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THERMODYNAMIC AND KINETIC PROPERTIES OF HYDROGEN ADSORPTION ON THIN IRON LAYERS

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Thermodynamic properties of hydrogen adsorption on iron layers evaporated under UHV conditions have been determined from calorimetric and volumetric measurements over the temperature range from 298 K to 363 K. Kinetic properties have been determined with the help of deconvolution of calorimetric curves and compared with the literature data on the sticking coefficient.

Keywords: calorimetry, hydrogen adsorption, kinetics, thermodynamics

Introduction

Calorimetry is an important technique for investigation of metal surfaces. It allows the determination of the differential heat of adsorption much more reliably than one can do with the use of any of the indirect methods. The differential heat of adsorption is a physical quantity most directly related to the energy of interactions in the adsorbed layer. Additional measurements of the equilibrium pressure in the gaseous phase as a function of surface coverage with the adsorbate makes it possible to determine basic thermodynamic properties of the adsorption system under investigation. On the other hand a continuous recording of the calorimetric signal in the form of thermoanalytical curves makes it possible to derive also some kinetic information, especially when the curves are submitted to the proper deconvolution procedure in order to reduce the effects of thermal inertia of the calorimetric vessel on the output signal [1].

The knowledge of the adsorption properties of the system Fe/H_2 is important in understanding many industrial processes involving hydrogen [2, 3]. The high chemical reactivity of iron requires to perform the adsorption measurements on surfaces prepared under ultra-high vacuum conditions. In a recent paper [4] we have presented results of measurements of differential heat of adsorption of hydrogen on thin iron layers evaporated under residual pressure of 30–40 nPa at a rate of about 2 nm/min to a thick-

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ness of approximately 100 nm. In the present communication we present in a more detailed form three adsorption isotherms for that system, the differential heat of adsorption presented as a function of degree of surface coverage, and the results of deconvolution analysis of calorimetric curves and their comparison with the kinetic information obtained from literature data on the sticking coefficient.

Experimental

The calorimetric system used in this study was described elsewhere [1, 5], thus only short description will be recalled. The calorimetric vessels of Beeck-type [6] mounted differentially are entirely made from Pyrex glass tubes. They consist of internal cylinders of 38 mm diameter. 100 mm length and thickness of the wall 0.1 mm mounted in external jackets of 60 mm diameter. On the outer surface of each inner vessel two Pt wires of 0.05 mm diameter are interwound. One of the windings is used as the calorimetric detector and the other as the calibration heater. The ultra-high vacuum is composed of three independent glass vacuum lines, each of them is based on two mercury diffusion pumps mounted in series and liquid nitrogen traps. The ultra-high vacuum conditions of a few nanopascals are obtained after repeated cycles of heating and cooling of the main part of the system, including the calorimetric vessels. The measurements of the ultra-high vacuum are realized with an ionization gauge, Groszkowski type with modulation, the high vacuum is measured by means of a standard Bayard-Alpert gauge. Spectroscopically pure hydrogen, purified additionally by diffusion through a palladium thimble, was collected in the calibrated volume between two spherical glass dosing valves. The pressure of the collected hydrogen was measured by a Mac Leod manometer. During evaporation the temperature of the calorimetric vessel was kept constant at the level of 220±5 K. After deposition the evaporated layers were annealed at 373±2 K.

Results and discussion

The pressures of hydrogen in the gaseous phase is equilibrium with the hydrogen adsorbed on iron layers as a function of the degree of surface coverage at three temperatures are presented in Fig. 1. The degree of surface coverage is expressed as a ratio of the number of hydrogen atoms adsorbed after each dose to the total number of surface iron atoms available on the deposited layer [4]. From Fig. 1 one can see that the maximal degree of surface coverage is 0.83 at 298 K, 0.64 at 323 K, and 0.61 at 363 K. With the use of the degree of surface coverage isotherms of the differential heat of adsorption at three temperatures are shown in Fig. 2. One can see that the initial heat of adsorption is independent of temperature in the limit of experimental error. The range of the surface where the heat of adsorption is practically constant and equal to the initial heat of adsorption is increasing with temperature. Most probably this behaviour is related to the existence on the iron surface more than one form of adsorbed hydrogen [1, 4, 7–10]. As the temperature is increased the weaker forms disappear. In Fig. 3 results of comparison maximal rates of heat evolution are presented during adsorption of hydrogen doses at various surface coverages obtained from deconvolution of calorimetric curves [1] and calculated from sticking coefficient data [4, 11]. The disagreement at low and middle coverages can be caused by damping of the calorimetric signal by thermal inertia, the deconvolution technique is not sufficiently effective for very fast input signals. Another

