AN INVESTIGATION OF GAS-SOLID INTERACTIONS BY THE FLASH-FILAMENT TECHNIQUE

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ABSTRACT

The chemisorption of nitrogen and carbon monoxide on molybdenum and rhenium wires has been studied at room temperature and above. A flash-filament technique was used, in a conventional ultra-high vacuum system. Desorption kinetics have been examined by flash desorption and slow desorption.

It has been confirmed that on molybdenum nitrogen chemisorbs into one binding state. At room temperature the initial sticking probability, $\sigma_o = 0.27$ and the saturation coverage, $N_{sat} = 2.2 \times 10^{14}$ mol.cm^{-2}. These values both fall with increasing surface temperature. The desorption of nitrogen was found to follow a second order reaction, indicating dissociative adsorption, and the activation energy of desorption was found to be 60.5 kcal.mole^{-1}, independent of coverage. Carbon monoxide was found to dissociate on molybdenum at high temperature, in contrast to its behaviour on tungsten, leaving the surface contaminated. The surface could not then be cleaned by heat alone.

On rhenium, carbon monoxide was found to chemisorb into two main states, designated α and β. These have been tentatively associated with a linear- and a bridge-bonded form. The initial sticking probabilities were $\sigma_{o\alpha} \approx 0.14$, $\sigma_{o\beta} \approx 0.035$, $\sigma_{o(\alpha+\beta)} \approx 0.17$, and $N_{sat\,\alpha} \approx 3.3 \times 10^{14}$, $N_{sat\,\beta} \approx 1.2 \times 10^{14}$, $N_{sat(\alpha+\beta)} \approx 4.5 \times 10^{14}$ mol.cm^{-2}. This behaviour is in contrast to that on tungsten, for which the β state is more highly populated than the α. The behaviour is discussed in terms of the differences in atomic structure of the two metals. The activation energies of desorption were found to be

29 and 46 kcal.mole^{-1} for the α and β states respectively. A third state, γ, which became populated only at very high coverage had a desorption energy of 26 kcal.mole^{-1}. The desorption behaviour indicated a first order reaction, and hence non-dissociative adsorption. The desorption energies did not depend on coverage.

As expected from chemical evidence, nitrogen was found not to chemisorb appreciably on a clean rhenium surface.