phosphate or chloride solution. The size of sample weighed could be reduced to advantage by the use of a micro-balance. Great care is necessary to prevent calcium contamination. The time necessary to make one determination after the stock solution is prepared varies from two to four hours and requires considerable practice and skill in manipulation of the apparatus. This method is recommended for those cases where the amount of calcium is too small to determine by the usual chemical methods.

We wish to express our appreciation to Dr. Allison for the use of his apparatus and for the many courtesies he has extended to us throughout the work.

Summary

A quantitative method for the determination of calcium by the magneto-optic method has been outlined.

The sensitivity of the apparatus to calcium is 3.74×10^{-12} g. Ca/cc. when the minima are read for either phosphate, chloride, sulfate or nitrate. This varies slightly with the observer.

Of these minima, the phosphate is the most satisfactory to read and the chloride is second.

The presence of excess chloride, nitrate, sulfate, phosphate, magnesium, sodium, or ammonium does not affect the results.

Duplicates will check each other and values obtained with permanganate titration within 10%.

AUBURN, ALABAMA

THE EFFECT OF AMMONIA ON THE POSITIVE ION EMISSIVITY OF IRON, NICKEL AND PLATINUM

BY A. KEITH BREWER

In a recent article[1] it was shown that adsorbed gases in certain cases affect the photoelectric threshold of metal surfaces in a manner identical to that occasioned by adsorbed alkali ions. To illustrate, the emission characteristics of iron in 5 mm. of ammonia at 80° are identical to iron 0.02 covered with K^+ ions; on the other hand, ammonia has only a small effect on the emissivity of platinum.

An obvious interpretation of these results is that some of the adsorbed ammonia molecules are dissociated into ions by the electrical forces at the iron surface and that the change in work function is due to the presence of the positive ions so formed. This interpretation is not necessarily the only one, however, since it is within the range of possibility that a layer of

[1] A. Keith Brewer, THIS JOURNAL, 54, 1888 (1932).

highly polarized molecules adsorbed on the surface could produce the same effect.   It is the object of this research to distinguish, in so far as is possible, between these two mechanisms of adsorption.

Apparatus.—The apparatus was essentially the same as that described in the previous communication; a resistance leak of 1.73×10^{10} ohms, made by the S. S. White Dental Manufacturing Company, was substituted for the 10^{11} ohm resistance, since extreme sensitivity was not necessary in the present instance.

The filaments tested were pure iron, nickel and platinum in the ribbon form and a potassium aluminum oxide promoted iron catalyst coated on platinum in the usual manner.[2]   The gases were prepared in the manner described before.

Method of Procedure.—All filaments were heated in hydrogen for several hours and then glowed in a vacuum until outgassing practically ceased.   Care was taken, however, not to heat the iron catalyst appreciably above redness.   The thermionic currents were measured for both ascending and descending temperatures, the latter giving the more consistent results.   All thermocouple measurements were checked at high temperatures with an optical pyrometer.

Results

The effect of various pressures of nitrogen, hydrogen, and ammonia on the thermionic emission of positive ions from iron is shown in Fig. 1.
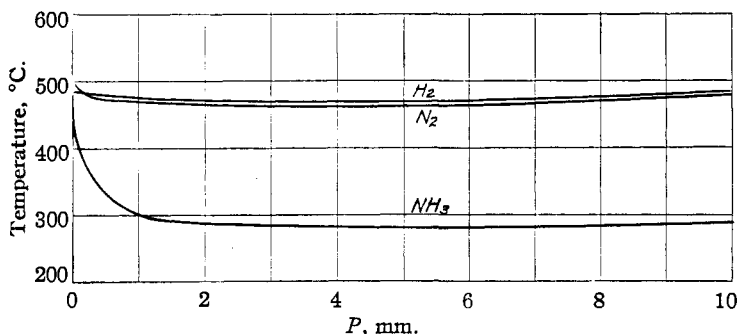

Fig. 1.—The effect of gas pressure on the temperature for equivalent thermionic currents from iron.

