HYDROGENATION OF OILS BY THE CONTINUOUS PROCESS.

PART V. MECHANISM OF CONTINUOUS HYDROGENATION OF OILS.

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The literature on the mechanism of the catalytic reduction of oils is vast and it is not possible to give an historical survey of all the previous work on the subject. In the present paper, the results given in the previous four parts have been examined in the light of the accepted principles regarding the mechanism of heterogeneous catalysis.

Adsorption plays a leading role in heterogeneous catalysis. The surface forces of the solid catalyst will cause an increase of concentration of any gaseous or liquid phase, which will help a general acceleration of reactions. Apart from this, the adsorption may be of a pseudo-chemical nature in that it is dependent on the existence of an affinity of an order approaching the ordinary chemical affinity between the solid and the liquid or gas adsorbed. The mechanism of catalytic reduction was at one time explained on the basis of the activated adsorption of hydrogen by the catalyst. However the activated adsorption of hydrogen alone failed to explain a number of reactions; and a number of other hypotheses were postulated.

Apart from the broad differentiation between specific and general adsorption, the surface of the catalyst is by no means uniform. Thus H. S. Taylor [*J. Phys. Chem.*, 1926, **30**, 145; *Proc. Roy. Soc.* (*A*), 1925, **108**, 107] has pointed out that the degree of unsaturation of an atom in the surface layer should depend on its position in crystal lattice. In Taylor's words "The surface of a granule may be regarded as composed of atoms in various degrees of unsaturation by neighbouring metal atoms, varying from those one degree less saturated than interior atoms to those which are only held to the solid surface by a single constraint. Moreover, since a gaseous atom of nickel can combine, for instance, with four molecules of carbon monoxide to form nickel carbonyl, it is not improbable that nickel atoms attached by a single valence to the remainder of the solid surface, will absorb three molecules of carbon monoxide, while nickel attached by two or by three constraints only would absorb, respectively two and one molecules of carbon monoxide." The heterogeneity of the catalyst surface may now be regarded as definitely established, but the above mechanical explanation may not represent the true non-uniformity. The work of Balandin (*Z. Phys. Chem.*, 1927, **126**, 267; 1929, **2B**, 289) explains the geometry of the catalyst surface and how the various organic molecules are held to the surface, in his 'Multiplet theory'.

Armstrong and Hilditch (*J.S.C.I.*, 1925, **44**, 701; *Trans. Faraday Soc.*, 1922, **17**, 670; *Proc. Roy. Soc.*, 1920, **98A**, 27; 1923, **103A**, 526; 1925, **108A**, 111) gave convincing proof for the formation of an adsorption complex between the unsaturated compound and nickel prior to hydrogenation. According to these authors the attraction between unsaturated organic compounds and unsaturated nickel is strong enough to loosen the nickel atom from its neighbouring atom or atoms, so that when catalytic change actually occurs, the nickel atom loses all contact with its neighbours. For the moment there may exist, actually apart from the solid surface, a combination of nickel-unsaturated complex and probably of hydrogen as well.

As regards the kinetics of hydrogenation, the data available is rather contradictory. Thomas (*J.S.C.I.*, 1920, **39**, 107), Armstrong and Hilditch (*Proc. Roy. Soc.*, 1919, **96A**, 137) and Brocklisty and Charnby (*Contri. Can. Biol. Fisheries*, 1933, **7**, 523–25) studied the kinetics of hydrogenation of oils in the *batch process*. Dougherty and Taylor (*J. Phys. Chem.*, 1923, **27**, 533) have studied the hydrogenation of benzene, and Pease (*J.A.C.S.*, 1923, **45**, 1196) the hydrogenation of ethylene, by the static method. From his experiments with olive oil, Thomas (*loc. cit.*) came to the conclusion that the addition of hydrogen at constant pressure, is a reaction of the first order. The results of Armstrong and Hilditch are in conflict with this view, in that, according to their experiments the hydrogenation is a linear function of time for as much as 40 to 80% of the total absorption of hydrogen.

Pease (*loc. cit.*) found a marked similarity between the conclusions reached as a result of his investigation and those of Armstrong and Hilditch. Lush (*loc. cit.*) showed that the absorption of hydrogen was independent of the flow of oil within certain limits, in a continuous method of hydrogenation of cottonseed oil.

