

The diffusion column of one substance may, by the bombardment of its molecules, accelerate, retard or even reverse the diffusion of another substance.

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[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE PHOTOELECTRIC PROPERTIES OF AMMONIA CATALYSTS

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RECEIVED OCTOBER 14, 1930

PUBLISHED JANUARY 12, 1931

An extended series of experiments carried out at this Laboratory has shown that reduced Fe_3O_4 is an excellent catalyst for the synthesis of ammonia¹ and that the activity is materially influenced by the presence of small amounts of impurities or promoters. A general investigation of the physical properties of these catalysts has been undertaken to determine, if possible, the function of the promoter, as well as add to our knowledge of surface catalysts.

An investigation of the thermionic properties *in vacuo* of a large number of possible catalysts carried out by Dr. C. H. Kunsman² has resulted in the discovery that these substances, for the most part, are excellent emitters of positive ions. A comparison of the positive ion emissivities and the catalytic properties³ showed that no direct relationship existed between different catalysts, although for a given catalyst it is possible that some such correlation does exist.

The present paper deals with the photoelectric properties of several of these catalysts both *in vacuo* and in the presence of nitrogen, hydrogen and traces of oxygen.

The catalysts chosen for this research were described by Almquist and Crittenden⁴ and are those which have received the greatest amount of study. The composition and activities of these catalysts are given in Table I.

TABLE I
DATA ON CATALYSTS

No.	Total Fe, %	Al_2O_3	K_2O	% NH_3 at 450°	
				30 Atm.	100 Atm.
918	72.86	3.30	5.49
920	72.58	..	0.20	1.57	3.43
921	71.99	1.31	..	5.35	9.35
922	71.99	1.05	0.26	5.80	13.85

The composition percentages are for the unreduced material.

¹ Larson and Brooks, *Ind. Eng. Chem.*, **18**, 1305 (1926).

² Kunsman, *J. Franklin Inst.*, **204**, 635 (1927).

³ Kunsman, *THIS JOURNAL*, **51**, 688 (1929).

⁴ Almquist and Crittenden, *Ind. Eng. Chem.*, **18**, 1307 (1926).

Apparatus and Method

A schematic drawing of the apparatus is shown in Fig. 1, and is essentially the same as that previously described by the writer.⁵

The catalysts to be tested were coated on platinum filaments in a manner described by Kunsman.⁶ Heating above visibility, which might result in sintering or premature fatiguing, was avoided in all except the first coated layer. The filaments were reduced in hydrogen at a temperature between 400 and 450°.

The temperature was measured by means of a platinum-platinum-rhodium thermocouple twisted tightly about the filament.

Commercial hydrogen and nitrogen were used after all traces of oxygen had been removed by glowing tungsten; moisture was removed by liquid air.

A hot mercury arc and a Hilger monochromatic illuminator were used as the source of ultraviolet light. The photoelectric current was measured with a Compton electrometer and high resistance shunt⁷ which enabled emission currents to be read from 10^{-15} to 10^{-10} amp.

The photoelectric threshold was determined by plotting the emission current per unit light intensity against the wave length. The intersection of the curve with the wave length axis is taken as the long wave length limit.

All measurements, unless otherwise specified, were made in the best obtainable vacuum, the pressure at all times being below the sticking point of mercury in the McLeod gage (10^{-6} mm.).

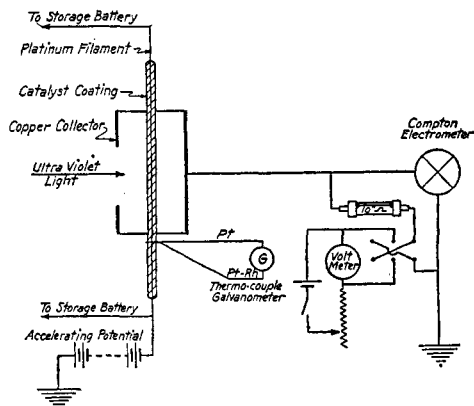


Fig. 1.

