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LETTER TO THE EDITORS

The Nickel-Fluorine Reaction in the Presence of Xenon

It was reported by Baker and Lawson (*1*) that the attack of fluorine on both nickel and palladium foils was enhanced by the presence of xenon. This conclusion was reached after studying surface replicas of the metal fluorinated in the presence and absence of xenon. Baker and Lawson suggested that the phenomenon could be due to a rate-determining surface step of the type discussed by Ritchie and Hunt (*2*). The xenon, by forming a chemical bond with adsorbed fluorine, could perhaps speed up a step such as dissociation, and so accelerate the overall rate. This appeared to be an interesting possibility, and it was decided to test it by further experimentation. The best starting point seemed to be to determine the kinetics of the nickel–fluorine reaction with and without xenon. The kinetics have not been reported below 573 K, although Jarry *et al.* (*3*) have worked above this temperature. Since it is difficult to follow the kinetics of the reaction using manometric or gravimetric methods, the transparency method (*4*) was employed.

EXPERIMENTAL

Fluorine was generated by electrolysis, purified by passage through sodium fluoride and cold traps, and stored in a metal cylinder. It was admitted to the vacuum system through a liquid nitrogen trap and stored in a glass bulb. During admission to the system, a cold finger attached to the storage bulb was used to hold the fluorine at liquid nitrogen temperature, and so trap out any hydrogen fluoride.

Xenon was supplied in bulbs; the quoted purity was 99% with the balance being krypton. Nickel was in the form of 99.99% pure wire.

The vacuum system used was the one described by Baker and Lawson (*1*), although it was slightly modified for the kinetic experiments. The transparency method depends on the fact that as a thin evaporated nickel film reacts with fluorine to form the transparent fluoride, the absorbance of the film decreases and so provides a measure of the extent of reaction. The reaction cell contained two parallel pyrex windows, onto the inner surfaces of which the thin films were evaporated from two nickel coils. The cell could be introduced into the beam of a Hilger 'Spekker' spectrophotometer, and the absorbance of the films determined. Filters were used so that the light passed through the cell was principally of 500 nm wavelength. This wavelength was selected since a spectrum run on AR nickel fluoride showed no absorption between 300 and 850 nm.

Heating of the cell was effected by placing a large insulated glass tube around it, and passing heated air through the tube. The temperature of the cell was measured by a thermocouple in contact with it.

In carrying out an experiment, the nickel coils were spot-welded onto the tungsten leads, and annealed by heating them at below 6×10^{-3} N m^{-2} in an Edwards 12E6 Coating Unit. During the annealing process a small quantity of nickel was evaporated. The two nickel coil assemblies were glass blown onto the cell and the cell was attached to the vacuum system. Baking of the cell then continued at 573 K for 1–3 days to remove moisture, the final pressure being below 1×10^{-3} N m^{-2}. The nickel was outgassed, and the film deposited at 490 K, the maximum pressure during deposition being about 3×10^{-3} N m^{-2}. The film was then heated at 490 K for about 1 hr to reduce the possibility of any spurious transparency changes caused by restructuring of the film. Following adjustment of the temperature to 473 K, the fluorine or fluorine/xenon mixture was admitted and the run commenced. At the completion of each run the fluorine was disposed of by pumping it through a vessel containing mercury.

Results and Discussion

The method of operation of the 'Spekker' is such that the reading (A) obtained at a particular time (t) is actually the absorbance of the unreacted film, measured relative to the fluorinated film. It follows from Lambert's law that the absorbance is directly proportional to the thickness of metal consumed. Assuming that the nickel fluoride forms a uniform isotropic film, the absorbance is directly proportional to the thickness of nickel fluoride.

Some of the results at 473 K, in which A is plotted against time, are shown in Fig. 1. It is not unusual for the results of an oxidation reaction to be scattered in this way, largely because of the difficulty of reproducing evaporated films (*5*).

The results were plotted on a log–log scale, and yielded slopes of 2.6–5.3. The rate law could therefore range from almost parabolic to logarithmic. Jarry *et al.* (*3*) reported an approximately parabolic law between 573 and 873 K. Within experimental error, it is clear from Fig. 1 that the presence of xenon had little effect on the reaction rate. If anything, the rate was reduced rather than enhanced.

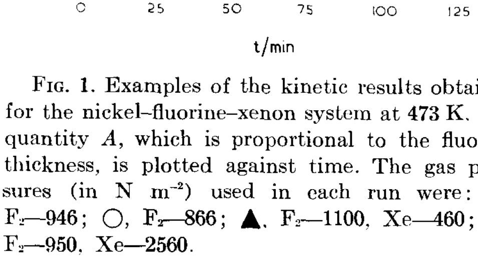

FIG. 1. Examples of the kinetic results obtained for the nickel–fluorine–xenon system at 473 K. The quantity A, which is proportional to the fluoride thickness, is plotted against time. The gas pressures (in N m^{-2}) used in each run were: ●, F_2—946; ○, F_2—866; ▲, F_2—1100, Xe—460; △, F_2—950, Xe—2560.

In view of Baker and Lawson's observations at 473 K (*1*), it is surprising that xenon did not affect the kinetics of the nickel–fluorine reaction. Replicas of the films failed to detect any roughened areas of the type found by Baker and Lawson. The appearance of the films was unchanged by the presence of xenon in the oxidizing atmosphere.

The solid reaction product which formed on the nickel surface was identified as NiF_2 by electron diffraction. Unfortunately, it was not possible to confirm that XeF_2 was formed in our experiments, and so we cannot be sure that the catalytic formation of XeF_2 was taking place over the evaporated films. The catalytic studies of Baker and Lawson were carried out using nickel foils. It is possible that the enhanced attack that they observed only takes place on a catalytically active surface.

Acknowledgments

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