

Raman Spectrum of Fluorine

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$D_+^{(0)}$, $D_+^{(1)}$, $D_+^{(2)}$, etc., respectively reduce under the symmetry in question.

For odd numbers of electrons the same procedure is used; the functions are however classified according to the appropriate two-valued group.³

This procedure will be illustrated in a paper now being prepared on the polarization of singlet-triplet transitions.

¹ D. S. McClure, *J. Chem. Phys.* **17**, 665 (1949).

² E. Wigner, *Gruppentheorie*, p. 198.

³ H. Bethe, *Ann. d. Physik* **3**, 133 (1929); H. A. Jahn, *Proc. Roy. Soc.* **164**, 117 (1938); W. Opechowski, *Physica* **7**, 552 (1940).

Raman Spectrum of Fluorine

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December 23, 1949

THE Raman spectrum of fluorine has not been observed up to the present time. Garner and Yost¹ made an attempt to obtain the Raman spectrum of the liquid but no Raman lines were found. Considerable improvements in the light sources and the speed of photographic plates have been made since that time. It was therefore decided to make an attempt at obtaining the Raman effect of fluorine gas at atmospheric pressure.

A water-cooled mercury arc lamp of 14 kw capacity, the type developed at the University of Toronto, with magnesium oxide-coated reflectors, was used. The irradiated portion of the quartz Raman tube was 14 in. long. The spectrum was recorded in 8½ hr. in a spectrograph with an $f/2.3$ camera lens on 103- a -F photographic plates.

Two weak Raman lines were found corresponding to the two mercury lines 4047 Å and 4358 Å. The observed Raman shifts were 891.4 cm^{-1} and 892.8 cm^{-1} , respectively. The mean, $892.1 \pm 2 \text{ cm}^{-1}$, is the first vibrational quantum ΔG_1 of the F_2 molecule.

Murphy and Vance² in calculating the thermodynamic properties of fluorine estimated ΔG_1 to be $856 \pm 17 \text{ cm}^{-1}$ by applying Badger's rule to the electron diffraction value of r_0 ($=1.48 \text{ Å}$). Adoption of the new experimental value of ΔG_1 here obtained will introduce changes in the thermodynamic functions calculated by them.

The author is grateful to Dr. G. Herzberg for suggesting the problem.

¹ C. S. Garner and D. M. Yost, *J. Am. Chem. Soc.* **59**, 2738 (1938).

² G. M. Murphy and J. E. Vance, *J. Chem. Phys.* **7**, 208 (1939).

Metallic Valences*

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December 2, 1949

TWO different sets of valences are now being applied to metals in alloys, that of Hume-Rothery,¹ Mott and Jones,² and Pauling.^{3,4} In the former, metallic valences approach a minimum of or nearly zero for the transition metals, whereas in the latter a maximum of about 5.78 is reached for the same metals.

Hume-Rothery⁵ has investigated the effect of manganese, iron, and nickel on the α/β brass equilibrium, assuming that the major factor influencing the ternary isothermal, solid-solubility boundaries is the electron-to-atom ratio. By comparison of predicted and experimental curves for isothermal solubility as a function of added transition element, he finds that if the metallic valences of copper, zinc, and aluminum are 1, 2, and 3, respectively, then the valences of manganese, iron and nickel are 2, 1, and 0.4–0.6, respectively.

Hume-Rothery⁵ states that, "... whatever may be the validity of Pauling's views regarding the numbers of electrons responsible for cohesion in the crystals of the transition elements, these numbers are not the effective valences of the atoms as regards their influence on the α/β equilibrium," and, "... the directions

of the curves are quite different from those to be expected for elements of valency 5 or 6."

Hume-Rothery's conclusions are valid only if copper and zinc have valences of 1 and 2, respectively. If one chooses a valence of 5.44 for copper, as suggested in Pauling's^{3,4} papers, and 3 for aluminum, one obtains a valence of 4.22 for zinc from the 550°C $\alpha/\alpha+\beta$ boundary in the copper-aluminum-zinc system. Using these values for zinc and copper, on examination of the empirical ternary solubility curves given by Hume-Rothery,⁵ the following valences are obtained: iron 5.44; manganese 4.22; and nickel 5.93–6.17. Pauling's⁴ values are zinc 4.44; iron 5.78; manganese 4.16 and 5.78; and nickel 5.78. Not too much reliance is to be placed on the exactness of the valences obtained, but the calculation outlined above does show that Pauling's valences, if changed slightly, form a self-consistent set.

