in order to emphasise the educational value of a study of animal life as well as that of botany.

The psychologists and educationists, led by such practical observers as Prof. Cyril Burt and Messrs. Cox, Earle, and Salter Davies, are meeting in joint session to hear and discuss the latest results of research on vocational guidance. The education of the industrial worker and expert will be reviewed by Sir Robert Blair, who will open a discussion on "The Conditions of Success of Technical Institutions." Mr. Wickham Murray will deal with the handicap

imposed by the present narrow spirit of university matriculation requirements on technical students, and Dr. W. M. Varley will speak for the claims of the "Local College" as a centre of educational activities for adolescents and adults, providing not only technical instruction but also opportunities of wide cultural study.

A lecture will be given by Dr. Ernest Barker on "Growth of National Character," and another by Mr. Percy Scholes on "Musical Education by means of Player-piano, Wireless, and Gramophone."

Catalysis and Oxidation.¹

By Prof. HENRY E. ARMSTRONG, F.R.S.

THE treatment of the subject must depend upon the definition that is given of the term. Is or is not *catalysis* to be regarded as the synonym of *chemical change in general*? Berzelius, the author (1835) of the term, who developed the conception, included among catalysts agents so diverse as sulphuric acid (*e.g.* the production of ether and the hydrolysis of starch); platinum, especially in the spongy form (*e.g.* the formation of water from hydrogen and oxygen and the oxidation of alcohol); and enzymes (*e.g.* the hydrolysis of starch by diastase). Such agents have, in common, the power of acting reversibly, so that they may eventually be recovered, if not soiled by some secondary change.

The need of a clear definition and limitation is obvious from the frequent use of the expression *contact catalysis*, as if there were several forms of catalysis. Such use of the adjective *contact* is superfluous, to say the least—as all chemical interactions necessarily involve *contact* of the substances concerned, whatever their character: if the expression have any meaning, it can only be that of chemical change in general, for which we need no other specific term.

I would urge that the term catalysis be limited to actions *at and influenced by solid surfaces*: in other words, the catalyst is either an extended solid surface or a finely divided, particulate agent—in suspension, not in solution. I have specially developed this view in my recent Messel Lecture to the Society of Chemical Industry (Journal, 1922).

Since 1885, my contention has always been that chemical change is an electrolytic process. On this assumption, whilst electrolytes, in solution, may interact directly, chemical action between non-electrolytes is an indirect process, determined by the presence of an electrolyte compatible with the substances ultimately brought into interaction through its agency, because of its power of linking them in a conducting circuit. This agent I would term the *determinant*; it is necessarily an electrolyte.

In general terms, the equation of interaction may be written

where $\epsilon\delta$ is the electrolytic determinant.

I have specially considered the formation and nature of electrolytes in numerous communications to the Royal Society and elsewhere.² To give a specific illustration: alcohol and hydrogen chloride do not interact, except in the presence of water:

Hydrogen chloride and water together, however, form an electrolyte. The process of interaction, in their presence in association (as a composite electro-

lyte), may be less direct and more complex than is commonly supposed: perhaps broadly as follows:

Having the postulate referred to above in mind, I was able, in 1885, to predict not merely that oxygen and hydrogen cannot interact but that water alone would not suffice as determinant—that the water must be impure, *i.e.* an electrolytic conductor. The forecast has been verified by H. B. Baker. The criterion is a simple one. Over and over again, the correctness of this postulate has been verified experimentally, especially by H. B. Baker, whose masterly, long-continued inquiries are in no way appreciated as they should be. It has led me to affirm that gases cannot interact—except in the presence of a liquid determinant, if not of a catalyst. Aitken's work on the condensation of hydron, αOH_2 , to water, $(\text{OH}_2)_x$, may be interpreted from this point of view.

At least the chief distinction to be drawn between changes influenced by catalysts and those which occur in a wholly liquid medium is, that whereas, in the latter, the extent to which change takes place diminishes as the concentration is diminished, in the presence of a catalyst the rate of change is constant over a considerable period and apparently independent of the concentration *in the solution*: because of the attractive influence exercised by the catalyst and the consequent uniform and continued concentration of the hydrolyte at its surface.

