stronger than the material in the first test, and its ductility, as measured by the contraction of area, fell from 60 to 6 per cent.

This indicates that discrepant fatigue limits may be due to discrepant form. There is also another point to be noted. If, during a fatigue test of the usual type, the machine is stopped when slips have begun to develop, they will heal themselves during the period of rest and so confuse the final result. There are therefore several causes which together act to modify the results of a test on the fatigue limit of a material by the method of repeated oscillations.

I think that a fatigue limit of practical value can be determined from a looping test of the type described in my recent paper. That is to say, the load is applied and removed, and then reapplied and removed through a wider range, until at last a range is found at which looping appears. When this loop appears the fatigue range has just been passed. I have shown in my recent paper that an iron or mild-steel bar, when tested in this way, and when loops corresponding to considerable overstrain have been described, will show an elastic line again when re-tested again after a rest. (See Curve 5, sheet 1, "Phil. Trans." (1920).) But this process does not alter the real fatigue limit of the material, as can be seen from the curves.

A Study of Catalytic Actions at Solid Surfaces. X.—The Interaction of Carbon Monoxide and Hydrogen as conditioned by Nickel at relatively Low Temperatures.—A Practical Synthesis of Methane.

By E. F. Armstrong, D.Sc., F.R.S., and T. P. Hilditch, D.Sc.

(Received December 19, 1922.)

The investigation described in this communication had for its primary object the production of formaldehyde or methyl alcohol. In this aim we have been so far unsuccessful, but our results have led to the discovery of an action, which apparently has hitherto escaped notice, by which methane is formed. Apart from theoretical interest the method would appear to have important technical possibilities, either as a means of producing pure methane or of enriching of town's gas in methane, because by its use more methane is formed from water-gas than by other methods.

In order to make clear the course of the action about to be described it will be well briefly to enumerate some of the known interactions of carbon

monoxide and hydrogen on the one hand, and of the former gas and steam on the other.

The behaviour of carbon monoxide and excess of hydrogen over the temperature range 230–400° C. at the surface of metallic catalysts has been exhaustively studied by Sabatier and his co-workers,* who observed that, whilst copper, iron and platinum were without action, nickel, cobalt and palladium induced the formation of methane according to the equation :

$$CO + 3H_2 = CH_4 + H_2O.$$

Above about 300° C. (but not markedly below about 400° C.) carbon monoxide also decomposes in presence of finely divided metals as follows :—

$$2CO = C + CO_2.$$

Whilst the above hydrogenation process is a useful laboratory means of synthesizing methane, it is open to the important technical objections that hydrogen is required in practice in excess of the amount given by the equation, and that in any case an equal volume of hydrogen must be added to the cheaper water-gas to provide the theoretical mixture of one volume of carbon monoxide and three volumes of hydrogen. Since this extra hydrogen must in general be made from water-gas, the loss in gas volume becomes considerable and the yield of methane is in practice only about 15 per cent. of the total water-gas required.

Sabatier therefore indicated† conditions under which water-gas itself could be transformed into methane, or into the latter accompanied by hydrogen and carbon dioxide. This was effected by passing the gas over nickel at a relatively high temperature, 400–500° C., when both actions of hydrogenation and carbonization occur, and the total change may be given as :—

$$3CO + 3H_2 = CH_4 + H_2O + C + CO_2 ;$$

the deposited carbon is then exposed at the same temperature to a current of steam, which in presence of the nickel yields a mixture of hydrogen, methane and carbon dioxide and leaves the nickel ready for participation again in the first phase of the process.

Sabatier also pointed out‡ that both phases might be united, a mixture of

* Sabatier and Senderens, ' Compt. Rend.,' vol. 134, pp. 514, 689 (1902) ; ' Ann. Chim. Phys.' (8), vol. 4, pp. 424–428 (1905) ; Breteau, ' Etude sur les Méthodes d'Hydrogénation,' p. 22 (1911).

† French Patent 355900/1905.