Using the valences quoted above, one obtains exactly the same theoretical solubility curves as does Hume-Rothery. Giving copper a valence of 5.44, nickel has the highest valence of the three transition elements considered, whereas manganese has the lowest valence, a result in opposite order to that obtained by assuming copper to be univalent.

The particular ternary alloys considered by Hume-Rothery in his paper do not offer a means of distinguishing between the two viewpoints on valence, since both yield identical isothermal solubility curves.

Methods of choosing between the two valence sets are not plentiful since, in general, the two valence sets give results which are very close to each other. For example, Pauling⁶ has found that both valence ideas lead to the more-or-less complete filling of Brillouin zones for the gamma-alloys and other alloys with filled zone properties. One method of distinguishing between the two valence sets is to consider a ternary solid solution in which two of the components have valences for which Hume-Rothery and Pauling give identical values. If the third element is one on whose valence the two views disagree, different isothermal ternary solubility curves will be predicted on the basis of the two views. By comparison of calculated and empirical solubility curves, one may distinguish between the two points of view.

Even if constancy of electron-to-atom ratio, on which the above argument depends, is a valid concept one must, however, consider carefully the effects of electronegativity, relative atomic size, and the orbitals available for bond formation in all of the components of the solid solution.

These points will be discussed in a future paper.

The author wishes to acknowledge the aid given to him by helpful discussion and criticism of this paper by Dr. R. E. Rundle.

* This document is based on work performed in the Ames Laboratory of the AEC. Contribution No. 81 from the Iowa State College Institute for Atomic Research, Ames, Iowa.

¹ W. Hume-Rothery, *The Structure of Metals and Alloys* (The Institute of Metals, London, 1936).

² N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, London, 1936).

³ L. Pauling, *Phys. Rev.* **54**, 899 (1938).

⁴ L. Pauling, *J. Am. Chem. Soc.* **69**, 542 (1947).

⁵ W. Hume-Rothery, *Phil. Mag.* **39**, 89–97 (1948).

⁶ F. J. Ewing and L. Pauling, *Rev. Mod. Phys.* **20**, 112 (1948).

Macroscopic Space Charge in Electrolytes during Electrolysis

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December 19, 1949

IN a recent paper¹ Reed and Schrieffer claim to have observed non-linear potential gradients in a conducting electrolyte solution of *uniform* composition. Since this observation, if substantiated, would invalidate all work on the transference numbers of electrolytes by the moving boundary method, it appears essential to examine critically the conditions of their experiments. Poisson's relation requires the existence of a space charge ρ in

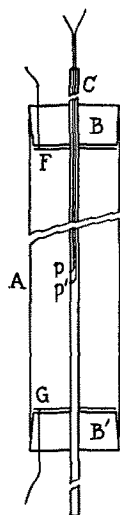


FIG. 1.

any region, such as a boundary layer, in which the composition, and hence the conductivity, κ , varies with the distance, x , i.e.,

$$\frac{d^2V}{dx^2} = \frac{i}{A} \frac{d}{dx} \left(\frac{1}{\kappa} \right) = -\frac{4\pi\rho}{\epsilon}.$$

Here i is the current and A the (uniform) cross-sectional area of the column. The magnitude of this space charge at a moving boundary was computed in 1897 by Kohlraush² for a typical case and he concluded that it is of no significance in transference experiments, a conclusion supported by all subsequent work. It is basic to the moving boundary method, however, that the potential gradient in the interior of a homogeneous conducting solution be given accurately by Ohm's law.

Reed and Schriever's work is subject to the criticism that, in the horizontal trough they used, the concentration gradients that tend to develop at the vertical electrodes are disturbed by gravity. Thus in the electrolysis of aqueous copper sulfate the concentrated solution of this salt formed at the anode falls to the bottom of their trough, while the dilute solution at the cathode rises. Erratically changing concentration differences must thus develop in an unstirred system and are by no means negligible.

