330. *The Disappearance of Carbon Monoxide in the Presence of Electrically Heated Nickel Filaments.*

By George Bryce.

Preliminary experiments showed that, when a nickel filament in a bulb cooled in liquid air was heated in low pressures of carbon monoxide to above 1200° Abs., the gas disappeared rapidly and completely. When the bulb was at room temperature the clean-up was slow, and it was practically zero when the bulb was at or above 100°. The pressure remained low so long as the liquid-air level on the bulb was maintained, and even when it receded considerably; but complete removal restored most of the initial gas pressure. Hence it seemed that the product was volatile or could migrate on glass without decomposition, if the temperature were not too high. This view was supported by experiments in which a short filament was heated in the upper part of a bulb, the bottom of which was cooled in liquid air. Afterwards there was nickel on the cooled part, but practically none directly opposite the filament, as ascertained by pipetting nitric acid into the cooled part of the bulb, and analysing this solution and also one obtained from the whole bulb interior.

Previous work on the clean-up of residual gas in vacuum tubes containing electrically heated filaments had shown that it may be due to either electrical or thermal effects. Campbell and Ryde (*Phil. Mag.*, 1920, **40**, 585, *et seq.*) proved that the electrical effects were almost absent if the potential across the filament was less than a critical value, and that in most cases only the thermal action occurred if the potential was less than 20 volts. Langmuir (*Chem. Reviews*, 1933, **13**, 147, where earlier references are given) studied chiefly the thermal action, and gave fairly simple chemical explanations of his results. In the present experiments, electrical effects were minimised by keeping the total potential drop along the filaments at 6—8 volts. The following thermal processes by which the nickel might remove the carbon monoxide were considered. (*a*) Adsorption or absorption of the carbon monoxide by the nickel filament could remove only a very small quantity of gas. (*b*) Homogeneous interaction of evaporated nickel atoms with carbon monoxide molecules, giving products of low vapour pressure. (*c*) Attack of the nickel filament by carbon monoxide: presence of an adsorbed layer, or striking of gas molecules, changing

the rate of evaporation of the metal. (*d*) Heterogeneous reaction of carbon monoxide on the nickel, possibly without the metal evaporating, giving products which are of smaller volume or can be condensed or adsorbed elsewhere. (*e*) Adsorption of carbon monoxide by nickel condensing on the bulb.

In general, for the investigation of these problems, methods must be used which can identify all of the possible types of clean-up, not only in simple cases where only one occurs, but also where the reaction is composite. Accurate determination of the rate of evaporation of the filament in a vacuum and in gas is important, as it shows whether the gas attacks the filament. Such determinations, as well as the other measurements, were carried out in the apparatus described below.

Experimental.

Apparatus.—Two cylindrical Pyrex bulbs were used, both ground to fit the same top, which was lubricated with Apiezon grease L. The top carried a pinch with 1-mm. diameter tungsten leads, to which were spot-welded lengths of 1-mm. diameter " gas-free " nickel, and between these was spot-welded 15 cm. of 0·0104-cm. diameter 99·9% nickel, so that it was held axially in the bulb. The bulbs were thoroughly cleaned and baked. The filament was out-gassed and annealed in one bulb at 1250° Abs. for several hours, at over 1400° Abs. for about 10 minutes, then quickly transferred to the second bulb, and after a further short flashing was as free as possible from gas. Gas pressures were read on a Pirani gauge calibrated against McLeod gauges (Campbell, *Proc. Physical Soc.*, 1921, **33**, 287). The gases were admitted to the reaction system from a calibrated pipette. The volumes of the different parts of the apparatus were found by expanding a known volume of nitrogen at known pressure into them. Pressure changes, when the temperature was varied, were determined for each bulb at a series of pressures and temperatures.

The carbon monoxide was prepared from nickel carbonyl (kindly given by the Mond Nickel Co.), which had been distilled several times in a vacuum from 15° to − 190° before use; it was purified by passage over potassium hydroxide and phosphoric oxide and then through a liquid-air trap.

