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Surface Potential Measurements on Nickel and Iron Films During the Chemisorption of Ammonia, Nitrogen, and Hydrogen

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The surface potential changes $\Delta\phi$ during the adsorption of ammonia, nitrogen, and hydrogen on evaporated films of nickel and iron have been studied. After little change of potential at low coverage, large positive $\Delta\phi$ values were obtained when ammonia was adsorbed at −78°C to high coverages on both metals. Since this potential increased with time and the adsorption was not reversible, chemisorption with dissociation was probable. The initial zero value of $\Delta\phi$ was explained by the $-NH_2$ radical and H atom having dipole moments of approximately the same magnitude but opposite in sign, the latter on a fully covered surface giving a $\Delta\phi$ of −0.4 volt. The positive potential was a consequence of an activated transformation of the H adatom from its interstitial surface site to one outside the surface between adjacent chemisorbed $-NH_2$ radicals with change of sign (and magnitude) of its dipole, as previously found in the CO + H, and O_2 + H systems.

At 20°C and above, a surface equilibrium was set up between chemisorbed $-NH_2$, $=NH$, and H radicals on nickel films as evidenced by the displacement in the $-NH_2$ direction (with increase in $+\Delta\phi$) by increasing either the hydrogen pressure or the ammonia pressure in the gas phase, and in the reverse direction by evacuation (thereby desorbing some hydrogen), by increase in temperature, or by working at low coverages.

There was no evidence of the formation of the N-atom complex $Ni\equiv N$, but with iron, a surface layer of $Fe\equiv N$ was formed and had a $\Delta\phi$ of −0.4 volt for a "fully" covered surface. With this latter metal, a surface equilibrium between $-NH_2$, $=NH$, $\equiv N$, and $-H$ radicals was set up. Thus, with high coverages of NH_3, $\Delta\phi$ was positive because of the presence of adsorbed "protonic" hydrogen atoms, but its bonding energy was less than on nickel, and hydrogen was spontaneously desorbed at 20°C, thereby causing $\Delta\phi$ to drift in a negative direction.

Comparatively little information is available about the nature of the adsorbed species present on the surface of transition metals when ammonia is chemisorbed; thus, the surface composition of the chemisorbed layer is still uncertain although such knowledge would be particularly valuable in discussions on the mechanism of the synthesis of ammonia. Recently, however, Ozaki, Taylor, and Boudart (*1*) from isotope effects, have shown that the rate-determining step on an iron catalyst was the rate of chemisorption of nitrogen on a surface predominantly covered with NH radicals. Similarly, analysis of the amounts of nitrogen and hydrogen present at the surface of a tungsten catalyst during the slow decomposition of ammonia has been made (*2*), but comparative data on iron or nickel are not available. However, Kemball (*3*), on the basis of deuterium exchange with ammonia chemisorbed on a large number of metals, including iron and nickel, in which only one hydrogen atom exchanged at a time, concluded that the adsorption was dissociative, and that chemisorbed $-NH_2$ radi-

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cals and H atoms were the predominant species. However, it seems clear that, with tungsten and iron films (*4*), more highly dissociated radicals are formed since hydrogen, in excess of that which would leave the surface covered with $-NH_2$ radicals, could be desorbed; moreover, it is well known that nitridation of the surface of many metals has been effected at high temperatures using ammonia gas.

The object of the present preliminary study was to obtain additional information from a study of the changes of surface potentials of nickel and iron films that occurred during the chemisorption of ammonia, nitrogen, and hydrogen, under various conditions.

