

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

THE EFFECT OF ADSORBED GASES ON THE PHOTOELECTRIC EMISSIVITY OF IRON AND PLATINUM

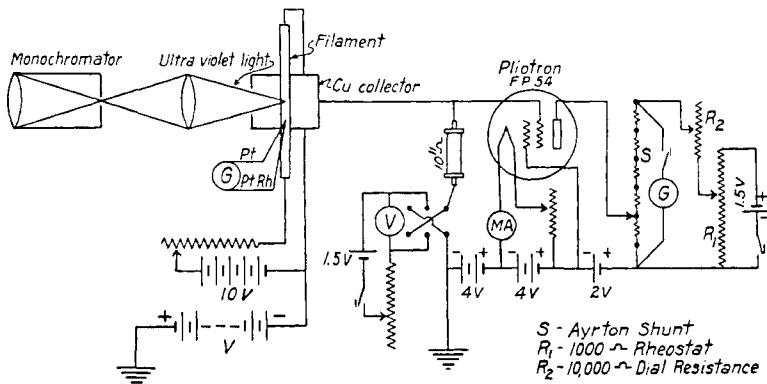
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The present research was undertaken to determine, as far as possible, the physical state of gases adsorbed on metallic surfaces, with the hope in view that this knowledge will contribute to our understanding of surface catalysis. The metals chosen for investigation were iron and platinum, while the gases used were nitrogen, hydrogen, ammonia, helium and oxygen. Thus the study comprises both excellent and poor catalysts for the synthesis of ammonia, as well as reactive and poisonous gases.

Apparatus.—The apparatus, illustrated in Fig. 1, is essentially the same as that described in previous papers,^{1,2} except that a Pliotron FP 54 four element vacuum tube was used in place of the Compton electrometer. The current sensitivity was 4.35×10^{-16} amp. per cm. galvanometer deflection; it was possible to read currents accurately from 5×10^{-16} to 10^{-11} amp. The sensitivity can be increased considerably beyond this point but it was not necessary in this research.



Method of Procedure.—It was found necessary to take special precautions for the removal of oxygen and water vapor from the gases. The nitrogen, hydrogen and helium were passed slowly through a tube filled with freshly reduced copper heated to 500°, dried with liquid air, and then stored in a balloon flask containing a tungsten filament. The gases were kept in contact with the incandescent tungsten for a day. The balloon flask was connected to the main system by a stopcock followed by a mercury seal to prevent grease contamination during operation. The gases were again passed through liquid air before entering the photoelectric tube. The ammonia was taken from a tank of liquid ammonia that had stood in contact with metallic potassium for years.

¹ A. Keith Brewer, *Phys. Rev.*, **38**, 401 (1931).

² A. Keith Brewer, *THIS JOURNAL*, **53**, 74 (1931).

The entire system was thoroughly flamed out before starting a series of runs. The filament was then heated to redness in about 2 cm. of hydrogen for an hour, after which the system was again flamed out and the filament heated *in vacuo* until it showed the normal long wave length limit, *i. e.*, a just detectable emission with $\lambda 2536$ for iron and a small emission with $\lambda 2653$ for platinum. An iron surface is readily purified but platinum requires considerable heating at 800° to give anything like a constant threshold, due to the difficulties of removing absorbed hydrogen.

Results with Iron

The factors given special attention in making this study were the effect of the gases on the intensity of emission as well as on the shift in the photoelectric threshold, the character of the wave length *vs.* current curves, and the effect of temperature on the sensitivity.

The data were taken with an accelerating potential of 9 volts plus the contact potential difference between the filament and collector; stopping potential measurements showed the latter to be near +1 volt. This potential was below the ionization potential of any of the gases studied so the possibility of ionization by collision did not exist.