These results were taken with a pure iron filament which had been heated to about 800° in a good vacuum for several hours before each series of runs.   The data do not represent the point where emissivity becomes detectable but rather the temperature at which the positive ion current was 8×10^{-13} amp.   Each gas was studied over the pressure range of 10 cm. to about 10^{-6} mm.   No conspicuous effect was observed above 1 cm. except a

[2] C. H. Kunsman, *J. Franklin Inst.*, **204**, 635 (1927).

slight rise in the temperature necessary to obtain the equivalent thermionic current.

The important thing to note is that an equivalent positive ion current can be obtained at 200° lower temperature in the presence of ammonia than in a vacuum; indeed a positive ion emissivity was detected at temperatures as low as 250°. The effect of nitrogen and hydrogen is small, both showing only a slight enhancement of the current over that obtained in a vacuum.

The effect of accelerating voltage on the positive ion emissivity from iron in these three gases at 1 cm. pressure is shown in Fig. 2.
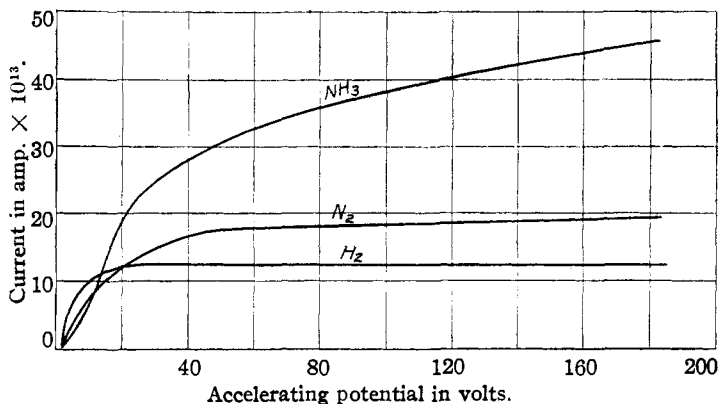

Fig. 2.—Effect of accelerating potential on the thermionic current: iron filament; gas pressure, 1 cm.

The curves for nitrogen and hydrogen were taken at the same temperature, while the ammonia curve was taken at about 200° lower. The curve for hydrogen shows saturation and is identical in shape to that obtained in a vacuum. Nitrogen gives only a partial saturation while ammonia completely fails to saturate. At only slightly higher pressures, the current in ammonia is proportional to the voltage. Thus since saturation is not obtainable with ammonia, the true difference in the relative emissivities of the gases would be greater than that shown in Fig. 1, especially at the higher pressures. Doubtless the failure to saturate is responsible for the flattening out and even turning up of the curves in Fig. 1 above about 5 mm. pressure.

The results obtained with a pure nickel filament are shown in Fig. 3. The accelerating potential was 45 volts, as was the case for iron.

It will be noted that the results for positive ion emission are quite similar to those obtained with iron. The outstanding difference is the lowering of the equivalent temperature for hydrogen, while nitrogen shows only a small effect. Ammonia again has a very pronounced effect on the emissivities, the equivalent temperature being almost as low as for iron.

Curves are included to show the effect of nitrogen and hydrogen on the negative ion, probably electron, emission.   It will be noted that nitrogen has only a small effect, while hydrogen lowers the equivalent temperature about 140°.   The curve for ammonia can only be approximated due to the rapid decomposition at the higher temperatures.   The temperature–current curves for ammonia show a detectable emission current at about 550°, where a decay with time sets in which becomes rapid at 655°; at 700° the electron emissivity almost entirely disappears.   It is interesting to note that this is the temperature range over which Kunsman[3] found the rate of decomposition of ammonia on nickel to be appreciable.
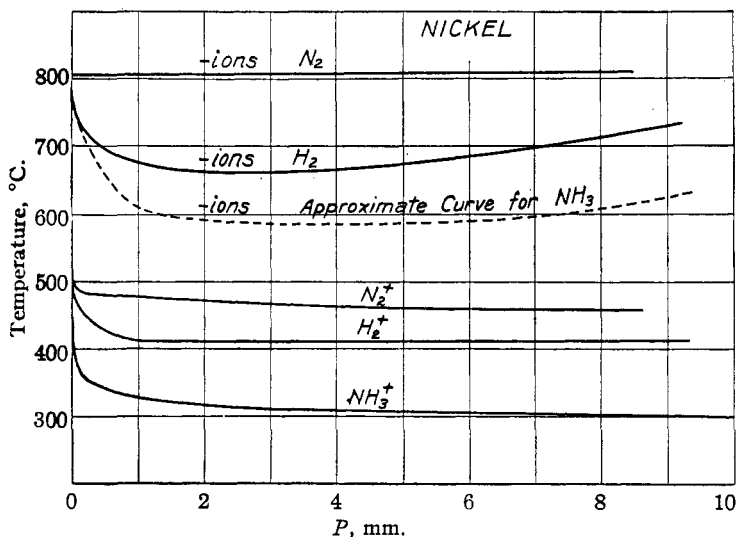

Fig. 3.—Effect of gas pressure on the thermionic emission of positive and negative ions from nickel.

The results obtained with platinum under conditions identical to those described for iron and nickel are shown in Fig. 4.

The salient features are that nitrogen has little or no effect on the positive ion emissivity, while hydrogen lowers the equivalent temperature more than 100°.   The effect of ammonia on the positive ion emission was very similar to its effect on the electron emission described for nickel.   A small emission current was detected at 325°, which increased only seven-fold at 500°.   From 500 to 600° the current increased only two-fold, but from this point on the increase was characteristic of thermionic emission.   At all temperatures below 600° the positive ion current in ammonia was not constant but decreased with time.

The data showing the effect of gases on the electron emission from plati-

[3] C. H. Kunsman, This Journal, **50**, 2100 (1928).

num were unsatisfactory due to the fact that the equivalent emission temperatures fluctuated between such wide limits. In general, however,
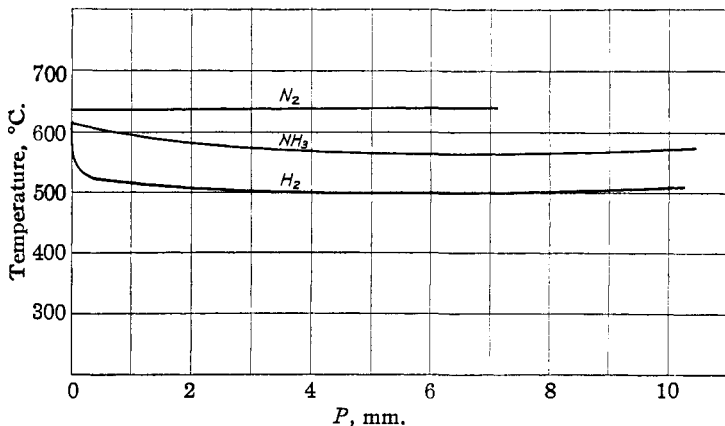

Fig. 4.—Effect of gas pressure on the temperature for equivalent thermionic currents from platinum.

nitrogen decreased the emissivity while hydrogen and ammonia showed an enhancement.
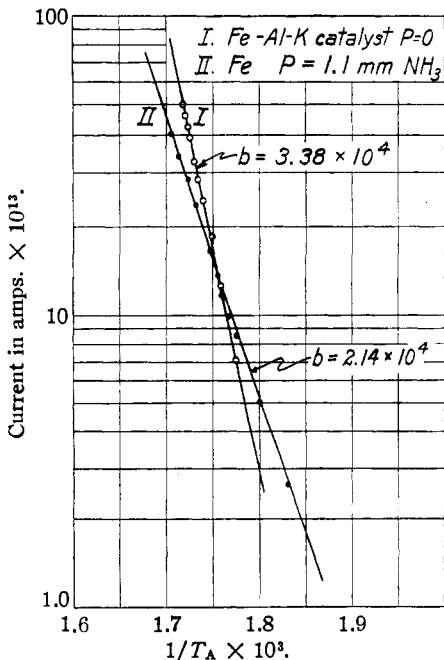

Fig. 5.—Emissivity curves for iron in ammonia, and for an Fe-Al-K catalyst.

