CCLXVI.—*Adsorption of Nitrogen by Condensed Atomic Platinum.*

By S. H. Bastow.

When metallic wires undergo vaporisation by heating to high temperatures, the phenomenon termed "clean up" is frequently noted, in that a steady diminution of the pressure of any residual gas occurs. The cases of tungsten and molybdenum in the presence of nitrogen have been investigated by Langmuir (*Z. anorg. Chem.*, 1914, **85**, 265; *J. Amer. Chem. Soc.*, 1918, **41**, 1139), and that of iron by Frankenburger (*Z. physikal. Chem.*, 1928, **139**, 386; *Z. Elektrochem.*, 1929, **35**, 9, 591). In the case of tungsten, a nitride, WN_2, is formed in the gas phase; this condenses to a brown solid, decomposing thermally only at very high temperatures and reacting with water to give ammonia. With molybdenum two "nitrides" are apparently formed in the gas phase. On condensation, one, present in larger quantity, is found to be stable up to 360°, but the other liberates its nitrogen at room temperatures; the molybdenum left on the glass undergoes a sintering process, and as a result the liberated nitrogen is not readsorbed on cooling.

Frankenburger noted no "clean up" of nitrogen by iron, but hydrogen readily disappeared. Under optimum conditions, one atom of iron condensing on the liquid-air-cooled glass surface removes one molecule of hydrogen. When the "hydride" is warmed to − 80° or to 0°, liberation of most of the hydrogen takes place and the iron undergoes a sintering process, so that, on re-cooling, a smaller quantity of "hydride" is re-formed or less hydrogen is occluded.

The reaction mechanism differs from that of tungsten and molybdenum in that the process is not a gas-phase reaction but occurs on condensation of the atomic iron. No "clean up" of nitrogen was noted by Frankenburger in the case of iron, and no synthesis of ammonia occurred in nitrogen–hydrogen mixtures, and he concluded that some activation of the nitrogen was necessary for this reaction.

We can depict these processes by the formal equations

$$(1)\ \text{Fe (atom adsorbed)} + H_2 \longrightarrow FeH_2$$
$$(2)\ FeH_2 \longrightarrow \text{Fe (sintered)} + H_2$$

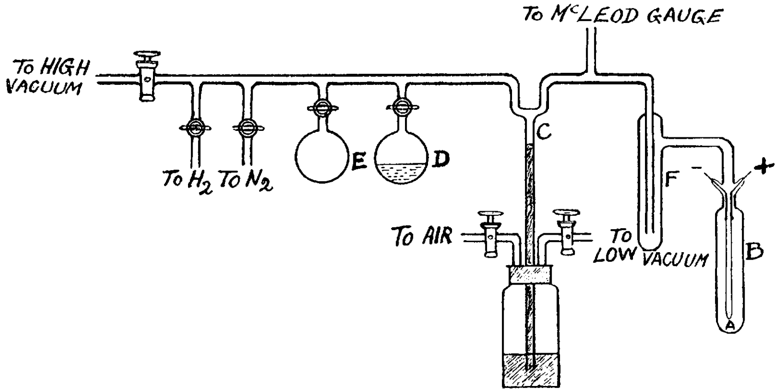
and it follows that the source of the energy change in the two reactions is the energy set free in the sintering of the iron, which evidently depends on the initial and the final state of aggregation of the iron.

In an investigation on the combustion of platinum (Wansbrough Jones and Rideal, *Proc. Roy. Soc.*, 1929, *A*, **123**, 202), it was noted that a slow clean up of nitrogen took place. It seemed of interest to examine this phenomenon in more detail because the formation of complexes of platinum with hydrogen is well known, and it seemed possible that an opportunity would be found in this case for examining how far the energy derived from the sintering of a metal could be rendered available for chemical reaction, either as energy of activation or, in addition, energy of reaction.

EXPERIMENTAL.

Apparatus, etc.—A looped platinum filament (*A*) was sealed with heavy platinum leads into a cylindrical glass bulb (*B*). The filament was connected, in series with a lampboard and a rheostat, to a constant electric supply, and could thus be raised to any desired temperature.