METHODS

The changes of surface potential $\Delta\phi$ were measured by the space-charge–limited diode technique. The convention of $\Delta\phi$ positive corresponding to a *decrease* in work function has been adopted in this paper. A refined version of the diode cell of Culver, Pritchard, and Tompkins (*5*) was used, since with their cell it was found that the voltage–current characteristics depended to some extent on its over-all temperature. Since the resistance of the filament, and therefore its average temperature, was maintained constant, the different characteristics were attributed to small changes in the temperature distribution along the filament. This lack of reproducibility was, however, completely eliminated by enclosing the filament leads in a glass sheath, through which water at constant temperature was circulated. Surface potential changes that were independent of the temperature of the cell were then obtained. Voltage–current curves for the diode were no longer parallel with ambient pressures greater than 10^{-4} mm Hg. When the pressure exceeded this value, the measurements were made immediately after opening the system to the pumps, probably at a pressure $\sim 10^{-5}$ mm Hg. There was, in general, no evidence of significant desorption for this short pumping time.

Films were deposited, after the usual thorough outgassing procedure, by evaporation from Specpure wires, in an ultrahigh vacuum system, and were presintered *in vacuo* at a temperature at least as high as that required in the subsequent adsorption experiments. Contamination of the films by mercury vapor was prevented by interposing two traps, cooled in liquid oxygen, during experiments with nitrogen and hydrogen, and in solid carbon dioxide–acetone mixture when ammonia was used.

Hydrogen was purified by diffusion through a palladium thimble; nitrogen was prepared by the thermal decomposition of sodium azide in presence of free sodium; and ammonia was obtained from a cylinder and, after condensation on sodium, was repeatedly distilled between traps before use.

RESULTS

Nickel Films

Adsorption of Ammonia

The results for the adsorption of ammonia on nickel at −78°C on two different films are summarized in Fig. 1. The amount of adsorbed is somewhat uncertain because of simultaneous adsorption on the walls of the cell. However, even after correction for this, using Kemball's data (*4*) for ammonia adsorption on glass, it was evident that the first doses of ammonia reaching the film caused little immediate change in the surface potential $\Delta\phi$ but after about 20 min, during which time doses were being added, $\Delta\phi$ became increasingly positive, reaching a saturation value of about 2.1 volts with increasing amounts adsorbed.

Now it is often true that a positive surface potential may be expected when a gas is physically adsorbed by a metal. However, this interpretation of the present results is most unlikely. Ammonia has a large permanent dipole moment of 1.45 D and it is estimated using the Helmholtz equation,

$$\Delta\phi = 4\pi\sigma\theta\mu \qquad (1)$$

(where θ is the fractional coverage, μ the dipole moment of the ammonia molecule, and σ the maximum number of adsorbed molecules per cm^2 surface, assuming hexagonal close packing and a cross-sectional area of the molecule rotating about the nitrogen atom as pivot) that $\Delta\phi$ should be about $+2.8$ volts when all the ammonia molecules are perpendicular to the surface with the positive end of its dipole outwards. It is therefore interesting that the isotherm of ammonia adsorption on graphite can be interpreted in terms of the repulsive interactions (*6*). It may be argued that, statistically, alternate molecules are aligned head-to-tail (because of the ease of inversion of the nitrogen atom) so that the permanent dipole effect is zero, but, even so, ammonia also has a high polarizability and the contribution to $\Delta\phi$ of the induced dipole, which is independent of the direction of the permanent dipole, would be quite substantial. It is therefore concluded that ammonia is not physically adsorbed; a more compelling argument is the observation that prolonged pumping at $-78°C$ which should effect, at least, partial desorption, does not change the $\Delta\phi$ value. Moreover, physical adsorption normally takes place extremely rapidly, whereas $\Delta\phi$ was found to increase slowly with a first order "rate constant" of 5.3×10^{-2} min^{-1} [i.e., the plot of log $(\Delta\phi_t - \Delta\phi_\alpha)$ against time was linear, $\Delta\phi_\alpha$ being the maximum value attained). This time dependence also eliminates a possible alternative mode of adsorption, viz., the formation of an undissociated chemisorbed molecule $Ni \leftarrow NH_3$ involving a charge-transfer process, since the process would not normally be an activated one.

