## Constitution of the Poly-acids

THE work of Keggin[1] has placed the constitution of the 12-heteropoly-acids, metatungstates and metamolybdates—for example, $R_3H[SiW_{12}O_{40}].aq$, $R_6[H_2Mo_{12}O_{40}].aq$.—on a sure basis, and has indicated that the poly-acid anions may be regarded as co-ordination structures, built up of polyhedra of oxygen ions in the manner first envisaged by Pauling[2]. The constitution of other groups of poly-acids, for example, those with 9 or 11 $MoO_3$ or $WO_3$ for each molecule of hetero-acid, is still quite unknown, as also is that of the second main series of poly-acids—the 6-poly-acids, such as the 6-molybdo-periodates.

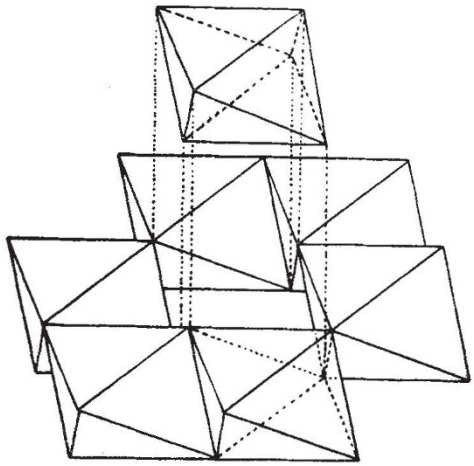

Fig. 1.

These have hitherto been regarded as satisfactorily expressed by the Rosenheim formula, $R_{12-n}[M^n(XO_4)_6]$, and there is good evidence that the central atom is, as shown, in 6-fold co-ordination. It may be predicted, however, from Goldschmidt's table of ionic radii, that the $Mo^{6+}$ and $W^{6+}$ ions must normally be found in 6-fold co-ordination with oxygen, as they are in known oxide structures, such as the 12-poly-acid anions. This conception leads to a new structure for the 6-heteropoly-acids and the related paramolybdates and paratungstates. It may readily be seen that six $MoO_6$ octohedra may be so arranged, by sharing corners with each of two neighbouring octohedra, that a hexagonal $Mo_6O_{24}$ annulus is built up. The central cavity of this structure is then the same size and shape as one of the $MoO_6$ octohedra, and can therefore accommodate another cation in the same 6-fold co-ordination (see Fig. 1).

It is suggested that this is the structure of the 6-poly-acid anions. The similarity between the paramolybdates (and paratungstates) and the 6-heteropoly-acids led to their formulation by Rosenheim as $R_5H_5[H_2(MoO_4)_6].aq$. Sturtevant[3] has recently shown that ammonium paramolybdate is correctly represented by the older formula $3(NH_4)_2O.7MoO_3.4H_2O$, or $(NH_4)_6[Mo_7O_{24}].4H_2O$. The relation of this to the 6-heteropoly-acids, for example, to $R_5[I(Mo_6O_{24})]$, is at once made clear if the paramolybdate is regarded as $R_6[Mo(Mo_6O_{24})]$, with the $Mo_6O_{24}$ structure built around a central $MoO_6$ octohedron in place of the $IO_6$ octohedron in the 6-molybdoperiodate.

Moreover, if some hydrolytic process, such as $[Mo(Mo_6O_{24})]^{8-} + H_2O \rightleftharpoons [Mo_6O_{21}]^{6-} + H_2MoO_4$ $[I(Mo_6O_{24})]^{5-} + 3H_2O \rightleftharpoons [Mo_6O_{21}]^{6-} + H_5IO_6 + H^+$ may be postulated in solution, it is possible that the grave discrepancies between the X-ray evidence and the considerable bulk of physico-chemical evidence as to the complexity of poly-acids in solution might be removed.

In the present state of the subject, a careful X-ray examination of the 6-poly-acids, including the paramolybdates and paratungstates, is urgently desirable.

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[1] Keggin, F. J., *Proc. Roy. Soc.*, A, **144**, 75 (1934).
[2] Pauling, L., *J. Amer. Chem. Soc.*, **51**, 1010, 2868 (1929).
[3] Sturtevant, J. H., *J. Amer. Chem. Soc.*, **59**, 630 (1937).

## Determination of the Relaxation Time for the Vibrational Energy of Carbon Dioxide

DURING the past year, we have made a series of measurements[1] on the absorption of sound in gases at ordinary and low temperatures. As is well known, such experiments are of great interest in connexion with the collision mechanism between molecules. These phenomena can also be studied by means of measurements on the dispersion of the velocity of sound. This method is followed by Eucken and his collaborators[2].

We investigated especially oxygen, carbon monoxide, hydrogen and nitrogen. On the other hand, Eucken has studied carbon dioxide and nitrous oxide, for the reason that for such gases the vibrational energy is great, so that dispersion measurements are easily made. Hence there was hitherto no immediate relationship between our measurements and those of Eucken.

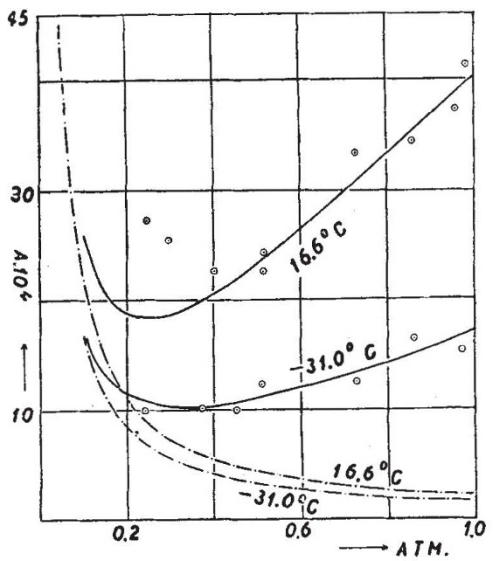


Fig. 1.

Recently we have made absorption measurements on well purified carbon dioxide, so that a direct comparison is possible with the dispersion measurements of Eucken. We have made measurements at 16·6° C. and −31·0° C., and have studied at each of these temperatures how the absorption of sound depends on pressure (frequency used, 304·4 kc.).