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The Emission of Alkali Atoms from Various Ammonia Catalysts

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An apparatus is described for measuring the rate of emission of alkali as positive ions and as neutral atoms from the ammonia catalysts. The results show that when the temperature of the catalyst is first raised to the emission point the number of atoms leaving the surface far exceeds that of ions. In the course of several minutes heating the emissivity of atoms decays to a negligible value. Atom emission is much more persistent from catalysts containing Al_2O_3 , also the temperature for equivalent ion currents is higher. Both atom and ion emission increase when sintering occurs, since the alkali can then diffuse

more readily to the surface. The factors determining the ratio of atoms to ions are discussed. Under the conditions where the alkali concentration at the surface amounts to several hundredths of a molecular layer the presence of the adions will lower the work function of an appreciable fraction of the surface to a point below the ionization potential of potassium, thus permitting the potassium to escape as neutral atoms. When the alkali concentration is small, however, the work function is close to that of pure iron and the potassium can escape only in the form of ions.

A COMPREHENSIVE investigation of the physical properties of the ammonia catalysts has demonstrated that these substances are excellent emitters of positive ions of the alkali with which they are impregnated,¹ and also that the alkali concentration at the surface never builds up to more than a few hundredths of a molecular layer.² In the present paper this investigation is extended to a study of the conditions underlying the thermal emission of neutral atoms from these catalysts.

The experimental procedure was similar to that described previously.^{3,4} It consisted of measuring photoelectrically the amount of alkali deposited on an iron reference electrode placed beside a catalyst filament. The catalyst was heated at a constant temperature for a period of one minute with retarding or accelerating potentials for the emitted positive ions placed between it and the reference electrode. Thus when the reference electrode was positive with respect to the catalyst only neutral atoms were deposited, but when the potential was negative it received both atoms and ions. The photoelectric current from the reference electrode gave

directly the amount of alkali deposited, when compared with standard emission curves.⁴ In operation all the ions emitted from the catalyst reached the reference electrode. This was not true for the atoms since the geometry of the tube made it possible for only one atom in fifty to be deposited.

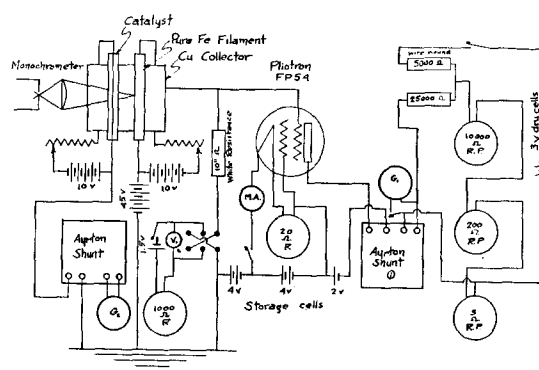


FIG. 1. A_s , 25,000 to 100,000 Ω ; R.P.=Yaxley wire wound radio potentiometer; R=Yaxley radio rheostats; V_1 =Full scale 1 volt; M.A., Full scale 150 m.a.; G_1 , 1 mm = 10^{-8} to 10^{-10} amp.

¹ C. H. Kunsman, J. Frank Inst. **204**, 635 (1927).

² A. K. Brewer, J. Am. Chem. Soc. **53**, 74 (1931).

³ A. K. Brewer, Phys. Rev. **38**, 401 (1931).

⁴ A. K. Brewer, Phys. Rev. **44**, 1016 (1933).

A diagram of the apparatus is shown in Fig. 1. It includes a simple and practical electric circuit utilizing the FP 54 Pliotron, for measuring the photocurrent.

The catalyst filaments were prepared in the usual manner, care being taken during the coating and reducing process not to raise the temperature over 450°C , to insure that the alkali was not evaporated before the tests were made. All filaments were approximately the same size, containing about 0.042 g of catalyst.

RESULTS

Typical results for potassium promoted catalysts are shown in Fig. 2.

The signs at the different points represent the potential placed on the reference electrode with

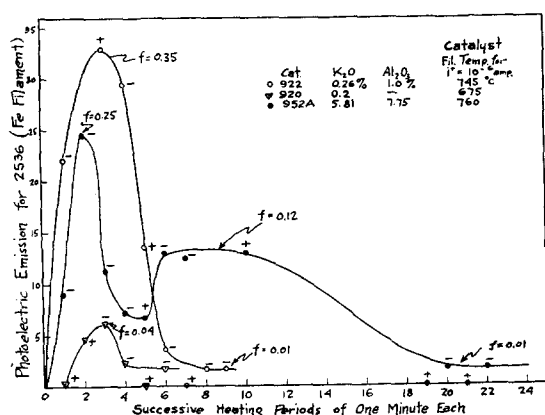


FIG. 2.

respect to the catalyst; 45 volts was used. The values of f are for the fraction of the surface of the reference electrode covered with the potassium emitted from the catalyst during a one minute heating period. After each heating period the reference electrode was restored to its original condition by glowing until the potassium deposit was completely removed.

The temperatures given are those at which the positive ion current was 1×10^{-6} amp. In the case of 920 this temperature remained fairly constant for some time; for 922 and 952 it dropped about 25° during the first few minutes of the heating period and thereafter remained fairly constant.