FIG. 1.



The bulb, into which nitrogen, hydrogen, or water vapour could be introduced from separate gas lines, could be evacuated through a high-vacuum line, consisting of a Langmuir mercury pump backed by a "Hyvac" pump. The pressure of gas in the system was measured by a sensitive McLeod gauge. The bulb and the gauge could be isolated from the rest of the apparatus by a mercury cut-off (*C*), and together they served as the reaction chamber. It was necessary to place a liquid-air trap (*F*) between the bulb and the rest of the system to prevent condensation of mercury and tap grease on the filament. Small depositions of hydrocarbon on the filament, which were sometimes unavoidable, made the filament glow unevenly. A small quantity of oxygen, admitted while the filament was hot, burnt off the hydrocarbons. By expanding nitrogen at a known pressure into the system from the bulb (E), of accurately-known volume, the volume of the system isolated by the cut-off could be determined. A Dewar vessel full of liquid air was placed round the trap F; from the fall in pressure, the correction due to cooling by the liquid-air trap was measured, and similarly for the bulb B.

The nitrogen, prepared from sodium nitrite and ammonium chloride, bubbled through sulphuric acid and passed successively over red-hot palladised copper, calcium chloride, and phosphoric anhydride, and was finally stored in a bulb over the last reagent. Hydrogen, prepared by electrolysis of baryta, was purified and stored in the same way.

The water vapour was obtained from a small bulb (D), partly filled with conductivity water.

The resistance of the hot filament, which was balanced against that of a coil of known resistance immersed in an oil-bath, was measured by a Wheatstone's bridge, operated by the heating current. A correction was made for the resistance and cooling effect of the leads, by using Langmuir's figures (*Physical Rev.*, 1930). The temperature of the filament is given by the equation

$$R_t = R_0\,(1 - 0{\cdot}00398t - 0{\cdot}00000058t^2)$$

where R_t = resistance of filament at $t°$,
R_0 = ,, ,, ,, ,, $0°$.

A check on these temperature measurements was made with an optical pyrometer, which was calibrated for reading the temperature of a glowing filament by observing the known melting points of various substances on a similar filament. From Langmuir's figures for the vapour pressure of platinum (*Physical Rev.*, 1914, **11**, 377), the amount of platinum evaporated during each experiment could be calculated.

Procedure.—The bulb B was evacuated and baked out for 3 hours at 300°, for 20 mins. at 400°, and then kept at 300°. When emission of gas had ceased, the filament was heated to about 1500° till it was completely out-gassed. The liquid-air trap was also baked out and then immersed in liquid air.

The bulb was cooled to room temperature, a small amount of nitrogen admitted, and its pressure measured. The bulb was then immersed in a Dewar flask full of liquid air, and the pressure again measured. The filament was heated to a suitable temperature, and the fall in pressure of nitrogen recorded. The liquid air in the Dewar flask was kept at a constant level by adding fresh liquid air every 5 mins. during a run. Thus the amount of nitrogen adsorbed could be calculated, and its relation to the amount of platinum evaporated determined. The initial diameter of the platinum filament was in all cases 0·075 mm., and its thinning during an experiment was generally less than 5%. The rate of thinning, and thus the increase of resistance with constant current, was calculated for each temperature. By decreasing the current appropriately, the temperature of the filament was kept approximately constant.

The results obtained are shown in Table I. It will be noticed that the ratio of platinum evaporated to nitrogen adsorbed is variable. This may have been due to one or both of two factors affecting the experimental error.

TABLE I.

Abs. temp. of filament (approx.).	*Press. decrease, mm. × 10^{-3}.	No. of mols. of N_2 adsorbed, × 10^{-16}.	No. of atoms of Pt evaporated, × 10^{-16}.	$\frac{N_2 \text{ adsorbed}}{\text{Pt evaporated}}$
1600°	5·6	8·393	4·83	1·736
1660	2·65	3·97	2·91	1·37
1660	1·45	2·175	1·83	1·19
1610	1·83	2·745	1·88	1·46
1610	0·50	0·75	0·603	1·25
1610	2·35	3·525	3·89	0·905
1690	1·80	2·73	4·63	0·59
1690	5·63	8·44	7·83	1·078
1720	8·8	13·2	6·56	2·01
†1650	1·80	2·77	4·10	0·676
†1630	1·24	1·87	3·56	0·53
†1680	2·24	3·37	6·37	0·53

* Several bulbs were employed during the course of the experiments.