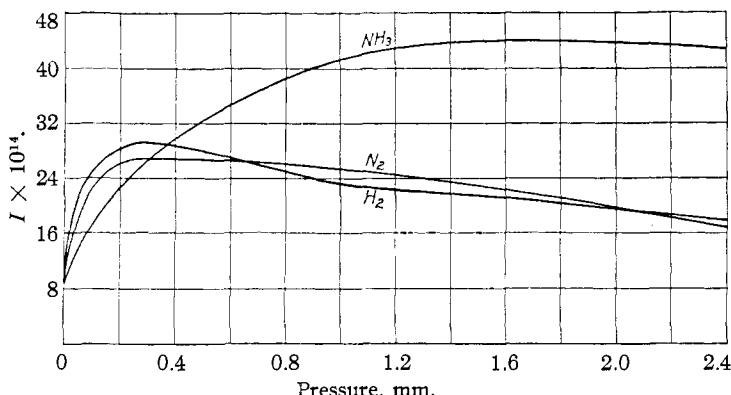


Fig. 2.—The effect of gases on the photoelectric emissivity of iron: V , 9; λ , 2300; temp., 215°C .

| Gas | V | λ | Temp. |
|--------|-----|-----------|-------------------------|
| NH_3 | 9 | 2300 | 215°C . |
| H_2 | 9 | 2300 | 215°C . |
| N_2 | 9 | 2300 | 215°C . |

The effects of various pressures of hydrogen, nitrogen and ammonia on the emissivity of iron are shown in Fig. 2. The measurements were all extended to 10 cm. pressure; the photoelectric current decreased only slightly with increasing pressure above 2.0 mm.

The emissivity curves for nitrogen and hydrogen are very nearly identical over the entire pressure range; the ammonia curve is distinctive in that the current enhancement for low pressures is less than that for nitrogen or hydrogen, while for high pressures it is materially greater. Oxygen

behaves quite differently in that when present in the most minute traces it materially lowers the emissivity. For instance, nitrogen, when passed slowly through a freshly reduced copper deoxidizer at 500° and thereafter held in contact with glowing tungsten for about fifteen minutes, still contained enough oxygen to give an emissivity definitely lower than nitrogen which had been held in contact with incandescent tungsten for ten hours. The amount of oxygen on the surface necessary to give a lowering of the threshold was too small to be estimated with any degree of precision.

Voltage *vs.* current measurements showed saturation to exist at pressures below the maximum points on the pressure *vs.* current curves; at higher pressures the current increased gradually with the voltage until ionization by collision set in, whereupon rapid increases were observed. At 10 cm. the current increase was but slightly less than linear with respect to voltage. At pressures below 0.4 mm. saturation was obtained for 2.0 volts accelerating potential.

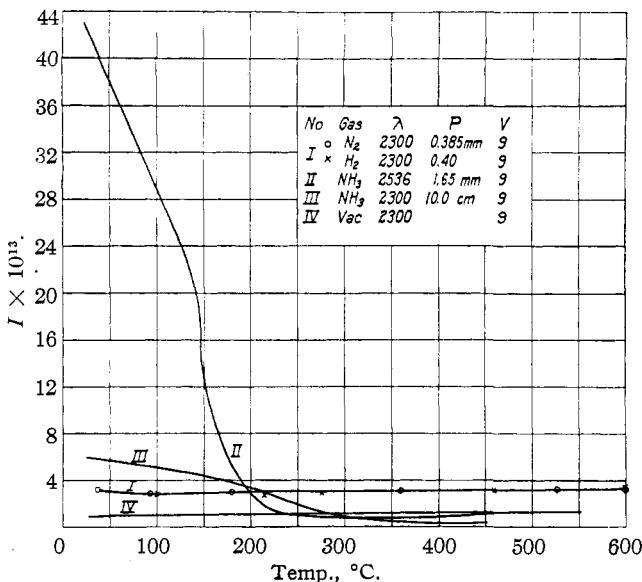


Fig. 3.—The effect of temperature on the photoelectric emissivity of iron in gases.

The effect of temperature on the emissivity is illustrated in Fig. 3. Line I shows nitrogen and hydrogen to be almost identical in their behavior, the points for nitrogen being just slightly the higher. Line IV is typical of the results obtained when the pressure becomes too low to read on the McLeod gage, without making any attempt to degas the iron; the curve for degassed iron is similar but somewhat lower. The temperature coefficient for ammonia differs from that for nitrogen and hydrogen, since it ab-

normally increases the emissivity at temperatures below 200°. The curves are all completely reversible when the products of decomposition of ammonia were not allowed to accumulate.