It is therefore likely that ammonia is dissociately adsorbed on a nickel film at $-78°C$ in agreement with Kemball's conclusion. Thus, the H–NH_2 bond energy is 104 kcal/mole compared with 103 kcal/mole for the H–H bond in the hydrogen molecule which is adsorbed as atoms, even at $-183°C$; similarly, dissociation into H atoms and radicals takes place when CH_4 and H_2O are chemisorbed on nickel at low temperatures.

At $-78°C$, therefore, the surface is populated with chemisorbed H atoms and $-NH_2$ radicals. If it is now *assumed* that the $-NH_2$ group has a positive dipole outwards from the surface such that its $\Delta\phi$ at full coverage is about $+0.4$ volt, then since the surface saturated with H atoms has a $\Delta\phi$ of approximately equal magnitude but opposite in sign, the initial over-all value of $\Delta\phi \sim 0$ can be explained.

To account for the development of a large positive $\Delta\phi$ with time and increasing coverage, it is recalled (*5*) that when H atoms are chemisorbed at $-183°C$ on a nickel surface that is already covered with chemisorbed carbon monoxide, the $\Delta\phi$ increment is about $+2$ volts; similarly (*7*), when H atoms are admitted to a saturated layer of chemisorbed oxygen on nickel, the negative $\Delta\phi$ is first made more positive by converting the layer to hydroxyl groups, and then further H-atom adsorption again produces a large change of $\Delta\phi$ (~ 2 volts) in the positive direction. Now, although H atoms are normally adsorbed interstitially in the surface to give $\Delta\phi \sim -0.4$ volts ($\theta = 1$), when adjacent surface nickel atoms have already engaged in chemisorption, the H atom occupies a position between these chemisorbed groups at a distance of ~ 1 Å from the metal surface with a virtual positive charge of about half the protonic charge.

With NH_3 at low coverages, $-NH_2$ and H^- atoms are the main surface species (the minus superscript refers to the sign of the dipole outwards from the metal), whereas at full coverage, each H atom will be flanked by $-NH_2$ radicals and will therefore tend to transform to the H^+ form with an accompanying large positive increase in $\Delta\phi$ to give an expected value of from $+2.0$ to $+2.4$ volts, as indeed was found. However, for the $CO + H + Ni$ system at $-183°C$, the $\Delta\phi$ values are dependent on the order of addition, being -0.60 volt for CO on a saturated H-atom layer and $+0.70$ volt for H atoms on a CO-covered surface; thus, for transformation of H^- atoms to H^+ atoms a small activation energy is required. Its magnitude is probably less than 10 kcal/mole, which is the estimated value of the heat of desorption of the H^+ atoms. A similar dependence of $\Delta\phi$ on order of addition is found in the $O_2 + H$

+Ni system but the bonding energy of the "protonic" hydrogen is stronger.

