3000, the percentage of methyl alcohol rose to 19.5, but the production sank to 71 grams per hour for the 250 c.c. of normal zinc chromate used.

Further data relative to the performance of zinc-oxide/chromium-oxide catalysts of various compositions have been published by M. C. Molstad and B. F. Dodge[2]. The percentage of methyl alcohol obtained at a pressure of 178 atm., with a space velocity of 25,000, (from which the space-time-yields can also be calculated if required), are given below. The composition of the catalyst is expressed in atomic percentages of the two metals (Table 40).

Table 40.

Composition of catalyst		Temperature	Per cent conversion	
Zn	Cr	°C.	At beginning of test	At end of test
100 (Pure ZnO)	0	400	6.0	4.0
96	4	350	4.8	3.9
88	12	350	9.4	7.5
		375	11.5	10.6
75	25	375	14.0	13.7
58	42	350	10.8	16.2
		375	12.6	14.4
39	61	300	0.2	4.0
		325	3.3	10.2
		350	7.6	13.0
		375	8.6	12.6
		400	8.2	10.4
		425	6.3	7.1
0	100 (Pure Cr_2O_3)	400	6.5	6.8

It will be noted, firstly, that pure chromium oxide is somewhat more active than pure zinc oxide and, secondly, that, as the atomic percentage of chromium is increased above about 60, the activity of the catalyst, in place of decreasing with use, rose during the period of the test, for details of which reference should be made to the original paper. From curves connecting the composition with

---

[1] Ind. Engng. Chem. 20, 960 (1928).

[2] Ind. Engng. Chem. 27, 134 (1935).

the performance, the most active catalysts after use for some time correspond with equal atomic percentages of zinc and chromium in the mixture, although the highest initial activity was given by catalysts containing 75 atomic per cent of zinc and 25 of chromium.

c) Formation of Higher Alcohols.

While, with normal catalysts of the above types under ordinary conditions of use, the process—save possibly for slight methane formation—leads to the production of almost pure methyl alcohol, the reaction may be modified either by changing the conditions or, more effectively, by incorporating other components with the catalyst, in such a way that considerable quantities of higher alcohols are formed. In general, a relatively high reaction temperature, or a slow rate of passage, or catalysts containing an alkali, favour the formation of these higher products.

The alcohols produced vary greatly with the conditions and with the catalyst. P. K. Frolich and W. K. Lewis[1] give the following analysis of the liquid product obtained with a zinc chromite catalyst containing potash, at a working temperature of 460—490° and a pressure of 240 atm (Table 41).

Table 41.

Alcohol	Percentage in product
Methyl	17.8
Ethyl	2.3
Propyl (mixture of isomers)	33.4
Butyl (mixture of isomers)	2.5
Amyl (mixture of isomers)	9.0
Higher alcohols	Trace
Water	35.6

It will be noted that the temperature employed is considerably higher than that normally used for the synthesis of methyl alcohol.

G. T. Morgan, D. V. N. Hardy and R. A. Procter[2] found that, although the alkalisation of manganese chromite catalysts greatly increased the proportion of higher alcohols in the product, the rate of formation of liquid products as a whole was, in most cases, substantially decreased. Rubidia, however, acted very effectively, without decreasing the liquid yield. Some results of these workers with rubidium and potassium hydroxides under comparable conditions are summarised in Table 42.

Table 42.

Impregnating metal	Percentage, by weight, of impregnating metal	Yield of liquid product g. per hr.	Methyl alcohol in product Per cent	Carbon present as compounds other than methyl alcohol Per cent
None	—	62	80.5	13
Rubidia	2.3	61	75.5	23.1
	4.4	62	67.2	33.1
	9.8	53	49.7	46.0
Potash	1.5	47	81.8	16.4
	4.9	33	50.7	48.6
	8.4	24	52.2	43.4
	11.9	27	49.0	46.3

The mixture of higher alcohols contained, as in Frolich and Lewis' work, only a relatively small percentage of ethyl alcohol; but G. T. Morgan and R. Taylor[3] were able to obtain a product containing appreciable quantities of this alcohol by using a cobalt-zinc-manganese catalyst containing potash. Under the conditions employed, however, considerable methane formation occurred.