† In these experiments the nitrogen was admitted after the film had been laid down in a vacuum.

(1) It was never possible to start an experiment with a clean glass surface, for a thick layer of platinum (probably some 50 molecules thick) was deposited during the out-gassing of the filament.

(2) The measurement of temperature was not precise. As the filament thinned considerably and unevenly during out-gassing and during an experiment, resistance–temperature curves could not be trustworthy, and checking with the optical pyrometer was unsatisfactory as it could not be read accurately to within 10—15°. Such a variation would mean a possible error of ± 50% in the calculated amount of platinum evaporated. Nevertheless, the ratio of the nitrogen to platinum deposited is extraordinarily high and approximates to the value obtained by Frankenburger for iron and hydrogen.

If the nitrogen in the system is completely cleaned up by the platinum, and the bulb is kept in liquid air, no measurable desorption of nitrogen takes place; but if the Dewar vessel containing the liquid air is removed from the bulb for only 30 secs., which allows of only very slight warming of the film through the glass, an appreciable quantity of nitrogen is liberated which is not re-adsorbed on cooling. If, on removal of the liquid air, the bulb is immersed in a water-bath and allowed to attain room temperature, all the nitrogen is given off, and less than 50% is readsorbed on cooling. More prolonged warming decreases the amount readsorbed, and if the bulb is baked out for 10 mins. at 200°, none of the nitrogen is readsorbed.

There are, apparently, two distinct stages in the sintering of a film. On allowing the film to warm to a definite sintering temperature, above that at which it is condensed but still well below 0°, a certain definite amount of the nitrogen adsorbed is liberated irreversibly. This corresponds to a collapse of the presumably spongy structure of the film.

On warming the bulb to room temperature for, say, a minute, and then re-immersing it in liquid air, only about two-thirds of the nitrogen is readsorbed, and practically the same net amount of nitrogen is readsorbed if the above process be repeated. Prolonged warming, however, sinters the film slowly, and after about one hour's sintering only about one-fifth of the nitrogen is readsorbed on immersion in liquid air. The following figures were obtained for the fall in pressure in terms of 10^{-3} mm. of mercury :

N_2 adsorbed in forming the film.	N_2 readsorbed after sintering at room temp. (15°) for 1 min.	10 mins.	60 mins.
4·48	1·28	1·20	0·82
6·4	5·0	3·4	2·9 (16 mins.)
7·60	4·4	2·8	2·0
7·07	5·5	3·9	1·9
3·56	1·83	0·40	0·10

Similar experiments on films deposited successively on the same surface indicated that, although the first very rapid collapse still occurred, yet the second stage was slower. The following two series of three experiments were made successively on the same glass surface, the bulb being baked out between each experiment; the units are as before.

N_2 adsorbed.	Period of sintering. 1 min.	10 mins.	60 mins.
6·13	2·43	2·0	1·3
6·50	3·13	2·60	2·05
4·83	2·65	2·20	1·90
6·50	2·70	2·52	2·03
7·10	3·46	3·02	2·62
6·86	3·68	3·36	3·00

Experiments with unimolecular films of platinum were not successful, owing to the fact that considerable amounts of platinum were deposited during the out-gassing of the filament. A small movable glass shield was used to screen half the glass surface, but the heating effect of this screen during an experiment, and the slowness with which it cooled in the low gas pressures used, made the reading unsatisfactory. There were, however, indications that unimolecular platinum films sintered in much the same way as the thicker films.

Effect of Adsorption on Chemical Behaviour.—The following experiments were made to test the effect of the active surface on the chemical behaviour of the adsorbed nitrogen.

