

Mercury Traps

THE interesting investigations of Messrs. Hughes and Poindexter¹ showed that a trap lined with alkali metal is as satisfactory as a liquid air trap, for preventing mercury vapour diffusing back into a vacuum system from a mercury pump. This method offers several advantages, with one disadvantage: it is difficult to clean commercial alkali metals and to avoid the introduction of various impurities (for example, organic vapours, hydrogen, carbonic dioxide) in the vacuum system. However, there exists one method—the glass-electrolysis—which enables very clean sodium to be introduced into closed glass vessels. This elegant method can be easily applied to any normal glass or pyrex glass apparatus by providing the mercury trap with an incandescent cathode and immersing it partially in molten sodium salt. We have already used a similar method in the manufacture of photoelectric cells.²

Mr. Ansiau, of this University, is at present experimenting with this method; the results will be recorded later.

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¹ F. E. Poindexter, *J. Opt. Soc. Am.*, **9**, 629; 1924. A. Ll. Hughes and F. E. Poindexter, *Phil. Mag.* (6), **50**, 423; 1925.

² L. Marton and E. Rostas, *Zeit. f. Techn. Phys.*, **10**, 52; 1929.

Dispersion of Sound in Several Gases, and its Relation to the Frequency of Molecular Collisions

MEASUREMENTS on carbon dioxide, carbon disulphide, sulphur dioxide, and ethylene show that the dispersion of sound in these gases is sensitive to pressure. In each case the dispersive region shifts to higher frequencies with increasing pressures or, conversely, the velocity of sound at a given frequency increases as the pressure is diminished until a constant value is attained. At 30° C. and 451,000 cycles sec.⁻¹, for example, the velocity of sound is constant in carbon dioxide below about 350 mm., in carbon disulphide below about 100 mm., and in ethylene below about 40 mm. The corresponding heat capacity ratios are 1.4 for carbon dioxide, 1.4 for carbon disulphide, and nearly 1.33 for ethylene; thus in each case only translational and rotational terms continue to participate in the sound wave under these conditions. In sulphur dioxide at 200 mm. the dispersion between 94 and 451 k.c. is only about 1.2 m. sec.⁻¹ at 30° C., indicating that frequencies above the present experimental range are necessary to demonstrate by the acoustical method that sulphur dioxide is not a linear molecule.

The temperature dependence of the dispersion of sound in carbon dioxide and carbon disulphide has also been studied. In carbon dioxide at 770 mm. the difference between the velocity of sound at 92 and at 9 k.c. is negligible at 60° C., whereas at 10° C. it is about 5.0 m. sec.⁻¹. Similar behaviour is manifest in carbon disulphide at about 320 mm.

The dispersion of sound in binary mixtures of ethylene with argon and nitrogen is exactly that calculated from pure ethylene at a corresponding partial pressure. It is concluded from this that the vibrational energy of ethylene is not excited by collisions with molecules of these gases. In hydrogen-ethylene mixtures, on the other hand, the effective heat capacity of ethylene rises sharply on the introduction of small quantities of hydrogen, and it is necessary to suppose that a collision with a hydrogen molecule is about ten times as likely to excite ethylene

as a collision with another ethylene molecule. The analogy of this result to recent chemical evidence on the decomposition rates of the ethers is striking.

Because air, nitrogen, argon, propane, and pentane appear to be without dispersion (+0.2 m. sec.⁻¹) between 9 and 451 k.c. in the same apparatus it is believed that the measurements reported above are free from serious errors due to tube effects.

A quantitative description of the dependence of the dispersion of sound on pressure, temperature, and frequency has been obtained by incorporating in the dispersion theory of Einstein² the suggestions of Herzfeld and Rice³ and of Heil⁴. If it is supposed that equilibrium between translational and internal energies is incomplete in high-frequency sound waves (H and R) and that only molecules of exceptionally high translational energy can excite molecular vibrations (H), an expression results which closely resembles that given by Einstein (and consequently that of Kneser⁵ but which involves two additional constants. The first may be called the collision energy, and determines the temperature coefficient of the dispersion of sound much as the activation energy determines that of a chemical reaction rate. The second is dimensionless, and represents the fraction of collisions possessing the collision energy which result in vibrational excitation. For carbon dioxide these quantities are respectively about 4×10^{-13} ergs and 0.01. These magnitudes may be understood when it is remembered (Heil) that on collision less than half of the translational energy may be converted into vibrations, and that the type of collision necessary to excite a transverse vibration must be directionally extremely specific.

It is possible that a small potential energy wall may also impede the energy transfer. The two constants cannot be separated without assumption if more than one vibrational state of the molecule contributes to its heat capacity. Under these conditions a fine-structure should appear in the absorption band or, conversely, points of inflection should be manifest in the dispersion. These may be studied at constant frequency by lowering the temperature or pressure in the dispersive region.

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¹ In agreement with Kneser, *Ann. Phys.*, **11**, 777; 1931.

² *Sitz. ber. Akad.*, 380; 1920.

³ *Phys. Rev.*, **31**, 691; 1928.

⁴ *Z. Phys.*, **74**, 31; 1932.

⁵ *Ann. Phys.*, **11**, 761; 1931.

Spectrum of Trebly Ionised Lead

THE spectrum of trebly ionised lead, which has been studied by several authors ending with S. Smith¹, requires modification in several respects. I have shown that $7p^2P-7d^2D$ is really $7p^2P-8s^2S$ and confirmed this by obtaining further combinations with the $8s^2S$ term. This provides a series of 2S terms the values of which can be accurately calculated by Hicks's formula. $6s^2S$ comes out equal to 340180, giving an ionisation potential of 41.9 volts.

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¹ *Phys. Rev.*, **36**, 1; 1932.