**b. Apparent energy of activation and heat of $O_2$ adsorption.** The half-life values in Table 3 are normalized to a 1-$cm^2$ surface area. When the logarithm of the reciprocal half-life is plotted against the inverse temperature, an apparent activation energy of $30 \pm 2$ kcal/mole is obtained from the slope of this Arrhenius plot.

It is possible to obtain a value for the heat of oxygen adsorption by plotting the logarithm of $K_2$ values in Table 3 against the reciprocal of the temperature. An approximate value of $12 \pm 3$ kcal/mole is obtained from the slope of the Clausius-Clapeyron plot. This value obtained for heat of adsorption is consistent with the picture of an oxygen-poisoned surface where the heat of oxygen adsorption on a fully covered surface would be expected to be relatively low.

**c. Added oxygen.** Again a brief investigation of the effect of added oxygen on the reaction rate has been made. Added oxygen has been found to retard the reaction; this is evident in Table 2 where the half-life values are listed and found to increase with oxygen content. In order to determine if added oxygen has the same poisoning effect as product oxygen, the reaction rate data for the three runs listed in Table 2 have been plotted according to Eq. (4). According to this equation, the curves for the three runs should coincide. It has been found that within experimental error these curves do overlap. Thus, it has been concluded that added oxygen has the same poisoning effect as product oxygen.

An examination of the reaction rates for the decomposition on palladium and iridium and the previous work on platinum shows that the order of catalytic activity is Pd > Pt > Ir. This is in line with the other kinetics results where a comparison of rate equations indicates that oxygen is most strongly adsorbed on iridium and least effective on palladium. The poisoning by oxygen is intimately tied in with the ability of the metal to form stable metal oxide films plus the catalytic activity of that layer.

This characteristic is probably related to a common fundamental property of these metals but more work is needed to establish this assumption.

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# Surface Composition of Equilibrated Copper-Nickel Alloy Films

Previous work (*1–3*) on copper-nickel alloy films equilibrated at 200°C confirmed the existence of a wide miscibility gap at this temperature. In agreement with thermodynamic data an alloy phase I ($\approx$20 at. % Ni) coexists with a phase II ($\geqslant$95 at. % Ni). Moreover, evidence was found suggesting that for films prepared by subsequent vacuum deposition of the two metals, followed by sintering at 200°C, the crystallites of phase II tend to be enveloped by the alloy phase I. Consequently, the composition of the surface differs strongly from the average composition of the bulk and remains constant in a wide range of bulk compositions. Pronounced differences between surface and bulk were also assumed by Takeuchi (*4*) for granular copper-nickel alloys.

In the present note are reported selective chemisorption measurements carried out to determine the composition of the surface of copper-nickel alloy films. In addition, the catalytic activity for alloy films of various Cu:Ni ratios was measured, using benzene hydrogenation as the test reaction.

Nickel is known to chemisorb hydrogen strongly at room temperature, whereas hydrogen chemisorption on copper is negligible. Since the physisorption of xenon per unit surface area is equal for copper and nickel, it may be expected that the following ratio

$$\alpha = \frac{\text{number of H atoms adsorbed at saturation}}{\text{number of Xe atoms adsorbed at saturation}}$$

is indicative of the nickel content of an alloy surface. This statement is, however, only valid if chemisorption is indeed governed by the composition of the surface and not by some average bulk property such as the hypothetical number of holes in the *d* band calculated for the average overall composition.

The present measurements, therefore, should allow us to distinguish between these two concepts. If the surface composition governs hydrogen chemisorption, $\alpha$ should be equal for all alloys with equal surface composition, whereas $\alpha$ should vary with overall composition if the second model holds, which moreover predicts $\alpha$ to be zero for all diamagnetic alloys (0–40 at. % Ni).