Results

Catalyst 918.—In the study of the coated filament used in these researches the question arose as to the effect of the method of coating on the threshold. A comparison was made, therefore, of a pure iron ribbon and a platinum filament coated with catalyst 918. The results in both cases were substantially the same, showing that the coating process had little or no effect.

⁵ Brewer, *Phys. Rev.*, **35**, 1360 (1930).

⁶ Kunsman, *J. Phys. Chem.*, **30**, 525 (1926).

⁷ Brewer, *Rev. Sci. Inst.*, **1**, 325 (1930).

The photoelectric threshold for pure but not outgassed iron is given by Hamer⁸ as $2870 \pm 40 \text{ \AA}$. Cardwell⁹ gives the threshold for outgassed iron to be very near 2580 \AA .

Lines 1 and 2 of Fig. 2 show the results obtained in the present experiments with pure iron. In the figure the wave length in \AA . units is plotted against the deflection per unit light intensity expressed in purely arbitrary units, which are different for the various lines. Line 1 was taken with a non-outgassed filament at room temperature and shows a threshold very near 2860 \AA ., which is in agreement with the value given by Hamer for similar conditions.

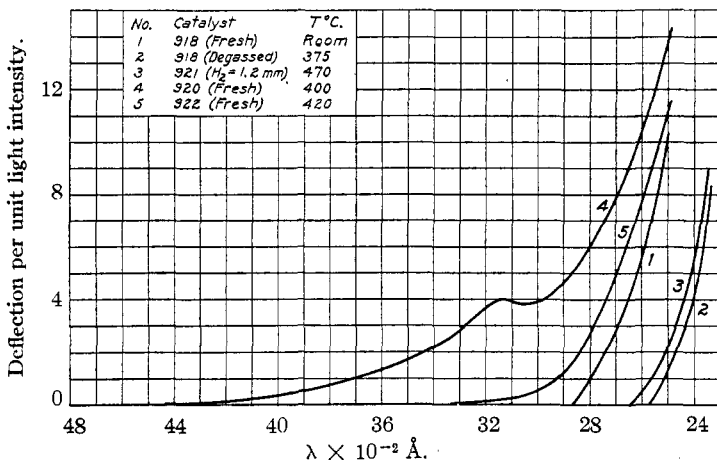


Fig. 2.

The threshold of a fresh filament appeared very sensitive to temperature. Above 200° the threshold started to shift toward shorter wave lengths. After heating at 650° for about twenty-four hours, the threshold shifted to a position as shown by line 2, in which condition it showed a very slight temperature coefficient for temperatures below 700° . The threshold as given by line 2 lies very close to 2575 \AA ., which is in good agreement with the value given by Cardwell for outgassed iron.

Catalyst 921.—The small quantity of alumina present in 921 had very little or no effect on the threshold as compared to that of pure iron (918). The threshold for the fresh filament was very close to that given by line 1 of Fig. 2, while the degassed filament showed a barely detectable emission for $\lambda 2653 \text{ \AA}$.; the threshold, therefore, lies between these two values. The curve itself agreed very well with line 2 of Fig. 2.

Nitrogen and hydrogen had little effect on the photoelectric emissivity,

⁸ Hamer, *J. Opt. Soc.*, 9, 251 (1924).

⁹ Cardwell, *Proc. Nat. Acad. Sci.*, 14, 439 (1928).

tending to increase the intensity. This effect was most pronounced in the neighborhood of 1 mm. pressure. Line 3 of Fig. 2 is for 921 in hydrogen at 1.2 mm. pressure. It will be noted that the threshold is shifted about 85 \AA . to the red over that for vacuum conditions. The effect of nitrogen is very similar to that of hydrogen; oxygen in traces produced no noticeable result.

Catalyst 920.—The positive ion emissivity from the potassium promoted catalyst has been observed by Kunsman² to be large but unstable. This may also be said to be true for the photoelectric emissivity.

The effect of temperature on the photoelectric emissivity was measured for ascending and descending temperatures as well as for the steady state and was found to be quite different from that observed for 918 and 921.