I have long thought—and the evidence in favour of the interpretation is increasing daily—that so-called gaseous interactions always take place at the surfaces with which the nominally interacting gases (plus the necessary determinant) are in contact—the surface playing the part of catalyst, by serving to attract and hold the determinant. It may be questioned whether Moureu's refined studies of oxidation do not furnish complete evidence of this view. In some instances the substances which he has successfully used as inhibitors of the oxidation of acrolein have been of such low volatility that they can scarcely have been present, except in most minute proportion, in the gas above the liquid: if so, it may be legitimate to suppose that oxidation is confined to the liquid state. All turns on the proportion of inhibitor that is necessary.

We are not entirely clear, however, as to the function of the catalyst—whether or no it be included

^{*} The H in brackets is that which may be supposed to take the place of (OH) originally in the alcohol. Some such process as this may be at the root of the Walden inversion.

¹ Address delivered at the second of the triennial conferences of the Institut International de Chimie Solvay on April 22.

² Proc. Roy. Soc., 1886, 40, 268; A, 78, 264, 1907; A, 79, 586, 1908; A, 81, 80, 1910; A, 84, 1912; A, 86, 604, 1914; 90, 73. British Association Report, 1885; J. Chem. Soc., 1895, 1122.

in the circuit or whether it merely serve to attract and hold the determinant, together with the substances the interaction of which it determines. Taking the case of hydrogen and oxygen interacting at a platinum surface, it is open to question whether the platinum be coupled with both gases at adjacent points, the determinant acting as an electrolytic conductor between the two; or whether the determinant be merely adherent to and concentrated upon the platinum, the two gases being attracted to it: thus forming the circuit within which change takes place.

The balance of evidence would seem to be in favour of the former explanation. Thus, platinum influences the interaction of hydrogen and oxygen but not that of carbonic oxide and oxygen. Carbonic oxide and various hydrocarbon vapours even have a protective and preventive action and *apparently* can displace both oxygen and hydrogen from a platinum surface. It might be that carbonic oxide is also more attracted by the liquid determinant. It is almost impossible to grant that any one of the gases can monopolise the surface. The behaviour of carbonic oxide, in fact, is in many respects peculiar and needs special discussion.

Evidence on the point is, perhaps, to be found in recent observations on the interaction of hydrogen and oxygen in presence of silver and gold (D. L. Chapman, J. E. Ramsbottom and G. G. Trotman, Proc. Roy. Soc. A., 197, 92). Bone and Wheeler have shown that both metals are more active after heating in hydrogen but not if heated in oxygen. Chapman and his fellow-workers show that absorbed oxygen acts as an inhibitor, apparently owing to the formation of a film of metallic oxide, whilst absorbed hydrogen does not appreciably diminish or increase the activity of the metal. They have further found that the two gases interact, even at the laboratory temperature, in the presence of a silver film deposited on the inner surface of the vessel in which they are confined. The explanation of the inhibiting effect of the film of oxide may be that, being strongly alkaline, the film holds the *trace of acid* which normally serves as electrolytic determinant. Whether silver act as the catalyst and determine interaction at ordinary temperatures—because it merely attracts the electrolytic determinant and the two gases to its surface—or because either or both of these is absorbed by it, must apparently be left an open question.

The special activity of catalysts, due to their particulate character, may be ascribed to the influence they exercise in maintaining a high "surface concentration" of the interacting substances. On this account, the primary action exercised by the enzyme takes place during the earlier, in fact, a considerable period, at a linear rate; only as the products of change accumulate and the action is reversed to an appreciable extent or the enzyme is neutralised or lamed by products of change is the rate of change perceptibly diminished. This is well illustrated by curves showing how urea is hydrolysed by urease, according as the product of change, ammonia (which but lames the enzyme, as the action is not sensibly reversible), be allowed to accumulate or be neutralised by an acid too weak to affect the enzyme.

Enzymes have a peculiar and rigidly *selective* activity—it is on this account that they form a special class of catalyst. They, therefore, influence the hydrolysis of specific hydrolytes; there is no reason to regard their hydrolytic influence as exercised in any peculiar manner.