In the continuous method, the kinetics of reaction are generally followed by the space-time-yields. As the reaction, however, proceeds in a logarithmic manner along the length of the tube, the percentage conversion in one passage over the catalyst represents an integrated reaction over the whole length of the tube. In the present work the velocity coefficients, *i.e.*, the reaction in unit space is calculated by the formula

$$K = 2{\cdot}3 \text{ R} \log \frac{a}{(a-x)} \quad \cdot\cdot \quad \cdot\cdot \quad (1)$$

where R is the rate of the oil flowing over the catalyst and K is the apparent velocity coefficient. Calculations of the apparent velocity coefficients by this equation gave concordant values at all rates, only in the case of the nickel wire catalyst at 140°, 160° and 180° (*cf.*

Part I, *This Journal,* **20A**, 95–109), but discordant values were obtained for the results at 95° and 120°, and to a lesser extent at 200°. Similarly, nickel hydroxide-silica gel catalyst gave concordant values only at 100°, 160° and 200°. The other catalysts showed a variation in the values of K at all temperatures (*cf.* Parts II and IV, *This Journal,* 1938, **21A**, 285–93; 307–19).

As the adsorption depends on the association between the unsaturated compound and the catalyst, the apparent velocity coefficients calculated as above, are a measure of this association at a particular rate, in unit length of the catalyst. The variation of the values of K shows that the extent of association of the unsaturated compound with nickel is a function of the rates, and in the case of almost all catalysts the variation could be expressed by an equation similar to the one for adsorption process, *i.e.*,

$$K = K'R^{1/n} \quad \cdots \quad \cdots \quad \cdots \quad (2)$$

K′ and *n* being positive constants (*cf.* Parts II and IV, *loc. cit.*).

From the equations (1) and (2) a general equation applicable to all catalysts at all temperatures is

$$K' = 2\cdot3\ R^{1-1/n} \log \frac{a}{(a-x)} \quad \cdots \quad \cdots \quad (3)$$

When $1/n$ approaches zero K will be equal to K′. K′ has been referred to as the corrected velocity coefficient. The value of *n* is a measure of the adsorption of the reactants on the surface.

Relation between temperature and K′.—The relation between the corrected velocity coefficients and temperature is shown in Fig. 8 (Part I) in the case of nickel wire catalyst, and in Fig. 8 (Part IV) in the case of groundnut oil hydrogenated by nickel peroxide-kieselguhr, and olive, groundnut and cottonseed oils hydrogenated by nickel carbonate-kieselguhr catalysts. The curves for the three oils hydrogenated with the catalyst last mentioned, show the effect of the change in the composition of oil on the velocity of the reaction. It appears (*cf.* Part II, p. 289) that the high reaction velocity at 150° is due to the selective hydrogenation of olein which is maximum at this temperature, and the high velocity at 200° is similarly due mostly to the hydrogenation of linolein, the latter being not completely selective. In the case of cottonseed oil, a greater percentage of linolein in the oil inhibits to some extent the selective hydrogenation of olein at 150°, so that the reaction velocity increases continuously with temperature from 100° to 200°.

Relation between temperature and K.—A considerable variation in the apparent velocity coefficients K with rates was observed in the case of unsupported nickel carbonate and Raney's catalysts. As however, only two experiments were carried out at each temperature, the values could not be corrected by applying the equation (2). The relation between K and temperature for the unsupported nickel catalyst is shown in Fig. 3 (Part IV) which shows two flat regions between 100° and 140°, and 180°–200°, the velocity rising rapidly between 140° and 180°. The Raney's catalyst showed two maxima in the curve at 125° and 150° respectively and a high velocity at 200° (Fig. 8, Part I). Silica gel-nickel hydroxide (Fig. 6, Part IV) showed a feeble maxima at 150° after which the velocity rose continuously up to 230°. A reference to these results will be made later.

Relation between temperature and n.—In the adsorption isotherm represented by the equation $a = k\mathrm{C}^{1/n}$ which is used as the basis of equation (2), the variation of both k and n with temperature is in the same direction, *i.e.*, if the values of k decrease with increasing temperature, the values of n will also decrease and *vice versa*. Therefore, knowing the values of n, one can determine the relative adsorption at various temperatures.

In Table I the values of n at different temperatures in the case of the various catalysts are given.

TABLE I.