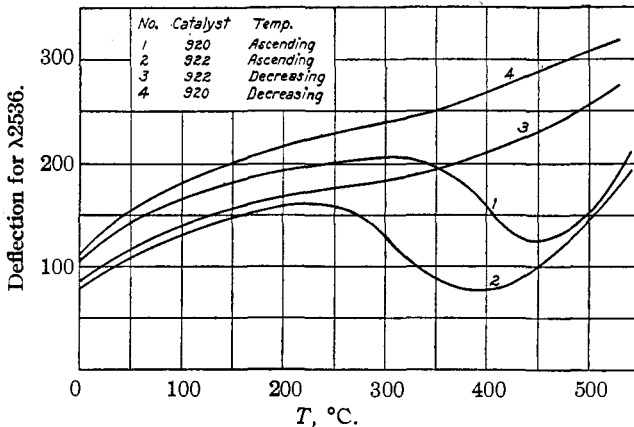


Fig. 3.

Curve 1 of Fig. 3 for a freshly reduced filament was taken with a rising temperature in which deflection readings were made as quickly as possible after each rise in temperature. It will be seen that the emissivity increased to a maximum in the neighborhood of 300° , followed by a minimum at 450° , and thereafter increased rapidly with temperature. At temperatures just below 600° the photoelectric emissivity became complicated by the thermionic emission of electrons. The approximate photoelectric emissivity up to 700° was measured by placing such a potential on the high resistance shunt that the thermionic current was just balanced out and then measuring the photoelectric current. The results showed little if any increase above 600° .

Line 4 of Fig. 3 is for descending temperatures, but otherwise was taken under the same condition as line 1. It will be noted that the pronounced minimum at about 450° is only faintly noticeable.

All experiments on the determination of thresholds were made under steady state conditions, the deflection following line 4 quite closely. At temperatures above 500° these conditions were reached fairly rapidly.

The threshold at room temperature was in the neighborhood of 3200 Å., as only a detectable emission was obtainable with λ 3130 Å. As may be expected from Curve 1, Fig. 3, the threshold shifts toward longer wave lengths with rising temperature. Line 4 of Fig. 2 shows the emission per unit intensity at 400° for various wave lengths; emissivity was just detectable at λ 4350 Å. and did not occur at λ 4900 Å.

It will be noted that the characteristics of line 4 are quite different from those of lines 1, 2 and 3. A small maximum is seen at 3100 Å., and the foot of the curve, rather than being sharp as is characteristic for pure substances, skirts the wave length axis for a long distance, as is characteristic of composite surfaces.⁵

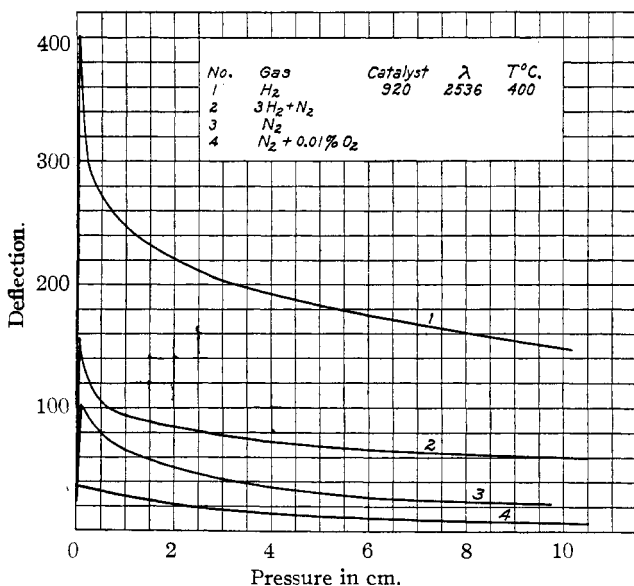


Fig. 4.

The effect of gases on the emissivity is shown in Fig. 4. These runs were taken for λ 2536 Å. at 400°, and with an accelerating potential of 45 volts.

The emission in hydrogen, nitrogen and the 3-1 mixture of the two gases reached a maximum at about 0.5 mm. pressure. The current intensity was some four times greater in hydrogen than in nitrogen and the 3-1 mixture gave values but slightly higher than did pure nitrogen. Nitrogen containing only a trace of oxygen (estimated at about 0.01%) dropped the emissivity to a point very close to that for pure iron.