The effect of gases on the long wave length limit is suggested by the character of the lines in Fig. 4. The curves are distinctly different from those obtained in the absence of a gas in that the metal does not have a sharp long wave length limit. Thus the lines in Fig. 4 skirt the wave length axis to no definite limit and do not end sharply at some specific wave length.

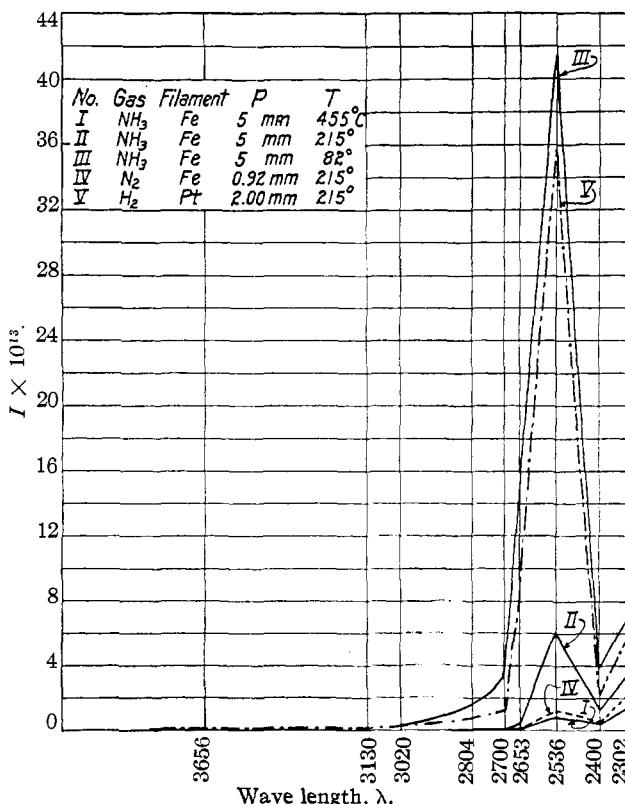


Fig. 4.—Characteristic wave length *vs.* emissivity curves.

Pure iron in a vacuum showed a just detectable emission for $\lambda 2536^{1,2}$ with a threshold near 2575 Å. In the presence of hydrogen the emissivity became negligible below $\lambda 2750$ and for nitrogen below $\lambda 2802$. Ammonia, however, gave a definite emissivity for $\lambda 3650$, the threshold lying near the limit of the visible, about 4000 Å. Expressed in equivalent volts the approximate thresholds are: vacuum 4.8 volts, hydrogen 4.5 volts, nitrogen, 4.4 volts and ammonia 3.1 volts. These values are for pressures just

above the maximum point in the curves shown in Fig. 2 and for room temperature.

The long wave length limit in oxygen when present even in small amounts was too low to be measured. One millimeter of nitrogen containing near 0.01% oxygen dropped the threshold to near 2300 Å.; *i. e.*, it raised the work function from 4.8 volts to more than 5.4 volts. Under these conditions there was just about enough oxygen present in the entire system to cover the filament with a monomolecular layer. Since the lowering of the threshold took place immediately upon the introduction of the oxygen and since the system was so designed that the probability of the average oxygen molecule striking the filament surface was very small, the amount of the surface covered by oxygen must have been only a very small fraction of a monomolecular layer. Continued heating in gas of this composition lowered the threshold to a point where an emissivity could no longer be detected.

Results with Platinum

The effect of gas pressure on the emissivity was investigated between 10 cm. and the best vacuum that could be obtained. Characteristic results are plotted in Fig. 5. The emissivity curves given are for $\lambda 2300$ Å. and for $\lambda 2700$ Å.; the temperature of the filament was 215° . The same gas was used throughout each series of runs except for ammonia, where the system was evacuated and refilled between each pressure measurement to prevent the accumulation of any products of decomposition.

The data were all taken starting with high pressures and temperatures working toward the low, though after the filament had once been heated to the maximum temperature used, all points were reproducible when approached from either side.