Catalyst	Temp. °C.	n groundnut oil	Temp. °C.	n olive oil	Temp. °C.	n cottonseed oil
Kieselguhr-Nickel carbonate ..	100–180	2	110–150	4	107	1·5
	200	4	166	3–4	130	1·7
			180–200	3	151	2·0
					177	3·0
					200	4·0
Nickel wire ..	95–120	6				
	140–180	very high				
	200	high				
Kieselguhr-Nickel peroxide	100–190	3				
	200	4				
Monel wire ..	180–200	4				
Silica gel-Nickel hydroxide ..	120	4				
	140–160	high				
	180	4				
	200	high				
	230	4				

The value of n for olive oil is four and remains constant from 110° to 150°. At higher temperatures the value drops to three and remains constant from 180°–200°. With groundnut oil the value is two and remains constant between 100°–180° but rises abruptly to 4 at 200°. In the case of cottonseed oil the values increase continuously from 1.5 to 4 from 100° to 200°. With nickel wire n is fairly high between 140°–200°, while at 95° and 120° the value is 6.

The analysis of the curves obtained by plotting n against temperature in the case of olive, groundnut and cottonseed oils show that each curve is a combination of two curves: (a) where n rises continuously with temperature as observed in the case of cottonseed oil due to the adsorption of linolein, and (b) where n decreases first very slowly with temperature from 100° to 150° and rapidly at higher temperatures. The fact that the part (b) is predominant in the case of olive oil shows that it favours the hydrogenation of olein. Previous discussion as regards the relation between K′ and temperature has shown that the velocity of hydrogenation of olein rises to a maximum from 100° to 150° and drops down at higher temperatures. As the reaction velocity depends on the adsorption, the adsorption of olein rises continuously from 100° to 150°. The constant value of n from 100° to 150° for olive oil suggests that the part (b) is due to the third reactant in the process, *viz.*, hydrogen.

Activated adsorption of hydrogen on metal catalysts.—The total reaction in the process of hydrogenation is a sum of a number of factors among which the activation of hydrogen is prominent. The adsorption of hydrogen on metals occurs in three stages: (1) Van der Waal's adsorption, (2) activated adsorption and (3) diffusion subsequent to activation which is a distinct process not related to the catalytic activity.

Benton (*Trans. Faraday Soc.*, 1932, **28**, 202) detected a three stage adsorption of hydrogen and carbon monoxide on copper, iron, nitrogen or iron, and hydrogen on nickel. In the case of hydrogen on nickel a fast activated adsorption between 0°–110° was noticed. Morzove (*Ibid.*, 1935, **31**, 659) similarly noticed a three stage adsorption on iron having a maximum activated adsorption at about 100° C. with a heat of activation as 20300 cals./mol.

Esmet and Harknes (*J.A.C.S.*, 1935, **57**, 1631) detected a three stage adsorption of hydrogen on promoted iron catalyst. Van der Waal's adsorption dropped down considerably at −78° from which temperature the activated adsorption became relatively fast. About 100° a second type of activated adsorption came into action. The activation starts at about 0° and rises upto 75° C. after which it gradually decreases up to 400°, the fall in the adsorption at 200° being about 25% of the adsorption at 100°. Thus the decrease of the activated adsorption of hydrogen in the range of temperature from 100° to 200° is very gradual and the constancy of the value of n in the case of olive oil may be due to this reason. The effect of the activated adsorption will be evident only when the substance to be hydrogenated is also adsorbed and the olein being selectively hydrogenated at low temperature, the effect is markedly seen in the case of olive oil.

A rough picture of the various factors (1, 2 and 3) involved in the reaction of hydrogenation and their relation to temperatures is shown in Fig. 1. These are (1) activated adsorption of hydrogen which decreases gradually from 100–200° (B, Fig. 1), (2) adsorption of olein which rises to a maximum rapidly from 120–150°, remains constant up to 170° and drops down rapidly above 170° (C, Fig. 1), and (3) adsorption of both linolein and olein but with ponderance of olein which increases continuously with temperature (A, Fig. 1).

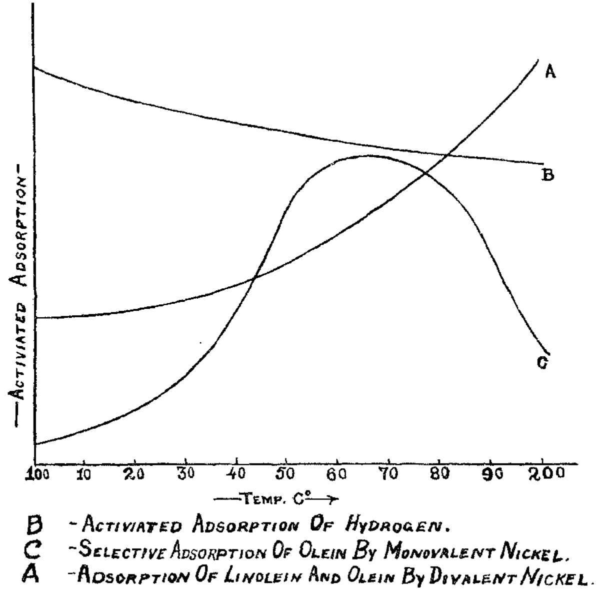

Fig. 1.

