Isotope Effects in Palladium-Hydrogen Systems

THE CONCENTRATION OF DEUTERIUM AND TRITIUM

Palladium dissolves the isotopes of hydrogen in a selective manner and can be used, therefore, to facilitate separation and concentration processes. Although simple absorption techniques permit high separation factors under equilibrium conditions, no satisfactory counter-current process capable of separation by absorption has yet been developed. Better results are obtained by using the electrolytic diffusion technique which allows kinetic separation factors to operate. These effects are discussed in the summary below which is based on a paper presented by Professor E. Wicke of the University of Münster to a Symposium held in the Chemistry Department of Queen's University, Belfast on "The Formation and Reduction of Surface Oxides, and Processes of Hydrogen Discharge and Exchange at Noble and Quasi-noble Metal Surfaces".

Electrolytic processes for the separation and concentration of hydrogen isotopes utilise the fact that the mixed water molecule HDO is more stable than H_2O, with the result that deuterium is concentrated in the liquid phase. The ratio of the equilibrium concentrations of deuterium set up between water and the mixed light and heavy diatomic molecules in the gas phase has been measured as 3.5 (1). Since the vapour pressure ratio is 1.07, the enrichment ratio between liquid and the gas works out as approximately 3.7 at room temperature. This ratio is obtained when water is electrolysed under equilibrium conditions.

The exchange equilibrium set up between the gas phase and palladium depends very much upon the concentration of gas dissolved in the metal. Differences in the equilibrium pressures of the isotopes increase with the amount of gas dissolved in the palladium. In the β solid solution the pressure ratio at 25°C is 6:1 for deuterium relative to hydrogen (2) and about 10:1 for tritium relative to hydrogen (3). In the dilute α solid solution, however, the equivalent value for deuterium relative to hydrogen is only 4:1 (2).

Relative to hydrogen, the low solubility of deuterium in palladium is shown in Fig. 1. Here the hydrogen/deuterium separation factors range from 2.4 at 25°C to 3.7 at −80°C. Measurements by Sicking (3) have
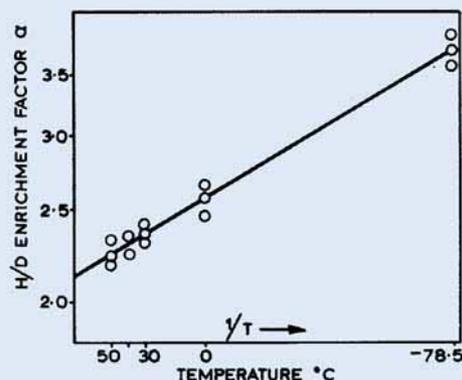

Fig. 1 Effect of temperature upon the equilibrium separation factor of hydrogen and deuterium between the gas phase and palladium (after Wicke and Nernst (2)). Relative to the concentration ratios which exist in the gas phase, hydrogen dissolved in the palladium is enriched by ratios ranging from 2.4 at 25°C to 3.7 at −80°C
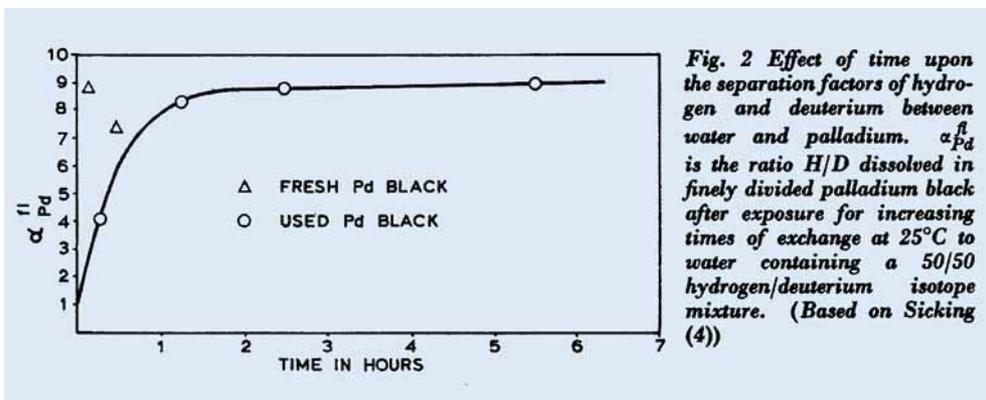
Fig. 2 Effect of time upon the separation factors of hydrogen and deuterium between water and palladium. α^{fl}_{Pd} is the ratio H/D dissolved in finely divided palladium black after exposure for increasing times of exchange at 25°C to water containing a 50/50 hydrogen/deuterium isotope mixture. (Based on Sicking (4))

recently shown a value of 2.8 for the hydrogen/tritium ratio at 25°C.

By combining the water-gas partition coefficient with that which is set up between gas and the palladium electrode, a separation factor for hydrogen/deuterium of $3.7 \times 2.4 = \sim9$, is arrived at. For hydrogen/tritium a value between 12 and 15 would be expected.