The curves show that the emissivity increases rapidly with the advent of gas to a maximum in the neighborhood of a few tenths of a millimeter pressure, after which it decreases slowly with pressure over the entire range investigated; the change between 1 and 10 cm. is very slight. The location and sharpness of the maximum depend both on the gas and on the wave length of the light. To illustrate, hydrogen always shows a sharp maximum for wave lengths considerably removed from the threshold, the sharpness gradually disappearing toward longer wave lengths. This is shown in the hydrogen curves for $\lambda 2300$ and $\lambda 2700$.

The emissivity in hydrogen, as is shown by Fig. 5, is large compared to that in nitrogen, ammonia, helium and oxygen. This enhanced emissivity is accompanied by a shift in the long wave length limit toward the red, as is illustrated by magnitude of the currents obtained with $\lambda 2700$ in the various gases. The threshold for oxygen lies near 2225 Å., for helium is near 2650 Å. and for nitrogen and ammonia it is near 2750 Å.

Hydrogen, on the other hand, gives the characteristic curve of a highly composite surface, as will be seen by line V in Fig. 4. Under most advantageous conditions an emission could just be detected with $\lambda 4078$, although $\lambda 3650$ is usually near the limit. The possibility of the observed currents being due to scattered light was removed by placing suitable screens in the path of the ultraviolet light before entering the monochromator.

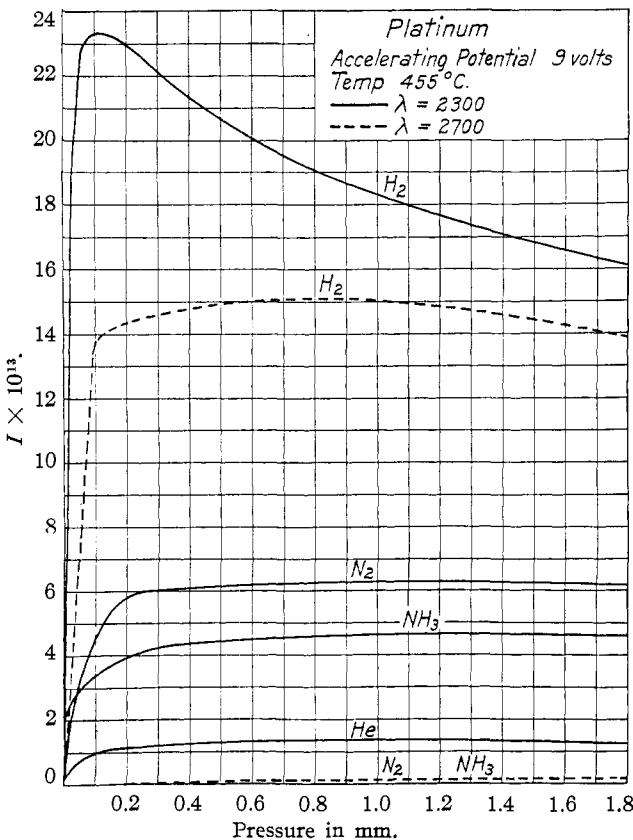


Fig. 5.—The effect of gases on the photoelectric emissivity of platinum.

The decrease in emissivity observed in oxygen is interesting in that it is not due to the normal gas molecules; the effect of oxygen on a cold filament is not materially different from that of nitrogen. As the filament is heated, the photoelectric current rapidly drops, the threshold finally shifting to below 2225 Å. This rapid shift in threshold is most pronounced when the filament has previously been heated in hydrogen for some time; under such conditions it is accompanied by the formation of water within the tube, even though the filament has been thoroughly glowed in a vacuum.

before introducing the oxygen. Apparently the first rapid shift in threshold is due to the removal of hydrogen from the platinum by the oxygen, followed subsequently by a combination between oxygen and platinum, since an appreciable emissivity cannot again be obtained without reducing in hydrogen.

The effect of temperature on the emissivity in various gases is illustrated in Fig. 6. In general, the data were taken while going from higher to lower temperatures, but the effects were all perfectly reversible. Curve 6 for the evacuated system is not for outgassed platinum but represents the condition where the pressure is too low to be read by a McLeod gage and where the filament is being lowered from 600° to room temperature.

