The Physical and Chemical Properties of Iron Carbonyl.

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This paper contains an account, as promised, of a study of the physical and chemical properties of iron carbonyl, similar to that already communicated to the Society on the properties of the analogous compound of nickel,[*] to which this forms the sequel.

The combination of iron and carbon monoxide was discovered by Drs. Mond and Quincke in 1891,[†] and the resulting compound called iron pentacarbonyl was isolated (as a coloured liquid), and examined by Drs. Mond and Langer [‡] in the course of the same year.

Our knowledge of this remarkable substance is derived entirely from the observations of the last-named investigators, and a few isolated observations of others—thus the late Dr. Gladstone determined its refractive indices and Dr. Perkin the magnetic rotation. The molecular refractive power and magnetic rotation are abnormally high, and the compound is diamagnetic; such remarkable properties naturally aroused considerable interest, but the lack of any further work on the compound is doubtless due to the great difficulty experienced in preparing quantities of the compound large enough to work with.

The peculiarities exhibited by this compound call for further attention, and we have examined the formation of the compound and its properties, both physical and chemical ; the investigation has been carried out on the same lines as that on nickel carbonyl,[§] and attention has been directed more particularly to the differences between the iron and nickel carbonyls, such as the difference in formula, colour, stability and, more especially, to the action of light on iron carbonyl.

We are indebted to Dr. Mond for two specimens of iron carbonyl with which the investigation was begun; latterly we have been able to prepare and use much larger quantities of the compound, and further work is still

[*] 'Roy. Soc. Proc.,' 1903, vol. 71, p. 427.

[†] 'Trans. Chem. Soc.,' 1891, vol. 59, p. 604.

[‡] 'Trans. Chem. Soc.,' 1891, vol. 59, p. 1090.

[§] *Loc. cit.*, and 'Trans. Chem. Soc.,' 1904, vol. 85, p. 203, p. 213.

in progress. The preparation of iron carbonyl in quantity is a long and tedious process; the yield obtained depends on a number of circumstances; the best conditions for the preparation of the compound are being investigated, and it is hoped that the observations made on this subject will form the subject of another communication.

Liquid iron carbonyl is described as a yellow liquid, with the formula $Fe(CO)_5$, boiling at $102°·8$ C. It is remarkable that nickel carbonyl, the compound of a metal whose salts are highly coloured, is colourless, while iron carbonyl is coloured, and the salts of iron have usually only a feeble colour. Also the difference in composition, coupled with the higher boiling point of the iron compound, caused by the introduction of more carbon monoxide, is a striking phenomenon. We considered it important to determine whether careful purification and drying of the compound would remove the colour, and to procure further analytical evidence bearing on its formula.

To purify the substance it was placed with some suitable drying agent (copper sulphate, barium oxide, zinc chloride, and pure phosphorous pentoxide were all found suitable) in one limb of a carefully-dried glass tube bent into the form of a V-tube; the other limb was empty. The tube was then exhausted by means of a side tube, filled several times with carbon monoxide, hydrogen or nitrogen, exhausted again, and then the side tube was sealed off. After standing in the dark for some time the iron carbonyl was distilled into the empty limb by placing this in a freezing mixture and the other limb in a beaker of water at about $50°$ C. The liquid was still of a pale yellow colour, even after standing several days over phosphorous pentoxide and distilling by feeble gas-light.

Another form of experiment showed conclusively that the colour is a definite property, and is not due to impurities. A tube bent into the form of an M was used, the liquid was allowed to stand in one limb for several days over anhydrous copper sulphate, distilled over into the bend, where it was allowed to stand for a week over pure phosphorous pentoxide, and then finally distilled into the empty limb of the tube. The operations were carried out in the dark, and the liquid still possessed its yellow colour. Consequently, it is concluded that the pure compound has a yellow colour. We have therefore not been able to confirm the opinion expressed by Armstrong[*] that the pure compound would be colourless.

For analysis the compound was purified as described above, and rapidly transferred to weighed glass bulbs in a vacuum desiccator, the bulbs sealed and weighed. The transference must be effected very rapidly, as the com-

[*] 'Proc. Chem. Soc.,' 1893, p. 58.

pound is exceedingly sensitive to air and moisture; a reddish precipitate is produced on standing if the liquid has been exposed even for a very short time to moist air.

The percentage of carbon monoxide was determined by combustion. It was found necessary, in order to get constant results, to pass a current of oxygen through the tube for a long time, while heated to a bright red heat, in order to completely oxidise the carbon which was deposited with the iron.

(1)   0·2680 gramme of the liquid gave 0·3000 gramme of carbon dioxide.

(2)   0·4336   „   „   0·4825   „   „

The estimation of the iron offered greater difficulties. Mond and Langer[*] decomposed the compound by heating to 100° C. with chlorine or bromine water in a sealed tube, and then weighing the iron as ferric oxide.

This method always gave slightly high results, and accuracy is limited because small quantities only can be used on account of the great pressure developed.

(3)   0·3417 gramme gave 0·1424 gramme of ferric oxide.

A bulb containing a weighed quantity of the liquid was broken under a chloroform solution of bromine, the gas evolved was passed through more of the same solution in a U-tube. When the reaction had ceased the solutions were evaporated to dryness, and the iron precipitated and weighed as ferric oxide.

(4)   0·7820 gramme gave 0·3209 gramme ferric oxide.

The best method of decomposing the compound was found to be treatment with alcoholic potash solution in a sealed tube at 100° C. When a bulb containing iron carbonyl was broken in alcoholic potash solution, beautiful colourless tabular crystals having a pearly lustre were at once produced; at the surface of the liquid these were at once oxidised by the air with the formation of a reddish brown precipitate.