‡ Sabatier, ' La Catalyse en Chimie Organique,' pp. 151–153 (1920 edition).

water-gas and steam being passed over the nickel at 400-500° C. He suggested that the following equation summarized the main action :—

$$5CO+5H_2+H_2O = 2CH_4+2H_2+3CO_2.$$

This equation is, in effect, merely a summation of the following processes :—

$$\begin{cases} 3CO + 3H_2O = 3CO_2 + 3H_2. \\ 2CO + 6H_2 = 2CH_4 + 2H_2O. \end{cases}$$

This introduces another action, namely, that between carbon monoxide and steam in presence of reduced metals such as iron, copper, nickel, etc.

Whilst this process is well known to proceed, in the presence of iron or iron oxide, by alternate reduction of iron oxide by the carbon monoxide, and oxidation of iron (or ferrous oxide) by the steam, we have shown elsewhere* that prepared copper effects the same ultimate change :

$$CO + H_2O = CO_2 + H_2,$$

by an entirely different mechanism, namely, the decomposition of formic acid transiently produced from the carbon monoxide and steam.

The present communication deals with the behaviour of water-gas (purified from sulphur compounds, etc.) in presence of various finely divided metals other than copper at temperatures between 200° and 300° C.

Experiments were made in which the volume and composition of the gas before and after passage over the prepared metals was measured, and the approximate volumes of gases which had disappeared and those of the products were thus deduced.

It was considered possible, in the first place, that combination of carbon monoxide and hydrogen might occur so that formaldehyde or one of its polymerides or transition products would be produced :

$$CO + H_2 = H.CHO ;$$

or, again, that the usual hydrogenation might take place, leaving excess of carbon monoxide unattacked :

$$3CO + 3H_2 = CH_4 + H_2O + 2CO.$$

In point of fact, neither of these take place in presence of nickel (except that towards 300° C. the latter sets in to a minor degree), the only action being one which has apparently hitherto escaped observation, namely,

$$2CO+2H_2 = CO_2+CH_4.$$

This action, although never complete, proceeds to a very considerable extent,

* This series of papers, Part IV, 'Roy. Soc. Proc.,' A, vol. 97, p. 265 (1920).

as may be instanced from the following experiment, in which purified water-gas was passed at the rate of 45 litres per hour and at 265° C. over 10 grams of prepared nickel supported on kieselguhr :

> Ten volumes of water-gas of the composition 7·1 per cent. CO_2, 38·0 per cent. CO, 41·4 per cent. H_2, and 4·4 per cent. CH_4 gave 5 volumes of gas containing 43·8 per cent. CO_2, 1·5 per cent. CO, 7·3 per cent. H_2 and 41·0 per cent. CH_4.

Thus 3·1 volumes CO and 3·8 volumes H_2 disappeared, producing 1·5 volumes of CO_2 and 1·7 volumes of CH_4.

Assuming that the excess of methane over carbon dioxide is due to normal hydrogenation, we may represent the action as :

$$\begin{cases} 0{\cdot}2\ CO + 0{\cdot}6\ H_2 = 0{\cdot}2\ H_2O + 0{\cdot}2\ CH_4, \\ 2{\cdot}9\ CO + 3{\cdot}2\ H_2 = 1{\cdot}5\ CO_2 + 1{\cdot}5\ CH_4, \end{cases}$$

or, to the nearest whole numbers,

$$2CO + 2H_2 = CO_2 + CH_4.$$

The " oxidation " of carbon monoxide to dioxide is somewhat paradoxical in view of the " reducing " conditions which obtain in the process, but it is very readily explained if our former work on copper* is considered in conjunction with the present investigation.

In the present experiments the gases were not dried and there would always be sufficient water present to initiate the action

$$CO + H_2O \rightarrow (H\,.\,COOH) \rightarrow CO_2 + H_2O,\dagger$$

which will be provoked by nickel at least as readily as by copper, and probably more readily, on the basis of general analogy between the activities of nickel and copper.

Consequently, if we consider two volumes of water-gas, $2CO + 2H_2$, the action may be expressed as

$$\begin{cases} \text{(i)}\ CO + H_2O = CO_2 + H_2, \\ \text{(ii)}\ CO + 2H_2 + H_2 = CH_4 + H_2O, \end{cases}$$

$$\text{or } 2CO + 2H_2 = CO_2 + CH_4.$$

It has not been possible to determine whether, in the rigorous absence of all moisture, this change would be suppressed (an argument which would definitely prove the mechanism of the process), because it is impossible to

* *Loc. cit.*

† Alternatively, some water would be formed by preliminary normal hydrogenation: $3CO + 3H_2 = CH_4 + H_2O + 2CO$ (left in excess).

eliminate the last traces of moisture from the catalyst and especially from its support, and because the participation to a minimal extent of the normal hydrogenation

$$CO + 3H_2 = CH_4 + H_2O$$

would furnish sufficient water to serve for the purpose of the preceding hypothesis.