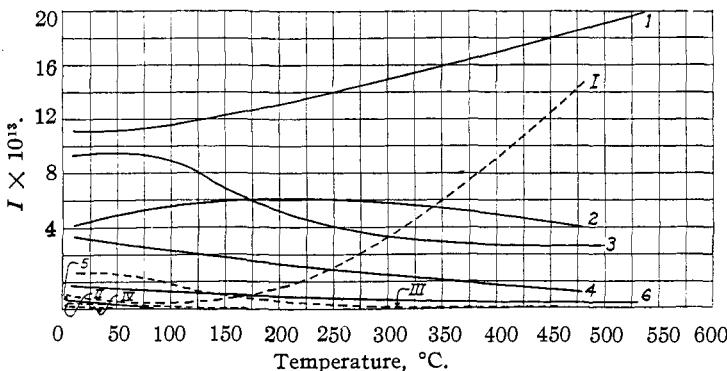


Fig. 6.—The effect of temperature on the photoelectric emission of platinum in gases.

| Curve | Gas | λ | P , mm. | Curve | Gas | λ | P , mm. |
|-------|-----------------|-----------|-----------|-------|-----------------|-----------|-----------|
| 1 | H ₂ | 2300 | 0.435 | III | NH ₃ | 2700 | 0.80 |
| I | H ₂ | 2700 | .435 | 4 | He | 2300 | .485 |
| 2 | N ₂ | 2300 | 1.7 | IV | He | 2700 | .485 |
| II | N ₂ | 2700 | 1.7 | 5 | O ₂ | 2300 | 10.00 |
| 3 | NH ₃ | 2300 | 0.80 | 6 | — | 2300 | vac. |

Curves 4 and 6 for helium and for the evacuated system show a small enhancement in emissivity with decreasing temperature, while Curve 1 for hydrogen shows a large positive temperature coefficient. Nitrogen exhibits only a small temperature effect. The ammonia curve is characteristic of this gas in that there is a pronounced increase in emissivity as the temperature drops from 200 to 100°, while above and below these points the temperature coefficient is small; the effect, however, is much less than for iron.

The emissivity in gas mixtures could be analyzed in a few instances. In the case of hydrogen on platinum the addition of nitrogen had no appreciable effect. The addition of nitrogen or hydrogen to ammonia had no effect on the enhancement of the emissivity from iron. For platinum,

on the other hand, the addition of hydrogen to ammonia raised the emissivity to a point corresponding to pure hydrogen.

Discussion of Results

No ambiguity can exist regarding the nature of the wave length *vs.* current curves, as illustrated in Fig. 4. They are distinctly the type of curves obtained only on composite surfaces;^{1,2} indeed, these curves can be exactly duplicated by those previously obtained from pure iron on which various amounts of potassium ions had been deposited. In the neighborhood of 0.5 mm. pressure the wave length characteristic for iron in hydrogen coincides with line 2, Fig. 2, of the previous communication¹ for an iron surface 0.002 covered with potassium ions. The results for nitrogen fall between Curves 2 and 3, and correspond with a surface 0.003 covered, while the maximum effect obtained with iron in ammonia corresponds to line 7 for a surface 0.02 covered with potassium ions.

In continuing the comparison between the photoelectric emission in gases and on composite surfaces it is interesting to note that for low gas pressures the sensitivity of the surface increases almost proportionally to the pressure, while Fig. 3 of the previous article shows the emission to be proportional to the concentration of potassium ions on the iron when the fraction of the surface covered is less than 0.04. The failure of the proportionality between pressure and current to extend over a wider range is doubtless due to three causes. First, saturation cannot be obtained above 0.4 mm. pressure. Second, the sensitivity is lowered by the presence of neutral gas particles, whether atoms or molecules, covering the surface. Third, the presence of space charges in the layers of gas near the surface materially lowers the emission current.

The physical status of the composite surface, capable of giving the observed effect, necessarily entails some degree of speculation. It safely may be said however, that since it affects the work function of the surface for escaping electrons, it is necessarily electrical in nature. Several possibilities may exist: a small percentage of the gas molecule striking the surface may become ionized by the surface forces; the surface may be covered with a highly polar layer of gases, in the "incipient ionization" stage as described by Sir J. J. Thomson;³ or a state of dynamic equilibrium may exist in which the gas is in all degrees of dissociation from normal molecules to complete ions, as prescribed by probability.

