ORTHOPARA AND ISOTOPE SEPARATIONS BY PREFERENTIAL ADSORPTION AT LOW TEMPERATURES

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SUMMARY

Although the catalysed conversion of ortho- to para-hydrogen has been known for many years, the separation of the two species by adsorption at low temperatures is a much more recent discovery. The separation of the spin species was first clearly recognized by Sandler during a study of hydrogen adsorption, at 90°K, on rutile and charcoal. The difference in extent of adsorption of ortho- and para-hydrogen was attributed to such strong hindrance of rotation of adsorbed hydrogen that one degree of rotational freedom is lost. A much more extreme example of the strong preferential adsorption of ortho-hydrogen at 20.4°K was encountered by Cunningham and Johnston during the course of a study of the rate of conversion of ortho- to para-hydrogen by paramagnetic salts adsorbed on an inert support of finely divided alumina. The conversion rate was found to be nearly independent of the ortho–para composition of the liquid hydrogen mixture in contact with the catalyst. This suggested that the catalyst surface was almost completely covered with ortho-hydrogen. A detailed analysis led to an ortho–para separation factor of 16 ± 3 at 20.4°K. That ortho-hydrogen is preferentially adsorbed was established conclusively by Cunningham, Chapin and Johnston as the result of experiments in which nearly pure ortho-hydrogen was prepared by successive adsorption and desorption on alumina in the absence of a paramagnetic salt. Para-deuterium was also separated by the same method. For both hydrogen and deuterium, molecules in the rotational state \( J = 1 \) are most strongly adsorbed. Separation of ortho- and para-hydrogen has also been observed by Moore and Ward using the method of gas chromatography.

Recent adsorption experiments in this laboratory using \( \gamma \)-alumina free of paramagnetic materials have confirmed the magnitude of ortho–para separation factors suggested in the work of Johnston et al. These have been found to be dependent on surface coverage, so a single value cannot be given. However, they fall in the range 6–13 for hydrogen and 1.8–3.0 for deuterium. It has also been found that the hydrogen isotopes, deuterium-hydrogen, can be separated by preferential adsorption with separation factors ranging from 5 to 200, depending on surface coverage. In addition, it has been observed that the magnitude of the isotope separation depends on the ortho–para concentration of each of the hydrogen isotopes undergoing separation.

The above experimental results have been accounted for by White and Lassettre in a recent article in which a theory is developed by considering...
the energy levels of a three-dimensional rotator. The Schroedinger equation for an adsorbed molecule on a plane surface has been solved for several simplified potential fields, leading to rotational and vibrational energies as functions of barrier height. The calculated separation factors, both ortho–para and isotope, are not in accurate quantitative agreement with the experimental results at a fixed surface coverage. However, the theory does predict all the effects observed to date, namely,

(1) molecules in the rotational state $J = 1$ (ortho-hydrogen, para-deuterium) are more strongly adsorbed than molecules in the ground state;

(2) predicted isotope separation factors are strongly dependent on the ortho–para composition of the isotope mixture.

Both the experimental and theoretical investigations are continuing in this laboratory in order to further elucidate the nature of the interactions of diatomic molecules, both heteronuclear and homonuclear, with surfaces.

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References