

The Raman Spectrum of Oxalic Acid

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LETTERS TO THE EDITOR

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The Conductance of Salt Crystals

Recently Rodebush and Cooke¹ criticized a paper of the author² in a way which hardly seems adequate.

(1) It is commonly known, as assumed in my article, that generally the conductance cannot be represented over the whole range of temperature by a single exponential. It was the aim of my investigation to show that for regions, where a simple exponential holds—this is always the case for unipolar conductors and sufficiently high temperatures—one can derive the *correct formula with constants of the right order of magnitude*. Then it is not difficult to generalize the result for more complicated cases. Of course one can derive the same formal expression by more or less vague analogies with reaction rates as has been shown sufficiently often since the time of Rasch and Hinrichsen.³

(2) Rodebush and Cooke's attempt of a derivation of the self-diffusion formula is not without contradiction within itself. It holds generally that properties belonging to a *stationary state*—and self-diffusion as well as electrolytic conduction refer to a stationary state—cannot be derived by analogies with the rate of a reaction without an explicit consideration of the reverse reaction. Rodebush and Cooke's reasoning contains instead of the reverse reaction only the loss of mobility of an activated ion which moved away from its former lattice point. *Therefore they describe the crystal in a state of increasing perturbation ("Fehlordnung"), not considering where the dislocated ions shall remain.* A consequent treatment, however, would require as reverse reaction the return of an activated ion into a normal lattice position; therefore one first has to assume that vacant lattice points are present. If Rodebush and Cooke had consequently carried through their reasoning they would have arrived at the conclusion that in equilibrium a certain fraction of the ions must be dislocated to irregular positions, leaving empty lattice points at their former positions; but this is just the model used by Frenkel⁴ and the author. In special cases such empty positions are present in the original lattice structure as in the cases of α -Ag₂J⁵ and α -Ag₂S⁶ which have been found after the author's first paper.

(3) Usually the methods of statistical mechanics and thermodynamics give more precise results in the treatment of states of equilibrium than in kinetic problems. Especially for the treatment of disturbances of a crystal lattice ("Fehlordnungs-Erscheinungen") the existence of which

can be concluded from numerous observations we refer to the fundamental papers of Schottky and Wagner.⁷ We mention, however, that the author's assumption of the existence of an *equivalent* number of "holes" and dislocated ions is not always true; for instance it may happen that the number of dislocated ions is negligible compared with the number of "holes" of both signs, which probably holds in the case of alkali halides.^{8,9}

W. JOST

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March 25, 1936.

¹ W. H. Rodebush and T. G. Cooke, J. Chem. Phys. 3, 834 (1935).

² W. Jost, J. Chem. Phys. 1, 466 (1933).

³ E. Rasch and F. W. Hinrichsen, Zeits. f. Elektrochemie 14, 41 (1908).

⁴ I. Frenkel, Zeits. f. Physik 35, 652 (1926).

⁵ L. W. Strock, Zeits. f. physik. Chemie B25, 441 (1934).

⁶ P. Rahlfs, Zeits. f. physik. Chemie B31, 157 (1936).

⁷ C. Wagner and W. Schottky, Zeits. f. physik. Chemie B11, 163 (1930); C. Wagner, Zeits. f. physik. Chemie, Bodenst. Festschrift, (1931), p. 177; Zeits. f. physik. Chemie B22, 181 (1933); C. Wagner, Physik. Zeits. 36, 721 (1935).

⁸ W. Schottky, Zeits. f. physik. Chemie B29, 335 (1935).

⁹ cf. W. Jost, Zeits. f. tech. Physik 16, 363 (1935).

The Raman Spectrum of Oxalic Acid

In a recent note Angus and Leckie¹ have taken exception to an observation of Hibben made in a previous publication.² This article recorded and discussed the Raman spectrum of oxalic acid in aqueous and alcoholic solutions, as the dihydrate and as the anhydrous compound. It was observed, in comparison with other organic acids, that the two C=O Raman shifts ($\Delta\tilde{\nu}$ 1645 and 1740) obtained from anhydrous acid and aqueous solution are anomalous. In alcoholic solutions the doubling of the carbonyl shift no longer occurred and one shift, $\Delta\tilde{\nu}$ 1755, resulted, which is more in accord with the carbonyl shift obtained from an ester, aldehyde or ketone. Consequently it was affirmed that, based on the magnitude of the two frequency displacements, the two carboxyl groups behave differently in aqueous solution and in the anhydrous acid, but identically in alcohol. The attribution of $\Delta\tilde{\nu}$ 1430 to an O-H shift in oxalic acid by Rao,³ Tschitschibabin's and the hexahydroxy formulas were discussed in detail.