To make the argument clear, it may be well to recapitulate and consider the formation of hydrone from hydrogen and oxygen. Being non-conductors, by my postulate above, these gases cannot interact:

By this same postulate, even the presence of "water" would not suffice:

Action would only take place in the presence of an electrolytic determinant:

As, however, the determinant would only be an electrolyte if present as liquid; and moreover, as the formation of liquid appears to be dependent upon the presence of a nucleus, *i.e.* of a surface, it is conceivable that no change would take place unless a catalyst (*k*) were present:

Finally, as interaction takes place in an electrolytic circuit, hydrogen is but indirectly "oxidised" whilst oxygen is hydrogenised

As this illustration shows, oxidation is not a direct but an indirect, *depolarising* effect.

It may be questioned whether water itself, as liquid, should not rank as a catalyst. In the interactions considered, it appears only as part of the electrolytic determinant and is necessarily to be thought of as present in the liquid state. Supposing, however, that in an entirely gaseous mixture—say, under the influence of an electric discharge—a sufficient number of hydrone molecules were temporarily brought into conjunction and formed liquid drops, would these suffice to determine interaction independently of any solid surface? It is possible that they would, if drops were formed under such conditions. The water, however, would not then be acting as catalyst but merely as part of the determinant: the rate of change would not be raised, as it is by solid catalysts.

The argument may be extended to the reverse process—the electrolysis of acidified water between platinum electrodes—and the assumption made that the perhydrone produced during the first stage,

is itself acted upon and hydroxylated during the second:

The "oxoperhydrone" thus formed is then hydrolysed into oxygen and hydrone, being itself acted upon, perhaps, as a composite electrolyte:

If the electromotive force or the current density be increased and the rapidity of attack sufficiently raised, the "oxoperhydrone" may be further hydroxylated:

Ozone may be pictured as formed by the hydrolysis of a "dioxoperhydrone" (also, perhaps, in the form of a composite electrolyte) thus produced:

In like manner, when concentrated solutions, particularly of sulphuric acid, are electrolysed, peracids are formed, which, in turn, according to the conditions, give rise to perhydrone, to oxygen or to ozone when hydrolysed.

Oxidation phenomena in general may be interpreted in a similar manner.

The suspended or inhibited oxidations which Moureu and his fellow-workers have studied so thoroughly in recent years, seem to be consistently accounted for by regarding them as involving the continued backward and forward hydroxylation of competing or antagonistic oxidisable compounds—*i.e.* as interference or reversal effects. I have long thought of the inhibition by hydrogen cyanide of the decomposition of perhydrone by platinum or yeast as due to the formation, in the first instance, of perhydrols and their reversible interaction

In result, the interactions here pictured have the same effect as those postulated by Moureu, the main difference being that the process is more clearly defined, as it is represented as "electrolytic" in all its stages. Moureu has usually assumed that the substance primarily concerned is oxidised to a "peroxide," $A(\text{O}_2)$, from which oxygen is transferred to the inhibitor, a second "peroxide" $B(\text{O})$ being formed, the primary "peroxide" being reduced to another "peroxide," $A(\text{O})$: the original molecules are reproduced by the interaction of these antagonistic "peroxides":

In their recent communication to the Chemical Society, however, Moureu and Dufraisse clearly contemplate the probability that platinum, acting as an oxygen carrier, oxidises the molecules of hydrogen and the interfering gas (H_2 , CO , C_2H_4 , etc.) simultaneously to form two antagonistic peroxides, which then interact, reducing each other.

The oxidation of the two oxidisable substances is and, indeed, must be effected in the same circuit, one of them acting as "depolariser," thereby raising the potential to the necessary extent: otherwise, one would not be oxidised at all or the "antagonism" would be incomplete.

Carbonic oxide may be taken in illustration. I have long wondered at the peculiar behaviour of this gas, in fact since I first read in the early 'seventies Groves' fascinating memoir on his gas battery and Faraday's earlier more complete observations on the combining power of platinum; in the former it is shown that carbonic oxide cannot be coupled with oxygen, as hydrogen can, to form a gas battery. Then came H. B. Dixon's discovery of the incombustibility of the dry gas and the increase in velocity of the explosive wave as the proportion of steam present was raised up to a certain maximum. I have more than once discussed the problem, particularly in 1904, in a brief communication to the Royal Society on "The Retardation of Combustion by Oxygen," (*Proc. Roy. Soc.*, 74, 86), in which I dealt with H. B. Dixon's observations on the retardation of the combustion of hydrogen by "excess" of oxygen and of Bone and Stocking's similar observations on ethane.

