Absorption Spectrum of Cobaltous Chloride in Deuterium Oxide

SMALL differences in the colour of solutions of copper sulphate and silver permanganate when dissolved in deuterium oxide instead of ordinary water have been reported by Bell[1], and Hein and Bähr[2] respectively. Displacement of the absorption lines in the spectrum of potassium chrome selenium alum $(KCr(SeO)_4 12 H_2O)$[3] and of several complex chromium salts[4] when H_2O is replaced by D_2O have also been observed. Bell's work was confirmed by Brodsky and Zanko[5], who made spectrophotometric measurements with copper sulphate in pure H_2O, 43·6 per cent and 92·7 per cent D_2O mixtures.

I have determined the absorption curves of anhydrous cobaltous chloride dissolved in H_2O and 99·6 per cent D_2O. These curves lie within the visible region between the wave-lengths of 4000 A. and 6000 A., and they were obtained by means of a wave-length spectrophotometer. Distinct differences were apparent, the molecular extinction coefficient in D_2O being smaller throughout the region of absorption, and the height of the maximum is lower. The accompanying table indicates the nature of these differences at various points of the curves. Up to 4900 A., the difference is practically insignificant; above 4900 A. it increases and appears to be greatest between 5300 A. and 5400 A., that is, at lower frequencies than the maximum.

Wave-length (A.)	4700	4800	4900	5000	5140	5300	5400	5600
Mol. extinct. coef. Solvent, D_2O ..	2·82	3·17	3·46	3·92	4·14	3·30	2·54	1·04
Solvent, H_2O ..	2·89	3·19	3·48	4·02	4·34	3·67	2·84	1·20

These differences are comparable to those obtained by Brodsky and Zanko for copper sulphate.

D. C. MARTIN.

Chemistry Department,
University of Edinburgh.
Sept. 14.

[1] Bell, NATURE, 137, 534 (1936).
[2] Hein and Bähr, Z. phys. Chem., 38, 270 (1937).
[3] Joos and Böhm, Phys. Z., 36, 826 (1935).
[4] Duhm, Z. phys. Chem., 38, 359 (1937).
[5] Brodsky and Zanko, Acta Physicochem. U.R.S.S., 5, 919 (1936).

Photo-electric Absorption of Radiation in Gases

A LETTER on the above subject by Page[1] and a reply by Menzel[2] have recently appeared in NATURE. While I am in agreement with most of Dr. Menzel's letter, I feel that discrepancies between theory and laboratory experiment in the above field are more radical than his remarks would appear to suggest.

Theoretical calculations are based on the assumption that interactions between neighbouring atoms or molecules may be neglected, so that the atomic absorption coefficient is a true constant, independent of temperature and pressure. Detailed experiments[3] have shown that this assumption is true only at low pressures. The transition-probabilities for the photo-electric process for cæsium, for example, are greatly reduced by the presence of only a few millimetres of the rare gases. Much larger effects are produced by active gases like hydrogen or by the interaction of cæsium with cæsium. It should be emphasized that the continuous state is much more sensitive to these pressure effects than the internal quantized states of the atom. These results indicate that it is not correct to base astrophysical calculations on the assumption that the absorption is proportional to the number of atoms present, except at low pressures. Thus 'atomic absorption coefficients' measured in the laboratory or deduced from one set of stellar data cannot, in general, be used to make calculations on a mass of gas at another temperature and pressure.

Even if we confine ourselves to the region of low pressures, the agreement between theory and experiment is by no means satisfactory. It has been shown that for hydrogen[4] and the alkali metals[5] the absorption should theoretically decrease monotonically from the series-limit in the direction of short wave-lengths. This conclusion is independent of any precise assumption concerning the form of the atomic field[5]. Experiments are available for potassium[6], rubidium[7] and cæsium[8]. For potassium and cæsium the absorption is found to reach a minimum a short distance from the series-limit and then to increase again in the direction of short wave-lengths. (For rubidium, it is probable that the minimum is just at the end of the observed region of the spectrum.)

A second prediction is that there is no discontinuity in the absorption at the series limit. This result has been rigorously calculated for hydrogen[9] and probably applies also to the alkali metals. In a recent paper[10], I have assembled strong experimental evidence which shows that the absorption changes sharply, by a factor of about two, at the series-limit. This discontinuity is found for hydrogen and for all the alkali metals, but for hydrogen its magnitude is probably small.

These discrepancies suggest that the present calculations omit some essential factor, or else that the normalization of the continuous states is not correctly treated. I believe, with Dr. Menzel, that the wave-mechanics will eventually yield a satisfactory theory for this problem. I think, however, that attempts to apply Kramers' formula (or the wave-mechanical modifications of it) to astrophysical problems may be very misleading and certainly must be so at high pressures. At present, it would appear to be necessary to admit that we have no theory of continuous absorption which is satisfactory in the sense of being well verified by terrestrial experiments. While Kramers' formula may be useful as a rough guide, it is safer to regard the opacity as a quantity which cannot be determined theoretically, and, in comparing one system with another, to remember that the atomic absorption coefficient is, in general, a function of the temperature, pressure and state of ionization of the gas surrounding the absorbing atom.

R. W. DITCHBURN.

Trinity College,
Dublin.
Sept. 12.

[1] Page, NATURE, 141, 1137 (1938).
[2] Menzel, NATURE, 142, 433 (1938).
[3] Braddick and Ditchburn, Proc. Roy. Soc., A, 150, 478 (1935). Ditchburn and Harding, Proc. Roy. Soc., A, 157, 66 (1936).
[4] Gaunt, Proc. Roy. Soc., A, 126, 654 (1930). Sugiura (see ref. 9 below).
[5] Phillips, Phys. Rev., 39, 905 (1932).
[6] Ditchburn, Proc. Roy. Soc., A, 117, 486 (1938). Lawrence and Edelfsen, Phys. Rev., 34, 233 (1929).
[7] Mohler and Boeckner, Bur. of Standards J. Research, Paper No. 96 (1929)
[8] Braddick and Ditchburn, Proc. Roy. Soc., A, 143, 473 (1934).
[9] Sugiura, J. Phys. Rad., 8, 113 (1927).
[10] Ditchburn, Z. Phys., 107, 719 (1937).