Our results, which are shown in Fig. 1,

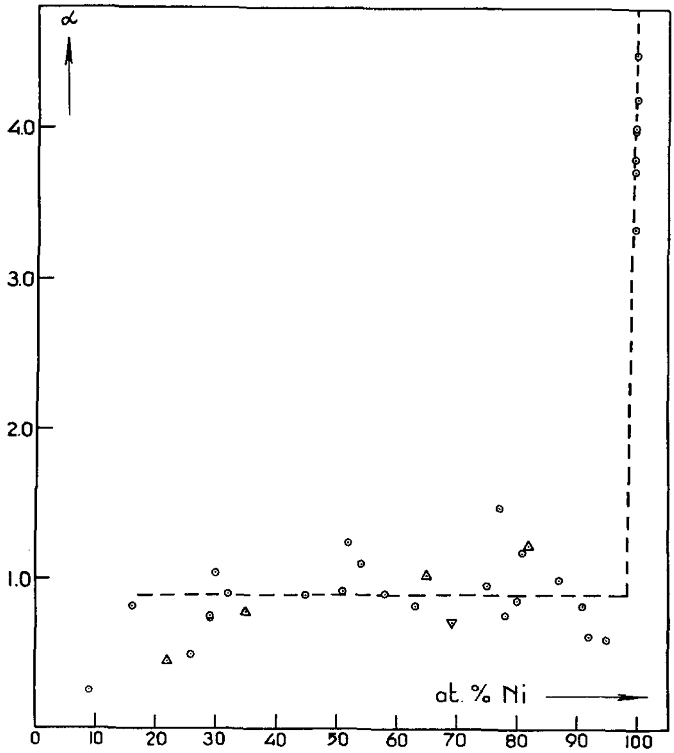

Fig. 1. Adsorption ratio as a function of film composition: ○, Ni deposited on top of Cu, films sintered at 200°C during 18 to 20 hrs; △, Cu deposited on top of Ni, films sintered at 200°C during 18 to 20 hours; ▽, Cu deposited on top of Ni, films sintered at 300°C during 14 hr.

clearly favor the first model. Although the points show a considerable scatter, $\alpha$ is independent of the overall Cu:Ni ratio for alloys containing 25–95 at. % of Ni. Furthermore, $\alpha$ is independent of the order in which the two metals are deposited. In these experiments the xenon monolayer adsorption at —196°C was determined by a manometric method. A Pirani gauge was used for dosing either gas. Hydrogen not adsorbed at room temperature, after a given portion of this gas had been admitted, was determined mass-spectrometrically using a MS 10 instrument. The hydrogen adsorption results were checked by a different method: After the surface had been saturated with hydrogen, a measured amount of deuterium was admitted to the cell and after equilibration the gas composition determined mass-spectrometrically. From the material balance the number of hydrogen atoms initially adsorbed on the film could be calculated. The results of the two methods were in satisfactory agreement. Various reasons can be given for the experimental scatter. We shall, however, not discuss them for the sake of brevity. Since the results show that $\alpha$ is typical of the surface composition, a more quantitative evaluation seems justified.

Assuming that hydrogen is adsorbed exclusively by nickel atoms, the nickel content $\gamma_{\mathrm{Ni,s}}$ of the adsorbing surface of any copper-nickel alloy film should be given by

$$\gamma_{\mathrm{Ni,s}} = \frac{\alpha \text{ alloy}}{\alpha \text{ nickel}}$$

For the alloys in the miscibility gap Fig. 1 shows that $\gamma_{\mathrm{Ni,s}} = 0.23 \pm 0.04$, which is in good agreement with the expectation that phase I forms the surface.

Typical results of catalytic experiments of benzene hydrogenation at 150°C are shown in Fig. 2, where the "activity pattern" is given, i.e., the rate per unit surface area is plotted versus the overall film composition. Under the conditions chosen the effect of self-poisoning due to formation of carbonaceous deposits is small, whereas under different reaction conditions self-poisoning may cause drastic changes in the activity pattern. In agreement with the adsorption results, the catalytic data show the following:

(1) The catalytic activity of the two-phase alloys seems to be independent of the composition except on the nickel-rich side of this region where the enveloping of phase II by phase I may be incomplete, because the quantity of phase I is very small.

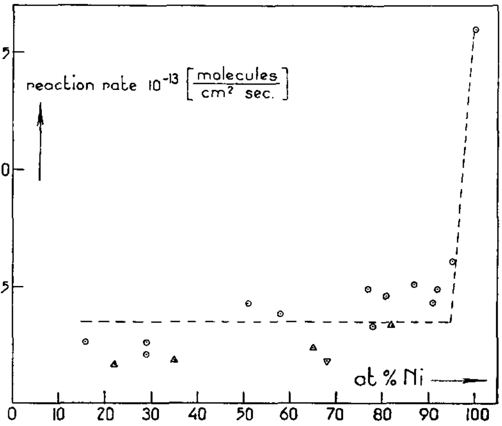

FIG. 2. Activity pattern for benzene hydrogenation at 150°C: $p_{\mathrm{H_2}} = 322$ torr, $p_{\mathrm{C_6H_6}} = 5.8$ torr. The symbols have the same meaning as in Fig. 1.

(2) The catalytic activity of sintered alloy films does not significantly depend on the order in which the two metals are deposited.

(3) The catalytic activity of the two-phase systems is a factor of roughly 4 or 5 lower than that of pure metals, which is in agreement with expectations for a catalyzing surface of alloy phase I.

(4) In the absence of self-poisoning, no maxima in the "activity pattern" are observed.

The present results seem to suggest that (a) the catalytic activity is as a first approximation proportional to the nickel concentration of the catalyzing surface $\gamma_{\mathrm{Ni,s}}$. (b) $\gamma_{\mathrm{Ni,s}}$ is for many films very different from the average Ni content of these films; (c) $\gamma_{\mathrm{Ni,s}}$ is equal to the value predicted by thermodynamic data and the assumption that in the two-phase system phase I prevails in the surface.

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