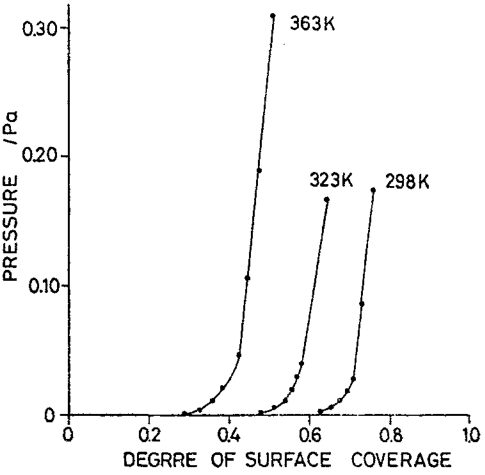

Fig. 1 Isotherms of hydrogen adsorption on evaporated iron layers

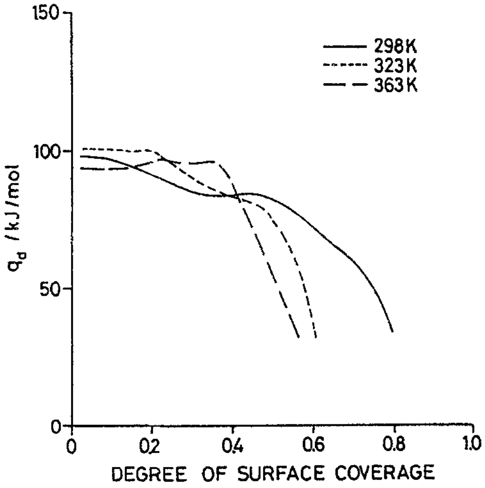

Fig. 2 Differential heat of adsorption of hydrogen on evaporated iron layers as a function of degree of surface coverage

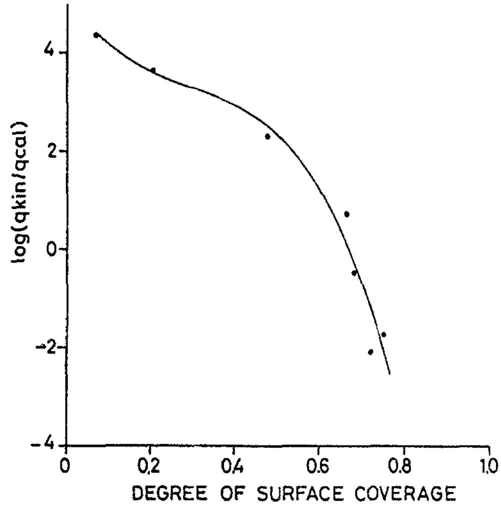

Fig. 3 A comparison of the maximal rates of heat evolution during adsorption of hydrogen doses at 298 K determined from kinetic data (qkin) [11] and from deconvolution of calorimetric curves (qcal) [1]

reason is that the rate of heat evolution determined from kinetic data is overestimated because the maximal pressure taken for calculations was determined from the number of molecules of hydrogen introduced to the reaction vessel and its volume. At high coverages the disagreement cannot be explained by metrological properties of the measuring techniques. The difference is probably related to the bulk properties of the deposited layer or its adsorption-induced reconstruction which could be detected by the calorimetric technique but could not be observed by surface potential measurements with the help of which the sticking coefficient data were collected.

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Zusammenfassung — Mittels kalorimetrischer und volumetrischer Messungen im Temperaturbereich von 298 bis 363 K wurden die thermodynamischen Eigenschaften der Wasserstoffadsorption an Eisenschichten untersucht. Die kinetischen Eigenschaften wurden mit Hilfe der Dekonvulotion kalorimetrischer Thermogramme ermittelt und mit Literaturangaben zum Haftkoeffizienten verglichen.