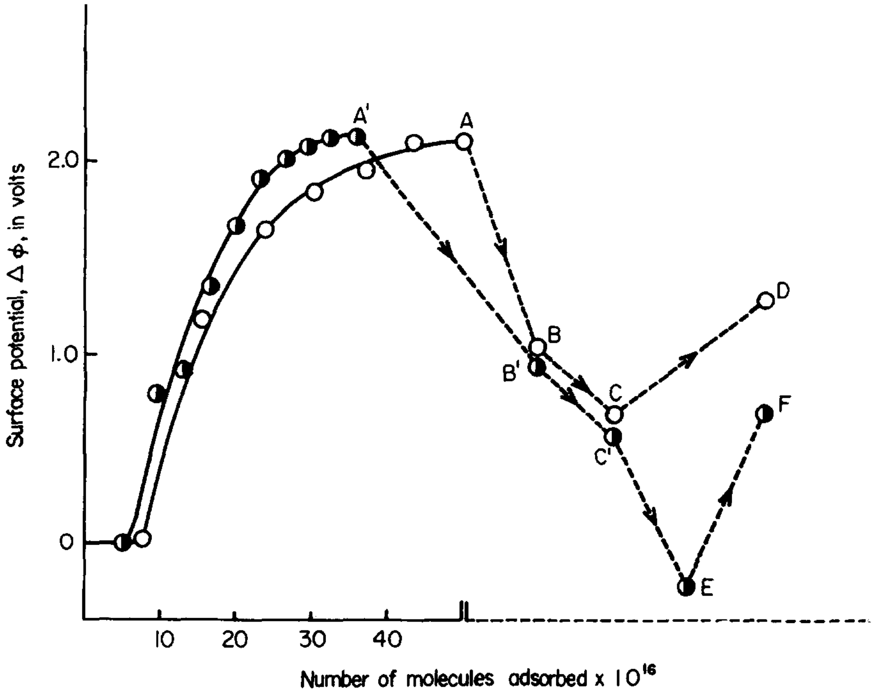


FIG. 1. Change of surface potential $\Delta\phi$ (volt) with amount of ammonia adsorbed (number of molecules × 10^{16}) for two different nickel films at −78°C (○, ◑). At point A, A′, film heated to 20°C with pumps isolated; at B, B′ evacuated at 20°C; at C, pumps isolated and excess ammonia added at 20°C and cooled at −78°C to give D; at C′, film heated to 130°C, excess hydrogen introduced and film cooled to −78°C to give $\Delta\phi$ at F.

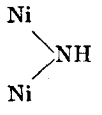
Now, in Fig. 1, each experimental point represents the maximum $\Delta\phi$ developed in time, i.e., on addition of a dose of ammonia, although the adsorption was extremely rapid, the value of $\Delta\phi$ increased at a fairly slow, measurable rate, the time taken to attain the maximum value decreasing with each additional dose, since fewer H^- sites were available as the coverage increased. It seems likely that it is this H^+ form that undergoes easy deuterium exchange and accounts for Kemball's result that only one "hydrogen" atom exchanges at a time.

On raising the temperature from −78°C to 20°C (Fig. 1) there is little desorption when the system is isolated but $\Delta\phi$ decreased to ~1 volt and the original $\Delta\phi$ is not restored on cooling to −78°C, although there is a slight increase (~0.1 volt). This result is explained by the further dissociation of the chemisorbed $-NH_2$ radical, a process which requires an activation energy higher than that for the H^- to H^+ transformation. A surface equilibrium that may be formally written in the form,

$$Ni{-}NH_2 \rightleftharpoons Ni{=}NH + Ni{-}H \qquad (2)$$

is then set up.

Thus, at coverages approaching saturation, provided that desorption is slight, $\Delta\phi$ becomes more negative on increasing and slightly more positive on decreasing the temperature. The effect is largely reversible. Equation (2) as written must be endothermic and the imino radical must have, as expected, a negative dipole outwards. Possible structures are (*i*) the bridged form



which is unlikely on geometric arguments since the chemisorbed ammonia would occupy 4 sites, (*ii*) the linear form Ni = NH or, (*iii*) the singly bonded form Ni → NH in which both electrons are donated from the metal; all of these structures would be expected to have a negative dipole outwards from the metal. Furthermore, taking the bond energy H–NH to be the same as that of H–NH_2, viz., 104 kcal, and noting that the Ni–H bond energy is 62 kcal decreasing to 52 kcal with increasing coverage [= ½ (dissociation energy of H_2 molecule + heat of adsorption of hydrogen molecules on nickel) (*8*)], then reaction (2) is endothermic unless the difference in bond energy between Ni–NH_2 and Ni=NH is greater than 42 kcal.

while addition of ammonia increased it to a value approaching its original magnitude of ~1 volt. When the temperature was further increased to 130°C, $\Delta\phi$ decreased to −0.2 volt and addition of hydrogen at this temperature followed by cooling to −78°C gave a $\Delta\phi$ value of 0.7 volt. All these results are consistent with the displacement of an equilibrium represented by Eq. (2).