The mixture contained in a sealed tube was heated to 100° C. for a short time, the tube cooled, opened (no pressure is produced by this decomposition), the contents washed out and evaporated to dryness. The residue was treated with nitric acid, again evaporated down, and the iron precipitated by hot caustic potash to separate it from aluminium which was dissolved out of the glass.

(5)   0·9465 gramme gave 0·3886 gramme ferric oxide.

* *Loc. cit.*

Several other methods of analysis were also tried, such as decomposing the carbonyl by heat, weighing the iron and measuring the carbon monoxide. A small bulb containing a weighed quantity of the purified iron carbonyl was placed inside a strong glass bulb, a glass tap was then sealed on to this, the bulb exhausted with a Töpler pump, the small bulb was broken and the carbonyl decomposed by heating to about 180° to 200° C., until no deposit of iron could be produced by heating a clear portion of the large bulb with a blow-pipe flame.

The carbon monoxide was then removed, by means of a Töpler pump, and measured; the bulb with the deposited iron was weighed, the iron dissolved off and the bulb weighed again after drying. In this process it was found that the glass was often attacked where the iron had been deposited and the high values obtained for the iron are doubtless to be attributed to this cause, and to the presence of carbon in the iron (see later). The following example illustrates the kind of result obtained by this method:—

(6)　0·4626 gramme gave 287 c.c. of carbon monoxide at 19° C. and 757 mm. and left 0·1371 gramme of iron.

	Fe.	CO.	CO by volume for 1 gramme.
Found—			
(1)	—	71·2	—
(2)	—	70·9	—
(3)	29·2	—	—
(4)	28·7	—	—
(5)	28·7	—	—
(6)	29·6	—	564·2 c.c. at 0° C. of 760 mm.
Calculated for Fe (CO)₅	28·57	71·43	571·4 c.c.
„　　　Fe (CO)₄	33·33	66·66	530·9 c.c.

The compound is therefore $Fe(CO)_5$.

Attempts were made to determine the ratio Fe : CO in the compound by passing nitrogen through a weighed or unweighed quantity of pure iron carbonyl and then through a glass tube bent twice on itself and heated in a bath so that the vapour was heated for some time and decomposed into iron and carbon monoxide; the iron was deposited in the tube and then weighed, the carbon monoxide was passed over hot copper oxide and weighed as carbon dioxide in a potash tube. It had been found previously that this process gave good results in the case of nickel carbonyl.

With iron carbonyl, however, consistent results could never be obtained. In the first place the compound is much more difficult to decompose completely than nickel carbonyl, and it was found that, in order to ensure complete decomposition, it was necessary, when keeping the bath at

180° to 200° C., to heat a small portion of the tube nearer the copper oxide tube nearly to redness. Even then it was always found that the sum of the weights of the iron and carbon monoxide was always less than that of the iron carbonyl taken. This was traced to the fact that the iron deposited was always contaminated with carbon, which was given off as hydrocarbons when the iron was dissolved in acids; also the weight of ferric oxide obtained from the iron was always less than it should have been. The ratio CO : Fe was usually about 4·5 to 4·8 ; this is readily accounted for by a small percentage of carbon in the iron. The presence of carbon in the iron would also tend to raise the percentage of iron as estimated by method (6).

Further evidence in support of the formula $Fe(CO)_5$ was afforded by experiments on the decomposition of the vapour enclosed in a space at a given pressure and measuring the pressure of the carbon monoxide produced; this was approximately five times the original pressure of the vapour. These experiments will be referred to later.

Molecular Weight.—Numerous vapour-density determinations have been made and will be described in another part of this paper. When no dissociation occurs the vapour density varied between 98 and 100, so that the molecular weight corresponds to the formula $Fe(CO)_5$ with a molecular weight of 198.

Two determinations of the molecular weight in benzene were made by the cryoscopic method: a weighed quantity of liquid in a bulb was broken under the benzene. Owing to the very great sensitiveness of the compound to air and moisture, the solution always began to turn turbid before the end of the experiment, even when the greatest care was taken to exclude moisture and the air in the apparatus had been replaced as completely as possible by nitrogen or carbon monoxide.

0·2956 gramme in 14·28 gramme benzene gave a depression of 0·524° C. Hence the molecular weight is 197.

0·3900 gramme in 14·20 grammes benzene gave a depression of 0·705° C. Hence the molecular weight is 194.

Specific Gravity of the Liquid.—Mond and Langer* gave the density of liquid iron carbonyl as 1·4664 at 18° C. compared to water at the same temperatures, or 1·4688 compared to water at 4° C. Gladstone† gave the density at 13°·4 C. as 1·474, at 15°·5 C. as 1·470, and at 22° C. as 1·460.

The specific gravity was determined with the aid of a small glass pyknometer (volume 2·2 c.c.) at temperatures from 0° C. to 80° C. Great care

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* *Loc. cit.*

† 'Phil. Mag.,' 1893, [5], vol. 35, p. 204.

was exercised to exclude moisture, and the experiments were carried out in a dim light; a very small amount of decomposition, indicated by the formation of minute bubbles of gas, always took place, which was more marked at the higher temperatures, and was doubtless caused by traces of moisture and air, so that the numbers obtained can only be regarded as approximate for the two highest temperatures. The specific gravity is in each case referred to water at 4° C.