In view of the fact that the catalyst surface is heterogeneous the two types of adsorption given in (2) and (3) may be due to two active centres having different degrees of unsaturation. The one which is more unsaturated will be capable of adsorbing both olein and linolein as stated in (3).

It will be shown in a subsequent communication that the life-tests of various catalysts showed a stepwise fall in the activity which is in agreement with the idea of active centres.

A maximum reaction of olein at 150° and linolein at 230° was postulated by Bloeman (*Fette Chem. Unchau.*, 1934, 41, 95–98; 1934, 41, 154–55; 1934, 41, 151–54) from theoretical considerations assuming the catalytic hydrogenation of oils as a reversible reaction. This observation is against the view previously put forward that the maximum reaction at 150° and above 200° is due to the selective adsorption of the reactants by two active centres.

Apparent heats of activation.—The apparent heats of hydrogenation were calculated for different oils and catalysts from the values of the corrected velocity coefficients by the equation:

$$\text{Log } K_2' - \text{Log } K_1' = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

In those cases in which the corrected velocity coefficients were not calculated, the apparent heats of hydrogenation were calculated from the values of K at a fixed rate at various temperatures. The values of E calculated for a temperature interval of about 20° C. are shown in Table II.

TABLE II.

Catalyst	Oil	Apparent E in Cals./mol at mean temperature °C.								
		110	120	130	140	150	160	170	190	210
Kieselguhr-carbonate ..	Olive		12·0		9·3		2·4		5·9	
	Groundnut	9·3		4·6		1·7		6·7	17·0	
	Cottonseed		9·8		12·7			10·3	10·6	
Kieselguhr-peroxide ..	Groundnut	7·8		5·9		7·6		6·3	6·7	
Nickel wire ..	,,	10·0		15·8		2·2		3·5	9·3	
Monel wire ..	,,							3·0	2·7	
Silica gel-Nickel hydroxide ..	,,	14·5		6·0		1·5		6·1	5·0	6·7

The correct values of the two processes, *viz.*, the hydrogenation by monovalent and divalent nickel will be obtained from the results observed with olive and cottonseed oils. Olive oil gives a value of about 10 Cals./mol. at 120° and 140° and the same value is obtained with cottonseed oil at all temperatures. This shows that the heats of hydrogenation in the two cases are practically the same. The same value is also given by nickel wire at 110° and 190°.

The apparent heat of activation calculated in the case of nickel peroxide catalyst after poisoning, from the values of K at rate 100 gives the following values:

Temp. ..	110	130	150	170	190	215	240	270
Apparent E ..	17·0	1·6	5·9	9·0	10·2	5·4	4·0	6·2

A high value for E is obtained at 110° and is of the order of the heat of activation of hydrogen which is 20 Cals./mol. At temperatures above 130° the values rise and remain constant at about 10 Cals./mol. at 170° and 190°. At temperatures higher than 190 the values again decrease, a minimum value being obtained at 240°. Unsupported nickel carbonate gives a value for E as 11.7 Cals./mol., calculated from the value of K at rate 100, between temperatures 135°–184°.

The heat of activation in hydrogenation of the oils is, therefore, very near to 10 Cals./mol. which is in fair agreement with the values given by various authors as shown below:

Reaction	Catalyst	E	Observer
Hydrogenation of ethylene	Copper	13·4	Pease and Harris
Hydrogenation of Benzene	Copper	10·0	Pease and Purdum
Dehydrogenation of hexahydrobenzene ..	Nickel	9·9	Zelinsky and Balandin
Dehydrogenation of Decahydronaphthalene ..	Nickel	10·0	Zelinsky and Balandin

The heat of activation of monel wire at 170° and 190° is much lower than the values for the other catalyst. It is well known that the addition of a promoter to a catalyst reduces the heat of activation.

Selectivity in the hydrogenation of oils.—This term, 'selectivity', is used in a vague manner and is generally referred to the selective hydrogenation of linolein only. An extensive amount of work has been done on the subject and a reference to the same has been made in Part IV. In recent years the selective hydrogenation is being studied from a different standpoint. This arises out of the tribasic character of the glycerine molecule and consequent non-identity of α- and β-substitution products, the hydrogenation having been found to take place in a stepwise saturation of a single molecule. The recent work by Hilditch and others (*J.S.C.I.*, 1935, **54**, 331–36 T; 336–38 T) on this problem is highly interesting although our experiments were not aimed at this aspect of the problem.