Surface potential changes obtained when ammonia was added to a clean nickel film at 20°C are shown in Fig. 2. The $\Delta\phi$ value was initially negative, reaching a minimum of −0.15 volt at $\theta \sim 0.4$, but with increased adsorption of ammonia a saturated value of +0.75 volt was found. This magnitude should be compared with values of 0.95, 0.70, 0.74, 0.9 volt obtained with films on which ammonia was first adsorbed at −78°C followed by heating the film to 20°C. The initial negative value is a consequence of the displacement of equilibrium (2) to the right at low coverages where the number of free sites is large, but with increasing adsorption of ammonia, and fewer available sites, the

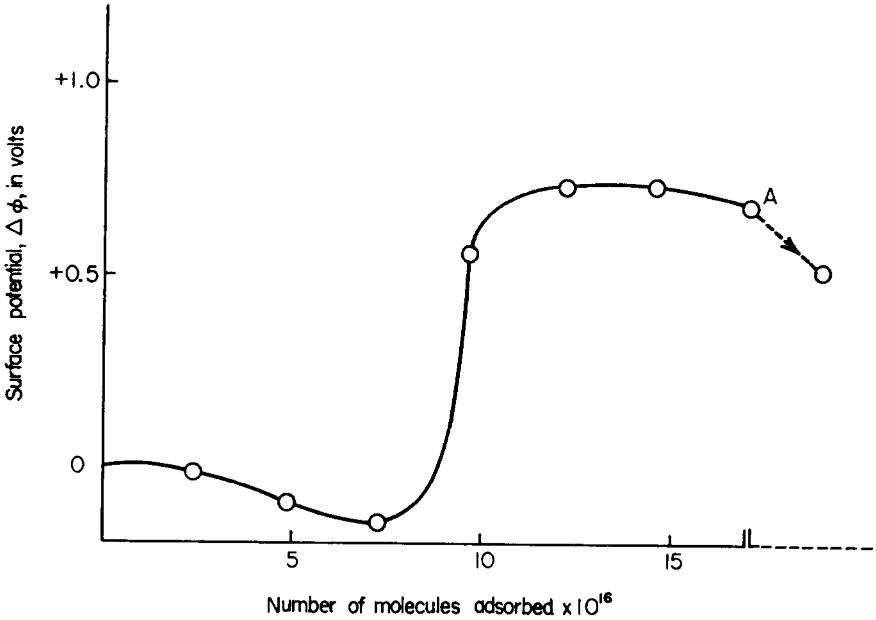


FIG. 2. Change of surface potential $\Delta\phi$ (volt) with amount of ammonia adsorbed (number of molecules × 10^{16}) for a nickel film at 20°C. At point A, film pumped causing decrease in $\Delta\phi$.

On leaving the system at point B overnight at 20°C, a small amount of hydrogen was evolved; this slight evolution has been previously reported by Singleton, Roberts, and Winter (*9*) who identified the gas by thermal conductivity measurements. This desorption was accompanied by a slight decrease in $\Delta\phi$, and on evacuation at this temperature, $\Delta\phi$ was reduced to 0.6 volt, equilibrium is displaced backwards to attain the equilibrium composition of a saturated layer.

Adsorption on a clean film maintained at 130–140°C gave somewhat irreproducible $\Delta\phi$ values; these were, in general, small in magnitude and negative in sign, the most negative recorded being —0.45 volt for a maximally covered surface. The variability of the results is related to the amount of hydrogen desorbed; thus, with a partially covered film from which no hydrogen had been desorbed, a small positive value was initially recorded but this changed spontaneously in a negative direction with time. However, cooling to 20°C in the presence of hydrogen restored $\Delta\phi$ to the expected value of 1.0 volt (cf. Fig. 1), and this was not changed significantly on further decreasing the temperature to —78°C.

Although the evidence is negative in type, there are no results which suggest that the imino radical dissociates further to the "nitride" complex, and in this respect nickel differs from iron (see later).