Catalyst 922.—The threshold for the cold reduced catalyst is very close to that given by line 1 of Fig. 2 for 918; the K₂O and Al₂O₃, generally considered to be in the form K₂Al₂O₄, have but little influence.

The effect of temperature on the emissivity is shown by lines 2 and 3 of Fig. 3, for ascending and descending temperatures, respectively. Line 2 shows a pronounced minimum at 400° which corresponds quite closely to that observed for 920; this minimum is almost completely absent for the descending temperatures.

The threshold of a freshly reduced filament at 420° as given by line 5 of Fig. 2 lies between $\lambda 3130 \text{ \AA.}$ and $\lambda 3342 \text{ \AA.}$ The shape of the curve lies intermediate between that for a pure surface (line 1) and that for a highly composite surface (line 4), indicating the presence of a small amount of material at the surface with a threshold above that of iron.

In the course of a week's use, in which the filament was repeatedly heated to 500° in nitrogen and in hydrogen and to 700° in a vacuum, the threshold gradually fell to a final value very close to that shown by line 3 for Catalyst 921. This comparatively rapid fatiguing is contrary to what might be expected from the results of Kunsman² on the thermionic emission of positive ions, which showed that 922 while not giving as large an initial positive ion emission as 920 is a far more constant source.

Fresh and photoelectrically fatigued filaments were compared, therefore, for positive ion emissivity with the result that the temperature at which an emission became detectable did not increase more than 10° throughout the fatiguing process, although the threshold shifted some 800 \AA.

In the presence of gases the photoelectric emissivity of a fresh filament was similar to that shown in Fig. 4 for 920 with the exception that the curves for nitrogen and for hydrogen very nearly coincided. Traces of oxygen had the same pronounced poisoning effect.

In this connection an attempt was made to show the effect of gases on the positive ion emissivity. The problem is complicated because positive ions of the type observed by Kunsman² as well as those observed by the writer¹⁰ are both emitted at about the same temperatures. The experiments showed that the temperature at which emission was detected was lowered from 50 to 100° by the presence of a millimeter of gas. Further increases in the gas pressure did not lower the temperature but did increase the current for large accelerating voltages since saturation does not exist in gases, the current becoming proportional to the applied voltage at atmospheric pressure.

Discussion of Results

The thermionic emission in gases from various surfaces is doubtless intimately related to their catalytic properties.¹⁰ This, however, cannot be said for photoelectric emission only in so far as the photoelectric threshold is a measure of the surface forces. Photoelectric emission is generally considered to be confined to the removal of electrons from the emitting

¹⁰ Brewer, *J. Phys. Chem.*, **32**, 1006 (1928).

surface;⁶ no satisfactory evidence exists for the emission of either positive or negative ions by this means. Thus these experiments cannot be interpreted to give a direct picture of the mechanism of reaction. Photoelectric emissivity is, however, a sensitive test for the composite nature of surfaces and so may serve to help define a catalytic material.

In the case of Catalyst 918, we see that the long wave length limit agrees exactly with that of pure iron. From this the conclusion can be drawn that the surface forces, image and intrinsic,¹⁰ of the reduced Fe_3O_4 are identical to those of pure electrolytic iron.

The sharp feet of lines 1 and 2 are indicative of the fact that surface is uniform and not composite. Had the emitting material and hence the long wave length limit varied from point to point over the surface, the above lines would have turned off asymptotic to the wave length axis.

The increase in work function, as is shown by the shift in threshold from 2860 Å. to 2580 Å. during the outgassing process is characteristic of photoelectric emission and is probably due to the removal of a layer of highly polarized gas molecules from the surface.

The close similarity between the values obtained for 918 and for 921 indicates that there is no free aluminum on the surface of the Al_2O_3 promoted catalyst, and also that Al_2O_3 (possibly FeAl_2O_4), if it exists at the surface at all, is present in very small quantities.

Catalysts 920 and 922 offer a marked contrast to 918 and 921 in two respects: they possess pronounced temperature coefficients (Fig. 3); and the threshold curves, rather than having the usual sharp feet, skirt the wave length axis for a long distance (Curves 4 and 5, Fig. 2).