Selectivity in the ordinary sense is supposed to increase at higher temperatures. Analysis of cottonseed oil hydrogenated by the batch process shows that at 150° olein rather than linolein is selectively hydrogenated, though at temperatures below 140° and above 160° the velocity of hydrogenation of linolein is much faster. In the case of oils which contain higher percentage of linolein, the velocity will change with temperature in the manner shown by curve A in Fig. 1. It has been stated that this curve is due to the hydrogenation of both the linolein and the olein. Had it been only due to the selective adsorption of linolein, then an oil like olive oil which contains about 85% of olein or ethyl oleate, should have a very low velocity of reaction at 200°. The fact that both these substances show a high velocity at 200° proves that olein is also adsorbed as much as the linolein, though at the higher temperatures the latter may suppress the adsorption of the former to a considerable extent. Analysis of the cottonseed oil hydrogenated at temperatures above 160° (*cf.* Part II) has shown that the velocity of hydrogenation of both linolein and olein increases with temperature. Williams (*J.S.C.I.*, 1927, **46**, 446 T) has shown that in case of cottonseed oil, the relation between the divergence from complete selectivity "D" and temperature is linear, "D" having a lower value at higher temperature. The results indicate that though the velocity of hydrogenation increases with temperature, the difference in the velocity of the hydrogenation of linolein and olein becomes more at higher temperature.

Active Centres of Nickel and Adsorption of the Reactants.—A number of considerations given so far have shown that the catalytic hydrogenation is the sum of three factors, *viz.*, (1) activation of hydrogen, (2) activated adsorption of olein at 150° and (3) the activated adsorption of both linolein and olein from 100–240°. It is clear from the discussion given in the last paragraph that the adsorption in (3) does not appear to be selective though the linolein, owing to its higher unsaturation, is preferentially adsorbed. It has also been pointed out that the difference in the velocities of hydrogenation of linolein and olein due to (3) becomes more at higher temperatures.

Although the precise nature of activation is not yet understood, all recent experimental work on catalysis is leading back to the ideas closely approaching the old intermediate compound theory and is giving stronger support to the view that the valency forces are involved in activated adsorption. There is no reason, therefore, to abandon the conception of active centres. The specific effects observed in the present case may be attributed to the mono- and di-valent nickel atoms present on the surface. The selective adsorption (2) of olein may be due to the monovalent nickel while the adsorption in (3) may be due to the divalent nickel atoms. The divalent nickel atoms will adsorb linolein in preference to olein but when the percentage of the latter is considerable, it may absorb olein as well. The monovalent atom, on the other hand, will be capable of adsorbing only the olein. It is, therefore, probable that there are two active centres of nickel in the catalyst surface having specific affinity for either olein, or both the olein and linolein. The monovalent nickel adsorbs only the olein, the adsorption being appreciable at 125°, reaches to a maximum at 150° and decreases at higher temperatures. The divalent nickel adsorbs both olein and linolein. The adsorption is appreciable even at temperatures lower than 100° and increases gradually above 200° having maxima at about 240°.

SUMMARY.

A brief survey of the literature on the mechanism and kinetics of hydrogenation is given.

The apparent velocity of the reaction was calculated by the formula $K = 2.3 \; R \log \frac{a}{(a-x)}$ which gave concordant values only in the case of nickel wire catalyst at 140°–180° and at other temperatures in the case of silica gel catalyst.

The variation in the apparent velocities with rates in the case of the rest of the catalysts was expressed by the equation $K = K'R^{1/n}$, which is a special case of the general equation

$$K' = 2 \cdot 3 \; R^{1-1/n} \log \frac{a}{(a-x)}.$$

Considerations regarding the change of K, K′ and n with temperatures show that the catalytic hydrogenation is a sum of the three factors, *viz.*, (1) activated adsorption of hydrogen which decreases very slowly from 100°–200°, (2) activated adsorption of olein by monovalent nickel which becomes appreciable above 125°, reaches a maximum at about 150° and decreases gradually at higher temperatures, and (3) activated adsorption of both the linolein and olein by divalent nickel which is appreciable even below 100°, and increases gradually with temperature reaching a maximum at about 240° C.

The results show that the optimum temperature for the catalytic hydrogenation of oils is 180° at which all the factors contribute to the high velocities observed.

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