Little if anything of a quantitative nature is known regarding the effect of polarized or "incipiently ionized" molecules on the work function, hence it cannot be told whether such a surface state will satisfy the demands of the emissivity curves. Since the curves are identical with those obtained for surfaces sparsely covered with ions, the most probable inter-

³ J. J. Thomson, "The Electron in Chemistry," J. B. Lippincott, Co., 1923.

pretation to adopt is that a fraction of the gas molecule striking the surface is completely dissociated into ions; it is reasonable to assume that the ionized gas is present in various degrees of dissociation in dynamic equilibrium with the ionized and normal molecules. In this connection, Kobosew and Anochin⁴ compute the ionization potential of the average hydrogen molecule on platinum to be of the order of 4 volts.

The ionization of gases at metallic surfaces has long been recognized in thermionics. It was first pointed out by H. A. Wilson⁵ and has been discussed in detail by O. W. Richardson⁶ from the point of view of thermionic emission. Erikson⁷ has shown that the mobilities of the ions from alkali-free platinum in air are identical with air ions and concludes that the ions most probably come from gas molecules dissociated on the platinum.

Schmidt⁸ has calculated the conditions under which hydrogen may be dissociated into ions at metallic surfaces and has shown his deduction to be in agreement with the observed facts found in the catalytic hydrogenation of organic compounds. The writer has shown certain correlations between temperature and work function in thermionic emission in gases,⁹ and has proposed a mechanism for surface catalysis in which the problem is considered as a special case of thermionic emission in gases.¹⁰ The present results furnish another method of attacking the problem of ionization of gases at metallic surfaces wherein it is possible to estimate the degree of ionization over a definite pressure region and also to show the effect of the adsorbed ions (adions) on the work function of the surface.

The condition established by the presence of ions adsorbed on a conducting surface may easily be understood from the following considerations. Becker¹¹ has shown from thermionic studies that barium ions adsorbed on tungsten behave in a manner analogous to that which would result from a grid placed at an atomic diameter from the surface and charged positively with respect to the surface. This same analogy is even more strikingly shown in the recent photoelectric studies. The effect of the adsorbed ions is exactly that of a grid covering the surface where the grid spacings correspond to the distance between the ions; thus for conditions where the fraction of the surface covered by ions is small the *grid spacings* are large compared to the distance between the grid and the surface.

On leaving a conductor an electron must do a certain amount of work

⁴ Kobosew and Anochin, *Z. physik. Chem.*, **13**, 18 (1931).

⁵ H. A. Wilson, *Phil. Trans. Roy. Soc.*, **A197**, 415 (1901).

⁶ O. W. Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green & Co., New York.

⁷ H. A. Erikson, *Phys. Rev.*, **26**, 625 (1925).

⁸ O. Schmidt, *Z. physik. Chem.*, **118**, 195 (1925).

⁹ A. K. Brewer, *Proc. Nat. Acad. Sci.*, **13**, 592 (1927).

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

¹¹ J. A. Becker, *Trans. Am. Electrochem. Soc.*, **55**, 21 (1929).

against the image and intrinsic forces of the surface; this work may be expressed in equivalent volts, ϕ , which under ordinary conditions lies between 3 and 6 volts. In thermionics the value of ϕ is obtained directly from the Richardson equation, $I = AT^{1/2} e^{-e\phi/kT}$, while in photoelectrics it is given by the relation $\phi = h\nu_0 - \phi_0 e$, where ν_0 is the threshold frequency and $\phi = 12345/\lambda$.

The immediate effect of a positive grid near the surface is to lower ϕ_0 and hence to lower ν_0 by an amount depending on the strength of the field of the grid at the point of exodus of the electron; adsorbed negative ions will tend to raise the work function. In thermionics this point of exodus is where the work function is lowest, *i. e.*, where the grid field is the highest, hence close to the adsorbed positive ion. In photoelectrics, on the other hand, the electron leaves at whatever point the quantum strikes. If the distance between ions is large compared to an atomic diameter, the work function will vary over a wide range depending on whether the electron escapes from a point near the adion or at the maximum point removed. There is little possibility of an electron being emitted from the adion itself, since the second ionization potential of the ion requires more energy than is ordinarily available.