1. *Action of water on adsorbed nitrogen.* A large amount of nitrogen was adsorbed as before, and while the bulb was immersed in liquid air, a relatively large amount of water vapour was admitted to the reaction chamber, and condensed and frozen on to the film surface. The bulb was then sealed off from the rest of the apparatus and opened while still immersed in liquid air. The sides of the bulb were washed with conductivity water squirted in by a pipette, and after about ½ hour the water was removed and tested for traces of ammonia. Fresh Nessler solution was used, and the colour produced was measured by a sensitive colorimeter. This was checked against the colour given by standard solutions of ammonium chloride of approximately the same concentration. In all cases but one, ammonia was detected in measurable quantity: the following table shows the amount formed, together with that which would have been formed if all the adsorbed nitrogen had been reduced. The ratio between these two quantities (last col.) may be termed the " efficiency factor."

Expt.	NH_3, g. × 10^6.			Expt.	NH_3, g. × 10^6.		
No.	Found.	Calc.	Ratio.	No.	Found.	Calc.	Ratio.
1	2·59	4·42	0·59	5	14·6	17·65	0·83
2	Nil	3·44	—	6	10·5	19·3	0·54
3	9·0	16·3	0·55	7	9·3	13·6	0·68
4	5·88	17·4	0·34				

In Expt. 2, the glass tubing was sucked in while being sealed off under a vacuum; a blast of hot air would thus be admitted to the film, which probably sintered.

The most probable chemical reactions involved in the synthesis of ammonia from nitrogen and water in the presence of sintering platinum are

$$(1)\ N_2 + 6H_2O \longrightarrow 2NH_3 + 3H_2O_2$$
$$(2)\ N_2 + 6H_2O + 3Pt \longrightarrow 2NH_3 + 3Pt(OH)_2$$

It is possible that part of the oxygen is liberated in a reactive form because, when the ammoniacal solution was tested with a solution of potassium iodide and starch, a faint blue coloration was frequently observed, indicating the presence of an oxidising agent. It was not possible to estimate this, for the colour was very faint, but it was regarded as indicating that hydrogen peroxide or a higher oxide of platinum had been formed during the reaction.

In Expts. No. 5 and 7 the bulbs were already coated inside with a thick platinum film. In fact, bulbs that had been used in previous experiments were washed, baked out, and used again. The average of the efficiency ratio in these cases is higher than in the other cases, in which only platinum condensed on the bulb during outgassing was present before the run was started.

(2) *Action of hydrogen on adsorbed nitrogen.* Experiments on the adsorption of hydrogen by the platinum film could not be rendered quantitative. On admission of a known quantity of hydrogen, there was an instantaneous adsorption of a small fraction of the gas. If the bulb was immersed in liquid air as soon as the filament glowed, there was a sudden large adsorption of gas, many times greater than in the case of nitrogen in any one experiment. A slower, but still large, adsorption followed.

When the temperature of the filament was raised to a white heat, and the bulb baked out, the hydrogen could be desorbed. This would point to the filament adsorbing most of the hydrogen itself. Baking out of the bulb while the filaments were kept cold, however, resulted in the desorption of a large quantity of hydrogen, pointing to the definite combination of the volatilised and condensed platinum with hydrogen. There was thus a possibility that, if nitrogen and hydrogen were adsorbed by the cold platinum, ammonia would be formed.

Purified hydrogen was, therefore, admitted to the film, on which a large amount of nitrogen was adsorbed. As before, ammonia was estimated by Nessler solution, comparison being effected with solutions from blank experiments carried out with no nitrogen present at all (these gave values of 2×10^{-7} g.). The results are expressed as before in the accompanying table.

	NH_3, g. × 10^5.		
Expt. No.	Found.	Calc.	Ratio.
1	1·0	1·86	0·54
2	0·86	2·3	0·37
3	0·45	1·13	0·40

On introduction of nitrogen and water vapour into the bulb, at liquid-air temperature, with the platinum film completely sintered, no trace of ammonia was obtained; nor were similar experiments with hydrogen and nitrogen successful in producing ammonia.

To test whether the nitrogen adsorbed by the spongy structure of the film was more active than that adsorbed by the more solid parts of the film, the following experiments were carried out.