In addition to the above, which comprised the greater portion of the article in question, it was stated: "No shifts corresponding to those at approximately $\Delta\tilde{\nu}$ 1650 and 1750 of the anhydrous acid were observed in the hydrate. This

does not preclude the possibility that they may be extant, but if so they are very much weaker than the same shifts in the dehydrated acid." It is principally with this remark that Angus and Leckie disagree, as they state: "... the Raman spectra obtained from the saturated aqueous solutions of oxalic acid and from the dihydrated oxalic acid crystals are substantially the same." However, they add: "Our results, obtained from crystals which were definitely dihydrate crystals, agree with those of Rao . . ." and, "Since Hibben's conclusions that the two carboxyl groups behave differently depend to a large extent on the difference in the spectra of the anhydrous and hydrated crystals we submit that such conclusions may be invalidated by his comparing the spectrum he obtained for his anhydrous crystals with Rao's spectrum for the solid."

The last quotation leaves such an erroneous impression that it is necessary to correct it. As pointed out in the first paragraph of this note, the different behavior of the two carboxyl groups is predicated on the observed magnitudes of the two carbonyl shifts and not on a comparison of the anhydrous, or hydrated material with the solution, consequently these conclusions are not affected by the presence or absence of such shifts in the hydrated material.

The apparent weakening of these lines in the anhydrous acid and their greater weakening (or absence) in the hydrated compound were explained by this writer as possibly attributable to chelation. If Angus and Leckie's observations are correct this explanation would be without significance. Nevertheless Rao's results cannot be cited in entire support of themselves since his published photographs show clearly that in the hydrate or anhydrous acid (it is immaterial to the argument which he used) the relative intensities of the carbonyl frequencies are markedly reduced as compared with the solution, in contradistinction to the first statement of Angus and Leckie's previously quoted. The intensities published by Rao are: (for $\Delta\tilde{\nu}$ 1640 and 1740, respectively) crystal: 00, 1; solution: 1, 3; or approximately a 66 percent decrease taking $\Delta\tilde{\nu}$ 845 as a reference standard. It is unfortunate that in republishing Rao's data Angus and Leckie omitted the intensities, which indicate an agreement with the present writer.

The fact that carbonyl shifts may weaken is already well known from the spectra of acid salts. So far as the hydrate is concerned Zachariasen⁴ from x-ray measurements has concluded that the C—O bond in this compound is at least part of the time a single bond, and that this substance is not a normal hydrate of oxalic acid.

It is believed that some of the difficulties of interpretation may have arisen in the use of an unfiltered mercury spectrum as a source of excitation. The O—H band, unusually sharp, falls in approximately the same position as the C=O shifts and the 4730 Hg line overlaps in the same position.

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Geophysical Laboratory,
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January 21, 1936.

¹ Angus and Leckie, *J. Chem. Phys.* **4**, 83 (1936).

² Hibben, *J. Chem. Phys.* **3**, 675 (1935).

³ S. Rao, *Zeits. f. Physik* **94**, 536 (1935).

⁴ Zachariasen, *Phys. Rev.* **45**, 755 (1934).

Reply to Dr. Hibben's Letter

Dr. Hibben's criticisms may be answered very briefly. His suggestion that our results for the dihydrate crystals are vitiated by incomplete filtration of the 4047A Hg line is incorrect since we used a strong solution of NaNO₂ as a filter and the 4047 undisplaced Hg lines were very weak on the plates. His second quotation from our letter tends to misrepresent the arguments put forward by us. We must maintain our view that Rao's crystals, showing frequencies at approximately 1660 and 1760 cm⁻¹, were dihydrate crystals and that Rao's results, therefore, support our own observations. We have satisfied ourselves that our results are correct.

The purpose of our letter was merely to indicate differences in results which, as we pointed out, *may* invalidate some of Hibben's conclusions. We do not think that the point at issue is sufficiently important to merit an extended controversy.

W. ROGIE ANGUS
ALAN H. LECKIE

University College,
London, W.C.1.,
February 19, 1936.

Metallic Binding According to the Combined Approximation Procedure

A combined approximation procedure has been proposed by one of us¹ for the calculation of the chemical interaction between atoms. In this method the atomic kernel is treated according to Thomas-Fermi and the valence electron by a Schrödinger equation. The total action of the kernel upon the valence electron—inclusive of the Pauli principle—then goes over into an additional potential in the Schrödinger equation, which can be taken approximately from the spectra. The application to K₂ and KH gave plausible results, however, on account of the omission of higher approximations they were still not absolutely convincing. We have therefore applied the combined approximation procedure to the problem of metallic binding. Here one can easily take into account the interactions between the valence electrons to a higher degree of approximation than in single molecules.

It was established in the beginning that the law $-1/r + (A/r)e^{-2\kappa r}$ for the total field of the kernel gives a good approximation in the case of the free Mg atom: When A and κ were so determined that the lowest s term and p term of Mg⁺ were rendered correctly, then Ritz's method (with r_{12} in the eigenfunction) yielded good results for the ground term of Mg. For the alkali metals A and κ were determined from the two lowest s terms with the aid of one-parameter hydrogen-like eigenfunctions. Since the field of the ion determined in this way runs a rather flat course, it is sufficient in the first approximation to set the valence electron in the lattice equal to a plane wave. The interaction of the kernels arising from their overlapping is