Temp.	Sp. gr.
0·0° C.	1·494
16·5° C.	1·468
40·0° C.	1·421
61·5° C.	1·382
80·0° C.	1·351

These specific gravity determinations were made with a specimen of the carbonyl kindly supplied by Dr. Mond. When a much larger quantity was available this was purified, and further determinations were made with a much larger pyknometer (volume 7·1100 c.c.), using the same precautions (in this case there were no signs of any decomposition).

Temp.	Sp. gr.
0·0° C.	1·4937
21·1° C.	1·4565
40·0° C.	1·4330
60·0° C.	1·3825

These results agree fairly well with those given above, but are naturally more trustworthy on account of the larger quantity of material used.

The coefficient of expansion for 0° C. to 21° C. is 0·00121, for 21° C. to 40° C. is 0·00128, and for 40° C. to 60° C. is 0·00142. The mean coefficient of expansion is, therefore, about 0·00138.

By extrapolation on the curve the specific gravity at the boiling point, 102°·5 C., is 1·310. The molecular volume is, therefore, 149·6. At the melting point, −20° C., the specific gravity is 1·53 and the volume of the molecule is then about 128.

The values of the specific gravity of the liquid at 0° C. and 60° C., taken with the critical temperature (288° C., for which see p. 565), give the following Waterston formula for the relation between the volume v and the temperature t° C. :—

$$v = 1·974 - 0·5307 \log (288 - t).$$

Refractive Indices.—Gladstone* determined the refractive indices of the carbonyl for several of the lines of the spectrum and found that, as in the case of nickel carbonyl, the compound had a very large molecular refractive power and an enormous dispersive power. It was, therefore, unnecessary to investigate this property minutely, and two determinations only were made for sodium and thallium light with an Abbé refractometer by Mr. A. Hutchinson of the Mineralogical Department.

$$\mu \text{ for Na light} \ldots\ldots\ldots \quad 1\cdot519$$
$$\mu \quad \text{,, Tl} \quad \text{,,} \quad \ldots\ldots\ldots \quad 1\cdot528 \quad \text{at } 22^\circ \text{ C.}$$

These values agree very closely with those found by Gladstone—$1\cdot5180$ and $1\cdot5289$.

Melting Point.—The pale yellow liquid crystallises when cooled to a pale yellow solid which melts at $-19^\circ\cdot5$ C. to -20° C. At the temperature of liquid air the solid entirely loses its colour, which it gradually recovers on warming up again.

Vapour Pressure and Boiling Point.—The vapour pressure was determined by the statical method as in the case of nickel carbonyl.

A wide barometer tube, drawn off to a fine capillary at one end, was carefully cleaned and placed upright in a vessel of pure dry mercury, in a room lighted by a feeble gas jet. A small tube containing iron carbonyl was now introduced, the whole exhausted thoroughly by means of a Fleuss pump and sealed off at the end. The pressure was then read off by means of a kathetometer, while the tube was surrounded by a bath at various temperatures. Observations taken after cooling and allowing the tube to stand showed that no appreciable amount of decomposition took place under the conditions of the experiment. The results are appended below :—

Temp.	Pressure.
$-7\cdot0^\circ$ C.	$14\cdot0$ mm.
$0\cdot0^\circ$ C.	$16\cdot0$,,
$16\cdot1^\circ$ C.	$25\cdot9$,,
$18\cdot4^\circ$ C.	$28\cdot2$,,
$35\cdot0^\circ$ C.	$52\cdot0$,,
$57\cdot0^\circ$ C.	$133\cdot0$,,
$78\cdot0^\circ$ C.	$311\cdot2$,,

Next day at $18^\circ\cdot9$ C. the pressure was $29\cdot4$ mm.

The boiling point given by Mond and Langer is $102^\circ\cdot8$ C. at 749 mm. Several determinations of the boiling point were made, all of which gave a

* *Loc. cit.*

result slightly lower than this. Thus, it was found that the liquid boiled at 101°·8 C. at 736 mm., at 102°·0 C. at 744 mm. and at 102°·7 C. at 764 mm. The values for 0° C. and 102°·7 C. give the following Rankine formula for the relation between the vapour pressure p in millimetres of mercury and the absolute temperature T: $\log p = 7·349 - 1681/T$. This fits in very well with the results for the intermediate temperatures.

Critical Temperature.—It was found by trial experiments that the liquid could be heated in a glass tube under pressure to temperatures considerably above its boiling point without undergoing noticeable decomposition. Its critical temperature was, therefore, determined by placing some liquid in small thick-walled capillary tubes, exhausting, sealing-off, and then heating the tubes in an air or paraffin bath until the meniscus disappeared. The tubes were about one-third to one-half full of liquid, and though no deposit of iron was produced, yet the tubes burst after heating several times to the critical point. In several determinations it was found that the meniscus disappeared between 285° C. and 288° C.

The formula $T = 0·66\,T_c$, where T_c is the absolute boiling point and T the absolute critical temperature, is usually applicable to liquids which are not associated in the liquid or gaseous state near the boiling point, and was found to be applicable to nickel carbonyl; it should, therefore, be applicable here. Taking the boiling point as 102°·5 C., the critical temperature should be 289°·2 C., a value agreeing very closely with the number found experimentally.

The critical density of iron carbonyl is calculated to be 0·49, the value for nickel carbonyl is 0·46. The critical pressure calculated from the Rankine formula for the vapour pressure is 29·6 atmospheres.