Nitrogen was adsorbed in the usual way, and the bulb was warmed to room temperature for 1 min. and then re-immersed in liquid air. Only a small fraction of the nitrogen was readsorbed. On adding water and testing for ammonia, only about 20% of the available re-adsorbed nitrogen had reacted to give ammonia. Results of two experiments are given below :

N_2 originally adsorbed, g. × 10^5.	N_2 readsorbed after collapse of spongy structure, g. × 10^5.	NH_3, found, g. × 10^6.	NH_3, calc. from N_2 readsorbed, g. × 10^6.	Ratio.
1·65	1·03	4·6	12·5	0·37
1·73	0·93	3·3	11·3	0·29

Discussion.

The experiments described indicate that platinum atoms adsorbed on a cooled surface in an unsintered or partially sintered state, possess the power of occluding or combining with both nitrogen and hydrogen at low temperatures. On elevation of the temperature, sintering takes place, resulting in the liberation of the gases. The reaction in the case of nitrogen may thus be formulated

$$(1)\ \text{Pt (atom adsorbed)} + N_2 \longrightarrow PtN_2,$$
$$(2)\ PtN_2 \longrightarrow \text{Pt (sintered)} + N_2,$$

and is in every way analogous to the case of iron and hydrogen. Even partially sintered platinum may retain nitrogen and liberate and readsorb it reversibly.

Whilst these two reactions are coupled, the energy set free is dependent on the initial and the final state of division of the platinum. It is clear that even isolated platinum atoms adsorbed on a glass surface are not completely unsaturated, and that the sintered material is not in a macro-crystalline state.

The heat evolved in (1) and (2) will thus be variable, and it is difficult to decide, in calorimetric experiments on heats of adsorption, how far the second reaction does not occur with reactive metals. It is certain that the critical energy increment for the second reaction when the original platinum is highly disperse is small, for gas liberation and sintering will occur at temperatures well below 0°, and it is possible that the heat evolution would be by no means inconsiderable. No information has been obtained as to how far the assemblage of platinum atoms may proceed to the crystalline state and still retain the power of taking up nitrogen in the stoicheiometric ratio. In the presence of hydrogen, ammonia is formed. If Frankenburger's experiments with iron may be taken as analogous, the hydrogen must also be adsorbed. Since the process is exothermic, the reaction

$$(3)\ PtN_2 \text{ (adsorbed)} + PtH_2 \text{ (adsorbed)} + 2H_2 \longrightarrow Pt \text{ (sintered)} + 2NH_3$$

might be imagined to proceed with a critical energy increment identical with that necessary for decomposition according to reaction (2), one much less than for the direct catalytic formation of ammonia.

The experiments with water vapour indicate, however, that endothermic reactions can take place, for the reaction

$$N_2 + 6H_2O + 3Pt \longrightarrow 2NH_3 + 3Pt(OH)_2$$

requires some 92·6 kg.-cals. per g.-mol. of nitrogen, a direct confirmation that the free-energy change on sintering in reaction (2) in no way differs from the free energy of an ordinary chemical reaction.

The finely divided platinum is thus not acting in a catalytic manner, but as a source of energy resulting from the process of sintering. Under suitable conditions this energy may supply the critical energy increment for a catalytic reaction, or the critical energy increment and the necessary energy for an endothermic reaction.

Although the efficiency factors for the ratio of nitrogen adsorbed to ammonia formed cannot be regarded as strictly reproducible, yet the factor is some 60% with the most active unsintered deposits, and only some 30% with those partially sintered, thus supporting the contention that the energy changes involved in reactions (1) and (2) are dependent on the initial and the final state of aggregation of the platinum, and that the chemical reactions necessary for the formation of ammonia require a definite minimum amount of energy, which may or may not be attained in the elementary reaction, *viz.*, the partial sintering of platinum.

Summary.

It is shown that platinum, when condensed in a thin film on a very cold glass surface, adsorbs nitrogen strongly. A roughly quantitative relation is established.

The structure of the film and the effect of heat upon it are examined.

The adsorbed nitrogen is shown to react with hydrogen or water to form ammonia.

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