Accepting the postulate at the root of the argument in this essay, inasmuch as the oxidation of carbonic oxide is a process involving the electrolysis of water,

action should not take place at a platinum surface, at

ordinary temperatures, because the heat of oxidation of carbonic oxide is below that of hydrogen: the change would be endothermic. Probably, the combustion of carbonic oxide is never a direct effect but is determined by a minute quantity of hydrogen, acting as adjuvant, produced initially when the combustible mixture is inflamed or sparked:

To repeat what I said in 1904, "It is necessary to remember, that whereas both oxygen and water molecules diminish in stability as the temperature rises, the stability of hydrogen peroxide must be at a maximum at a high temperature—since its formation from oxygen and water is an endothermic process. In fact, it is to be supposed that water is readily oxidised at temperatures such as prevail in combustions. If, however, the formation of water be regarded as involving the changes

it follows that water and oxygen will mutually hold each other in check: so that when electrolytic gas is exploded there will be a deficiency of oxygen, as it were, owing to its conversion into hydrogen peroxide, which may be regarded as relatively if not entirely inoperative as an oxidising agent, at high temperatures, in presence of oxygen. On the other hand, when excess of oxygen is present, the water—which is the effective catalyst—will be more or less held back, also in consequence of its oxidation to hydrogen peroxide."

Whether or no the changes pictured above could equally well take place at a cold platinum surface would be open to question, were it not that platinum is known to determine the interaction of hydrogen and oxygen. There is no reason to suppose that carbonic oxide could not enter the circuit of change, as a depolariser, under such conditions. The difference in behaviour at low and high temperatures is, therefore, probably the consequence of differences in the stability of some of the compounds concerned.

As to the form in which carbonic oxide primarily enters into the circuit of change, it is not unlikely

that it is as the hydrol $\text{C} \begin{array}{c} \text{H} \\ \diagup \\ \text{O} \\ \diagdown \\ \text{OH} \end{array}$ rather than as

formic acid. Obviously, such a compound would be of low stability and the need of a high proportion of steam, to secure the combustion of carbonic oxide at the maximum rate, may be accounted for by the assumption that the presence of this hydrol, in sufficient proportion, is only to be secured in this way.

The immediate product of the hydroxylation of the hydrol, $\text{C} \begin{array}{c} \text{H} \\ \diagup \\ \text{O} \\ \diagdown \\ \text{OH} \end{array}$, would be the "perhydrol"

$\text{C} \begin{array}{c} \text{H} \\ \diagup \\ \text{O} - \text{OH} \end{array}$, a still less stable compound. At ordinary temperatures, at a platinum surface immersed in an atmosphere of hydrogen, carbonic oxide and hydrone, this perhydrol would be antagonised by a corresponding "hydroxyperhydrone" or "oxoperhydrol" and

the two would interact reversibly to their mutual destruction:

At high temperatures, such perhydrols would no longer be formed and the direct combustion of the carbonic oxide with the aid of hydrogen, acting as depolariser, would be effected without their interference and with special readiness.

One other case of apparently anomalous protection against oxidation may be referred to—that afforded by so-called rustless steel and the more recently introduced soft alloy staybrite. The former is a chromium steel, the latter an alloy of iron, nickel and chromium, as free as possible from impurities. That chromic acid will protect iron against oxidation is well known. It may be supposed that, in an alloy of iron with chromium, in which the chromium is properly distributed, both materials undergo surface oxidation to perhydrols, which act reversibly, so that at most a layer of molecular thickness is affected, a coating being formed which may well correspond with the (?) unimolecular layer of oxide upon the surface of the far more sensitive metal aluminium.

It is permissible to suggest that the influence of certain dyestuffs in checking the "fogging" of an undeveloped photographic plate may perhaps be traceable to the initial production of antagonistic perhydrols by simultaneous hydroxylation of the sensitive film and the coloured material.