The increase in emissivity with rising temperature places these catalysts in the same general class with oxide coated filament such as barium or strontium oxide on platinum. While this peculiar temperature effect has been observed on oxide filaments by many investigators, its cause is still a matter of conjecture. Case¹¹ feels that in heating the oxide the pure metal is to some extent set free, thus increasing the threshold since the long wave length limit is much higher for the pure metals than for the oxides. Becker¹² has obtained excellent evidence to support his contention that the activity of oxide coated filaments is due to metallic barium on the surface of the barium oxide. Crew,¹³ on the other hand, feels that during the heating process a thin film of the base metal of the filament becomes built up over the surface and that the work function of this film decreases with temperature. The characteristics of the threshold curves in Fig. 2 should throw much light on this question.

The distinctive shape of Curves 4 and 5 in Fig. 2 for the long wave

¹¹ Case, *Phys. Rev.*, **17**, 398 (1921).

¹² Becker, *ibid.*, **34**, 1323 (1929).

¹³ Crew, *ibid.*, **28**, 1265 (1926).

length limit shows unquestionably that the photo electrons are emitted from a composite surface similar in nature to that described where potassium was electrolyzed into platinum.⁵ The long wave length limit for iron is very close to 2575 Å., while that for pure potassium is 5600 Å. in layers of one or more molecules deep. The thresholds for K_2O and $K_2Al_2O_4$ are unknown, but they must be at least as low, probably lower, than for pure iron, since the presence of oxygen, even in traces, drops the long wave length limit to that given by line 2, Fig. 2, for pure iron.

The threshold for 920 at 400° is about 4450 Å., while for 922 under the same conditions it is about 3330 Å. Not only are both of these values far below that for pure potassium, but the current intensity was comparatively low for $\lambda 3130$, which line is near the maximum wave length sensitivity for potassium.

The conclusion to be drawn from the above consideration is, therefore, that the composite emitting surface in both cases is one of potassium and iron, and that the quantity of free potassium on the surface is small, far less than a monomolecular layer. It will be noted that the ratio of free potassium to iron in 922 is small compared to 920, in spite of the fact that the total potassium contents have the ratio of 26 to 20.

These observations substantiate the contentions of Case and of Vecker that the activity of the oxide is due to a small amount of the metal which has become reduced.

The increase in photoelectric emissivity with rising temperature can only come from an increase in the amount of free potassium on the surface. In Fig. 3 Curves 1 and 2 show an increased emissivity with temperature to about 350° followed by a minimum near 450° with an increase thereafter up to about 700°. The minimum is only faintly evident for descending temperatures or for constant temperatures. The most probable explanation of these results is that the increase up to 350° is due to an increased dissociation of K_2O , yielding free potassium, just as was pointed out by Becker for oxide coated emitters. Above 350° evaporation from the surface decreases the free potassium content and results in the minimum at 450°. Above this temperature the diffusion of potassium through the iron to the surface again caused the emissivity to rise. Since the rates of migration and evaporation, as well as the dissociation of K_2O decrease with temperature, Curve 3 of Fig. 3 should not show a pronounced minimum for decreasing temperature.

An idea as to the possible source of the free potassium can be had from the character of the emission curves. Catalyst 920 contains only iron and K_2O , hence the potassium must come from the dissociated oxide. Catalyst 922 is made by reducing a mixture of Fe_3O_4 , Al_2O_3 and K_2O , during which process all the K_2O is supposed to combine with the Al_2O_3 to form $K_2Al_2O_4$. The potassium must come, therefore, either from the

dissociation of the $K_2Al_2O_4$ or from some K_2O which is left uncombined in the iron. Since the long wave length limit shows that the ratio of elemental potassium to the total potassium content is greatly reduced by the presence of the alumina, either the quantity of uncombined K_2O is small or else the $K_2Al_2O_4$ dissociates at such high temperatures that evaporation prevents the accumulation of any appreciable quantity of potassium in the iron. The fact that 922 fatigues rapidly favors the idea that much of the elemental potassium comes from free K_2O within the iron; the similarity of Curves 1 and 2 to 3 and 4 of Fig. 3 points to a common source. This contention is also substantiated by the fact that although the catalyst readily fatigues to the point where the amount of free potassium is negligible, as shown by the photoelectric emissivity, the positive ion emission occurring at higher temperatures is not greatly reduced.

