

hydrogen ions, and at electrode II the reverse process occurs.

The E.M.F. of the cell may be expressed as follows :

$$E = \frac{1}{F} \left\{ \left[\frac{1}{2}(D_{H_2})_{T_1} + \frac{1}{2} T_1 \Delta S_1 - NeI - (W_{H^+})_{T_1} \right] - \left[\frac{1}{2}(D_{H_2})_{T_2} + \frac{1}{2} T_2 \Delta S_2 - NeI - (W_{H^+})_{T_2} \right] \right\},$$

where D_{H_2} is the heat of dissociation of hydrogen, that is, decrease in heat content, and ΔS the corresponding entropy change at the temperature shown; I represents the ionization potential of hydrogen, and W_{H^+} the free energy of solvation of 1 gm.-ion hydrogen ions at the temperature subscribed. In so far as the constituent parts of the E.M.F. may be considered as belonging to the two electrodes individually, the potential of the hydrogen electrode at temperature T_1 is represented by the terms in the first square bracket, and that of the hydrogen electrode at temperature T_2 by the terms in the second.

The free energy terms considered above are unquestionably functions of temperature, and it follows, therefore, that the potential of the hydrogen electrode changes with temperature.

The above analysis of the electrode process, which is essentially that used by various authors including Butler³, neglects, of course, all thermo-electric effects in the metal leads in the outside circuit and the contribution to the E.M.F. of the liquid junction potential, both of which effects would, it is presumed, be considerable.

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¹ Gilbert, P. T., *Discussions of the Faraday Society*, 1, 320 (1947).

² Harned, H. S., and Ehlers, R. W., *J. Amer. Chem. Soc.*, 54, 1350 (1932).

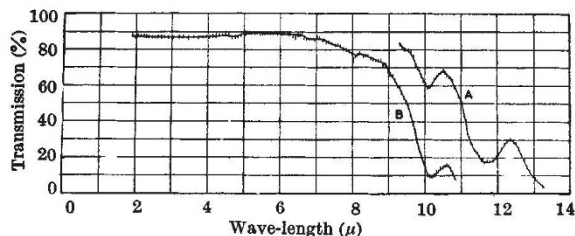
³ Butler, J. A. V., "Electrocapillarity" (Methuen, 1940).

Absorption of Magnesium Oxide in the Infra-Red Region

IN 1935 Barnes, Brattain and Seitz¹, investigating the absorption of magnesium oxide in the infra-red, reported some forty or so fine absorption lines in the range from 6μ to 15.6μ . In 1934 Fock², using fumed magnesium oxide, had reported the eigen-frequency to be at 17.3μ , with subsidiary maxima at 14.8μ , 6.8μ and 25μ , but no fine structure. Such a fine structure was hitherto unknown for face-centred cubic crystals, though it has been reported for quartz³ and calcite⁴. The theory advanced by these authors to explain the fine structure is based on the interaction of crystal vibrations as originally suggested by Born and Blackman⁵; but the assumptions which lead to the details of the fine structure do not appear to be correct⁶.

This fine structure does not seem to be consistent with any form of lattice theory of infra-red absorption, and a further investigation, therefore, appears to have both theoretical and practical interest.

The curves reproduced here are typical results in the range up to 14μ for specimens of different thickness. Values of the percentage transmission of cleaved specimens of artificially grown magnesium oxide, obtained from the same firm which supplied Barnes, Brattain and Seitz, were taken at a mean separation of 0.07μ , using a large rock-salt prism spectrometer. Each point is the mean of two results



Curve A, specimen 0.075 mm. thick; curve B, specimen 0.467 mm. thick. Slit-width covers a band of approx. 0.1μ . Vertical lines indicate probable error

obtained from two separate runs through the spectrum, and in no case did the values at any one wave-length differ by more than 2 per cent. Each result in each run is the mean of three results taken consecutively. Experiments showed that by using a Welsbach mantle as the source of radiation, the scattering within the apparatus is negligible; but that with a Nernst filament as a source some five to ten per cent of the radiation at 11μ was due to scattering from the high-energy peak in the spectrum of the Nernst filament.

It will be seen that the fine structure reported by Barnes, Brattain and Seitz has not been confirmed. Two distinct subsidiary maxima have been found, one at 10.1μ and the other at 11.7μ .

The curves for various thicknesses are consistent with each other, that is, they all give the same value for the extinction coefficient at any one given wave-length. This is not the case in the results of Barnes, Brattain and Seitz, where the detailed shape of the absorption spectrum differs considerably for specimens of different thickness. Further, the curve for a specimen of 75μ thickness (curve A) shows that it becomes practically opaque beyond 13.3μ , while a specimen of the same thickness was found by Barnes, Brattain and Seitz to have at least 10 per cent transmission up to 15.6μ , indicating that there must have been considerable scattering of the short wave-length radiation from their source, which was a heated platinum strip.

Preliminary results in the region from 14μ to 25μ show that the eigen-frequency is at 17.3μ , as reported by Fock, with subsidiary peaks at 14.8μ and 24.2μ . The absorption maximum at 6.8μ , found by Fock, has not been confirmed, and is probably due to absorbed water, as a cleaved specimen left out in the air for some weeks showed an absorption at 6.5μ , which vanished as soon as the specimen was cleaned by rubbing with clean chamois leather.

To sum up, the fine structure observed by Barnes, Brattain and Seitz has not been confirmed. The eigen-frequency is at 17.3μ , and there are subsidiary maxima on the short wave-length side of the eigen-frequency at 10.1μ , 11.7μ and 14.8μ , and at 24.2μ on the long wave-length side.

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² Fock, J., *Z. Phys.*, 90, 44 (1934).

³ Silverman, S., and Hardy, J. D., *Phys. Rev.*, 37, 176 (1931).

⁴ Silverman, S., *Phys. Rev.*, 39, 72 (1932).

⁵ Born, M., and Blackman, M., *Z. Phys.*, 82, 551 (1933).

⁶ Blackman, M., *Phil. Trans.*, 236, 103 (1936).