The Mechanism of Carbon Monoxide Removal.—Deposition of nickel on the bulb was always associated with the disappearance of carbon monoxide, which in itself suggests that the gas combines with the deposited metal. Evidence in favour of this view of the nature of the reaction is first given by excluding the other possible reactions already mentioned. Later it is shown directly that freshly evaporated nickel can take up carbon monoxide.

The clean-up first became appreciable with the filament just above 1200° Abs., and was too fast for measurement above 1450° Abs. Short tests in bulbs of 2·55 and 5·25 cm. diameter and at different pressures showed that the rate was independent of bulb diameter and of gas pressure between 0·1 and 10^{-4} mm. Hg. The reaction was followed up to 1 mm. Hg pressure and, although here, in order to obtain an appreciable pressure change, the filament had to be thinned so rapidly that it was difficult to obtain accurate data, yet the rate appeared to continue to be independent of pressure.

According to Smoluchowski's formula, the number of collisions made by a carbon monoxide molecule in traversing a linear distance d is $3\pi d^2/4\lambda^2$, where λ, the mean free path, is equal to 9·92 cm. at 25° and $7{\cdot}5 \times 10^{-4}$ mm. Hg pressure (Dushman, " High Vacuum "). If this is assumed to apply approximately to the passage of nickel atoms through carbon monoxide, it can be calculated that the above variation of conditions varies the number of collisions made between filament and bulb between the limits 7×10^{-4} and 3000. Since the rate was independent of gas pressure over this wide range, the mechanism of homogeneous reaction between nickel atoms and carbon monoxide molecules must be rejected.

A series of experiments was carried out in which a run in carbon monoxide with the bulb in liquid air was interposed between two similar ones in a vacuum. Initially, the resistance of the filament, which was in a Wheatstone bridge, was set to the desired value, and several readings of the middle temperature were taken by a disappearing-filament pyrometer with magnifying objective, thus giving directly to about 5° the brightness temperature for $\lambda = 0{\cdot}665\,\mu$ (Forsythe, *Trans. Faraday Soc.*, 1919, **15**, 21). These were corrected to the Kelvin scale by using a graph from Forsythe's results as given in International Critical Tables, 1929. The resistance of the filament was kept the same throughout all three experiments. These tests were carried out at temperatures between 1300° and 1450° Abs., and showed that within the experimental error the rate of evaporation of nickel in carbon monoxide was the same as in a

vacuum. In order to avoid possible loss of nickel by volatilisation of the product, air was admitted to the reaction bulb after an experiment before the liquid air was withdrawn. After this it was rinsed with concentrated nitric acid, and the nickel determined as described in the following paper. Actually, the filament thinned only 10—15% more rapidly in carbon monoxide at 0·03—0·01 mm. Hg than it did in a vacuum. The effect was thus just within the limits of detection, and is probably to be attributed to factors such as the difference in temperature distribution along the filament when heated (1) in a vacuum and (2) in a low pressure of carbon monoxide. It is interesting to compare this behaviour of annealed filaments with low pressures of carbon monoxide and that shown in the Mond nickel process. Intermittent activation of the powdered nickel mattes is necessary in the latter process, and accounts for the ease with which the tetracarbonyl volatilises from them; and in addition, very much higher pressures of carbon monoxide are used.

The foregoing results, together with the fact that the rate of clean-up is independent of the pressure, show that the reaction is not a surface attack of the wire by the gas.

With the bulb in liquid air, either of the following reactions, if they occurred at the surface of the filament, would give products of low vapour pressure: (1) $2CO \longrightarrow C + CO_2$, (2) $CO + Ni \longrightarrow NiO + C$. The disappearance did not, in fact, depend on these * for the following reasons: (*a*) the carbon monoxide could be recovered quantitatively by heating the bulb at over 150° (blank experiments without evaporating nickel showing that heating to this temperature had no appreciable effect in freeing gas from the glass itself); (*b*) the gas freed by heating in this way did not condense on recooling, and reaction (2) was excluded further by the fact that (*c*) there was no clean-up with the bulb at 100°.

