RATE OF $^{14}\text{N}_2$ DESORPTION FROM THE SURFACES OF NITRIDES IN THE PRESENCE AND ABSENCE OF $^{15}\text{N}_2$ IN THE GAS PHASE

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The rates of $^{14}\text{N}_2$ desorption from the surfaces of nitrides have been measured in the presence and absence of $^{15}\text{N}_2$ in the gas phase. Whatever the adsorption heat and the form of surface species, the adsorption of $^{15}\text{N}_2$ molecules does not affect the rate of $^{14}\text{N}_2$ desorption.

INTRODUCTION

Occurrence of individual steps of catalytic reactions, in particular the adsorption of atoms and molecules, may be accompanied by noticeable energy evolution. This can lead to a non-equilibrium vibrational energy distribution of adsorbed molecules. The probability of such distribution is still an open question. Along with the assumptions supporting the existence of super-equilibrium distribution and, consequently, the acceleration of the reaction [1,2], there exists a view [3,4] that these phenomena are hardly probable and are of no practical significance.

From the experimental standpoint this problem seems to be most easily resolved by studying the adsorption interaction of...
molecules with the surface. The idea of the experiment is as follows. It is necessary to measure the rate of desorption in two cases: (i) \( W'_D \) is the rate of desorption in vacuum, i.e. under irreversible conditions, when the adsorption process and, thus, generation of excited particles can be neglected; and (ii) \( W_D \) is the rate of desorption of one isotope under reversible conditions, i.e. with the simultaneous occurrence of adsorption of another isotope.

If \( W'_D = W_D \), the energy evolved during the adsorption of the second isotope is not used to accelerate desorption of the first isotope. If \( W'_D < W_D \), the energy exchange affects the rate of desorption. It is necessary, however, to keep in mind a condition, which is methodically not easy to fulfill. In both cases the desorption rate measurements must be made at the same surface coverage, \( \theta \). This is especially important for inhomogeneous surfaces, because even a small decrease in \( \theta \), which is inevitable during \( W'_D \) measurements, may lead to a drastic inhibition of the desorption and, thus, to erroneous conclusions.

On the whole, the less sensitive the method, i.e. the higher the amount of surface particles that must desorb during \( W'_D \) measurements, the higher the probability to conclude that the equilibrium distribution is disturbed, whatever, the real mechanism is.

We believe that the methodical aspect and accumulation of reliable experimental data are of primary importance for the solution of this problem. It is of interest to establish reliably the events of conservation of the energy distribution and its distortion.

The attempts to clarify this problem as applied to adsorption-desorption processes have been made in a number of studies. For example, the authors of [5,7] studied the interaction of CO with Pt, Pd and Ru and found the desorption rate to depend upon CO pressure in the gas phase and to be much higher than the desorption rate in vacuum. However, these results are quite ambiguous because the analysis of the procedure indicates that desorption in vacuum occurs at far smaller sur-