The most serious error in Reed and Schriever's work probably arises, however, from their choice of electrodes. Every material used by these workers is incompletely reversible. The stresses and imperfections in practically all crystalline metals render them unsuitable for quantitative potentiometric measurements.

To avoid these errors we believe that the experiment should have been set up in a vertical tube for gravitational stability. Moreover, the potential gradient along the column of solution can best be explored by using as probes a pair of closely spaced reversible electrodes fixed relative to each other, and independent of the working electrodes.

Although we were quite certain of the outcome, an experiment was set up with the simple equipment shown in Fig. 1. The vertical glass tube A , about 30 cm long and 5½ cm in diameter, was fitted with the stoppers B , B' through the centers of which ran a vertically movable glass tube C , carrying insulated silver wires. These wires were sealed through the wall of the tube with fused silver chloride to form the probe electrodes, p , p' , about 6 mm apart. For the working electrodes F and G flat helices of heavy silver wire were used. The electrodes were given a coating of silver chloride electrochemically, thus making the probe electrodes reversible. After filling the apparatus with 0.003*N* KCl, three series of measurements were made with about 2, 4, and 6 volts across the terminals. The potential differences between the probes: 43, 89, and 131 mv, respectively, remained constant, within a few tenths of a millivolt, throughout the length of the tube A . However, after the current had been on for about a half hour the

gradient near the bottom cathode dropped by nearly a millivolt in the case of the two higher currents and increased slightly near the anode, since solution tends to become more concentrated at the bottom and less concentrated at the top.

This experiment, admittedly relatively crude, gave no indication of any appreciable space-charge effects in the uniform solution. We believe that it indicates the type of experiment that Reed and Schriever might better have carried out to test the presence, or much more probable absence, of any significant deviations from Ohm's law in solutions of electrolytes.

¹ C. A. Reed and W. Schriever, *J. Chem. Phys.* **17**, 955 (1949).
² Kohlraush, *Ann. der Physik* **62**, 209 (1897).

Erratum: Raman Effect, Infra-Red Absorption, Dielectric Constant, and Electron Diffraction in Relation to Internal Rotation

[*J. Chem. Phys.* **17**, 591 (1949)]

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ON page 594 of this paper the Raman frequency 859 cm⁻¹ of asymmetrical tetrachloroethane should be 959 cm⁻¹. According to the private communication of Mr. A. Opler who kindly pointed out this misprint, the infra-red absorption frequencies observed by him are in excellent agreement with our Raman frequencies. The fact that no further normal frequency was observed by the infra-red absorption would be another experimental evidence for the only one configuration of asymmetrical tetrachloroethane molecule.

On the same page "the chlorine atoms or polysubstituted ethanes" should be "the chlorine atoms of polysubstituted ethanes"

The Photo-Decomposition of Acetaldehyde: Individual Rate Constants by the Sector Method

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December 15, 1949

HADEN AND RICE¹ have reported the use of intermittent illumination in the high temperature photolysis of acetaldehyde. Without absolute intensity measurements the independent results from such measurements are values of the ratio k_t/k_p , where k_p and k_t are, respectively, rate constants for chain propagation and chain termination. Combined with the best absolute value of $k_p k_i^{1/2} k_t^{-1/2}$ (obtained from absolute measurements of quantum yields of the reaction under steady illumination), this ratio gives $k_i k_p$ and $k_i k_t$, k_i being the quantum yield of the primary process.

Haden and Rice used two temperatures only, and their light intensities were low enough to permit deviations from the kinetic $I_{\text{abs}}^{1/2}$ law, with consequent greater complexity, and uncertainty, in the interpretation of the sector results.² Figure 1 shows the $\log(k_t/k_p) - 1/T$ plot of results now obtained by the sector method, at a variety of temperatures and at light intensities for which the square root law is valid. Haden and Rice's results are plotted as solid points and show good agreement. The straight line gives an activation energy -10.4 kcal./mole (± 1.0), corresponding to $E_i - E_p$.

The activation energy of the steady reaction, $E_p - \frac{1}{2}E_i$, has been variously reported as 8.6,³ 9.6,⁴ 10.0⁵ kcal./mole, the light intensities used increasing in the same direction. Haden and Rice have used Leermakers' value of 10.0 kcal./mole on the ground that the others require correction for the monomolecular chain termination, which is responsible for the discrepancies in activa-