The number obtained by dividing the absolute critical temperature by the critical pressure, which is proportional to the volume of the molecule, Van der Waals' constant b, is 18·9, the corresponding value for nickel carbonyl is 15·5 and the value for carbon monoxide is 3·7. Hence the volume of the molecule of iron carbonyl is 5·1 times larger than that of carbon monoxide, while 4·2 represents the ratio for the nickel carbonyl.

The latent heat of iron carbonyl is 39·45 calories per gramme, and the Trouton constant, molecular latent heat divided by absolute boiling point, is 20·6, a value identical with that for nickel carbonyl.

The molecular volume of iron carbonyl at its boiling point is 150, so that taking 7·0 as the volume of the iron atom, we get 28·6 as the volume of each carbon monoxide molecule, a number smaller than that found for nickel carbonyl, *i.e.*, 32·2. Liquid carbon monoxide at its boiling point has a molecular volume of 35, so that a greater contraction would take place in

the formation of liquid iron carbonyl from liquid carbon monoxide and iron, if that were possible, than in the formation of nickel carbonyl under similar conditions.

The similarity between many of the constants of nickel and iron carbonyls is very striking, in spite of the fact that the substances differ so widely in their boiling points and stability.

Vapour Density and Dissociation.—Two vapour-density determinations were made by Mond and Langer* by V. Meyer's method in an atmosphere of hydrogen at the temperature of boiling xylene. The results were 93·8 and 92·4, the theoretical value is 98, so that slight dissociation is indicated.

A number of trial experiments showed that iron carbonyl vapour dissociated quietly without explosion when heated to a high temperature alone or in an inert gas.

A series of vapour-density determinations were made by V. Meyer's method in various gases at different temperatures in order to show the effect of temperature, of admixture with inert gas or carbon monoxide and of the rate of diffusion on the dissociation of iron carbonyl. Owing, however, to the great stability of the iron compound and its slow rate of dissociation, these effects are not so clearly seen as in the case of nickel carbonyl. In fact, so slowly does iron carbonyl dissociate, that accurate determinations can only be obtained at the lowest temperatures where no dissociation occurs, and at the highest temperatures where complete dissociation is rapid; at the intermediate temperatures the dissociation is so slow that diffusion to the cooler parts of the tube takes place and the end-point of the evolution of gas is extremely uncertain.

Several series of determination of the vapour density were also made by Hofmann's method to show the effect of pressure and temperature on the dissociation of iron carbonyl; but again, owing to the slow rate of dissociation, the experiments had to be prolonged for an inconveniently long time before even an approximately constant volume was obtained. In these experiments it is advisable to protect the vapour as far as possible from light, since the decomposition of the iron carbonyl by light, which takes place at low temperatures, is thus minimised.

The results obtained are tabulated below. The percentage dissociation is calculated by means of the formula

$$p = \frac{D - d}{4d} \, 100.$$

* *Loc. cit.*

Vapour Densities determined by Meyer's Method.

Temperature of the bulb.	Gas filling the tube.	Vapour density $(H = 1)$.	Percentage of $Fe(CO)_5$ dissociated.	Remarks.
129° C. (amyl alcohol)	Carbon monoxide...	93·7 } 93·2 }	1·2	No visible deposit of iron.
	Nitrogen	90·1	2·2	
	Hydrogen	86·2 } 88·7 } 87·5 }	3·0	Distinct deposit of iron.
155° C. (turpentine)	Carbon monoxide...	82·6 78·0	4·6 6·4	
	Nitrogen	36·4	42·3	Extensive deposit extending over large area of tube
182° C. (aniline)	Carbon monoxide...	44·9 } 44·0 }	30·1	„
	Nitrogen	27·4	64·4	„
216° C. (naphthalene)	Carbon monoxide...	20·2	96·3	„
	Nitrogen	20·0	97·5	„

Vapour Densities by Hofmann's Method.

Temperature.	Pressure.	Vapour density $(H = 1)$.	Percentage of $Fe(CO)_5$ dissociated.	Remarks.
78° C.	195	99·8	—	
	195	98·4	—	
	212	100·0	—	
	288	99·8	—	
100° C.	126	98·3	—	
	179	98·6	—	
	204	97·2	—	No visible deposit of iron.
	225	97·1	—	
	298	99·5	—	
130° C.	136	95·0	0·8	
	192	95·7	0·6	
	216	96·2	0·5	
	242	94·5	0·9	
	325	95·0	0·8	
141° C.	261	86·6	3·3	
155—160° C.	274	70·2	9·9	Extremely faint deposit of iron.
	354	88·1	2·81	
179° C.	249	40·4 } 40·4 }	35·6	Very extensive deposit of iron; on cooling much undecomposed iron carbonyl condensed
	334			
	406	44·2	30·2	
	574	45·6	28·8	

These results show very clearly the effect of increase of temperature and of diminution of pressure in increasing the dissociation, the effect of carbon

monoxide in diminishing the dissociation observed in an inert gas at the same temperature.   The increased dissociation in a light inert gas as compared with a heavy one is shown by the values in hydrogen and nitrogen at 129° C.

The rate of dissociation of the vapour at various temperatures was also studied in an apparatus very similar to that used by Mittasch* for the dissociation of nickel carbonyl.   Owing to the small vapour pressure of iron carbonyl the range of pressures of undissociated vapour is very limited.

The rate of dissociation is very slow at temperatures below 180° C., but appears to be complete at that temperature.   The reaction is reversible, but the reversal takes place very slowly.

