

Fugacity of Hydrogen in Gas Mixtures

THE USE OF SILVER-PALLADIUM MEMBRANES

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A 25 per cent silver-palladium membrane has been successfully used in this laboratory (1, 5, 6) to directly determine the fugacities of hydrogen in hydrogen-containing fluid mixtures. This application depends on the fact that this alloy is permeable only to hydrogen and has been commercially used to prepare ultra-high purity hydrogen. Some information is available on various aspects of the diffusion of hydrogen through silver-palladium alloy membranes. This includes the effects of temperature, pressure (2) and water vapours (7) on the diffusion rate, solubility of hydrogen in palladium alloys (4, 8), maintenance of dimensional stability (3), and fabrication techniques (1).

In the present series of investigations pure hydrogen is maintained on one side of the membrane and on the other side is a mixture containing hydrogen. At equilibrium through equality of chemical potentials, the fugacity of pure hydrogen at the temperature and equilibrium pure hydrogen pressure is equal to the fugacity of hydrogen at the same temperature and equilibrium mixture pressure and composition. The fugacity of the pure hydrogen can be readily and accurately calculated from the P-V-T data on hydrogen. The technique therefore provides a powerful tool to directly determine fugacities of hydrogen as a component in a mixture without having to determine the partial molar volumes (a laborious and tedious way) and also serves as a means of evaluating the various predictive methods such as the equations of state as applied to mixtures.

The equipment consists of the palladium-silver membrane, which is in the form of a

coil made of 40 feet of 25 per cent silver-palladium tubing, 0.063 in. o.d. and 0.003 in. wall. This coil is located inside a high pressure vessel which is maintained at constant temperature by an oil bath. The coil is brazed with a short piece of nickel tube ($\frac{3}{16}$ in. o.d.) at one end and sealed at the other. The nickel tube is connected by a swage-lock fitting to a stainless steel fitting welded to a stainless steel manifold plate. The manifold plate closes the mouth of the pressure vessel which is equipped with a suitable enclosure cap and gaskets to ensure a leak-proof closure. The system has provisions for evacuating, charging gases to either side of the membrane separately and for sampling for analysis. This cell is kept at constant uniform temperature and the pressures on two sides of the membrane are measured separately by a standard dead weight piston gauge assembly provided with diaphragm null pressure indicators.

The studies made so far include determination of fugacities of hydrogen in the hydrogen-propane system (1, 5) up to 138°C and a mixture pressure of 2500 p.s.i.a., the hydrogen-butane system in the single phase (5) and two phase (6) regions and the hydrogen-propane-butane ternary system (5). In the study of the vapour-liquid system it is important to note that at equilibrium the fugacity of pure hydrogen in the tube is equal to the fugacity of the hydrogen in both the liquid and the vapour mixtures.

In conclusion, we evaluate the vapour and the liquid phase thermodynamic properties by directly measuring the fugacity of hydrogen in the hydrogen-hydrocarbon mixtures. We

do this by using a silver-palladium membrane permeable only to hydrogen.

References

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Organometallic Compounds as Reagents in Organic Synthesis

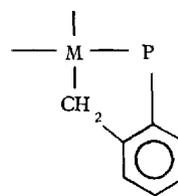
PAPERS AT THE CHEMICAL SOCIETY MEETING

One symposium during the Joint Annual Meeting of the Royal Institute of Chemistry and the Chemical Society held at the University of Sussex was devoted to organometallic compounds as reagents in organic synthesis. An increasing number of research groups is studying the reactivity of coordinated organo-ligands. During this meeting subjects ranged from the industrial use of organometallic complexes as catalysts in the production of organic compounds to simple stoichiometric reactions involving similar reagents. The bulk of this work was concerned with complexes of the transition metals.

Among the papers concerned with the platinum metals, B. L. Shaw (University of Leeds) concisely reviewed the metallation of C-H bonds, particularly of the type:



Q=P or N donor, i.e. a donor ligand which contains an "active" hydrogen. Several examples are known and in all these complexes the ligand functions as a chelate, bonding through both the donor atom (P or N) and a M-C σ -bond. Shaw has been examining systems centred on P atoms, where the tendency to form the M-C bond is enhanced by having bulky substituents on P. The best group to undergo metallation is the *o*-tolyl group illustrated. The facility with which such reactions proceed falls in the order *o*-tolyl > *p*-tolyl > phenyl > *n*-propyl



and for the other ligands on the metal as Me > I > Br > Cl.

D. Clark (Imperial Chemical Industries HOC Division) gave an explicit account of the problems encountered in the vinyl acetate process involving palladium-copper catalysts. He recounted much of the current thought behind the process and described the effect of trace amounts of Cl⁻ on the chemistry involved. In passing he mentioned that Pd^I had been observed although the precise nature of the derivative was not considered.

R. F. Heck (Hercules Inc., Wilmington) gave a most impressive account of the variety of arylation, alkylation, and carbo-alkoxylation reactions that may be carried out with organo-palladium compounds. Essentially he was concerned with the reactivity of the highly active species (RPdX) and the substitutions that may be carried out at unsaturated carbon atoms using this reagent. Many reactions depending on R and the substituents on C=C were described. High yields of olefins are reported (75 per cent). If CuCl₂ is present Pd⁰ is reoxidised to Pd^{II}; hence reactions may be catalytic in palladium.

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