Adsorption of Nitrogen and Hydrogen

Adsorption of nitrogen on a clean nickel film at —183°C gave a saturation $\Delta\phi$ value of +0.23 and +0.22 volt on two separate films, in close agreement with Mignolet's value (*10*) of 0.21 volt. On heating to —78°C, more than half the adsorbed nitrogen was evolved and $\Delta\phi$ decreased to 0.1 volt; at 20°C, there was complete desorption and $\Delta\phi$ was zero. The heat of adsorption of this loosely bound nitrogen has been measured isosterically (*12*) and calorimetrically (*13*) and found to be ca. 10 kcal/mole. It is probable, as Trapnell (*14*) has suggested, that molecular chemisorption with partial dissociation of the $N{\equiv}N$ triple bond had occurred, though physical adsorption cannot be ruled out.

Hydrogen was then adsorbed "on top" of this nitrogen layer, causing a slight decrease of $\Delta\phi$ from +0.23 volt to +0.12 volt, followed by a small increase to 0.18 volt, after which no further hydrogen was taken up. On heating to 20°C, nitrogen was desorbed and a value of $\Delta\phi = -0.22$ volt corresponding to a partially covered atomic hydrogen layer was obtained.

In other experiments, it was found that nitrogen was adsorbed at —183°C on a saturated hydrogen layer ($\Delta\phi = -0.32$ volt) to give a $\Delta\phi$ value of +0.4 volt, again in close agreement with Mignolet (*11*). As before, nitrogen was completely desorbed at 20°C, and a $\Delta\phi$ of —0.3 volt, corresponding to the H-atom layer, recorded. In this case, the nitrogen was probably physically adsorbed and would be expected to give a more positive $\Delta\phi$ increment than when it was molecularly chemisorbed on the clean metal film.

There was no evidence of formation of ammonia during these mixed gas adsorptions and desorptions, nor when nitrogen and hydrogen were in contact with a nickel film at 100°C on nickel films. There is, however, some evidence (*15*) of slight dissociative adsorption of nitrogen on supported nickel catalysts at higher temperatures in the presence of hydrogen, presumably with subsequent formation of —NH radicals.

Iron Films

Adsorption of Nitrogen and Hydrogen

When nitrogen was admitted to a clean iron film at —183°C a maximum $\Delta\phi$ of +0.28 volt was observed; the shape of the surface potential isotherm, shown in Fig. 3, suggests that the adsorbed molecules were mobile. However, on raising the temperature of the film to 20°C, there was partial desorption followed by readsorption and $\Delta\phi$ became negative, the actual magnitude, around —0.2 volt, varying with the period of time that the film was left at a particular temperature. Thus, a maximum value of —0.40 volt was recorded after heating for 10 hr at 130°C, although values of —0.22, —0.25, and —0.21 volt were obtained for shorter periods. There seems little doubt that the positive dipole layer should be ascribed to molecular chemisorption which transformed to a negative layer of nitrogen atoms when the necessary activation energy was acquired. Although the evidence was slight, it would