In a further paper, R. Taylor gives the distribution of the individual alcohols in products obtained with three catalysts of different constitution (Table 43).

---

[1] Ind. Engng. Chem. 20, 354 (1928). [2] J. Soc. chem. Ind. 51, 1 T (1932).
[3] Proc. Roy. Soc. [London], Ser. A 131, 533 (1931).

The products also contained aldehydes and acids, which were removed before the fractionation of the alcohols, and the product from the first of the catalysts given was hydrogenated with nickel before distillation, to remove unsaturated bodies.

Table 43.

Alcohol	Wt. of alcohol (g.), per kg. of crude product		
	Catalyst Cu-MnO-CoS	Catalyst Mn-Cr-Rb (oxide)	Catalyst Zn-Mn-Co-K (oxide)
Methyl	220	420	198
Ethyl	200	12	86
n-Propyl	50	43	17
n-Butyl	16	—	4
iso-Butyl	3	69	11
n-Amyl	6	—	1
β-Methyl butyl ..	2	8	1.5
n-Hexyl	2	—	—
β-Methyl amyl ..	—	6.5	—
n-Heptyl	< 1	—	—
Residue	1	89	1.5

Taylor points out that the first catalyst, which contained no alkali, gave a greater proportion of higher alcohols with straight chains than was the case with the second catalyst, which gave relatively large quantities of, for instance, isobutyl alcohol. The catalysts containing cobalt gave increased quantities of ethyl alcohol: indeed, it will be noticed that the copper-manganese oxide-cobalt sulphide catalyst led to a far greater production of this alcohol than the zinc-manganese-cobalt-potash catalyst previously used.

As already mentioned, aldehydes are always present in the reaction product, and the mechanism by which higher alcohols are formed may be one of successive aldolisation[1], i. e. by means of processes of the type:

$$R\cdot CHO + R'\cdot CH_2\cdot CHO \longrightarrow R\cdot CHOH\cdot CHR'\cdot CHO \xrightarrow[-H_2O]{} R\cdot CH:CR'\cdot CHO$$

$$\xrightarrow[+H_2]{} R\cdot CH_2\cdot CHR'\cdot CHO \xrightarrow[+H_2]{} R\cdot CH_2\cdot CHR'\cdot CH_2OH,$$

but F. **Fischer**[2] has put forward a mechanism involving the direct addition of carbon monoxide to alcohols with production of acids, the course postulated being:

$$CH_3\cdot OH + CO \longrightarrow CH_3\cdot COOH \xrightarrow[H_2]{} CH_3\cdot CHO \xrightarrow[H_2]{} CH_3\cdot CH_2\cdot OH$$

in addition to reactions such as:

$$2CH_3\cdot COOH = (CH_3)_2CO + CO_2.$$

It may be noted that acids, aldehydes and ketones are found in varying quantities, according to the catalyst and conditions employed, in the reaction mixture: further, D. V. N. **Hardy**[3] has synthesised acetic acid in fair yields from methyl alcohol and carbon monoxide, although with a mixed dehydration catalyst (copper phosphate).

A complicated mixture of alcohols and other organic bodies may also be made by alkalised iron or cobalt catalysts at high pressures. Considerable work on this type of process has been carried out with this type of catalyst by F. **Fischer** and his co-workers, who have given the name synthol to the mixture produced. Suitable conditions, with a catalyst consisting of iron impregnated with alkali, are a temperature of 400—420° and a working pressure of 150 atm.[3]; and, whereas impregnation of the iron catalyst with strong alkalis leads to insoluble oily products, the use of iron together with weak bases results in the

---

[1] G. T. **Morgan**: Proc. Roy. Soc. [London], Ser. A 127, 246 (1930).

[2] Ind. Engng. Chem. 17, 576 (1925).

