

On the Possibility of a Chemical Synthesis of Diamond

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Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$4.00 per page) will not be made and no reprints will be furnished free.

The Temperature Dependence of Viscosities of Liquids and Activation Energy

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June 12, 1947

VARIOUS types of exponential equations for the temperature dependence of viscosities of liquids are to be found in the literature, and some of the well-known equations have been referred to by me in a recent paper.¹ The equation proposed by Eyring *et al.*²

$$\eta = Z \exp[E_{vis}/RT], \quad (1)$$

in which η = the viscosity, Z = the "frequency factor," and E_{vis} = the "activation energy" per mole for viscous flow, and the theoretical background of it continues to attract attention. However, the term E_{vis} needs some clarification. Following the theory of Eyring, the energy required to push two molecules apart to provide a suitable site for the jump of a moving molecule from one equilibrium position to the next is synonymous with the energy needed to break a "bond," and this quantity represents the "activation energy." Based on this theory, I obtain the following equation:

$$\eta = Z \exp[\gamma(M/D-d)^{\frac{1}{3}} \cdot N^{\frac{1}{3}}/RT] \\ = Z \exp[f(\cos 30^\circ)^2(\sigma + \delta) \cdot N/NkT], \quad (2)$$

where the symbols correspond to those employed in another paper.³ According to the same paper,

$$\frac{\gamma(M/D-d)^{\frac{1}{3}} \cdot N}{N^{\frac{1}{3}}} = N \cdot f(\cos 30^\circ)^2(\sigma + \delta)$$

stands for the energy needed to break N "bonds" in a molal volume of V_c cs. Substituting for $\gamma(M/D-d)^{\frac{1}{3}}$ by its equivalent $2kN(T_c - T)$ as given by the Eötvös law, we have

$$\eta = Z \exp[2k \cdot N(T_c - T)/RT] = Z \exp[2(T_c - T)/T]. \quad (3)$$

Taking out logarithms, we have

$$\ln \eta = (\ln Z - 2) + (2T_c/T) \quad (4)$$

or

$$\log_{10} \eta = (\log_{10} Z - 0.87) + 0.87(T_c/T). \quad (5)$$

Adding $\ln V^{\frac{1}{3}}$ to both sides of Eq. (4), we obtain

$$\ln \eta \cdot V^{\frac{1}{3}} = (\ln Z \cdot V^{\frac{1}{3}} - 2) + (2T_c/T). \quad (6)$$

The close resemblance between (6) and an equation proposed and tested by Thomas⁴ viz.,

$$\ln \eta \cdot V^{\frac{1}{3}} = (c - k') + k'(T_c/T) \quad (7)$$

can now be clearly seen. Comparison of (6) and (7) gives $c = \ln Z \cdot V^{\frac{1}{3}}$ and $k' = 2$. It is of significance to note that the values of k' when expressed in logarithms to the base 10, as given by Thomas in his Table II, lie between 0.6 and 1.1, giving a mean of 0.85, which is in good agreement with the value of 0.87 given by Eq. (5).

Equation (6) leads us to another important conclusion that the usual method of estimating the "activation energy," according to the relation $E_{vis} = R[d \ln \eta / d(1/T)]$ from the linear plot of $\ln \eta$ vs. $1/T$, is unreliable. According to Eq. (4) or (6), such a plot gives the slope as $2T_c$, whereas it ought to be

$$\frac{\gamma(M/D-d)^{\frac{1}{3}} \cdot N^{\frac{1}{3}}}{R} = 2(T_c - T)$$

in accordance with Eqs. (2) and (3). It appears that the incorporation of a volume term ($V^{\frac{1}{3}}$) in the non-exponential part of the Eq. (6) or (7) is superfluous, but it need not be stated so definitely at this stage without a thorough investigation. However, whether the incorporation of $V^{\frac{1}{3}}$ in the non-exponential term should be made or not, the exponential term which stands for the "activation energy" remains unaffected. The identity of Eqs. (6) and (7) provides an indirect test of Eq. (2). A detailed examination of Eq. (2) is in progress. It may be tentatively stated that this equation is in harmony with the basic postulates incorporated in my previous paper.³

¹ M. S. Telang, J. Phys. Chem. **50**, 384 (1946).