It is this variation in work function from point to point over the surface that is responsible for the shape of the wave length *vs.* current curves obtained for composite surfaces. ϕ_0 no longer has a definite value for the entire surface, but varies from point to point depending upon the nearness of the adsorbed ions. Thus the wave length *vs.* current curves do not have the sharp feet characteristic of pure surfaces but skirt the wave length axis for long distances.

The presence of comparatively few ions adsorbed on the surface has an extremely large effect on the work function of an emitter. When the fraction of the surface covered by K^+ ions is 0.001, the threshold is shifted from 4.8 to about 4.65 volts; a 0.01 fraction shifts ϕ to 3.9 volts, while 0.02 reduces it to 3.1 volts. The values given are derived from the point where the emission becomes detectable; the true threshold doubtless is materially lower, as will be seen from the peculiar shape of the wave length *vs.* current curves. While these values are for K^+ ions, they will not differ markedly for any singly charged ion. From the above it follows that the sphere of influence of an adsorbed ion is strong even at a distance of ten times the ionic radius. The chemical analogy of these considerations is that when the fraction of the surface covered by adsorbed ions is but 1% of the total, the critical increment for electrons is shifted by about 23,000 calories.

The marked inhibiting effect of minute traces of oxygen on the photoelectric emissivity is readily understood in the light of the above considerations. The oxygen, upon combining with the iron, is attached to the

surface in the form of negative ions. It is obviously impossible to apply a lattice structure to an iron surface so sparsely covered with oxygen; however, the linkage most probably resembles that in FeO, which has a sodium chloride structure. If the oxygen is on the surface in the form of O⁻⁻ ions, an abnormally high increase in the work function per ion density would result.

Application to Surface Catalysis.—A quantitative application of these results to surface catalysis cannot be made at this time, since neither the rate of ion formation nor the distribution of ions for mixed gases can be told with certainty. From a qualitative point of view, however, these findings are in accord with the theoretical conclusions of Schmidt,⁸ since the relative ionization of hydrogen appears to be much greater on platinum than on iron. Further, they are in general agreement with the ionic mechanism of catalysis presented by the writer some time ago.¹⁰ This mechanism, which is a direct application of thermionic emission in gases to surface catalysis, has been materially simplified and strengthened by recent studies of chemical action in the glow discharge¹² wherein it has been shown that the reactivity of positive ions is high compared to that of other active states, that the reaction is always initiated by ions of only one of the reactants, and that the number of collisions an ion must make with neutral molecules for reaction to take place is small, being from 10 to 40. Thus it will be seen that a catalyst, on the basis of this mechanism, need produce ions of only the reacting gas to initiate the reaction.

Kunsman¹³ has shown that iron is an excellent catalyst for the decomposition of ammonia while platinum is relatively poor. On the basis of the above mechanism, therefore, ammonia should be highly ionized on iron and only slightly on platinum. The results in general are in agreement with this point of view. The addition of hydrogen to ammonia had no appreciable effect on the emissivity of iron in ammonia, indicating that hydrogen does not replace ammonia at an iron surface. When hydrogen was added to ammonia on platinum, however, the emissivity rose to that for pure hydrogen; apparently it is the hydrogen which is the more dissociated on platinum. It is possible that the preferential adsorption of hydrogen by platinum is responsible for its low catalytic activity.

The glow discharge studies have shown that the synthesis of ammonia is initiated primarily by N₂⁺ ions. The relatively high ionization of nitrogen on iron, combined with the fact that nitrogen had no appreciable effect on the emissivity from platinum in the presence of hydrogen, indicates that under the conditions of ammonia synthesis iron is the better source of N₂⁺ ions and hence according to the ionic mechanism should

¹² Brewer and Westhaver, *J. Phys. Chem.*, **34**, 153, 2843 (1930); Brewer and Kueck, *ibid.*, **35**, 1281 (1931); Brewer and Miller, *THIS JOURNAL*, **53**, 2968 (1931).

¹³ C. H. Kunsman, *ibid.*, **50**, 2100 (1928); **51**, 688 (1929).

be the better catalyst. Platinum, however, should be the better catalyst for reactions initiated by positive hydrogen ions. The glow discharge studies show the synthesis of water to be initiated by H_2^+ ions. The experimental results in both cases are in apparent conformity with the theory.