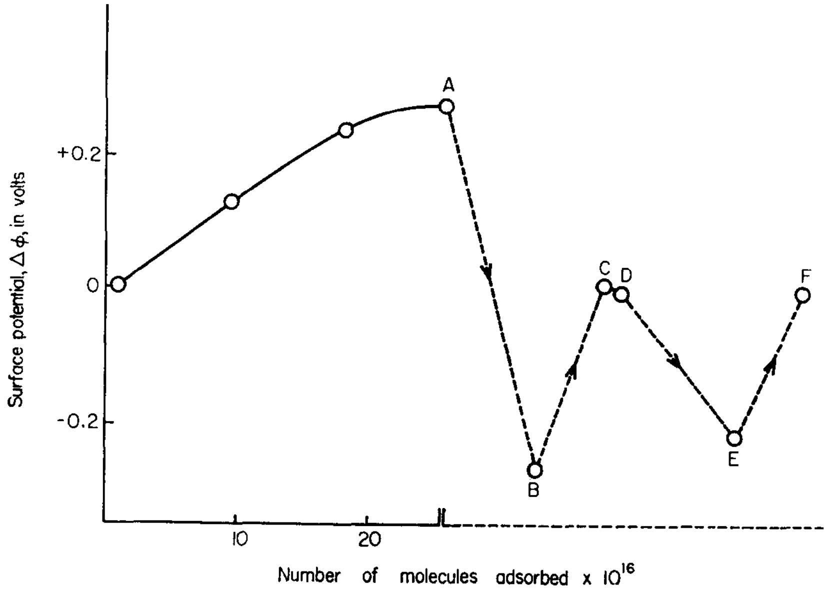


FIG. 3. Change of surface potential (volt) with amount of nitrogen adsorbed (number of molecules × 10^{16}) at —183°C on an iron film. At point A, temperature raised to 130°C with pumps isolated; some desorption followed by some readsorption occurred to give point B after cooling to 20°C; at B, hydrogen added to give C which drifted to D after 1 hr at 20°C; at D, temperature raised to 130°C with pumps isolated, hydrogen added and desorbed ammonia condensed in traps; on cooling to 20°C, point E obtained; at E, nitrogen added and point F obtained.

appear that this transformation proceeds, at least in part, by a desorption–adsorption mechanism suggesting that surface dissociation (without desorption) required a higher activation energy than that of N_2 desorption.

The transition from molecular to atomic form was more clearly evident when nitrogen was adsorbed at 20°C on a clean film. Immediately after addition of each dose of nitrogen at low coverages, $\Delta\phi$ increased momentarily to $+0.04$ volt and subsequently, over a period of minutes, decreased to -0.02 volt. A minimum value of -0.08 volt was observed when no further adsorption occurred; according to Beeck (*13*), dissociative adsorption ceases at 20% "coverage," presumably because of the rapid increase of activation energy with increasing adsorption; therefore, if nitrogen atoms were uniformly distributed over the surface, $\Delta\phi$ would attain a value of -0.4 volt on a surface "fully" covered with nitrogen atoms.

Addition of hydrogen at 20°C to an iron film previously covered with nitrogen at 100°C with a $\Delta\phi$ of -0.25 volt, effected an increase to $\Delta\phi = +0.07$ volt, which drifted spontaneously to -0.04 volt, due probably to the formation and subsequent desorption of ammonia which was condensed in the liquid-oxygen-cooled traps. Similarly, heating this film to 100°C in presence of a large excess of hydrogen gave a value of $\Delta\phi = -0.22$ volt and a further amount of ammonia was found to have been condensed in the trap.

In another set of experiments, adsorption of nitrogen at 20°C on a nearly saturated H-atom layer changed $\Delta\phi$ to $+0.01$ volt at the point when nitrogen was just detectable in the gas phase. With another film, previously covered with hydrogen, $\Delta\phi$ increased to about 0.0 volt when nitrogen was first detectable in the gas phase, but when the film was left in contact with excess nitrogen at 130°C for some hours, $\Delta\phi$ decreased to -0.45 volt, a value consistent with that expected for Fe≡N on a "fully-covered" surface.

Adsorption of Ammonia

The results obtained when ammonia was added to two separate iron films at 20°C are summarized in Fig. 4. As with nickel films, for the first few additions of gas, $\Delta\phi$ was around zero (although with iron this extended to much higher coverages, viz., ~50%), but with increasing adsorption, $\Delta\phi$ attained a maximum value of +0.65 volt. The close agreement of the results on the two films was partly fortuitous since throughout the later additions $\Delta\phi$ spontaneously drifted to lower values with an accompanying evolution of hydrogen. Thus, evacuation at 20°C which effected further desorption of hydrogen, reduced $\Delta\phi$ to +0.05 volt, while heating to 130°C caused a further reduction to —0.37 volt, i.e., corresponding approximately to the value expected for a "fully" covered Fe≡N layer (—0.45 volt).