Chemical Reactions of Iron Pentacarbonyl.—An examination of some of the simpler reactions of iron carbonyl was made in order to study its chemical nature and stability in comparison with nickel carbonyl, the reactions of which have already been described.†   The action of the halogens in solution in pure dry carbon tetrachloride on normal and decinormal solutions of iron carbonyl in the same solvent was first investigated ; the solutions were mixed in a nitrometer and allowed to stand, the gas evolved measured and tested and the solid examined.

Chlorine and iron carbonyl react fairly rapidly to produce a solid and carbon monoxide, which was measured, and showed that the decomposition was complete.   The solid was found to be a mixture of ferrous and ferric chlorides, the ferrous chloride could never be obtained quite free from ferric, but by using a large excess of chlorine practically pure ferric chloride could be obtained.   The gas appeared to be practically pure carbon monoxide and to contain no carbonyl chloride.

Bromine reacts with iron carbonyl very slowly, in fact much more slowly than iodine reacts with nickel carbonyl.   Five c.c. of a decinormal solution of iron carbonyl and 1 c.c. of normal bromine solution should evolve 22·4 c.c. of gas, 15 c.c. of gas had been evolved in six hours, 19·5 c.c. in 20 hours, and the reaction was practically complete in 35 hours.   The solid salt consisted chiefly of ferrous bromide with minute traces of ferric salt, the gas was pure carbon monoxide.   This reaction shows the much greater stability of the iron compound over the nickel compound, which is decomposed by bromine in a few seconds after mixing.

Iodine reacts extremely slowly with iron carbonyl to produce carbon monoxide and ferrous iodide ; in decinormal solution the reaction had only proceeded to the extent of 70 per cent. in three days.

Iodine monochloride in chloroform solution reacts with iron carbonyl much

* 'Zeit. Phys. Chem.,' 1902, vol. 40, p. 1.
† 'Trans. Chem. Soc.,' 1904, vol. 85, pp. 203—222.

in the same way as it does with nickel carbonyl; ferrous chloride is precipitated and iodine liberated, the solution becoming purple, the free iodine then reacts very slowly with the residual iron carbonyl.

The whole reaction is a very slow one, and the salt at first precipitated is ferrous chloride with no trace of ferric salt and no iodide, a little iodide appears before the formation of chloride is complete, but no ferric salt is produced.

Iodine trichloride in chloroform solution reacts slowly with iron carbonyl, producing a solid deposit and evolving gas ; no free iodine is produced for a long time. The solid is again ferrous chloride free from ferric chloride, and contains very little iodide until the reaction has been proceeding for some time.

Cyanogen gas does not appear to react at all with iron carbonyl liquid or vapour, and in alcohol solution the reaction is extremely slow.

Cyanogen iodide in chloroform solution reacts very gradually, the solution first becoming red and then purple and a brown solid is deposited. The solvent contains free iodine and the solid is ferrous cyanide mixed with a little ferrous iodide.

The action of the halogen hydrides was examined in the gaseous state and also in chloroform solutions.

Hydrochloric and *hydrobromic acid* gases had no action on iron carbonyl even after allowing the mixture to stand for weeks in the dark. Dry *hydriodic acid* gas was introduced into an exhausted glass bulb containing a small glass bulb full of iron carbonyl, which was then broken. On standing, a dark brown crystalline solid was produced, which was found to be ferrous iodide, and at the same time carbon monoxide and hydrogen were liberated.

In chloroform solution hydrochloric acid and hydrobromic acid react slowly with iron carbonyl, the former more slowly than the latter. In each case pure ferrous salts were produced and hydrogen and carbon monoxide were evolved. With a chloroform solution of hydriodic acid the reaction was more rapid and was complicated as in the case of nickel carbonyl by the liberation of iodine.

The reactions of iron carbonyl described above are exactly parallel with the corresponding reactions of nickel carbonyl, only differing in rapidity, which is much less owing to the greater stability of the iron compound. There is a more marked difference to be observed in some of the other reactions.

With *sulphur* dissolved to carbon bisulphide or xylene, iron carbonyl does not react at all in the cold, neither does it react with *nitric oxide*, in both cases differing markedly from nickel carbonyl.

Hydrogen sulphide also has no action on iron carbonyl, but an alcohol solution of the gas reacts extremely slowly to produce ferrous sulphide, carbon monoxide and hydrogen.

Nitric acid in carbon tetrachloride or ether solution reacts rapidly with iron carbonyl to produce a mixture of ferrous and ferric nitrates, carbon monoxide with some hydrogen and reduction products of nitric acid.

Concentrated sulphuric acid reacts rapidly with iron carbonyl, the mixture first darkens, carbon monoxide and hydrogen are evolved, mixed with a little iron carbonyl vapour; the liquid then becomes paler in colour as the reaction is completed. The salt formed is pure ferrous sulphate, so that the reaction may be expressed by the following equation :—

$$Fe(CO)_5 + H_2SO_4 = FeSO_4 + 5CO + H_2.$$
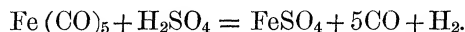
The rapidity of the reaction is very much greater than in the case of nickel carbonyl; this is the only reaction yet observed which is more rapid than the corresponding reaction with nickel carbonyl.

To complete the comparison between the nickel and iron compounds in so far as the reactions of nickel carbonyl have been described, the reaction of iron carbonyl with *benzene* in presence of *aluminium chloride* was examined. Four grammes of iron carbonyl and 10 grammes benzene (five molecules) were poured on to 28 grammes powdered aluminium chloride (five molecules) in a tube, which was then sealed off and heated for two hours to 100° C. The mixture became very dark in colour, and on opening the tube some pressure caused by carbon monoxide and a little hydrochloric acid gas was observed.

