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Note on Dipole Moments of Molecules in Solution

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LETTERS TO THE EDITOR

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Structure of Potassium Tetroxide

Up to the present time the structure of potassium tetroxide has not been determined. E. W. Neuman[1] on the basis of magnetic measurements concludes that this compound contains O_2^- ions and that its formula is KO_2. Klemm and Sodomann,[2] however, have shown that the formula K_2O_4 containing the ion $O_2^{--} \cdots O_2$ is also consistent with the magnetic data because of the paramagnetism of the oxygen molecule. Therefore the structure of potassium tetroxide cannot definitely be stated by the study of magnetic properties only.

At the suggestion of Professor J. A. Kasarnowsky we have undertaken an x-ray investigation of this substance. A pure sample of potassium tetroxide was prepared in this laboratory by S. Reichstein who also determined its density. By taking powder photographs and using the Hull-Davey charts we were able to establish a tetragonal face-centered lattice of the calcium carbide type.[3] The elementary cell contains four potassium atoms and eight oxygen atoms and has the following dimensions: $\mathbf{c}=6.72$A, $\mathbf{a}=5.70$A, $\mathbf{c}/\mathbf{a}=1.178$. The density calculated from the dimensions of the unit cell is $\delta_{\text{calc}}=2.15$ in agreement with the density value $\delta_{\text{meas}}=2.158$ measured in a pycnometer. The space group is $D_{4h}^{17}-F4/\mathbf{mmm}$. The coordinates of the four potassium atoms are 000, $\frac{1}{2}\,\frac{1}{2}\,0$, $\frac{1}{2}\,0\,\frac{1}{2}$, $0\,\frac{1}{2}\,\frac{1}{2}$ and those of the eight oxygen atoms are $\frac{1}{2}\,0\,0\pm U$, $0\,\frac{1}{2}\,0\pm U$, $0\,0\,\frac{1}{2}\pm U$, $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\pm U$. By comparing the calculated and observed intensities we obtained for the parameter U the value $U=0.095$, which corresponds to a distance between adjacent oxygen nuclei of $d_{0-0}=1.28\pm0.07$A.

The structure we have found for the potassium tetroxide lattice is quite analogous to that of SrO_2 and BaO_2[4] and may be considered as a rocksalt lattice elongated in one direction because of the shape of the anion. The SrO_2 and BaO_2 lattices, however, contain doubly charged oxygen ions O_2^{--} while KO_2 contains singly charged ions O_2^-. These data allow us to conclude that the formula of the highest potassium oxide is KO_2 in concordance with the views of Pauling and Neuman.[1]

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Moscow,
April 25, 1936.

[1] E. W Neuman, J. Chem Phys. **2**, 31 (1934).
[2] W Klemm und Sodomann, Zeits. f. anorg. u. allg Chem **225**, 273 (1935).
[3] M v. Stackelberg, Zeits. f. physik. Chemie **B9**, 437 (1930).
[4] J. D. Bernal, E. Djatlowa, J. Kasarnowsky, S. Reichstein and A. G. Ward, Zeits. f. Krist. **A92**, 344 (1935).

Note on Dipole Moments of Molecules in Solution

The suggestion has been made by H. O. Jenkins* that the moment of a polar molecule dissolved in a nonpolar solvent fluctuates about a mean μ_0 in a manner given by

$$dP(\mu)=Ce^{-(\alpha/T)(\mu/\mu_0-1)^2}d\mu \tag{1}$$

so that the observed moment is

$$\overline{\mu^2}_{\text{obs}}=\frac{C\int_{-\infty}^{+\infty}e^{-(\alpha/T)(\mu/\mu_0-1)^2}\mu^2d\mu}{C\int_{-\infty}^{+\infty}e^{-(\alpha/T)(\mu/\mu_0-1)^2}d\mu}, \tag{2}$$

where $dP(\mu)$ is the chance the moment has a value between μ and $\mu+d\mu$; μ_0, C, and α are constants characteristic of the dipole and the solvent and T is the absolute temperature. A theoretical derivation of expression (1) is given below.

(Jenkins showed that if one assumes the dipoles in a molecule such as *p*-dinitrobenzene behave independently with regards to this fluctuation and further that the latter is of a period which is relatively low compared to that of the orientation of the dipole in the local field, he can account for the existence of a moment in such a symmetrical molecule. Also, he can accurately predict the value to be expected for symtrinitrobenzene were he to use the available data for the dinitro compound to calculate the constant μ_0. The success of the predictions so made for the above case and for quinone, beryllium acetylacetonate and basic beryllium acetate provide support for Eq. (1) from an empirical standpoint. Attention is called to the fact that the invariant nature of the polarization with respect to the temperature is also thus accounted for.)

To explain the observed discrepancy between the values for the dipole moment as obtained from the dielectric constant measurements on the gas and on dilute solutions of the polar substance in a nonpolar solvent, K. Higasi[1] considered the change in μ_{gas} due to the induced moment in the medium immediately surrounding an ellipsoidal polar molecule. He concluded that

$$\mu_{\text{sol}}=\mu_{\text{gas}}(1+2\pi qAn),$$

where A is a function of the shape of the solute molecule, the position of the dipole in it, etc., q is the polarizability per molecule of the solvent and n is the number of solvent molecules per unit volume. For the purpose of the present discussion it is not necessary to specify the dependence of μ_{sol} so completely; it is sufficient to state

$$\mu_{\text{sol}}=\mu_{\text{gas}}(1+fn), \tag{3}$$

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where f is a function characteristic of the solute and solvent. It can be shown that if one circumscribes around the dipole a sphere large enough just to include the solute molecule the contribution of the material outside this sphere to the change in μ_{gas} vanishes. To evaluate f one must consequently integrate the induced polarization over the volume included between the surface of the polar molecule and that of the circumscribing sphere. Since this volume is of molecular dimensions, n should not be given the averaged macroscopic value but one which fluctuates appreciably about a mean n_0. Hence μ_{sol} of Eq. (3) is really an instantaneous value (μ). In the simple argument to be given below it is implicitly assumed that whatever the instantaneous n happens to be, it is uniform for the entire volume over which the intergration is performed. Further consideration will show, however, that the final equation is not necessarily restricted by this assumption since the form of f is left unspecified.

