

of output is observed by purging the cell with nitrogen and blowing hot filtered air through it in place of the usual feed-gas while the cell is at operating temperature.

Applications

Diffusion cells have three potential fields of application:

- (1) As a means of purification to ultra-pure standards of hydrogen obtained from cylinders or other sources. In this instance the ultra-pure hydrogen is required for specialised applications, as for example in the heat-treatment of stainless steels or other metallurgical processes, or in the semiconductor or chemical industries.
- (2) As a means of obtaining pure hydrogen from a cheap but low-grade hydrogen-containing gas, for example cracked

ammonia, hydrocarbon reformer gas, petroleum reformat streams or other industrial process gases.

- (3) As a means of removing unwanted hydrogen from process gases.

In all these applications the diffusion process offers substantial advantages over some other possible systems, in that the cells are very compact and robust, require little attention and have a reclaim value on account of their palladium alloy content.

References

- 1 Atlantic Refining Company, U.S. Patent 2,773,561
- 2 J. B. Hunter, *Platinum Metals Rev.*, 1960, 4, 130
- 3 Atlantic Refining Company and J. Bishop & Co., U.S. Patent 2,961,062
- 4 *Platinum Metals Rev.*, 1962, 6, 47-48
- 5 A. S. Darling, *Platinum Metals Rev.*, 1958, 2, 16-22
- 6 Johnson, Matthey & Co., Limited, British Patent 825,973

Rhodium as a Polymerisation Catalyst

FURTHER STUDIES ON POLYBUTADIENE PREPARATION

The use of aqueous solutions of rhodium salts as stereo-specific catalysts in the polymerisation of 1, 4 butadiene has recently been reported by the research laboratories of the United States Rubber Company. This development may make possible the large-scale production of *cis*-polybutadiene by the commonly-used technique of emulsion-polymerisation.

Further aspects of this work have now been reported from the laboratories of the Shell Development Company, Emeryville, U.S.A., by A. J. Canale, W. A. Hewett, T. M. Shryne and E. A. Youngman (*Chem. & Ind.*, 1962, (24), 1054). These workers demonstrated that, in addition to *trans*-1, 4 polymerisation of butadiene possible with Rh^{3+} salts, a much broader steric control over such polymerisations is possible with other ions and complex compounds of the platinum group metals. Under the polymerisation conditions studied, for example, almost complete *trans*-1, 4 additions were obtained using rhodium trichloride, cyclo-octadiene rhodium chloride and iridium trichloride as catalysts. Palla-

dium, in the form of palladium chloride or ammonium chlorpalladate, gave high proportions of 1, 2 polymerisations but the polymers had low molecular weights. One of the highest proportions of *cis*-1, 4 additions obtained resulted from the use of ruthenium trichloride with triphenyl phosphine or tri-*n*-butyl phosphine. Cobalt catalysed polymerisations, however, yielded the highest proportion of *cis*-1, 4 polymers, and also gave the highest molecular weights.

The fact that certain compounds that normally inhibit the "classical" free radical polymerisations had no effect on the reaction studied indicates that a completely different mechanism is operative in these instances. While no specific mechanisms have been suggested to date, it is clear that the ligands, the nature of the transition metal ions and their valency states exert powerful influences on the steric course of the polymerisation, its rate and the molecular weight of the products. It is postulated that the transition metal hydride may play a part in the initiation of some polymerisations.