Nevertheless, we are of opinion that this explanation is the most consistent with prior knowledge as well as the simplest of what at first appears to be a puzzling transformation.

Another possible explanation deserves some consideration, although the experimental evidence is against it:—It is known* that aldehydes are, under certain conditions, polymerized to fatty acid esters in presence of finely divided metals. Thus it might be supposed that the following changes take place, methyl formate formed from formaldehyde breaking down into carbon dioxide and methane:—

$$2CO+2H_2 \rightarrow (2H\,.\,CHO) \rightarrow (H\,.\,COOCH_3) \rightarrow CO_2+CH_4.$$

Against this must be set the fact that we have been unable to detect the slightest trace of either of these compounds. A large volume of the gases emerging from the catalyst has been thoroughly scrubbed through a small quantity of water and the solution carefully examined. The solution exerts some slight reducing action on ammoniacal silver nitrate and on mercuric chloride, as in the absence of any catalyst,† but in no instance was the iodoform test responded to, as would have been the case in presence of traces of formaldehyde; further, careful fractionation through an 8-pear Young-Thomas column revealed no trace of any liquid boiling below 100° C. (methyl formate or methyl alcohol).

The trace of water-soluble matter in the gas produced is thus exactly similar to that formed when water-gas and steam are passed over prepared copper, *i.e.*, it answers to tests characteristic of formic acid but not to those which would indicate formaldehyde or methyl alcohol.

We have confirmed Sabatier's observations‡ that formaldehyde is reduced to methyl alcohol in presence of hydrogen and nickel (when it also suffers partial decomposition into carbon monoxide and hydrogen), but find that methyl alcohol is not converted to methane under similar conditions.

Another factor is that, so far as we have been able to ascertain, there is no

* This series, Part III, 'Roy. Soc. Proc.,' A, vol. 97, p. 262 (1920).

† 'Roy. Soc. Proc.,' A, vol. 97, p. 267 (1920).

‡ Sabatier and Mailhe, 'Compt. Rend.,' vol. 144, p. 824 (1907).

experimental evidence to be obtained that hydrogenation of carbon monoxide or dioxide goes in successive stages. As already mentioned, with carbon monoxide and hydrogen no indication has been given, either at the lowest temperature of hydrogenation or under other conditions, that either formaldehyde or methyl alcohol are produced :

$$CO+H_2 \rightarrow H.CHO+H_2 \rightarrow CH_3OH+H_2 \rightarrow CH_4+H_2O.$$

Methane appears to be produced alone in the actual hydrogenation process, except for the change discussed in this paper when the hydrogen is reduced to an equal volume with the carbon monoxide.

Similarly, when carbon dioxide and hydrogen are passed over the catalyst no sign of the above compounds nor of carbon monoxide has appeared, as would be expected in a reduction by stages.

Indeed, in the case of carbon dioxide we have passed equal volumes of this gas and hydrogen over prepared nickel and have observed only consumption of the hydrogen with production of methane, leaving excess of carbon dioxide untouched :

$$4CO_2 + 4H_2 = 3CO_2 + CH_4 + 2H_2O.$$

The gas changes produced in two experiments may be quoted in illustration of this :—

(*a*) with equal volumes of carbon dioxide and hydrogen at 255° C., 1 volume of carbon dioxide and 4·1 volumes of hydrogen disappeared, whilst 0·9 volumes of methane were observed to have been produced ;

(*b*) with an original mixture of 1 volume of carbon dioxide and 2 volumes of hydrogen at 250° C., 1 volume of carbon dioxide and 3·7 volumes of hydrogen disappeared, whilst 1·1 volumes of methane were observed to have been produced.

Consequently we consider that the actual hydrogenation process proceeds direct from carbon dioxide or monoxide to methane and water.

