

The Raman Effect and the Dissociation of KHSO_4

W. H. Shaffer and D. M. Cameron

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gas at 25°C shows the calorimetric value to be about 8 e.u. lower than the spectroscopic value. This indicates about 8 e.u. zero-point entropy in the ordinary crystal of tetramethylmethane at the absolute zero, due to randomness caused by lack of equilibrium. There is an abnormal rise in the heat capacity of the solid prior to a transition at 140°K. In this region only is there evidence of hysteresis.

Giauque and associates have found a similar state of affairs for carbon monoxide^{3a} and nitrous oxide^{3b} and predicted the occurrence of the phenomenon in the case of organic compounds. Pauling has discussed the situation for some simple molecules.⁴

In view of the large discrepancy in the case of tetramethylmethane one must view entropies of organic compounds calculated from calorimetric data assuming a perfect crystal (i.e., zero entropy at the absolute zero) with considerable doubt even though they be based on heat capacities taken down to liquid hydrogen temperatures or lower.

At present the only source of a reliable value or the entropy of neopentane is a calculation based on spectroscopic data and a knowledge of the moments of inertia. Such a calculation yields a value of 79.85 e.u. at 25° and 1 atmos. neglecting nuclear spin. This value is the translational and rotational entropy 73.98 e.u.¹ plus the entropy of vibration (5.87 e.u.) calculated from the Raman frequencies determined by Rank and Bordner,⁵ using the following multiplicities: 335, (2); 414, (3); 733, (1); 925, (3).

The complete calorimetric data will be submitted for publication in the near future.

JOHN G. ASTON
GEORGE H. MESSERLY

School of Chemistry and Physics,
The Pennsylvania State College,
State College, Pennsylvania,
April 23, 1936.

¹ Kassel, J. Chem. Phys. **4**, 277 (1936).

² Huffman, Parks and Barmore, J. Am. Chem. Soc. **53**, 3876 (1931).

^{3a} Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).

^{3b} Blue and Giauque, *ibid.* **57**, 991 (1935).

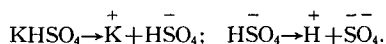
⁴ Pauling, J. Am. Chem. Soc. **57**, 2680 (1935).

⁵ Rank and Bordner, J. Chem. Phys. **3**, 248 (1935).

The Raman Effect and the Dissociation of KHSO₄

It has been found by Rao¹ and others that a study of the Raman effect offers a means of determining the degree of dissociation of concentrated solutions, where other methods are not applicable, and thus supplies valuable information with respect to the physical and chemical properties of such solutions. Woodward,² Nisi,³ and Bell and Jeppesen⁴ have observed the Raman effect in KHSO₄ at one concentration but made no observations on the change in the degree of dissociation with the concentration.

They found that HSO₄⁻ ions occur in a concentrated aqueous solution of KHSO₄ and that these ions partially dissociate into H⁺ and SO₄²⁻. This is precisely what might be expected from chemical considerations which indicate that KHSO₄ would dissociate in two stages:



Since other studies of the Raman effect in concentrated solutions indicate that normal salts are completely dissociated at all concentrations, and that in strong acids the degree of dissociation increases with dilution, it is of interest to consider what happens in the Raman spectrum of an acid salt like KHSO₄ when the concentration of the solution is changed.

By means of a high speed spectrograph of low dispersion the Raman effect was photographed in four aqueous solutions of KHSO₄ of the following concentrations: 13, 21, 28, 34 percent. The solutions were enclosed in the usual type of Wood tube and illuminated by mercury arc lamps. The Raman spectra were excited by the 4358A and 4047A lines. The frequencies of the observed Raman lines expressed in wave numbers (cm⁻¹) for concentrations of 13 percent and 34 percent have been recorded in Table I.

TABLE I.

CONCENTRATION	HSO ₄ ⁻	HSO ₄ ⁻	SO ₄ ²⁻	—	—
13%	1058	917	978	611	438
34%	1040	906	975	599	436

The ions to which these observed Raman lines have been attributed are indicated by the headings of the columns in the table. There is a change in frequency of the Raman lines with the dilution of the solution. A similar effect has been observed by Woodward and Horner⁵ and also by Bell and Jeppesen⁴ in the case of aqueous solutions of H₂SO₄. The reality of such a change in frequency due to a change in concentration has been questioned by Mitra⁶ but his observations on aqueous solutions of magnesium sulphate and lithium sulphate were concerned only with the Raman line 981 cm⁻¹ which has been attributed to SO₄²⁻. For this line the change in frequency due to the change in the concentration of the solution is small compared to the changes observed for the other lines.

From a comparison of the intensities of the Raman lines as indicated by the microphotometer curves, the relative degrees of dissociation of the solutions with respect to the

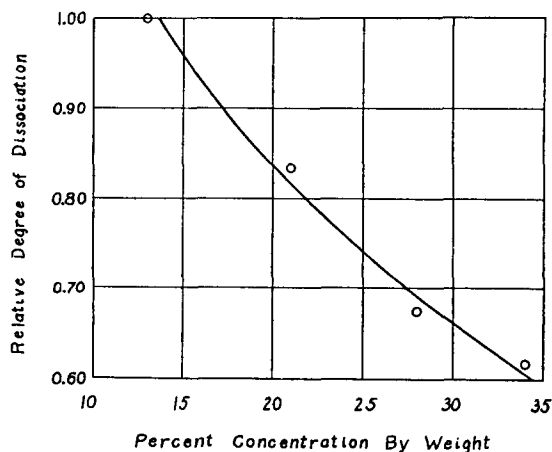


FIG. 1

degree of dissociation of 13 percent solution have been calculated and recorded in Table II. These results are also

TABLE II.