² H. Eyring, J. Chem. Phys. **4**, 283 (1936); S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 477.

³ M. S. Telang, "On the theory and application of the relation between surface tension and orthobaric densities," J. Chem. Phys. (to be published).

⁴ L. H. Thomas, J. Chem. Soc. 573 (1946).

On the Possibility of a Chemical Synthesis of Diamond

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June 6, 1947

RECENT attempts to synthesize diamond by transforming graphite to diamond under thermodynamically favorable conditions of pressure and temperature having so far failed,¹ it would seem worth while to examine the possibilities of a chemical synthesis by a process of polymerization.

It is of interest that the only synthetic material formed in many of experiments carried out over the last seventy years, positively identified as diamond by x-ray diffraction tests,^{2,3} is that said to have been produced by J. B. Hannay² in 1880. Though the evidence supporting Hannay's claims recently adduced by Bannister and Lonsdale³ is very strong, real proof can be achieved only by a successful repetition of Hannay's work. Hannay's method was to heat a mixture of light paraffin, bone oil (mainly pyridine),

and lithium in a sealed iron container. Only three of eighty cylinders tried withstood the temperature of a red heat. These conditions, inadequate to transform graphite to diamond, might conceivably have produced diamond directly by a process of polymerization.

Parsons,⁴ in his Bakerian lecture to the Royal Society of London, states that he tried to repeat Hannay's work, but in the very long list of experiments described at the end of his paper he gives very few details about these particular experiments. With the improved facilities now available it would seem worth while to try to check and possibly to extend Hannay's work. In addition to the light paraffins previously used, other substances possessing more of the diamond structure such as derivatives of methane III,¹⁻³ cyclopropane,⁵ and tricyclo (3.3.1.1)⁶ decane (adamantane) might repay investigation along these lines.

¹ P. W. Bridgman, *J. Chem. Phys.* **15**, 92 (1947); P. L. Gunther, P. Geselle, and W. Rebertsch, *Zeits. f. anorg. allgem. Chem.* **250**, 357 (1943).

² J. B. Hannay, *Proc. Roy. Soc. (London)* **30**, 188 (1880).

³ F. A. Bannister and K. Lonsdale, *Mineralog. Mag.* **26**, 309 (1943).

⁴ C. A. Parsons, *Phil. Trans.* **A220**, 67 (1919).

⁵ M. Beesley and J. Thorpe, *J. Chem. Soc.* **117**, 602 (1920); see also A. M. Patterson and L. Capell, *The Ring Index* (Reinhold Publishing Corporation, New York, 1940), p. 172, Compound 1191.

⁶ W. Nowacki, *Helv. Chim. Acta* **28**, 1233 (1945); see also A. M. Patterson and L. Capell, *The Ring Index* (Reinhold Publishing Corporation, New York, 1940), p. 275, Compound 2034.

The Nature of the Hydrogen Bond in KHF_2

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June 9, 1947

THE discovery of the residual entropy of ice at low temperatures, and its explanation in terms of a double minimum potential curve for the proton in the O—H—O hydrogen bond,¹ raised the question whether F—H—F system also had a double minimum potential curve. We had undertaken to answer this question by measuring the entropy of KHF_2 by heat capacity measurements from low temperatures and from the reaction $\text{KF}(s) + \text{HF}(g) = \text{KHF}_2(s)$. This work was interrupted in 1943 and is only now being completed. However, the heat capacity curve for KHF_2 was finished. In the interval the excellent measurements of Ketelaar² on the infra-red absorption and reflection spectra of KHF_2 have become available to us. These more complete spectra make untenable the earlier postulate of Buswell, Maycock, and Rodebush,³ which was followed by Glockler and Evans.⁴ However, our heat capacities are not consistent with Ketelaar's explanation of his data. We wish to propose the following interpretation of all these data.