In Table I it was pointed out that K_2O in itself is a catalytic poison and that only when combined with Al_2O_3 is it an effective promoter. The photoelectric data, however, show that both 920 and 922 possess the same types of heterogeneous surfaces, and that the work functions are quite similar. This apparent conflict is doubtless due to the fact that the photoelectric properties of 922 are determined by the uncombined K_2O while the ability of $K_2Al_2O_4$ to promote catalysis may offset the poisoning action of the remaining small amount of free K_2O .

The mechanism involved in the poisoning action of K_2O is uncertain and is receiving further investigation. It seems probable, however, that it is due to the dissociation of K_2O which takes place at the operating temperature (450°) and that the free potassium and not the oxide is the actual poison.

The writer is especially indebted to Dr. C. H. Kunsman for his criticisms and the constructive interest he has taken in this research; also to Mr. Joseph Reuter, instrument maker, and to Mr. Leonardo Testa, glass-blower.

Summary

A study of the photoelectric properties of several types of catalysts used in the synthesis of ammonia has yielded the following results.

The unpromoted iron catalyst made from reduced magnetite has the same photoelectric threshold as electrolytic iron; both show no temperature coefficient over the range investigated. The aluminum oxide promoted iron catalysts also have the photoelectric properties of pure iron. From this it follows that the surface forces for pure iron and reduced magnetite are identical, that no free aluminum collects on the surface of the promoted catalyst, and that the concentration of any aluminum oxide on the surface must be small.

The photoelectric properties of iron catalysts containing K_2O and

$K_2Al_2O_4$ are very different from those of pure iron. The emissivity increases markedly with temperature as is the case for oxide coated filaments, indicating dissociation of the potassium oxide at elevated temperatures. The long wave length limit lies intermediate between that of iron and that of potassium, showing the surface to be sparsely covered with elemental potassium. The long wave length limits show clearly that the ratio of elemental potassium to the total potassium content is greatly reduced by the presence of aluminum oxide.

The photoelectric properties of the $K_2Al_2O_4$ promoted catalyst appear to come from the K_2O which has failed to combine with the Al_2O_3 . It is suggested that the poisoning action of K_2O alone is due to the ease with which it dissociates, and that it is the free potassium which is the actual poison.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE SOLUBILITY OF HYDROGEN FLUORIDE IN BENZENE AND IN OCTANE

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RECEIVED OCTOBER 17, 1930

PUBLISHED JANUARY 12, 1931

The study of the solubility of gaseous hydrogen fluoride in organic solvents was begun in an attempt to obtain more information about the polymer H_2F_6 whose existence has been indicated by Simons and Hildebrand from considerations of the density of the gas.¹ While the results have not aided greatly in this connection, an example of an unusual type of solution has been found in the case of hydrogen fluoride dissolved in benzene.

Apparatus.—The apparatus, the design of which is shown in Fig. 1, was made entirely of copper with all permanent joints sealed together with silver solder. The three vessels of which the apparatus consisted were held together with screw connections. Two of the vessels were held in separate constant temperature baths; the one served as container for the liquid hydrogen fluoride and the other for the solution. The third vessel, which fastened on the bottom outlet of the solution container, was the constant volume sample tube. Copper is a suitable material for this apparatus, for hydrogen fluoride in the absence of an oxidizing agent, such as oxygen from the air, is without action on it, and oxygen was rigorously excluded.

Materials Used.—The anhydrous hydrogen fluoride was made in the manner described by Simons² and distilled directly into the apparatus, which had been carefully cleaned, dried and filled with dry nitrogen. The

¹ Simons and Hildebrand, *THIS JOURNAL*, **46**, 2183 (1924).

² Simons, *ibid.*, **46**, 2179 (1924).