The Composition and Properties of the Product.—The initial pressure at room temperature was read on the McLeod gauge, the gas cleaned up under various conditions, and the nickel in the deposit analysed colorimetrically. The results are given in Table I.

TABLE I.

Temp. (Abs.) in middle of filament.	Diameter of bulb, cm.	Initial quantity of CO, g.-mol. $\times 10^{-6}$.	Quantity of nickel obtained, g. $\times 10^{-5}$.	Ratio, $\frac{\text{CO (mols.) cleaned up}}{\text{Ni (atoms) deposited}}$.
1352°	2·55	1·66	5·0	1·96
1338	2·55	2·16	7·36	1·73
1312	2·55	2·16	5·17	2·46
1387	5·25	3·88	12·5	2·22
1297	2·55	2·16	5·0	2·56
1360	5·25	2·53	6·0	2·49
1380	2·55	2·37	6·25	2·23

The mean value for the ratio CO/Ni is 2·24. No systematic change in this ratio was found under the various conditions, suggesting that its value is not due to chance averaging, but that two carbon monoxide molecules combine with each nickel atom, or at any rate that the product is a subcarbonyl. A further indication that such is the case is the following. After cleaning up some carbon monoxide, the filament was cooled, and a similar dose admitted. None of this gas disappeared even after long intervals whilst the bulb was at — 190°, but if the liquid air was withdrawn for about a minute, and replaced, some had gone. Further slight temporary heating removed a little more, but a limit was reached when about half of the second dose had disappeared. Since secondary removal by the films formed from the primary clean-up did not occur appreciably at — 190°, it must require a low activation energy, and presumably depends on the addition of carbon monoxide to the already partly saturated carbonyl. The specific nature of the forces involved was shown by the fact that nitrogen (Frankenburger, Mayrhofer, and Schwamberger, *Z. Elektrochem.*, 1931, **37**, 473) was not cleaned up under similar conditions. Moreover, carbon dioxide was not affected by the hot metal filament.

Since preliminary observations had indicated that the product formed at — 190° was unstable at 100°, further experiments were carried out on the clean-up at a series of bulb temperatures, and also on the recovery of gas initially cleaned up with the bulb at — 190°. With the bulb in a slurry of solid carbon dioxide in acetone, the rate of removal was measurable with the filament at 1250—1500° Abs., and was independent of pressure between 0·07 and

* This finding is interesting in relation to earlier controversies (Sabatier and Senderens, *Bull. Soc. chim.*, 1903, **29**, 249; Charpy, *Compt. rend.*, 1903, **137**, 120) as to whether nickel at high temperatures decomposed carbon monoxide, but the earlier work related to higher pressures where there was a zone of heated gas at the interface.

10^{-4} mm. Hg. The gas could be cleaned up to very low pressures and kept so, either with the whole bulb at — 80°, or if the cooling mixture evaporated half-way down. The gas disappeared 4 or 5 times faster with the bulb at — 190° than at — 80°, and at the latter temperature the ratio CO/Ni lay between 0·4 and 1 instead of 2 to 1 at — 190°. More rapid sintering of the nickel deposit, or impurities from the glass competing with the carbon monoxide, would account for both these results. With the bulb at room temperature, only about 10^{-1} mol. of carbon monoxide was removed per nickel atom deposited.

All of the carbon monoxide originally cleaned up with the bulb at — 190° was released by heating the bulb to above 150° for a short time, and, after such treatment, no appreciable readsorption took place on cooling again. Some gas was freed by heating to — 80° for a considerable time. After an hour at room temperature 70% was liberated. These results give some indication as to the stability of the compound formed. No more than 5—10% was readsorbed when the bulb was reimmersed in liquid air, this being due to sintering of the condensate and to contamination from impurities in the glass, as shown in the next section.

