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H–D ISOTOPIC EQUILIBRIUM IN THE SYSTEM GASEOUS HYDROGEN–SOLUTION OF HYDROGEN IN PALLADIUM

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To determine the separation factor for the hydrogen isotopes H and D in the segregation taking place between free hydrogen and hydrogen dissolved in palladium, we employed the single-stage separation effect under static conditions. After equilibration, the isotopic composition of gaseous hydrogen was determined†. The hydrogen was then evacuated to a residual pressure of several millimeters and then the hydrogen dissolved in palladium was desorbed by raising the temperature to 180–200°C and its isotopic composition determined. The separation factor was found from the concentrations of deuterium and hydrogen in both phases. The isotopic composition was determined by the measurement of thermal conductivity using TSh-1 thermistors as detectors. This analytical method requires thorough purification of the hydrogen. Oxygen was removed over reduced chrome–nickel catalysts at 160–180°C. Hydrogen was then passed through silica gel columns and a trap immersed in liquid nitrogen to eliminate moisture. Nitrogen was removed by low-temperature sorption on activated carbon. Hydrogen containing 10% of deuterium was used. The experiments yielded the temperature variation of the separation factor over the range between -187° and 120°C (Fig. 1). In the range between -20° and 120°C the temperature variation of the separation factor α can be represented by the equation $\log \alpha = -0.50 + 226/T$. Our values in the above temperature range agree with the results in Ref. 1, where the separation factor was determined in a chromatographic column with mass-spectrometric isotopic analysis. Thomas and Smith[2] obtained somewhat smaller values

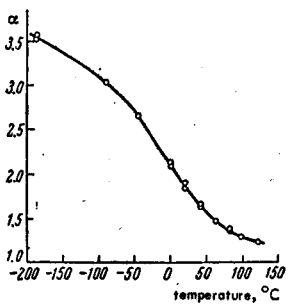


Fig. 1. Temperature dependence of the separation factor α.

† The time required for equilibration (several hours) was determined in preliminary experiments.

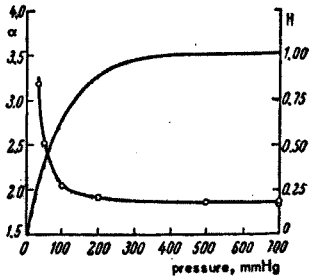


Fig. 2. Dependence of the separation factor α and the relative capacity of palladium with respect to hydrogen on the pressure of the gas at 20°C.

of α at 80° and 100°C using a chromatographic procedure with isotopic analysis by the thermal conductivity method. In the temperature range between -20° and 120°C the capacity of palladium with respect to hydrogen is virtually constant but at low temperatures the extent of sorption of hydrogen greatly increases: at 80°K it is three times as great as at room temperature. We also investigated the variation of the separation factor with pressure in the range between 35 and 700 mmHg at 20°C using the same experimental technique. The results are presented in Fig. 2, which also shows the variation of the solubility of hydrogen in palladium with pressure. The change in solubility was calculated from the material balance equation on the basis of measurements of the equilibrium concentrations of deuterium in both phases and in the initial hydrogen. At constant solubility of hydrogen in palladium the separation factor remains unchanged. When the solubility falls, the separation factor greatly increases.

SUMMARY

1. A study has been made of the temperature variation of the separation factor for the hydrogen isotopes (H and D) in the equilibrium between molecular hydrogen and hydrogen dissolved in palladium. Between 20° and 120°C the heat of isotope exchange is 1080 cal g-atom^{-1}. The heat of reaction falls greatly as the temperature is reduced.
2. Investigation of the pressure dependence of the separation factor showed that the latter increases sharply as the pressure falls.

1. "Proceedings of the International Symposium on Isotope Separation", North Holland Publ. Co., Amsterdam, 1958.
2. C. O. Thomas and H. Smith, J. Phys. Chem., 63, 427 (1959).

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