A comparison of the positive ion emissivity of pure iron in ammonia with a potassium impregnated iron catalyst in a vacuum is given in Fig. 5.

The catalyst was No. 922, the photoelectric properties of which were described in a previous communication;[4] it was shown to have an appreciable potassium content at the surface. This catalyst was chosen particularly because of its excellent emission properties for positive ions.

The effect of the ammonia pressure for all pressures above 0.1 mm. on the positive ion work function was negligible. The emissivity at all pressures followed very closely, the Richardson equation $i = A T^{1/2} e^{-b/T}$ the value of b varying between 2.08×10^4 and 2.17×10^4.

[4] A. Keith Brewer, THIS JOURNAL, **53**, 74 (1931).

The interesting thing to note is that pure iron in ammonia is a slightly better emitter of positive ions at low temperature than is iron impregnated with potassium. The temperature coefficient for the catalyst is somewhat higher, however, so it is the better emitter at high temperatures. It should be recalled that special care was taken in the preparation of the catalyst filament so that its emissivity would not be impaired.

Discussion of Results

The presence of positive ions adsorbed on a surface (adions) can be detected either by the lowering of the electron work function or by an enhancement of the positive thermionic current. This is clearly illustrated in the study of platinum coated glass filaments,[5] where it was shown that the electrolysis of K^+ ions to the emitting surface resulted in an enhancement of the thermionic and photoelectric emission of electrons as well as the thermionic emission of positive ions.

The mechanism by which adions lower the electron work function has been discussed in detail for photoelectric emission.[1] This mechanism, which is essentially the same for thermionic emission, is that adsorbed ions possess the properties of a positive grid placed about one molecular diameter from the surface, the effective potential of the grid being determined by the concentration of the ions. The work ϕ_0 expressed in volts which an electron must do to escape from a pure surface is now decreased by ϕ_G, the potential of the grid, so the observed work ϕ will be

$$\phi^- = \phi_0^- - \phi_G$$

This accounts for the results given in Fig. 3, where the equivalent temperature for the negative thermionic current is materially lowered by hydrogen and ammonia. The temperature lowering is due to a decrease in the work necessary to remove an electron brought about by the presence of positive ions adsorbed on the surface. These results are similar to those obtained for the photoelectric emission of electrons, where the lowering of the work function indicated the presence of adsorbed positive ions.

The detection of the presence of positive adions by the enhancement of the positive ion current can be seen from the following discussion. Consider a surface on which the concentration of ions is n per sq. cm. Let the velocity component of the ions be u, v and w, where w is normal to the surface. Since only the w component aids in the escape of the ions, and since due to the work function of the surface only those ions having a velocity component between w_0 and ∞ can overcome the surface forces, the number of ions leaving 1 sq. cm. of surface per second is given by[5]

$$N = n \sqrt{\frac{kT}{2\pi m}} \, e^{-mw_0^2/2kT}$$

[5] A. Keith Brewer, *J. Phys. Chem.*, **32**, 1006 (1928)

where T is the absolute temperature, m the mass of the ion and k is the Boltzmann constant. Since $1/2\ mw_0^2 = e\phi$, the equation can be simplified to the form

$$i = n\ \sqrt{\frac{kT}{2\pi m}}\ e^{-e\phi/kT} = AT^{1/2}\ e^{-b/T}$$

where $i = N$ ions per second and b is Richardson's work function. From this it follows that i increases directly with n. It is not a proportionality, however, since the positive ion grid while lowering the work function for electrons raises it for positive ions, $i.\ e.,\ \phi^+ = \phi_0^+ + \phi_G$, where ϕ^+ is again the observed work function in volts. ϕ_G will not be as effective for an ion adsorbed on the surface, however, as for an ion coming from within the metal, since the apparent distance of the ion grid from the surface is no greater than the dimensions of the ion; hence the ion will not necessarily pass through the entire grid field.