The dark mass was mixed with ice, when some ferrrous chloride dissolved and some ferrous hydroxide was precipitated, treated with hydrochloric acid and distilled in steam. Benzaldehyde and benzene came over first followed by a crystalline fluorescent solid; the residue in the flask was dissolved in benzene, dried and distilled, when a crystalline solid was obtained which was found to be pure anthracene, so also was the small quantity of solid which distilled in steam.

The final products of the reaction in this case are, therefore, precisely the same (namely, benzaldedyde and anthracene) as those produced by using nickel carbonyl. In the cold the reaction proceeds slowly, with the production of benzaldehyde and no anthracene, again precisely as in the case of nickel carbonyl.

Decomposition by Light.—Mond and Langer* state that liquid iron carbonyl is rapidly decomposed by light, giving rise to a solid product and

* *Loc. cit.*

carbon monoxide. Determinations of the percentage of iron in the compound made by them indicated that the formula was $Fe_2(CO)_7$, but the body was not obtained in a pure state. This behaviour to light constitutes the most striking difference between the carbonyls of iron and nickel, and was therefore examined more fully.

The decomposition was first investigated over mercury in a barometer tube. A weighed quantity of liquid iron carbonyl in a sealed bulb was introduced into a barometer and the bulb was then broken, after which the tube was exposed to light.

In the laboratory on bright days in February the decomposition was extremely slow, but on the same days in direct sunlight the decomposition was rapid and the evolution of gas was completed in a few hours. Exposure to the electric arc only induces the change very slowly, and a strong acetylene flame is almost without action. The volume of gas evolved (which was found to be pure carbon monoxide) was then measured and the solid collected. The solid was found to consist of beautiful, lustrous, hexagonal plates of an orange colour, which, when pure, retained their lustre for a very long time on exposure to ordinary air, and indefinitely in dry air; if, however, the decomposition had not been completed and the solid was contaminated with traces of the liquid compound, rapid change occurred and the compound sometimes took fire.

The following are two typical examples of experiments made in this way :—

(1)   0·0905 gramme iron carbonyl gave 4·7 c.c. of carbon monoxide.
(2)   0·2970   „   „   18·4   „   „

According to the equation

$$2Fe(CO)_5 = Fe_2(CO)_7 + 3CO, \tag{1}$$
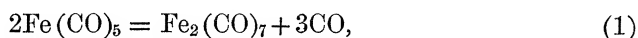
there should have been produced 15·5 c.c. and 50·9 c.c. of carbon monoxide respectively, whereas the equation

$$2Fe(CO)_5 = Fe_2(CO)_9 + CO \tag{2}$$

requires 5·2 c.c. and 17 c.c. of carbon monoxide respectively.

It would, therefore, appear that the formula of the solid compound is $Fe_2(CO)_9$ and not $Fe_2(CO)_7$, and that the decomposition induced by light is represented by equation (2) above. This result was confirmed by carrying out the decomposition in a large glass bulb out of contact with mercury.

A small sealed bulb filled with iron carbonyl was introduced into a large glass bulb, which was then sealed on to a glass tap, dried carefully,

and exhausted with a Töpler pump. The small bulb was then broken and the whole exposed to light for some days, after which the carbon monoxide was pumped out and measured. In these experiments it was practically impossible to get the decomposition completed, since the bulb became covered with a deposit of the solid, which cut off the light.

The following are typical examples :—

0·6006 gramme of the liquid carbonyl gave 33·2 c.c. of carbon monoxide and left 0·501 gramme of solid. Theory requires 34·3 c.c. of gas and 0·557 gramme of solid.

0·5076 gramme gave 32 c.c. of gas. Theory requires 33·8.

Decomposition was incomplete, as shown by behaviour of solid, and by the fact that on admitting air to the carbon monoxide a deposit of iron oxide was produced. Another type of experiment also served to confirm the above conclusively :—

A carefully dried glass bulb of about 250 c.c. capacity was fitted with a small mercury manometer, thoroughly exhausted, and filled with dry iron carbonyl vapour, the pressure of which was measured at a definite temperature. The bulb was then exposed to light until no further change took place ; after the bulb had been brought to the original temperature, the pressure was found to have been reduced to one-half its former value, as required by equation (2) above.

None of the specimens of the solid carbonyl prepared by either of the foregoing methods was found to be pure enough to give good results on analysis. The specimens prepared over mercury always retained small globules of mercury too small to be visible, but whose presence became evident during combustion, while the specimens prepared in glass bulbs were always contaminated with a little of the liquid, which either caused spontaneous combustion of the sample or decomposed quietly and left some oxidation product poor in carbon. The percentages of carbon monoxide obtained were too high for $Fe_2(CO)_7$, 63·6 per cent, and too low for $Fe_2(CO)_9$, 69·2 per cent.; thus, for example, 65·0 and 66·5 per cent. of carbon monoxide were obtained in two combustions.

We therefore examined the decomposition of the liquid in various solvents and succeeded in obtaining the compound in a pure state.

Iron pentacarbonyl dissolved in dry ether or petroleum ether and exposed to sunlight, undergoes rapid decomposition with evolution of carbon monoxide and formation of large reddish orange crystals of the solid carbonyl. To obtain the pure solid compound in quantity, the solution was sealed up in a dried and exhausted glass tube, and exposed to light. Owing to the unavoidable exposure to air during the transference, a small amount of a precipitate

of an oxidation product was sometimes produced. When a quantity of the solid carbonyl had been formed, the tube was opened (a considerable pressure of carbon monoxide was always produced), and the precipitate was removed easily by shaking the tube and pouring off the liquid, when the precipitate, which is very light and settles slowly, is poured off with the liquid, and the crystals remain behind. The crystals were then washed two or three times with the solvent and rapidly transferred to a desiccator containing sulphuric acid and solid paraffin. When prepared in this way they retain their lustre, and show no signs of change for a long time on exposure to air.

