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Extensive measurements on the thermodynamic and kinetic properties of hydrogen in metals and metallic solid solutions both at high and low (>300 K) temperatures have shown that much of the previously existing data are in error due to the use of "pure" metal samples containing concentrations of interstitial or substitutional impurity elements higher than that of the species being studied.
In general the behavior of H in "defect" solids can be understood in terms of simple models in which the distribution of the H-atoms between "normal" lattice sites and low-energy trapping sites is a Fermi-Dirac function. At high temperatures its Boltzmannian approximation is adequate.
FINAL REPORT

THERMODYNAMICS AND KINETIC PROPERTIES
OF INTERSTITIAL SOLID SOLUTIONS
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by

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1) STATEMENT OF PROBLEM

The central problem in this work centers around the behavior of interstitial atoms in metals, metallic solid solutions, and "defect" solids in general. The core theme is the interaction between interstitial atoms and lattice discontinuities in the form of foreign atoms (substitutional or interstitial) and/or such mechanical discontinuities as lattice vacancies and low-energy traps related to dislocations. The manifestations of such interactions upon the thermodynamics and kinetic properties of interstitial solutes, principally hydrogen atoms, have been investigated by making thermodynamic and diffusivity measurements.
BRIEF OUTLINE OF RESEARCH FINDINGS

Much of the work performed during this reporting session has centered on the kinetic properties of hydrogen in metals. Diffusion coefficients D for hydrogen in silver, platinum and palladium as a function of temperature have been measured using the time-lag permeability method.

In the case of silver D in the range 974-1123K is given by the relation:

$$D = (8.55 \pm 0.65) \times 10^{-7} \exp \left( -\frac{(3.62 \pm 0.40) \times 10^3}{T} \right) \text{m}^2/\text{sec}.$$ 

In the case of Pd, the diffusivities were measured in the T-range 769-1219K. This temperature range extends through the high-temperature range in which the only previous data (those of Gol'tzov, et al., Fiz. metal metalloved, 29, 1305, (1970)) had revealed a large positive deviation from Arrhenius behavior. This investigation showed no such anomaly and ln D vs. 1/T was linear in the entire T-range. The diffusivity can be described by:

$$D = (2.83 \pm 0.15) \times 10^7 \exp \left( -\frac{(10.93 \pm 0.65) \times 10^3}{T} \right) \text{m}^2/\text{sec}.$$ 

Despite the importance of platinum as an electrode material, no D-measurements had been made above 890K. The present measurements in the range 831-1236K showed no diffusion anomalies and resulted in the representational equation:

$$D + (6.47 \pm 1.73) \times 10^{-7} \exp \left( -\frac{(13.24 \pm 1.16) \times 10^3}{T} \right) \text{m}^2/\text{sec}.$$ 

In the thermodynamic studies, a careful investigation of the energy of solution of H-atoms $\tilde{H}_1$ in Mo-Nb-H ternary solutions spanning the entire composition range from pure Mo to pure Nb shows that $\tilde{H}_1$ varies linearly with the Nb-concentration despite the large extremum in the density-of-states curve. This behavior is in stark contrast to the predictions of the screened proton model for metal-hydrogen systems.
Theoretical work has been done on the effects of trapping sites, either foreign substitutional atoms or lattice discontinuities. An experimental system, based upon EMF measurements, has been constructed which enables the H-diffusivity in Pd-X films to be measured at low temperatures (300-400K). Condensation at trapping sites becomes critical at such temperatures. The apparatus has been used successfully to study H-diffusion in Pd-Ag, Pd-Au, and Pd-Cu membranes in the temperature region specified.

The work on H-trapping as revealed by H-measurements may be summarized as follows:

(a) Hydrogen trapping in iron

It is well-known that the diffusivity of hydrogen in iron drops by several orders of magnitude in the narrow temperature range 300-340K. This phenomenon has been explained by H-trapping at sites in the Fe lattice of depth $\Delta \varepsilon \approx 60$ kJ/mol and density $\phi = 8.5 \times 10^{20}$ m$^{-3}$. The H-atoms are in local equilibrium in a given infinitesimally small volume in the diffusion gradient. The distribution of H-atoms between "normal" and "defect" sites is a modified Fermi-Dirac function. It has been shown that $\lambda$ the ratio of the diffusivities in the defect crystal (containing traps), and a perfect (trap-free) crystal is given by

$$\lambda = \left[ \frac{x}{(\phi + x)} \right]^2$$

where $x = \exp \left( -\frac{\Delta \varepsilon}{kT} \right)$.

(b) Effect of Substitutional Solutes on H-diffusivity

Case 1 (Trapping) - In this case the substitutional (u) atoms create sites which act as traps for H-atoms. Equations have been developed on the basis of microscopic reversibility theory which are in good accord with the severe reduction in H-mobility observed.

Case 2 (Anti-trapping) - In this case the U-atoms create sites in which H-atoms have a higher energy than these in "normal" unperturbed interstitial sites. This is the situation for noble metal atoms dissolved in palladium. A theory based on the absolute rate considerations shows, as found experimentally, that even up to high U-atom concentrations, antitraps have virtually no effect on H-mobility provided the traps are "high" enough.

In addition to the above two cases a theoretical approach to the effect of lattice dilation or contraction due to the addition of U-atoms has been made.
New work has been performed in which elements belonging to the Group V of the Periodic Table have been used as the doping elements in Pd. The substitutional elements Ti and V were used in an initial series of diffusivity measurements.

In all cases, the diffusivities obeyed the Arrhenius relation. Both Ti and V atoms create trapping sites for hydrogen and the mobility of hydrogen decreases as the concentration of substitutional solute increases. However, the trapping sites are shallow in comparison to trapping sites created by dislocations and the thermodynamic and kinetic properties of the system can be described adequately by using classical Boltzmann statistics.

The diffusivity measurements on Pd-Ti and Pd-V alloys were carried out with the express purpose of detecting a Fermi condensation of the H-atoms at low temperatures. The shallowness of the trapping sites was surprising.

The diffusivity measuring system has been modified so that D-values can be determined at temperatures low enough to enable condensation and the concomitant drastic decrease in mobility to be observed.

In other theoretical work it has been shown that the diffusivity of H in deformed palladium provides an ideal system for the study of Fermi condensations of H-atoms. Recent (R. Kirchheim, *Scripta Metall.*, 14, 905 (1980)) measurements of the diffusivity of H in deformed Pd at 295K show a drastic decrease in H-diffusivity D at hydrogen-metal ratio of \( \Theta_1 \approx 10^{-4} \). At high concentrations the D values are constant. This behavior has been shown to be consistent with a density of \( 10^{-5} \) traps/lattice atom of depth \( \sim \) kJ/mol.

Work has been performed on the diffusivity and permeability of hydrogen in molybdenum using the time-lag method employing molybdenum membranes prepared by electron beam melting and cleaned by argon ion
etching. Measurements were also made on membranes prepared in this manner and subsequently coated with palladium. This combination of techniques has allowed previous inconsistencies connected with the presence of oxide films to be clarified.

The diffusivity is given by:

\[ \ln D (\text{m}^2/\text{sec}) = -17.547 \pm 0.0684 + \frac{(1.266 \pm 0.0688) \times 10^3}{T} \]

The solubility (premeability/diffusivity) \( \theta \) is:

\[ \ln \theta \left( \frac{\text{mol H}_2}{\text{m}^3 \text{MPa}} \right) = \ln \frac{\phi}{D} = 8.703 - \frac{7.863 \times 10^3}{T} \]
The publications ensuing from this work are listed in the following compilation:


