A Hydrogen Singing-flame Ionization Detector

THE sensitivity of an ordinary hydrogen flame ionization detector to hydrocarbons has been found to be two to three times higher when the detector flame 'whistles' or 'sings'. Further investigation of this phenomenon has disclosed the probable reasons for the enhanced sensitivity and has uncovered other useful characteristics of the singing-flame detector. 'Singing' hydrogen diffusion flames were first noted more than 160 years ago¹, shortly after the discovery of hydrogen. A number of investigators^{2,3} have since investigated the characteristics of such flames; however, no practical application of this unusual phenomenon appears to have been made.

A drawing of a hydrogen flame ionization detector of the type used in the present investigation is given in ref. 4. However, the rod electrode was replaced by a cylindrical platinum gauze electrode surrounding the burner tip in order to improve the ion-collection efficiency. Sample gases containing known concentrations of propane in nitrogen were used for calibration. With the optimum hydrogen and air flow rates, the ionization detector in both the singing and quiescent stages gave a linear response up to at least 15,000 p.p.m. propane in nitrogen. However, the ion current from the singing flame was 2.7 times higher than with the normal detector flame over the entire range of propane concentrations.

Of primary interest is the reason for the greatly enhanced sensitivity of the detector when resonating. Time exposure photographs of our detector flame showed it to be spherical when quiescent and elongated when singing. In 1866, Töpler⁵, using stroboscopic methods, found that the singing hydrogen diffusion flame was, in fact, an oscillating flame. Drawings of his observations are given by Gaydon and Wolfhard⁶. In brief, Töpler's work showed that each oscillation was caused by a small flame at the burner orifice growing into a tongue of flame which separates from the burner tip and burns out; a small flame remains in the burner orifice for the next cycle. The output from our singing-flame detector was shown on a cathode ray oscilloscope to have a periodic waveform with a frequency of about 1,600 c/s, the same as that of the emitted note. Higher ion production in the singing flame, therefore, probably results because the flame surface area is larger and because the vibrating flame is ejected clear of the burner tip, thereby preventing quenching of the flame at the burner rim as occurs with the normal diffusion flame.

Besides the increasing sensitivity of the singing-flame detector, which would be particularly useful for trace hydrocarbon analysis, the wave-form output of the detector also makes it amenable to a.c. amplification with its inherent advantages (stability, cost, compactness, etc.) over d.c. amplification. The rectified output of the singing-flame detector is exceptionally steady in contrast to the erratic response of a turbulent or premixed flame⁷.

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Energy Gap of β Silver Selenide

AN interesting variation of apparent measured intrinsic band gaps of β (low temperature) silver selenide prepared by different methods has been noted. Melt-grown silver selenide has been determined to have a band gap of 0.04–0.1 eV at about 300° K^{1,2}. When prepared as a powder at temperatures under 100° C³ silver selenide has a gap of 0.07–0.1 eV. This same silver selenide when sintered at 200° C (above the β - α phase transition) for 15 min and then remeasured in the same temperature range exhibits a different band gap, 0.2 eV.

Another method developed by us in which basic solutions of silver and selenium are reduced by hydrogen at pressures in excess of 2,000 lb./in.² at temperatures of approximately 200° C yields silver selenide having an apparent band gap of 0.2 eV that remains constant on sintering at 200° C.

Measurements on silver selenide prepared by the two methods were carried out in the same manner. Powder samples were compacted into pellet form (1.27 cm diameter with thickness up to 0.4 cm) using pressures of 70,000 lb./in.² and the electrical resistivities and Hall effects were measured using the Van der Pauw technique⁴ in the range of temperature from $1,000/T = 4$ to about $2.7/^\circ\text{K}$.

Our results tend to confirm the statements of Simon *et al.*² (who investigated melt-grown silver selenide) that the use of Hall or electrical resistivity measurements as a function of temperature in the range of temperatures from $1,000/T$ of 4 to $2.6/^\circ\text{K}$ tend to give slopes from plots of $\ln RT^{3/2}$ versus $1,000/T$ or $\ln \rho$ versus $1,000/T$ which, assuming no degeneracy and intrinsic conditions, are not readily interpretable in terms of simple intrinsic energy gaps.

While Simon *et al.*² have mentioned the difficulty in associating a definite meaning to 'energy gap' determinations, they have not mentioned a factor which may influence the interpretation of the slopes determined as above, namely, the effect of dissolved silver, that is, the electrical state of small amounts of silver in the β silver selenide lattice. It is conceivable that the changes in the silver concentration change the Fermi level and that the actual band gap remains constant. Our results above may suggest that the state of silver in the silver selenide could change on undergoing a phase transition, and, as inferred in previous publications^{5,6}, the role of silver either in undergoing a phase transition or the change in solubility with decreasing temperature may give rise to precipitation of silver (especially on cooling) or to silver in interstitial sites. It is suggested that the effect of excess silver and its role in the lattice could account for the different 'activation energies' observed, especially as varying degrees of order or disorder in the lattice are possible.

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RADIOCHEMISTRY

Thermal Annealing of Tellurium resulting from Isomeric Transition in Solid Sodium Tellurate

LITTLE attention has hitherto been directed to the chemical effects of radioactive decay in ionic crystals. Two papers are devoted to β -decay. Baro and Aten¹ have examined the distribution of arsenic-77, formed by