The percentage of carbon monoxide was then determined by combustion, using the same precautions as in the case of the liquid. The method of estimating the iron after decomposing the solid by heating in a sealed tube with bromine water was found unsatisfactory, and after trying several methods it was found that, if the compound were dropped slowly into pure nitric acid in a weighed crucible, complete decomposition took place, with effervescence and without loss of iron. The resulting liquid was then evaporated to dryness on a water bath, the ferric nitrate decomposed by careful ignition, and the ferric oxide weighed.

The following results were obtained by these methods :—

(1)   0·2470 gramme gave 0·2655 gramme CO_2.
(2)   0·3178   „   „   0·3417   „   „
(3)   0·1839   „   „   0·1992   „   „
(4)   0·5791   „   „   0·2534 gramme Fe_2O_3.
(5)   0·3450   „   „   0·1515   „   „

Found—

	CO.	Fe.
(1)......................	68·4	—
(2)......................	68·4	—
(3)......................	68·9	—
(4)......................	—	30·6
(5)......................	—	30·7
$Fe_2(CO)_7$ requires ...	63·60	36·40
$Fe(CO)_4$ „ ...	66·66	33·33
$Fe_2(CO)_9$ „ ...	69·20	30·80

The solid compound is therefore $Fe_2(CO)_9$, or *diferro-nona-carbonyl*. The solid prepared in this way forms large hexagonal plates, often 3 or 4 mm. in breadth, but always rather thin. It is very sparingly soluble, in fact practically insoluble, in ether, petroleum-ether, and benzene, but is slightly soluble in methylal, alcohol and acetone, and much more soluble in pyridine to form a

reddish solution. When dissolved the compound becomes much more sensitive to air and moisture, and deposits a reddish precipitate. We have not yet succeeded in recrystallising the compound. The crystals are slightly diamagnetic, but less so than the liquid. The density of the solid at 18° C. is 2·085, and its molecular volume is therefore about 174. If two gramme-molecules of solid $Fe(CO)_5$ were converted into $Fe_2(CO)_9$, then 256 volumes would become 174, or a contraction of about 33 per cent. would ensue.

On heating solid iron carbonyl, as stated by Mond and Langer, liquid iron carbonyl is produced, and some solid, probably iron, is left. We find that this change takes place at about 100° C. Under a pressure of carbon monoxide up to 150 atmospheres, there is no rapid change below 95° C., but at this temperature the solid is completely converted into liquid iron carbonyl, though traces of a yellowish-brown solid are sometimes left. Quantitative experiments were made on the decomposition at 100° C. in a stream of hydrogen, and showed that the decomposition could be represented by the following equation :—

$$2Fe_2(CO)_9 = 3Fe(CO)_5 + Fe + 3CO.$$
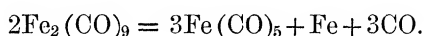
Liquid iron carbonyl, when exposed to light under a pressure of 75 to 125 atmospheres of carbon monoxide in the tube of a Cailletet pump, decomposes without any apparent diminution of the rate of transition. For this purpose the liquid was placed in a small tube kept in position by a plug of glass wool so that the liquid never came in contact with the mercury. If, however, the sealed tube containing liquid iron carbonyl, or a solution of it in ether, be heated to any temperature between 60° and 100° C., while exposed to light, no solid separates even after several hours, whereas below 50° C. solid is formed in about half an hour. This is also true when the liquid is under a pressure of 50 to 100 atmospheres of carbon monoxide. The solution which had been exposed to light at a temperature above 60° C. even on cooling gave no deposit of solid, showing that no decomposition had been caused by the action of light at these temperatures. And this is confirmed by the fact, which will be proved later, that if solid had been produced in solution it would at this temperature have formed a solution of an intense green colour.

The decomposition of liquid iron carbonyl dissolved in ether, amylene, or petroleum-ether (B.P., 30° to 40° C.) by light, takes place slowly at the temperature of liquid air. The solutions become solid, and, after exposure to sunlight for about three hours inside a vacuum vessel of liquid air, and then allowing to warm up in the dark, a faint deposit of solid was observed.

In spite of the fact that pressure is not effective in preventing the

decomposition by light, the reaction is reversed slowly under a slight pressure of carbon monoxide at the ordinary temperature in the dark. Tubes containing iron carbonyl alone, or in solution, which had been exposed to light so that they contained some of the solid carbonyl, on standing at the ordinary temperature in the dark for some weeks, were found to contain no solid ; so that the solid had absorbed the carbon monoxide which had been evolved, and had been completely reconverted into the liquid. These observations are of considerable interest and importance in their bearing on the question as to whether the action of light is exothermic or endothermic. If the light reaction is not endothermic, then we must assume the action of carbon monoxide on the solid carbonyl, and the change backwards into the liquid carbonyl is attended by an absorption of heat. Further experiments must be made to settle the question.

When solid iron carbonyl is heated alone, as stated above, no change takes place below 100° C., at this temperature a solid and a *green* liquid are formed. But if the solid be heated with liquids such as ether, petroleum-ether, or toluene, change begins at about 50° C., the solid decomposes and the liquid acquires an intense green colour. The intensity of the green colour is so great that the solutions are almost opaque, even in thin layers ; in more dilute solutions the absorption spectrum showed a distinct band in the yellow These green solutions, on exposure to light, again deposit yellow crystals of the solid carbonyl, and become colourless.