Finally, some reference to the oxidases may not be out of place. These are commonly spoken of as enzymes but they are in no way comparable with

these, in so far as they act selectively. They are only selective in the broad sense, that they are effective agents in determining the oxidation of compounds of a particular general type. Thus so-called tyrosinase will determine the oxidation of phenolic compounds of a certain type—not of tyrosin alone. This is true of "oxidising" organisms, such as *Bacterium aceti* and *B. xylinum*. The behaviour of *B. aceti* is altogether peculiar—although active towards ethylic and normal propylic alcohols, it has no action upon either methylic or isopropylic alcohol. At present we know so little of the process at work that it is impossible to attempt any precise explanation of these peculiarities. It may be suggested, however, that they are traceable both to configurational and energy differences in the systems concerned; moreover, it is clear that something more than the simple, direct oxidation of the alcohol is to be contemplated and that cross-interactions may be at work. Maybe we shall have little success in interpreting such actions until we no longer think "on paper" but have clear conceptions of the solid configuration of molecules. The oxidases may well be discarded from the class of enzymes and regarded as simple catalysts—of a parity with platinum black.

Not a few mysterious processes may be open to interpretation in accordance with the principle developed in this essay. The peculiar behaviour of phosphorus is a case in point—especially the dependence of the appearance of luminosity upon the partial pressure of the oxygen and the phenomena of intermittent luminosity to which Lord Rayleigh has recently directed attention. Little can be said with advantage, however, until we know far more of the several stages of the oxidation process—which may well be as complex as that of the interaction of nitric acid and metals.

Genetical Investigations.

THE practical value of chromosome studies is perhaps nowhere better demonstrated than in the wheats, where the species belonging in different groups have different multiples of 7 as their chromosome number. In hybrids between species with different numbers of chromosomes, the peculiarities in the hybrid behaviour are largely explained by the history of the chromosomes, some of which pair in meiosis while others remain single.

Sax and Gaines¹ draw several conclusions from a study of hybrids between emmer wheats (28 chromosomes) and vulgare wheats (42 chromosomes), which have been grown through several generations. The various segregates tend ultimately to have the same chromosome numbers as the original parents. This is accomplished through sterility or loss of chromosomes in forms with intermediate numbers, as has been found also in the *Enotheras* and in other cases. Segregates with 28 chromosomes resemble the emmer wheats, while those with 42 have most of the vulgare characters. This indicates that the 7 extra pairs of chromosomes determine most of the vulgare characters. The chromosome behaviour would lead to the expectation that ordinary Mendelian segregation would occur in characters, such as presence or absence of awns, yellow or black awns, and red or white grain, which are common to both the emmer and vulgare groups of wheats; while aberrant segregation would occur in regard to characters which distinguish the two groups. This is largely borne out by the

results of experiment. Some of the segregates show combinations of typical emmer and vulgare characters, which indicates that the 7 unpaired chromosomes (which are irregularly distributed in meiosis) independently determine particular characters of the vulgare group.

Another interesting result, obtained by Mr. and Mrs. Sax,² is derived from a cross between *Ægilops cylindrica*, a grass found in Italy, the Balkans, and neighbouring countries, and Marquis wheat, one of the most productive varieties of *Triticum vulgare*. *Ægilops*, like the emmer wheats, is tetraploid, having 28 chromosomes. The F_1 hybrid with *T. vulgare* is pentaploid (35), but unlike the crosses between tetraploid and hexaploid wheats, there are only 6 or 7 bivalents in meiosis (instead of 14), the remaining 21 chromosomes remaining univalent or unpaired. Nevertheless, the tetrad divisions are run through with very few irregularities, some of the univalent chromosomes apparently dividing in the first meiotic division while others divide in the second. The F_1 hybrids are in general intermediate between the parents, and are almost but not completely sterile.

The authors point out that this species of *Ægilops* and another both contain all the characters which distinguish the vulgare from the emmer wheats; and they suggest that the hexaploid vulgare wheats may have arisen through a spontaneous cross between *Ægilops* and a tetraploid (emmer) wheat. Irregular distribution of the unpaired chromosomes, of which there would probably be 14, would occasionally

¹ Sax, Karl, and Gaines, E. F., 1924, "A Genetic and Cytological Study of certain Hybrids of Wheat Species," *Journ. Agric. Research*, 28: 1017-1032, pls. 2.

² Sax, K. and H. J., 1924, "Chromosome Behaviour in a Genus Cross," *Genetics*, 9: 454-464, pls. 2.