A comparison of the curves for 922 and 952A shows that the maximum rate of emission of atoms is smaller for the latter although the total

quantity emitted is materially larger. The continuous emission of atoms from 952A is much greater than the curves illustrate since the rate of atom clean up became so slow at 760°C that from the 6 to the 20 minute periods the filament was heated at 800°C . The higher temperatures necessary for corresponding emission currents from filaments containing Al_2O_3 is doubtless intimately associated with the slowness with which these catalysts undergo sintering. Catalyst 920 reduces directly to a firm homogeneous mass, 922 does not sinter until heated to about 750°C , and 952A remains in a granular easily powdered form at all temperatures below 1000°C .

Since only one neutral atom out of fifty is deposited on the reference electrode the curves show that the emission of atoms at the maximum point exceeds that of ions by a factor of about 1000 for 922, 642 for 952A and 172 for 920. After a steady state has been established, however, the atom emission becomes less than one percent of the ion current.

A total positive ion current of 1×10^{-6} amp. corresponds to 2.43×10^{-8} g of potassium per minute. If all the potassium were given off as ions 920 would emit for 2.86×10^8 minutes. At the maximum rate for the combined emission of ions and atoms 922 would become alkali free in about 3 minutes; when the steady state was reached, therefore, the catalyst must have been nearly alkali free.

While the results given are for positive ion currents of 1×10^{-6} amp. ion currents of the order of 10^{-14} amp. can be detected with the electrical circuit used at temperatures from 350 to 450°C depending on the type of filament. The smallness of these currents, necessarily, makes it impossible to measure accurately the ratio of ions to atoms at these temperatures. The measurements do indicate, however, that atom and ion emission begins at about the same temperature for fresh filaments. Since the atom emission decreases more rapidly with time, a worked-in filament will show very little atom emission at temperatures where the ion emission is appreciable.

Results similar to those shown above were obtained for sodium, rubidium and caesium. The general characteristics were the same as for potassium.

DISCUSSION OF RESULTS

Becker⁵ has suggested that the ratio of ions to atoms (E_p/E_A) emitted from a conducting surface may be expressed by the equation.

$$E_p/E_A = e^{(\phi - I)/KT},$$

where ϕ is the surface work function and I is the ionization potential. Since ϕ for iron is about 4.8 volts and I for potassium is 4.3 volts $E_p/E_A = e^2 \times 10^3$, at 1000°A. This shows that the probability of an atom leaving in the neutral form is exceedingly small.

In the present experiment the conditions are complicated by the fact that the work function of the iron is changed by the presence of the potassium. The photoelectric studies of ammonia catalysts² show 920 and 922 to possess the properties of highly composite surfaces due to the presence of small amounts of potassium on the surface. The work function as obtained from photoelectric measurements varies over the surface from 4.8 to 2.8 volts for 920, and from 4.8 to 3.4 volts for 922; since the photocurrent for $\lambda 2800$ is greatly enhanced for these catalysts over that for pure iron the work function of an appreciable fraction of the surface must be as low as 4.3 volts, hence the emission of both atoms and ions is to be expected. Since the work function increases with decreasing potassium it follows that when it rises above 4.3 volts the emission of atoms will largely cease. It is not surprising, therefore, that atom emission is appreciable only at the beginning of the heating period.

Recent experiments³ show that potassium dissolves slowly in tungsten at 300°C and rapidly at 500°C. Similar results were obtained with iron although the solution occurs at a slightly lower temperature. As the temperature is raised the dissolved alkali diffuses to the surface and is

again emitted as positive ions provided the concentration is small, and as ions and atoms if the concentration is high. The ability of potassium to diffuse through the iron increases materially with the temperature.

Previous photoelectric measurements showed the work function of iron² to be unaffected by the presence of alumina, hence the positive ion emissivity should be unaffected provided the concentration of alkali at the surface is the same.⁶ Since the temperature for the same ion currents increases with the alumina content the rate of diffusion of alkali must be slower than for pure iron; this accounts for the difference in the temperature of emission for the two types of filaments.

The difference observed in the emission of atoms from 920 and 922 is due primarily to the difference in temperatures for equivalent ion currents. In general it is found that sintered emitters give off ions at a lower temperature than do nonsintered emitters. Thus in the case of 922, when the sintering temperature is reached the potassium is able to diffuse through the body of the catalyst and in virtue of this temperature being high it is necessarily followed by a rush of alkali to the surface. Since a small amount of alkali results in a large decrease in the work function, it follows that the chance of an atom leaving in the neutral form is enormously enhanced; for instance, if the surface is five per cent covered with potassium the work function is lowered to between 3.5 and 4 volts which is well below the ionization potential of potassium. The poor diffusibility of the alkali in 952A, is largely responsible for the atom emission continuing for such a long period of time, and also for the fact that the emission never becomes large although the potassium content is high.

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

⁵ J. A. Becker, Trans. Am. Electro Chem. Soc. **55**, 21 (1929).

⁶ A. K. Brewer, J. Am. Chem. Soc. **54**, 4588 (1932).