In practice the detection of gas ions on a metallic surface by an increase in the positive ion current is complicated by the fact that positive ions are always given off from hot surfaces even in the best vacuum and after a thorough baking out. These inherent ions, consisting of dissolved alkali, adsorbed gases and charged atoms of the metal itself, can be detected by a sensitive measuring apparatus, similar to that used in the present case, at temperatures from 450 to 600°, depending on the metal.

For the reasons just given, it is impossible to say with certainty whether positive adions exist in cases where the gas has only a slight effect on the emissivity of the metal, for instance, hydrogen on iron and nitrogen on platinum. In cases like hydrogen on platinum and nickel, and ammonia on iron and nickel, however, the enhancement is so great that it seems impossible to dispute the presence of positive adions.

The presence of adions from the adsorbed gas is again brought out by the temperatures for the two curves in Fig. 5; the emissivity is shown to be almost identical for ammonia on iron and for potassium on iron. The photoelectric studies[4] of catalyst 922 show it to possess the properties of a surface two per cent. covered with K^+ ions. Using this as a basis of comparison it might be assumed that two per cent. of the ammonia molecules of the surface are ionized at any given instant when the ammonia pressure is above 0.1 mm. Since i increases with n if the change in ϕ_G with n is neglected, it follows from a comparison with ammonia that the concentration of hydrogen ions on nickel is about one per cent. of the total adsorbed molecules, assuming the surface to be completely covered with adsorbed hydrogen.

The fact that iron in an atmosphere of ammonia gives off positive ions as copiously as do the best of potassium impregnated iron emitters, raises the question as to whether the ions come from the ammonia which has actually dissolved in the iron or from the adsorbed film of ammonia

on the iron surface.   An idea of the point of exodus of the ions can be had from the work function of the surface, *i. e.*, from the value of b.

b is a measure of the work done in removing an ion from some point near the surface to a point outside the sphere of electrostatic image attraction (10^{-4} cm. from the surface).   The electrostatic image attraction is given by $F = e^2/4x^2$ where x is the distance of the ion from the surface. The work done in removing an ion from the plane $x = 0$ would be infinite, but owing to the finite dimensions of the ion there is always a lower limit to x; also the intrinsic force at the surface is operative at distances of less than one molecular diameter.   The work done in removing an ion from a point at distance d from the surface to a point outside the range of surface forces is given by

$$w = (^1/_4) \int_d^\infty (e^2/x^2) \, dx = e^2/4d$$

Since $w = bk$ where k is Boltzmann's constant, it is possible to calculate d when b is known, by the equation $d = e^2/4bk$.   The value of $b = 2.1 \times 10^4$ obtained for ammonia on iron gives d to be 1.9×10^{-8} cm.   This value assumes that the image force is the only one that is appreciable at distance d and also that none of the work represented by b goes into dissociation of the ammonia molecule into ions.

The x-ray values for the diameter of NH_3 are 3.4×10^{-8} cm., while the kinetic theory value is 4×10^{-8} cm.   If it is assumed that the positive charge is located at the outermost point on the ion, 4×10^{-8} cm. from the surface, then it follows that b must represent work other than that of removing the ion from the surface against image forces.   Since ϕ_G is small for the removal of a charge from a point d cm. from the surface when d is of the order of atomic diameter, it is reasonable to assume that the excess energy may have gone largely into completing the dissociation of the ammonia.   On the other hand, if it is assumed that the positive charge is located near the center of the ammonia molecule, which is the natural assumption to make on the basis of a nucleus hypothesis of atomic structure, then it follows, since d is almost exactly one-half the molecular diameter, that the ammonia is largely dissociated by the surface forces and that the most of the work done by thermal agitation is the removal of the ion from the surface.   This latter interpretation, rather than the former, is in agreement with the photoelectric results obtained for ammonia on iron, wherein it was found that the concentration of positive ions on the surface decreased rapidly with rising temperature.

The values of b obtained for nitrogen and hydrogen on iron, however, suggest that part of the work done in removing an ion from the surface may be consumed in completing the dissociation of the gas.   For instance, the values of b for hydrogen and nitrogen are 3.45×10^4 and 3.66×10^4, respectively; there is but little change from 1 cm. to atmospheric pressure.