Adsorption of Carbon Monoxide on Nickel Evaporated in a Vacuum.—Direct experiments were made to find whether a condensate of vacuum-sublimed nickel retained the power, which the above results suggest that it has at the instant of its formation, of adsorbing carbon monoxide. The bulb was immersed in liquid air, and nickel evaporated from a well-aged filament in a vacuum of 10^{-5} mm. Hg or less. Neither radiation nor the stream of nickel could have heated the condensing surface much above — 190°. Immediately the filament cooled, a known quantity of carbon monoxide was admitted, and the resultant pressure was read on the Pirani gauge, from which the amount of sorption was determined. The quantity of nickel condensed was then found by analysis. Even under the best vacuum conditions and with the glass at liquid-air temperature, the metal first condensed was probably partly contaminated by gas from the glass. Sufficient nickel was therefore quickly vaporised to make it highly probable that the outer layers were gas-free, and the adsorption measured as soon as possible. The results are shown in Table II.

TABLE II.

Time to evaporate Ni, mins.	No. of layers of nickel on glass (1 layer = 10^{15} atoms per cm.^{2} geometrical area).	Residual pressure of CO after adsorption, mm. × 10^{-3}.	Pressure decrease due to adsorption, mm. × 10^{-3}.	No. of layers of CO taken up (1 layer = 10^{15} molecules per cm.^{2} of geometrical area).
60	0·3	28·5	1·6	0·16
60	0·9	21·4	3·8	0·38
10	47	6·0	20·4	2·1
5	12	5·0	7·4	0·75
5	17	16·4	11·5	1·2

Adsorption was rapid at — 190°, and thus did not require much energy of activation. It might be expected from the work of Roberts (*Proc. Roy. Soc.*, **1935**, **152**, 445) on hydrogen that fresh metal condensates formed in a vacuum would subsequently be able to adsorb certain other gases provided that the condensates were clean.

This experiment differed from the others in which the nickel was vaporised in presence of gas. In the present case the metal had formed a loose structure before the gas was admitted, and only the outer layers could then adsorb. Nevertheless, the specific surface of the nickel condensate was probably high (Gen, Zelmanov, and Shalnikov, *Physikal. Z. Sovietunion*, **1933**, 825), and this would account for the fact that in one experiment, if the geometrical surface was used as a basis of calculation, two layers of carbon monoxide were adsorbed.

Behaviour of Tungsten and Molybdenum in Carbon Monoxide.—Tungsten and molybdenum at the same temperatures as the nickel (1200—1500° Abs.) (or even up to 1800° Abs.) did not

TABLE III.

Temp. (Abs.) in middle of filament.	Diam. of bulb, cm.	Temp. of bulb.	Rate of clean-up of CO, g.-mol./cm.^{2} of Mo/sec. × 10^{10}.	Rate of evapn. of Mo, g.-atom/cm.^{2}/sec. × 10^{10} (from results of Jones, Langmuir, and Mackay, *loc. cit.*).
2046°	2·55	15°	2·7	1·3
2128	2·55	15	4·9	4·5
2240	5·25	15	59·0	23·0
1900	2·55	—190	8·5	—

cause any clean-up of carbon monoxide over long periods with the bulb at — 190° or at room temperature. It was only when molybdenum began to evaporate appreciably at temperatures above 1900° Abs. that clean-up took place, and the actual rates shown in Table III indicate a close correlation between the rate of evaporation of molybdenum atoms, and the removal of carbon monoxide molecules. This suggests that the mechanism of clean-up may be similar to that with nickel, and affords further confirmation of the view that with the latter metal it is not merely a thermal decomposition at the surface.

SUMMARY.

Processes by which nickel filaments might clean up carbon monoxide were considered, and new methods developed to identify and examine them. Carbon monoxide was cleaned up by nickel at temperatures above 1200° Abs., two molecules of gas disappearing per metal atom evaporated. The properties of the product (volatility, decomposition, and reaction with carbon monoxide) were studied, and it was shown to be stable at — 190°, but to decompose completely at 100°. The gas was adsorbed on the nickel as this condensed on the bulb. A similar mechanism is indicated for the clean-up of carbon monoxide by molybdenum above 1900° Abs. Neither nitrogen nor carbon dioxide was affected by hot nickel under similar conditions.

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