Let dN be the number of molecules of the solute having between n and $n+dn$ molecules of the solvent per unit volume in their shell of influence. The well-known expression for such a fluctuation[2] states

$$dN = B_0 e^{-(b/kT)(n-n_0)^2} dn,$$

where B_0 is a normalizing factor and b depends on the nature of the solute and solvent molecules. From (3)

$$(n-n_0)^2 = (1/f\mu_g)^2(\mu-\mu_0)^2.$$

Therefore,

$$dN = Ce^{-(\alpha/T)(\mu/\mu_0-1)^2} d\mu,$$

where

$$C = B_0(1/f\mu_g) \quad \text{and} \quad \alpha = (b/k)(\mu_0/f\mu_g)^2.$$

Eq. (2) follows immediately.

Thanks are due Professor Pauling and Dr. Jenkins for a number of interesting discussions.

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June 15, 1936.

* (Private communication. Manuscripts to appear in the J. Chem. Soc.)

[1] K. Higasi, Tokyo, Proc. Inst. Phys. Chem. Research **28**, 284 (1936).
[2] R. C. Tolman, *Statistical Mechanics*, p. 230.

Concerning the Amorphous and Crystalline Forms of Rubber Hydrocarbon

The coefficients of thermal expansion and the heat capacities of rubber hydrocarbon both in an amorphous and in a so-called crystalline form have been recently reported in two papers by Bekkedahl and Matheson.[1] According to these investigators, the amorphous form undergoes a transition of the second order in the neighborhood of 199°K. Above this temperature they found a rather abrupt increase of approximately 205 percent in the volume coefficient of thermal expansion and one of about 38 percent in the heat capacity. These phenomena are strikingly similar to those found in numerous studies on glasses in this laboratory and especially in the recent investigation on polyisobutylene by Ferry and Parks.[2] Thus, with the particular sample of polymerized isobutene employed, the *transition region* centered around 197°K and the subsequent increases in volume coefficient and heat capacity were 200 and 32 percent, respectively.

Bekkedahl and Matheson found that, by cooling the amorphous rubber hydrocarbon to about 230°K and then permitting it to warm up slowly over a period of days, their material could be obtained in a "crystalline" form. These "crystals" melted at 284°K with a heat of fusion of 4.0 cal. per gram. They also exhibited the previously-mentioned second-order transition at about 199°K but with somewhat smaller subsequent increases with rising temperature, i.e., about 165 percent increase in the volume coefficient of thermal expansion and 28 percent in the heat capacity. Two facts appear surprising and highly significant with these "crystals": (1) The value of the heat of fusion which is extremely low compared with the figures of 20 to 54 cal. per gram hitherto reported for various aliphatic hydrocarbons melting near room temperature,[3] and (2) the duplication of the second-order transition found previously for the amorphous rubber hydrocarbon.

The writer of this communication feels that these two facts can best be explained by the supposition that Bekkedahl's "crystals" really represent a mixture of amorphous and crystalline rubber hydrocarbon. Assuming that the second-order transition is solely due to the amorphous hydrocarbon, he estimates the percentage of this in the so-called crystals to be about 80 from the relative increases of the volume coefficients above 199°K. Similarly from the relative increases of the heat capacities above this transition, he estimates 71 percent amorphous material in the "crystals." These estimates check only roughly but in this connection it is important to note that the two types of measurements were made upon different samples and that the sample used for the specific heat measurements was contaminated with 2.8 percent oxygen. The presence of such a large percentage of amorphous substance in this "crystalline" form is not really surprising in view of the high molecular weight of rubber hydrocarbon and the probability that the material contains a variety of molecules representing various degrees of polymerization of C_5H_8. In fact, similar but not such extensive contamination of the crystalline form with amorphous material has previously been observed in this laboratory with such relatively simple substances as ethyl alcohol, n-amyl alcohol,[4] and lactic acid.[5] In the case of the last named, Parks, Thomas and Light, on crystallizing the liquid, obtained a two-phase system with about 12 percent amorphous material.

On the basis of his hypothesis of 71 percent amorphous material in the rubber hydrocarbon crystals of Bekkedahl and Matheson, the writer has obtained from their data an estimate of 17.4 cal. per gram for the heat of fusion of pure crystals. This estimate is of the same order of magnitude as the values reported previously for many other paraffin and olefin hydrocarbons melting above 200°K.

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Stanford University, California,
May 13, 1936.

[1] Bekkedahl, Bur. Standards J. Research **13**, 411 (1934); Bekkedahl and Matheson, *ibid.* **15**, 503 (1935).
[2] Ferry and Parks, J. Chem. Phys. **4**, 70 (1936).
[3] See, for example, Parks and Huffman, Ind. Eng. Chem. **23**, 1138 (1931).
[4] Parks, Huffman and Barmore, J. Am. Chem. Soc. **55**, 2733 (1933).
[5] Parks, Thomas and Light, J. Chem. Phys. **4**, 64 (1936).

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