The values of d computed from these quantities are 1.2×10^{-8} and 1.16×10^{-8} cm. for H_2^+ and N_2^+. It must be assumed therefore, for nitrogen, since d is less than the ion radius, that either thermal energy is consumed in completing the dissociation or the ions come from the gas which has dissolved in the iron. It is not possible at present to distinguish between these two suppositions.

The voltage–current curves shown in Fig. 2 are also indicative of the presence of adions on the surface. The fact that ϕ_G due to the adions is not constant over the surface, but is highest near the ions and diminishes to a small value at distances greater than 10 molecular radii removed, causes the effective work function of the surface to vary from point to point over the surface. This variation found on composite surfaces is always evidenced by a failure to obtain saturation.

Application to Surface Catalysis.—The photoelectric studies of the effect of adsorbed ions[1,6] has shown that the force field about positive adions is appreciable at distances ten times the ion radius. Recently Becker[7] has obtained an identical value from thermionic studies for the dimensions of this force field. Becker has shown further that the evaporation of neutral atoms is effected by the electrical fields at the surface and that the net force on an atom is much the same as on a negatively charged particle, the evaporation curves obtained for atoms being similar to those obtained for electrons. It seems probable that force fields of this type (combined image, intrinsic and adion) may be the basis of activated adsorption described by Taylor[8] and by Benton.[9]

As far as the mechanism of catalysis is concerned, the interpretation is primarily the same as that suggested from the photoelectric studies. If there is any connection between the dissociation of the adsorbed gas into ions and the mechanism of chemical action, then the data indicate that iron and nickel are excellent catalysts for the decomposition of ammonia, while platinum is comparatively poor. This is in agreement with the results of Kunsman on the decomposition of ammonia on these metals. Further, the data suggest that nickel and platinum might be excellent hydrogenation catalysts, which again is in agreement with experience. In brief it seems probable that a gas which appears to be appreciably dissociated into ions on a given metal, as is evidenced by a lowering of the work function for electrons or by an enhancement of the positive ion current, might be catalyzed by that surface in the case of reactions initiated by the gas in question. An exception to this may arise when one of the other gases present is selectively adsorbed; this is illustrated by the inhibition of the

[6] A. Keith Brewer, *Phys. Rev.*, **38**, 401 (1931).

[7] J. A. Becker, *Trans. Faraday Soc.*, **28**, 148 (1932).

[8] Taylor, *Chem. Rev.*, **9**, 1 (1931).

[9] Benton and Ulrich, THIS JOURNAL, **54**, 1820 (1932).

ionization of ammonia on platinum due to the hydrogen liberated from the decomposed ammonia.

These results are offered simply as an added proof of the contention that gases are dissociated into ions on metallic surfaces. If the present interpretation is correct, this dissociation as well as the types of surface forces outlined here must be taken into consideration in formulating a mechanism for adsorption and for surface catalysis.

The writer wishes to acknowledge the interest Dr. C. H. Kunsman has taken in this research.

Summary

Results are given showing the effect of nitrogen, hydrogen and ammonia on the thermionic emission of positive ions from iron, nickel and platinum.

The surprising fact noted is that at low temperatures a pure iron filament in ammonia emits positive ions more copiously than does even the best of potassium impregnated positive ion sources. Nickel also is only slightly less efficient than iron but the positive ion current from platinum is not materially increased.

Hydrogen exhibits an appreciable enhancing effect on platinum and nickel, for both positive and negative thermions. Nitrogen, however, shows only a slight effect on iron and nickel, and none on platinum.

The mechanism by which positive adions lower the work function for electrons and enhance the emissivity for positive ions is described.

Work function values for ammonia on iron indicate that the ion is emitted from a point 1.9×10^{-8} cm. from the surface. Since this distance is approximately equal to the radius of the ammonia molecule, it is interpreted as indicating that ions before emission resided on the surface in the completely dissociated state.

The bearing of these results on adsorption and surface catalysis is suggested.

WASHINGTON, D. C.