The pronounced effect exerted on the work function by the presence of only a sparse distribution of adsorbed ions on the surface, combined with the large sphere of influence about these ions, is of vital importance to any mechanism of catalysis in which electrical forces are involved. In thermionic emission it is generally felt that the electrons escape at the points on the surface having the lowest work function. Since the rate of chemical action is expressed by the same mathematical equations as is the rate of thermionic emission of ions, it seems reasonable to suppose that the reaction takes place primarily at the points of lowest critical increment. The results of Kunsman on the decomposition of ammonia on various catalysts are in qualitative agreement with this contention. These considerations suggest a very simple mechanism for action of promoters and poisons. Ions on the surface that lower the work function serve as promoters while those that raise the work function behave as poisons. An illustration of this may be had from the observed effect of oxygen ions on raising the work function of iron; oxygen is a pronounced poison in the ammonia reaction.

In line with the above point of view it is interesting to note that in every case investigated the thermionic and photoelectric work functions for degassed surfaces have been shown to be identical. Warner¹⁴ has studied tungsten, DuBridge platinum¹⁵ and Cardwell¹⁶ iron, cobalt and tantalum.

Since the thermion escapes at the point of lowest work function while the photoion escapes wherever the quantum strikes, these findings are conclusive proof that the field of force for a degassed surface is uniform over the entire surface. This suggests the possibility that the phenomena generally attributed to active points on catalytic surfaces may in reality be due to the large fields of force about the ions adsorbed on the surface.

The writer is indebted to Dr. C. H. Kunsman for the interest he has taken in this research.

Summary

An investigation of the photoelectric properties of iron and platinum in the presence of various gases shows that the metals do not exhibit the characteristic properties of a pure metal as is found under good vacuum conditions but rather possess the properties of composite surfaces. In-

¹⁴ Warner, *Phys. Rev.*, **38**, 1871 (1931).

¹⁵ DuBridge, *ibid.*, **31**, 263 (1928).

¹⁶ Cardwell, *ibid.*, **38**, 2033 (1931); *Proc. Nat. Acad. Sci.*, **14**, 439 (1928).

deed, it is possible to duplicate exactly the photoelectric characteristics of these metals by curves taken *in vacuo* in which the surface of the metal is partially covered with adsorbed ions. Taking curves of known ion density as a standard, the degree of dissociation of the different gases into ions is estimated.

Threshold measurements on surfaces of known ion density show the field of influence about an ion to extend out to many times its normal radius; at ten times the ion radius the field is of appreciable magnitude. This is true for both positive and negative ions, although the effect is opposite in sign.

It is suggested that the large field of force about the adsorbed ions might account for the phenomena generally attributed to "active centers," and, further, that the large effect of adsorbed ions on the work function of the surface might be responsible for poisoning and promoter action.

The observed ionization of nitrogen, hydrogen and ammonia on iron and platinum surfaces is shown to be in accord with an ionic mechanism for surface catalysis and with the activation results obtained in the glow discharge.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

**THE HEAT CAPACITY AND ENTROPY OF THALLOUS NITRATE
FROM 17 TO 300° ABSOLUTE. THE ENTROPY AND FREE
ENERGY OF NITRATE ION**

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In a previous investigation² the entropy of nitrate ion was calculated from data on barium nitrate. A similar evaluation of the entropy of nitrate ion has now been made from data on thallous nitrate. A discrepancy of 1.6 entropy units has been found between the two results. As in the previous work in this field the entropy of the solid salt at 25° has been determined from specific heat measurements carried down to the temperatures of liquid hydrogen. The accuracy of these measurements is considerably greater than the discrepancy found in the two calculated values for the entropy of nitrate ion and attention must therefore be directed to a re-examination of the existing data which have been used in the barium nitrate evaluation.

¹ Du Pont Fellow in Chemistry, 1929-1930.

² (a) W. M. Latimer and J. E. Ahlberg, *Z. physik. Chem.*, **148**, 464 (1930). For references to details of theoretical and experimental method, see (b) Latimer and Buffington, THIS JOURNAL, **48**, 2297 (1926); (c) Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928); (d) Latimer and Kasper, *ibid.*, **51**, 2293 (1929).