The action between equal volumes of carbon monoxide and hydrogen in presence of nickel or similar catalyst at temperatures below 300° C. is, however, mainly

$$2CO + 2H_2 = CO_2 + CH_4,$$

and we consider that this is due to one molecule of the monoxide and a molecule of water interacting and yielding a molecule each of carbon dioxide and of hydrogen—the latter, with the balance of hydrogen present, furnishing sufficient

hydrogen for the normal hydrogenation of a second molecule of carbon monoxide.

It is somewhat singular that this action has escaped notice previously.

Nickel is the most efficient catalyst of those which we have examined ; cobalt is also quite active (but apparently in a somewhat different direction). The change commences at about 180° C., somewhat lower than with nickel. This is another instance of the fact, which we have previously noted,* that until the temperature rises well above the stability limit of nickel carbonyl (180° C.) the latter complex is not sufficiently " unstable " for catalytic action to proceed freely.

In the case of cobalt the normal hydrogenation

$$CO + 3H_2 = CH_4 + H_2O$$

preponderates, and the carbonizing action

$$2CO = C + CO_2$$

also appears to take place to a considerable extent, so that the action

$$2CO + 2H_2 = CO_2 + CH_4$$

is here a subsidiary one.

Silver is inert, iron nearly so, whilst platinum and palladium are of minor activity in the present action.

The following mixed catalysts were also studied : copper-nickel, iron-nickel, cobalt-nickel, cobalt-platinum and cobalt-palladium. In all cases it was found that the action was less vigorous than when the corresponding single catalyst (cobalt or nickel) was employed.

At increased pressures (up to 6 atmospheres) the process proceeds much as at atmospheric pressure, except that in the case of nickel the minimum temperature of interaction rises with increasing pressure (*i.e.*, with increasing stability of nickel carbonyl at any given temperature).

We conclude this communication with some examples of the change effected with nickel or cobalt at varying temperatures and pressures :—

I. Approximately equal volumes of carbon monoxide and hydrogen passed over prepared nickel.

(i) At 280° C. and atmospheric pressure :

3·99 vols. CO + 3·95 vols. H_2 disappeared and 1·79 vols. CO_2 + 1·78 vols. CH_4 were produced

(or, $2CO + 2H_2 = 0{\cdot}9\ CO_2 + 0{\cdot}9$ vols. CH_4).

* This series, Part I., ' Roy. Soc. Proc.,' A, vol. 96, p. 45 (1919).

(ii) At 220° C. and 4 atmospheres pressure :

3·04 vols. CO + 2·74 vols. H_2 disappeared and 1·29 vols. CO_2 + 1·42 vols. CH_4 were produced

(or, $2CO + 1{\cdot}8\ H_2 = 0{\cdot}9\ CO_2 + 0{\cdot}9\ CH_4$).

II. *Mixture of one volume of carbon monoxide and two volumes of hydrogen passed over prepared nickel.*

At 220° C. and atmospheric pressure :

2·59 vols. CO + 5·12 vols. H_2 disappeared, producing 0·65 vols. CO_2 and 1·96 vols. CH_4.

This is accounted for by the following actions :—

{ 1·31 vols. CO + 3·93 vols. H_2 = 1·31 vols. CH_4 + 1·31 vols. H_2O (normal hydrogenation)
1·28 vols. CO + 1·19 vols. H_2 = 0·65 vols. CO_2 + 0·65 vols CH_4

(*i.e.*, $2CO + 1{\cdot}9\ H_2 = CO_2 + CH_4$).

III. *Approximately equal volumes of carbon monoxide and hydrogen passed over a prepared iron-nickel catalyst.*

At 250° C. and atmospheric pressure :

2·2 vols. CO and 2·3 vols. H_2 disappeared, producing 0·9 vols. CO_2 and 0·9 vols. CH_4.

IV. *Approximately equal volumes of carbon monoxide and hydrogen passed over prepared cobalt.*

At 180° C. and atmospheric pressure :

2·1 vols. CO and 4·2 vols. H_2 disappeared, whilst 0·4 vols. CO_2 and 1·4 vols. CH_4 were produced.

In this case the main action is evidently

$$CO + 3H_2 = CH_4 + H_2O,$$

whilst carbonization also occurred in spite of the low temperature of the experiment.

The process $2CO + 2H_2 = CO_2 + CH_4$ does not appear to proceed so readily with cobalt as with nickel.