In order to determine what kind of light was most effective in inducing this decomposition, small tubes containing a 10-per-cent. solution of iron pentacarbonyl in ether were exposed in different parts of a solar spectrum and also to sunlight under different coloured screens. It was found that most rapid decomposition occurred in the blue, then green, closely followed by yellow, and lastly red : exposure under red glass produces roughly about one-tenth the amount of solid produced under blue glass in the same time.

Exposure of the liquid in quartz tubes to the electric arc causes slow decomposition only, and the acetylene flame is still less active.

Colouring the ether solution with dyes was also tried ; cyanine and chlorophyll allow rapid decomposition, azobenzene retards the decomposition slightly, isatin and alizarine somewhat more.

It has already been stated above that the decomposition occurs readily in solution in petroleum ether and ether ; the same is true of alcohol ; in pure benzene the decomposition appears to be slower, but if the benzene contain traces of thiophene a black solid is deposited. Solutions of iron carbonyl in pyridine become dark red in colour when exposed to light, gas is evolved, but no solid is deposited except from strong solutions of about 50 per cent. by

volume. This is to be accounted for by the solubility of the solid in pyridine. Carbon bisulphide and nitrobenzene, which do not react with iron carbonyl in the dark, when exposed to light, react with the formation of solid precipitates.

The most striking result observed was with solutions of iron carbonyl in nickel carbonyl. These solutions are of a much paler yellow colour than solutions of equal concentration in other solvents. Thus for example a 10-per-cent. solution of iron carbonyl in ether has just the same intensity of colour as a 30-per-cent. solution in nickel carbonyl. A 10-per-cent. solution deposits no solid after exposure to bright sunlight for several weeks, a 25-per-cent. solution (by volume) deposits no solid from the liquid, but solid is deposited in the vapour space above the liquid; a 50-per-cent. solution deposits some solid both in the liquid and in the vapour space.

That no decomposition occurs in dilute solutions of iron carbonyl in nickel carbonyl is shown by the facts that no gas is evolved from these solutions, and that solid iron carbonyl is only sparingly soluble in nickel carbonyl. The absence of any change is not to be accounted for by the absorption of the active light by the nickel carbonyl, since the iron carbonyl has been shown above to be sensitive to light in the visible part of the spectrum which is not absorbed by nickel carbonyl. This fact was further confirmed by exposing a small tube full of iron carbonyl immersed in liquid nickel carbonyl to light, when decomposition was found to take place rapidly.

The following may be suggested as a simple hypothesis to account for the unique behaviour of nickel carbonyl as a solvent of iron carbonyl:—

The initial action of light on iron carbonyl might be represented by the equation

$$\mathrm{Fe\,(CO)_5 = Fe\,(CO)_4 + CO,}$$
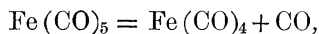
the hypothetical iron tetracarbonyl produced may be assumed to combine at once with a molecule of iron pentacarbonyl to produce the solid nona-carbonyl, thus:—

$$\mathrm{Fe\,(CO)_4 + Fe\,(CO)_5 = Fe_2\,(CO)_9.}$$

If this molecular mechanism of the light reaction be admitted, then there is no reason why iron pentacarbonyl may not form an analogous body of feeble stability by combining directly with nickel tetracarbonyl, thus:—

$$\mathrm{Fe\,(CO)_5 + Ni\,(CO)_4 = FeNi\,(CO)_9.}$$

A compound of this kind, though unstable in itself (since the vapour above the solutions contains iron carbonyl and the concentrated solutions deposit some solid), may yet be unacted upon by light. The existence of this compound is rendered probable by the fact that solutions of iron carbonyl in

nickel carbonyl have such a pale colour compared to solutions of the same concentration in other solvents.

The observations on the action of light on iron carbonyl under different pressures of carbon monoxide, at different temperatures and in solution in various solvents, will be continued as soon as the necessary sunlight is available.

The Electrical Conductivity of Dilute Solutions of Sulphuric Acid.

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§ 1.—*Introduction and Summary of Results.*

If the measure of the electrical conductivity of a solution be divided by that of the concentration expressed in gramme-equivalents per unit volume, we obtain a quantity which may be called the equivalent conductivity of the solution. If the conductivity of the solvent used be subtracted from that of the solution, the corresponding quantity may be taken as giving the equivalent conductivity of the solute.

As is well known, the equivalent conductivity of neutral salts when dissolved in water approaches a limiting value as the dilution is increased, and, in terms of the ionisation theory, this limiting value corresponds with complete ionisation.

With solutions of acids and alkalies, however, the phenomena are different. As dilution proceeds, the equivalent conductivity reaches a maximum at a concentration of about a one-thousandth or a two-thousandth of a gramme-equivalent per litre, and then falls rapidly as the dilution is pushed farther.

It has been supposed that this diminution of equivalent conductivity at extreme dilutions is due to interaction between the solute and the impurities which remain even in redistilled water.

Kohlrausch[*] has given evidence to show that the chief impurity in water carefully redistilled is carbonic acid, and Goodwin and Haskell[†] have corrected the observed values of the equivalent conductivity of nitric and

[*] 'Wissensch. Abhandl. d. phys.-tech. Reichsanstalt,' vol. 3, p. 193 (1900).
[†] 'Physical Review,' vol. 19, p. 369 (1904).