In general terms, if the dipole Fe–NH$_2$ is positive outwards of magnitude ~+0.4 volt, and Fe=NH and Fe≡N have dipoles of opposite sign with the latter having the larger magnitude, the results can be interpreted in the same manner as those obtained with nickel films. The main, and important, difference is that the surface equilibrium on an iron surface comprised a distribution of Fe–H, Fe–NH$_2$, Fe=NH, and Fe≡N, the corresponding Ni≡N not being formed under our experimental conditions. Thus, addition of nitrogen to a hydrogen-covered iron film, or of hydrogen to an atomic-nitrogen–covered film, caused a change of $\Delta\phi$ in the positive direction (cf. Fig. 3).

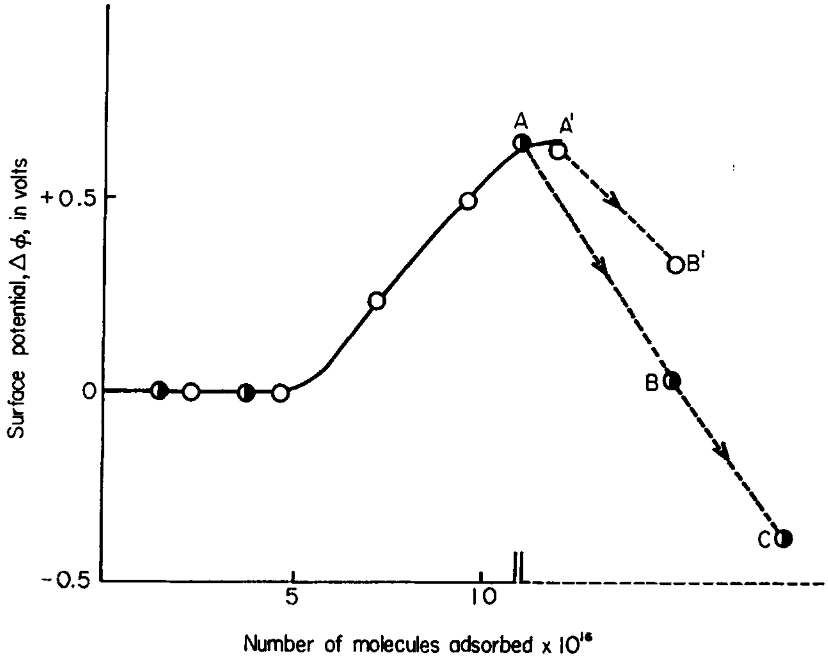


FIG. 4. Change of surface potential $\Delta\phi$ (volt) with amount of ammonia adsorbed (number of molecules × 10^{16}) at 20°C on two different iron films (○, ◑). Maximum $\Delta\phi$ of 0.65 volt drifted to B′ when system left isolated from pumps. For the second film, evacuation at 20°C gave B; on further heating to 130°C, point C obtained.

Again, when ammonia was adsorbed on a clean film at low coverages, the formation of the more highly dissociated forms was favored, but with increasing coverage the equilibrium was shifted to give Fe–NH$_2$ as the predominant species. This complex is, however, unstable at the higher temperatures, so that the equilibrium was changed to favor Fe=NH and Fe≡N as the main components, and there was simultaneous evolution of hydrogen; this reaction accounts for Kemball's observation that more hydrogen can be desorbed from an "NH_3-covered" iron film than corresponded to $Fe{=}NH_2$ as the sole remaining surface species.

Our results and conclusions are similar to those of Azuma (*16*) for the adsorption of N_2, H_2, and NH_3 on a W field emission tip. He deduces a $\Delta\phi$ value of -0.35 volt for a saturated $W{\equiv}N$ layer, and observes that the adsorption of NH_3 gives $\Delta\phi = +0.1$ volt which on heat treatment became negative when the tip was partially covered with N and H atoms (-0.5). He concludes that the activated step in the mixed adsorption (and in the ammonia synthesis) is the formation of $W{=}NH$ or $W{=}NH_2$ to which species he assigns a positive surface potential.

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