[3] J. chem. Soc. [London] 1934, 1335; 1936, 358

formation of watersoluble bodies. It may be noted that, of the alkalis, **rubidia** was most effective, as was also found by MORGAN, HARDY and PROCTER (loc. cit.) with catalysts of the mixed oxide type in the formation of higher alcohols.

E. AUDIBERT and A. RAINEAU[1] lay weight on the prevention of the reduction of the iron from its oxide form during use and recommend the employment of **iron phosphate or borate.** With these catalysts, the following yields per cub. m. of gas are reported:

	Grams		Grams
Organic liquids	118	Carbon dioxide	444
Gaseous hydrocarbons ..	97	Water vapour	48

The higher calorific value of the organic liquids was about 9000 calories per kilogram and that of the gaseous hydrocarbons 12,000 calories.

d) *Synthesis of Hydrocarbons.*

This fundamentally important modification of the hydrogen-carbon-monoxide reaction is based on the observation by F. FISCHER and H. TROPSCH that, as the reaction pressure is reduced, the formation of oxygenated condensation products is, in the presence of suitable catalysts, replaced by the production of condensed liquid hydrocarbons, the lighter fractions of which may be used as a substitute for natural petrol while the heavier fractions constitute a liquid fuel suitable for use, for instance, in engines of DIESEL type. It has also been found possible to produce satisfactory lubricating oils in this way; and, accordingly, the process forms a highly important method of manufacturing hydrocarbon oil products of almost every nature, starting from coke or any form of carbonaceous fuel: indeed, from the standpoint of natural economics, in countries possessing no natural oil deposits, the FISCHER-TROPSCH process—together with the alternative method of hydrocarbon production by the hydrogenation of coal—is certainly of an order of importance comparable with that, for instance, of the synthesis of ammonia. Further, while the hydrogenation of coal, as such, is associated with the loss of its by-products, the conversion of coke to hydrocarbons utilises a normal residue of the gas industry and may be coupled with the hydrogenation of selected tar products which are not required for other purposes.

The literature of the synthesis is very large; but for details of many of the main results, reference may be made to a summary by FISCHER[2], which contains a list of papers published up to 1934. An extensive summary has also been published in *Koppers Review*[3]; and reference may also be made to papers by ELVINS and NASH[4], AICHER, MYDDLETON and WALKER[5] and to extensive work by S. KODAMA, K. FUJIMURA and others[6].

In early work[7] FISCHER and TROPSCH found finely-divided **cobalt** to be the most suitable catalyst either alone or in conjunction with **iron** or with oxides such as **chromium oxide, zinc oxide** or **beryllium oxide.** Thus, with a mixed iron-cobalt catalyst, a yield of liquid or easily liquefied hydrocarbons of the order of 100 g. per cub. m. of water gas was obtained. Solid hydrocarbons were also produced, especially on using an **alkalised iron-copper catalyst.**

In general, catalysts containing a **cobalt** or **nickel** base are used at about 200°, and those containing **iron** at about 250°. Promotion of these metals with

---

[1] Ind. Engng. Chem. 21, 880 (1929). [2] Brennstoff-Chem. 16, 1 (1935).
[3] Koppers Rev. 2, Nr. 3 (1937).
[4] J. Soc. chem. Ind. 45, 876 (1926); 46, 473 T (1927); Fuel Sci. Pract. 5, 263 (1926).
[5] J. Soc. chem. Ind. 54, 313 T (1935); 55, 131 T (1936).
[6] For references to these, see FISCHER's summary (loc. cit.).
[7] Ber. dtsch. chem. Ges. 59, 830, 832, 923 (1925).

thoria and the incorporation of a porous carrier such as kieselguhr gives catalysts which are both highly active and resistant to decrease in activity during use, as is shown in the following table 44, which is taken from FISCHER's summary and represents the comparative performance of a number of catalysts of this class. The yields with iron and nickel are approximate only.

Table 44.