Solid KHF_2 shows absorption and reflection peaks at 1450 and 1222 cm^{-1} which are so much stronger than all others as to virtually assure the correctness of their assignment as fundamentals. The HF_2^- ion should have two infra-red active fundamentals, ν_3 , where the proton moves along the F—F line, and ν_2 , where the proton moves perpendicularly to the F—F line. The latter is degenerate. Also there is the inactive fundamental, ν_1 ,

which is a symmetrical F—F vibration. Ketelaar felt that the two observed peaks were too close together to be the two active fundamentals and that ν_2 would be "much lower than 600 cm^{-1} ." Hence he assigned the 1450 and 1222 cm^{-1} peaks to a doubling of ν_3 because of a double minimum potential curve. This is not possible because it would lead to a peak in the heat capacity curve near 20°K which is definitely not present⁵ (see Fig. 1). Consequently,

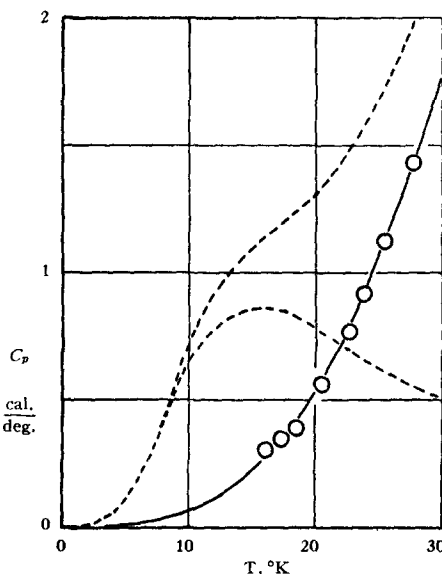


FIG. 1. The molal heat capacity of solid KHF_2 : circles, experimental; solid line, T^3 law for lattice vibrations; dotted curves, Ketelaar's model, lower the contribution from the ν_3 doublet above, upper the total including lattice vibrations.

we believe that 1450 and 1222 cm^{-1} peaks represent, respectively, the ν_3 and ν_2 fundamentals. In our opinion the more surprising point is not that ν_2 is so high but that ν_3 is so low. However, this hydrogen bond is considerably shorter than those previously studied so that there is no evidence against the assignment.

The HF_2^- ion has a center of symmetry both internally and with respect to the crystal, hence $2\nu_3$ is forbidden in the infra-red. The peak at 5099 cm^{-1} seems most likely to be $3\nu_3$. If we assume the peak at 4232 cm^{-1} to be $2\nu_3 + \nu_2$, then $2\nu_3$ should be approximately 3010 cm^{-1} . These levels show a large negative anharmonicity; indeed they approach somewhat the levels of an oscillator with a fourth power potential as calculated by Bell.⁶ There is no indication of any double minimum character with the F—H—F potential. The possibility of a very small potential hill has not been eliminated; however it must not be much higher than the lowest energy level.

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¹ W. F. GIAUQUE and M. ASHLEY, *Phys. Rev.* **43**, 81 (1933); L. PAULING, *J. Am. Chem. Soc.* **57**, 2680 (1935); W. F. GIAUQUE and J. W. STOUT, *ibid.* **58**, 1144 (1936).

² J. A. A. KETELAAR, *Rec. Trav. Chim.* **60**, 523 (1941).

³ A. M. BUSWELL, R. L. MAYCOCK, and W. H. RODEBUSH, *J. Chem. Phys.* **8**, 362 (1940).

⁴ G. GLOCKLER and G. E. EVANS, *J. Chem. Phys.* **10**, 607 (1942).

⁵ Other supporting arguments can be given for this conclusion, but they will be postponed until our full paper.

⁶ R. P. BELL, *Proc. Roy. Soc. London* **A183**, 328 (1945).