Absorption Processes

These unusually high separation factors are those predicted from the results of gas/water and gas/palladium equilibrium studies considered in isolation. It is, therefore, of interest to compare them with experimentally obtained water/palladium separation factors.

Determinations of this type by Sicking (4), Farkas (5) and others (6, 7, 8) have yielded equilibrium ratios for the hydrogen/deuterium concentrations ranging from 3 to 8.

The main experimental difficulty is that of obtaining true equilibrium and to facilitate this Sicking used finely divided palladium black. This he saturated with deuterium from the gas phase at one atmosphere and equilibriated the solid solution thus obtained with water containing equal quantities of hydrogen and deuterium. The results obtained are summarised in Fig. 2 which shows that 90 per cent of the deuterium originally dissolved in the metal is exchanged for hydrogen, and that only 10 per cent of the hydrogen originally present in the palladium remains in equilibrium with the 50/50 aqueous isotope mixture.

The prospect of developing isotope concentration processes which can utilise this powerful separation effect is, therefore, very attractive. Severe problems are encountered, however, in arranging the counter-current flow of solid and liquid phases which are required for the operation of such processes on a continuous basis. An effective continuous separation process based on the direct absorption method has not yet been developed.

Diffusion Processes

Deuterium diffuses through palladium more rapidly than hydrogen, and Bohmholdt (9) has shown that at room temperature $D_H/D_D = 0.7$.

This inverse isotope effect is caused by differences in the activation energies involved. That which governs the rate of diffusion of hydrogen through palladium is 5.8, the corresponding value for deuterium being 5.3 kcal/g atom. Under ordinary diffusion conditions, however, palladium membranes separate hydrogen preferentially from its isotopes. The total hydrogen flow is greater because palladium dissolves hydrogen preferentially and the higher concentration gradients thus built up outweigh the higher mobility of individual deuterium atoms. From the known solubility data on hydrogen and deuterium and the D_H/D_D ratio of 0.7 mentioned above, kinetic separation factors of about 1.7 at 25°C would be expected.

Such isotope separation effects are conveniently studied by using tubular palladium electrodes which function as either anodes or cathodes. Under anodic conditions the isotope mixture can be fed in gaseous form to the interior of the electrode. Gibmeier (11, 12) has shown that the anodic separation factor S_A is about 1.6, in good agreement with the diffusion separation factor S_D of 1.7 mentioned above. This factor is virtually independent of temperature.

At the cathode, however, a rather more complicated situation exists. The water/gas separation factor presents an additional stage in the concentration process and a kinetic separation factor S_K of $3.7 \times 1.6 = \sim 6$ would be expected at 25°C. As shown by Fig. 3, however, the experimental values are not only higher than those predicted, but are also exceedingly temperature sensitive. This behaviour was interpreted by Professor Wicke in terms of the isotope exchange effects known to occur (7) during dehydration and discharging processes at electrode surfaces.

At the same symposium in Belfast, Dr. R. V. Bucur (Institute for Stable Isotopes, Cluj, Romania) reported results of studies with several metals, including platinum, palladium and palladium alloys, of the presence of oxygen in either a physically or chemically sorbed form on the electrolytic separation factor for hydrogen and deuterium.

Dr. H. J. Bauer (University of Munich) reported the development of magnetic measurements of high precision which seemed likely to give valuable information on the form of the chemical binding in hydrided electrodes.
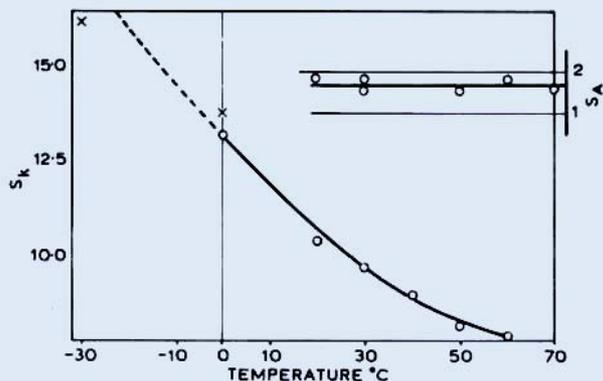

Fig. 3 Kinetic H/D separation factors S_K and S_A at tubular palladium cathodes and anodes plotted as a function of temperature (after Gibmeier (12)). At the anode the mixed isotopes can pass from the gas phase into the metal without restraint, and the separation factor S_A is approximately 1.6 and is unaffected by temperature. At the cathode, however, the additional water/gas separation stage must be accomplished before the mixed isotopes can enter the palladium. The hydrogen/deuterium separation factor S_K is higher than S_A and is very temperature sensitive

Other contributors to the symposium were as follows: Dr. A. S. Darling (Johnson Matthey), Dr. L. D. Burke (University College, Cork), Dr. C. Hinnen (C.N.R.S., Paris), G. Hodes (Queen's University, Belfast), Prof. B. Baranowski (Polish Academy of Sciences), R. C. Johnston (Queen's University, Belfast).

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