Base	Promoter	Support	Method of Preparation	Yield of product, in g. per cub. m. of gas	Number of days in use before reduction of activity to 80 per cent of original
Iron,	Cu-Mn + 0.4 % K_2CO_3	Silicagel	Decomposition of nitrates	30—35	8
	Cu	Kieselguhr	Co-precipitation	28	8
Nickel,	Th	,,	,,	100	30
	Mn-Al	,,	,,	105	35
Cobalt,	Th	,,	,,	110	30
	Th	,,	Decomposition	105	25
	Th	,,	Co-precipitation	105	> 30
	Th-Cu	,,	,,	105	60
Co-Ni		—	Alloy-skeleton from silicon alloy	85	12

From the above it will be seen that a very satisfactory catalyst both from the standpoint of performance and endurance appears to be **cobalt-thoria**, which may be made by the co-precipitation of cobalt and thorium nitrates, in the ratio for instance of 5 to 1, by means of potassium carbonate, in the presence of kieselguhr, the washed and dried paste being pelleted in the usual way. It is necessary to wash the catalysts free from alkali, otherwise low yields of liquid products are obtained.

Production of Gas for the Synthesis.

The most suitable ratio of carbon monoxide to hydrogen in the gas used for the synthesis varies with the catalyst employed. With cobalt, the ratio recommended is 1 to 2, corresponding with the primary reaction:

$$CO + 2H_2 = (CH_2)_n + H_2O\,,$$

but, with other catalysts, a higher proportion of carbon monoxide, e.g. equal volumes of this gas and hydrogen, may be used, particularly since the synthesis, with iron, at the higher temperatures which are necessary with this metal, follows a course represented by:

$$2CO + H_2 = (CH_2)_n + CO_2.$$

Ordinary water gas contains about 50 per cent of hydrogen and 40 per cent of carbon monoxide; but if, as is normally the case, a gas containing two volumes of hydrogen to one of carbon monoxide is required, it is readily possible to produce this by operating the water-gas plant at a relatively low temperature with a larger excess of steam than is normally used, in such a way as to reduce the carbon monoxide content and to raise that of hydrogen by promoting the alternative water-gas reaction:

$$C + 2H_2O = 2H_2 + CO_2$$

simultaneously with the normal main reaction:

$$C + H_2O = H_2 + CO.$$

By working in this way, a gas containing two parts of carbon monoxide, four parts of hydrogen and one part by volume of carbon dioxide may readily be produced, the carbon dioxide acting during the synthesis as an inert gas.

The carbon monoxide content of water-gas can also be decreased by partial catalytic interaction with steam, as in the continuous process for making hydrogen:

$$CO + H_2O = CO_2 + H_2,$$

but in this case an additional converter becomes necessary.

Further, in place of starting with coke or other solid fuel, coke-oven gas or natural gas may be used as a raw material, the methane contained in these gases being converted catalytically to carbon monoxide and hydrogen by interaction either with steam or with carbon dioxide:

$$CH_4 + H_2O = CO + 3H_2$$
$$CH_4 + CO_2 = 2CO + 2H_2.$$

By whatever method a gas of suitable composition is made, it is necessary, before using this, to free it as far as possible from *catalyst poisons*, especially sulphur. Sulphur present as hydrogen sulphide may be removed by passage through iron-oxide purifiers in the ordinary way; and this is followed by the removal of organic sulphur by passage through a heated purifier tower in which this sulphur is retained, for instance by an alkalised iron contact mass at 200—300°. Alternatively, the organic sulphur may be removed catalytically by conversion into hydrogen sulphide which is then absorbed in purifier boxes of ordinary type, the temperature used for this preliminary catalytic conversion of sulphur compounds being dependent on the catalyst used. It has been stated that for successful industrial operation, the synthesis gas, after purification, should not contain more than 0.002 gram of sulphur per cubic metre.

General Operation of the Synthesis.

A diagrammatic sketch of the arrangement of the plant is shown in Fig. 22: After purification from sulphur in *A*, the gas passes to the catalyst chamber *B*

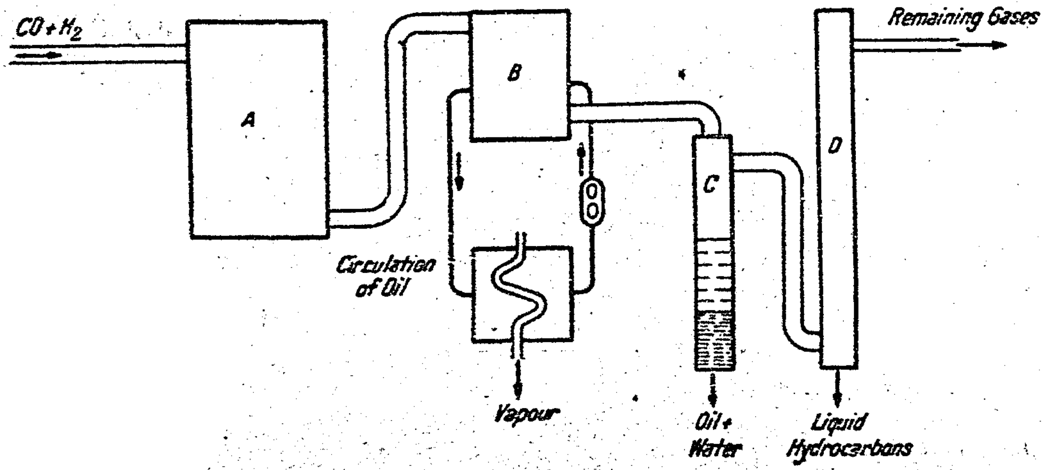


Fig. 22. Preparation of hydrocarbons from water gas.

which, with cobalt catalysts, is maintained at about 200°. This chamber may, in practice, with fresh catalyst be started at about 185°, the temperature being raised progressively as the activity of the catalyst falls; but the product is very sensitive to deviation from the experimentally determined optimum for the particular activity of the catalyst at any given time; and the correct working temperature should be maintained within 1°.

For this reason, means must be provided for the absorption of the relatively large heat of reaction. Thus, if the primary process be written:

$$CO + 2H_2 = (CH_2)_n + H_2O + 48 \text{ kg.-cals.},$$

about 600 kg.-cals. of reaction heat are developed during the conversion of each cubic metre of synthesis gas to hydrocarbon, an amount which, if uncontrolled, would suffice to raise the temperature of the gas by many hundred degrees. On account, however, of the relatively low reaction temperature, this control is not difficult and may very effectively be carried out by inserting thermal control tubes, through the catalyst mass. These tubes are fed either with heated oil or with high-pressure water at 185—215°; and, for effective control, no part of the catalyst should be more than about 1 cm. from a stabilising tube.

From the converter, the gas passes, usually by way of a wax trap, to a condensing system *C* and finally to active carbon scrubbers or oil washers *D*. In addition to volatile liquid hydrocarbons, some solid hydrocarbons are formed which, in view of their low volatility at the reaction temperature, remain on the catalyst and are removed periodically by washing with middle oil. This deposition can proceed to a considerable extent without greatly interfering with the activity of the catalyst.

Since the reaction involved consists in the conversion of permanent gases into liquid products, its course can conveniently be followed not only by the product which collects in the condenser but also by the gas contraction, namely by the ratio of permanent gases leaving the plant to the volume entering the converter. It is found possible to prevent methane formation almost entirely; and the contraction obtained may be up to 75 per cent, i. e. the exit gas may fall to one quarter of the volume of that entering.

The yield of liquid hydrocarbons is of the order of 100 to 130 g. per cub. metre of gas treated; and details of this yield, at a suitable gas rate, with a **cobalt-thoria** catalyst at 198°, in tests carried out by the staff of the *Fuel Research Station*, East Greenwich[1] are given in Table 45.

Table 45.