It should be remarked that whilst the earlier investigators appear to have directed their attention mainly to the alteration in composition of gases by passage over a catalyst, we have endeavoured to obtain quantitative data by observing in addition the contraction undergone by the gas during the process.

Under the conditions of our experiments, this involved differential readings between two gas-meters with gas flowing at from 25 to 100 litres per hour.

These measurements involve a possible maximum meter error of perhaps 2 per cent.; in addition, the analytical determination of a mixture of hydrogen and methane is open to small errors (eliminated, of course, as far as possible by duplicate analyses). Since the alterations in gas-volumes deduced from these data are also based on differences, any of the above experimental errors, if present, will have a cumulative effect on the final result.

It is therefore unreasonable to expect, in work of this character, an exact experimental accordance between the volumes of gases which have interacted; nevertheless, the data we have given are a sufficiently close approximation to establish that, in the case of nickel at all events, equal volumes of carbon monoxide and hydrogen are transformed into a mixture of carbon dioxide and methane from 200° C. upwards.

This process may prove of value in gas practice since the proportion of methane is 25 per cent. of the water-gas decomposed, whereas by any of the other processes referred to earlier in this paper the maximum possible amount is only 20 per cent.

The large amount of carbon monoxide in town's gas as at present manufactured has met with criticism, notably from Prof. W. A. Bone; this could be reduced by a partial application of the present process if it were technically feasible to remove the carbon dioxide simultaneously formed. Thus, the elimination of half the carbon monoxide present in fresh water-gas by this method causes a total gas-contraction of about 30–40 per cent. after the carbon dioxide produced has been removed.

On the other hand, if it were desired to manufacture pure methane the process would be repeated, the carbon dioxide produced being absorbed until only small proportions of carbon monoxide and hydrogen were left. In an actual experiment, after two passages of the gas over nickel at 240–250° C. and removal of carbon dioxide from the treated gas each time, the product contained 0·8 per cent. CO_2, 0·9 per cent. CO, 8·5 per cent. H_2 and 77·7 per cent. CH_4.

Passage of this gas over heated copper oxide produced a sample containing 3·8 per cent. CO_2, nil CO, 1·9 per cent. H_2 and 82·6 per cent. CH_4; to obtain pure methane this product is then fractionated at a low temperature, in order to eliminate nitrogen accumulated from the original water-gas and any remaining traces of hydrogen.

The method renders the preparation of pure methane in quantity very

simple: in technical practice repeated passage of purified water-gas over nickel at 240–270° C. would result in elimination of all carbon monoxide, since there is a slight excess of hydrogen over carbon monoxide in the original gas as obtained in the producer. Consequently the selective oxidation over copper could be omitted, when the process resolves itself into

(i) passage of purified water-gas over nickel until the carbon monoxide has disappeared;
(ii) removal of the carbon dioxide produced;
(iii) separation of methane from hydrogen and nitrogen by fractionation at low temperature.

Studies of Iridescent Colour and the Structure Producing it. III.—*The Colours of Labrador Felspar.*

By Lord Rayleigh, F.R.S.

(Received January 25, 1923.)

[Plate 1.]

§ 1. *Introduction.*

The brilliant colours displayed by reflexion at certain angles from a polished surface of labradorite, or Labrador felspar, have long been known, and specimens of the material are to be seen in most mineral collections. Several investigations of the origin of these colours have been published,* but I must confess that I have not been able to get clear ideas by studying them. The writers approach the subject primarily from the mineralogist's point of view, and much mineralogical detail is introduced which seems doubtfully relevant and (to me at least) difficult to follow.

Vogelsang's conclusion (translated) is: "The results of my investigations, so far as they concern the various colourations of labradorite, may be summarised as follows: A blue reflexion, due to a polarisation effect, is peculiar to a certain crystalline condition of the mineral. A golden yellow results from total reflexion on the included microlites, which consist of magnetic oxide of iron or of diallage as well; the association of these

* Reusch, 'Pogg. Ann.,' vol. 120, p. 95 (1863); Vogelsang, 'Arch. Néerland.,' vol. 3, p. 1 (1868). See also Brøgger, 'Mineralien der Syenite-pegmatitgänge,' p. 545 (1890).