PERCENT CONCENTRATION RELATIVE DEGREE OF DISSOCIATION	13	21	28	34
	1.00	0.84	0.68	0.82

shown as a curve (Fig. 1) with the degree of dissociation plotted against the concentration. From this curve the progressive dissociation of the HSO_4 ion is clearly seen. No lines attributable to the undissociated KHSO_4 molecule were observed even in the most concentrated solution. The fact that no undissociated molecules are present in solution is characteristic of normal salts, while the fact that the HSO_4 ion dissociates progressively is characteristic of acids. Thus the Raman method of investigation indicates that KHSO_4 has characteristics common to both acids and normal salts as would be inferred from chemical considerations.

W. H. SHAFFER
D. M. CAMERON

Mendenhall Laboratory of Physics,
Ohio State University,
April 20, 1936.

¹ I. R. Rao, Proc. Roy. Soc. A127, 279 (1930).

² Woodward, Physik. Zeits. 32, 212 (1931).

³ Nisi, Jap. J. Phys. 6, 1 (1930).

⁴ Ball and Jeppesen, J. Chem. Phys. 3, 245 (1935).

⁵ Woodward and Horner, Proc. Roy. Soc. A144, 129 (1934).

⁶ Mitra, Zeits. f. Physik 98, 740 (1936).

Quantum Mechanics and the Third Law of Thermodynamics

Rodebush¹ has recently discussed certain points concerning the third law of thermodynamics in terms of quantum mechanics. His recognition of the significance of quantum mechanics in considering the behavior of solutions and glasses at low temperatures we believe to be of interest, and we agree with the more important of his conclusions. However, there have arisen some questions of interpretation in which we differ from the statements of his paper. We have thought it of value to present here, as explicitly as possible and at the risk of some duplication of ideas, an outline of these points and a discussion of their bearing on the expected behavior of the systems under treatment. It is our opinion that the views presented below have been in the main accepted by investigators interested in the theory of the third law; however, so far as we are aware no equivalent discussion has been published.

Without entering into the question of the relation between statistical mechanics and thermodynamics, we accept as giving a value for the entropy of the system in which we are interested the expression $k \ln N$, in which N is the number of independent wave functions for the system compatible with our knowledge as to its condition. Following the plan adopted by Rodebush, we first discuss the case of an optically active substance.² An isolated molecule of such a substance in its lowest rotational and vibrational state and known to be in the dextro configura-

tion³ is to be represented by a single wave function corresponding to this configuration, and will have the quantum weight 1, and not 2. On the other hand, if the molecule is in one of the two lowest energy states corresponding to the accurate solution of the wave equation (as could be determined by an energy measurement extending over a period of time long compared to the time required for spontaneous dextro-levo conversion), it is to be represented by a single wave function which is either symmetric or antisymmetric relative to inversion about a center, and which is formed by linear combination of the dextro and levo wave functions. It will then not be known whether the molecule is a dextro or a levo molecule. Only in the case that neither its optical activity nor its (exact) energy is known can we assign to it the quantum weight 2.

By analogy with the simple case of the optical isomers Rodebush generalizes the many-minima problem exemplified by glasses and crystalline solutions with the following statement. "We have a number of configurations of the same energy separated by energy crests. By symmetric and antisymmetric linear combinations of wave functions,⁴ we obtain a total number of wave functions equal to the degeneracy; that is to say, the total number of configurations having the same energy. Thus, instead of each configuration having a distinct energy, each configuration has now a large number of closely spaced energy levels."

Here we prefer to state the situation in a somewhat different way, as follows. The system in its low temperature condition and known to have a particular configuration⁵ (one of N possible configurations) is to be represented by one of an appropriate set of N wave functions, corresponding to the N configurations. If not the configuration, but the energy of the system is to be investigated with great accuracy, by means of observations extending over a very long period of time, the set of wave functions of interest is that corresponding to accurate solution of the wave equation (these wave functions being linear combinations of those corresponding to the N configurations). The energy value found by experiment would be one of the multiplet of N levels corresponding to the low temperature condition. We cannot, however, make use of the two sets of wave functions simultaneously, but must use either the configuration wave functions or the multiplet wave functions, or some other equivalent set. In other words, both the configuration and the exact energy of the system cannot be simultaneously known. If either is known a single wave function (of the set of N) is sufficient to describe the system and the system will then have the quantum weight 1, and not N . However, if neither the configuration nor the exact energy of the system is known, we may use either set of N wave functions (or any other set formed from them by linear combinations) to describe it, and its quantum weight will then be N .

The behavior of systems on cooling to a very low temperature ($kT \ll h\nu$, where ν is the frequency of the lowest oscillational state) may be outlined in the case of an ideal solution somewhat as follows.⁶ If ν^* is the frequency of transition among the various configurations (as given by the corresponding resonance integral divided by h), the