Space velocity of synthesis gas	166 c.c. per hr. per c.c. of catalyst (201 c.c. per hr. per g. of unreduced catalyst)
Yield of hydrocarbons	128.8 g. per hr. per cub.m. of gas (0.026 g per hr. per g. of catalyst)
Gas contraction	130 c.c. per hr. per g. of catalyst (= 64.3 per cent)

The yield of liquid hydrocarbons may be raised still further by carrying out the synthesis in stages[2] with partial or substantially complete removal of liquid hydrocarbons between these stages; and, by a suitable arrangement of the respective sizes of the successive converters it is possible to bring about this increase in the yield per cubic metre of gas without increasing the total quantity of catalyst used. Thus, with three successive converters, Fischer and Pichler were able to obtain up to 141 g. of hydrocarbons per cub.m. of gas, not counting the paraffin wax and hydrocarbons boiling below 30° (Gasol). If these are included the yield rose to over 150 g. per cub. m. of gas. The catalyst used was **cobalt-copper-thoria**, prepared by precipitation and supported on kieselguhr. As has already been stated, the initial activity of the catalyst falls slowly during use.

The synthesis of liquid hydrocarbons in stages has also been studied by Aicher, Myddleton and Walker[3]. This work is of interest since ordinary water gas, containing about 48 per cent of hydrogen and 41 per cent of carbon monoxide, was used. In this case the catalyst employed contained a nickel base.

Composition of the Product.

The primary products of the Fischer-Tropsch process consist very largely of unsaturated hydrocarbons of olefinic type. The distribution of the various

---

[1] See Chem. and Ind. 57, 759 (1938).

[2] F. Fischer, H. Pichler: Brennstoff-Chem. 17, 24 (1936).

[3] J. Soc. chem. Ind. 54, 313 T (1935); 55, 121 T (1936).

classes of substance produced, arranged according to their volatility, is illustrated by Table 46, which represents a typical raw product[1] given by a cobalt catalyst.

Table 46.

Classification	Boiling Point	Percentage by weight, in product	Olefine content. Per cent by volume
Low boiling hydrocarbons (Gasol)	< 30°	4	50
Benzine	30—200°	62	30
Heavy oil	> 200°	23	10
Solid paraffins	M.P. 50°	7	—
Hard paraffins from catalyst chamber .	M.P. >70°–	4	—

The percentage of olefines decreases if the hydrogen-carbonmonoxide ratio is increased, or if nickel is used as a catalyst in place of cobalt; and, in general, as will be seen from the table, the higher-boiling fractions are less rich in olefines than those of lower boiling point. This is as would be expected, since polymerisation necessarily leads to a lesser degree of unsaturation.

It may be noted that, in addition to the direct production of benzine and diesel oil, lubricating oils of good quality may be made by subsequently still further polymerising the unsaturated constituents, for instance by treatment with about 5 per cent of aluminium chloride. This extension completes the series of oil products necessary both for internal combustion engines of every type and for mechanical use generally.

3. The Hydrogenation of Carbon Disulphide.

While it is not proposed to deal in the present section with the catalytic cracking of organic sulphur compounds in the presence of hydrogen, in such a way that the sulphur contained in these is converted into hydrogen sulphide, it will be convenient to include the simple hydrogenation of carbon disulphide from its similarity to carbon dioxide.

Sabatier and Espil[2] observed the formation of a body which they assumed to be methylene di-thiol, $CH_2(SH)_2$, on passing a mixture of carbon disulphide and hydrogen over nickel at 180°; but later work shows that this body is the mono-thiol, $CH_3 \cdot SH$. According to R. H. Griffith and S. G. Hill[3], methyl thiol may conveniently be prepared by leading a mixture containing equal volumes of hydrogen and of carbon disulphide vapour over a nickel sulphide catalyst at 250—300°, a suitable gas rate being 200 c.c. per minute with 15 c.c. of catalyst. The product is freed from hydrogen sulphide, for instance by passage through iron oxide, and condensed by means of a freezing mixture such as solid carbon dioxide in acetone. Purification is subsequently carried out by fractionation. Methyl thiol boils at 6°.

---

[1] Fischer: Brennstoff-Chem. 16, 1 (1935).

[2] Bull. Soc. chim. France (4) 15, 228 (1914).

[3] J. chem. Soc. [London] 1938, 717. — See also B. Crawley, Griffith: ibidem 720.