

Errata: The Intrinsic Viscosities and Diffusion Constants of Flexible Macromolecules in Solution

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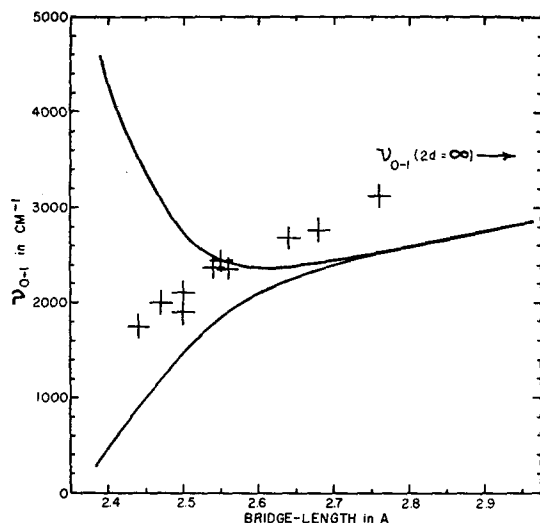


FIG. 1. Fundamental vibration frequencies of a hydrogen bridge.

the hydrogen atom moves in is the sum of two appropriate Morse potentials. By assuming no change in the oxygen-oxygen distance (the bridge length) during a vibration, we can treat the bridge length as a parameter in the calculations. Using the one-dimensional wave equation, we wish to find the energy levels and wave functions corresponding to the assumed potential function. Rather than attempt to obtain an exact solution by straightforward methods,⁴ we use an approximation method.

Since the potential function is the sum of two O-H Morse potential functions, we use as zero-order wave functions the normalized sum or difference of the wave functions appropriate to the O-H potential functions.⁵ With these, we find that the first-order energy levels are given by

$$H_{ii} = E_i + (1 \pm d_i)^{-1} (P_{ii} \pm Q_{ii}),$$

where the plus signs refer to the symmetrical states and the minus signs to the antisymmetrical states. E_i is the i th energy level of a single Morse well; $P_{ii} = \int_{-\infty}^{\infty} \phi_{Li} V_R \phi_{Li} dx$; $Q_{ii} = \int_{-\infty}^{\infty} \phi_{Li} V_L \phi_{Li} dx$; and $d_i = \int_{-\infty}^{\infty} \phi_{Li} \phi_{Ri} dx$. ϕ_{Li} and V_L are the wave functions and potential associated with the left-hand Morse well and analogously for ϕ_{Ri} and V_R . The P_{ii} are standard gamma-function integrals. The Q_{ii} and d_i are not standard integrals but can be evaluated using the method of saddle-point integration.

From band-spectra measurements of the O-H molecule,⁶ we evaluate the parameters of the wave and potential functions. We can then find the values of the energy levels as a function of the bridge length. Since each unperturbed energy level splits into a symmetrical and antisymmetrical level, there are four possible transitions from $i=0$ to $i=1$, two Raman active transitions, and two infrared active transitions. The theoretical frequencies of the infrared transitions are plotted as a function of bridge length in Fig. 1. For comparison the experimental frequencies given by Lord and Merrifield² are indicated by the crosses in Fig. 1.

Comparing the experimental frequencies to the theoretical frequencies reveals two facts. First, the calculated results for transitions from $(H_{00})_a$ to $(H_{11})_s$ show the same general trend as the experimental results. The observed frequency shifts resulting from the formation of a hydrogen bridge are about 25 percent smaller than the calculated shifts. Second, there seem to be no experimental data for transitions from $(H_{00})_s$ to $(H_{11})_a$.

Considering the first point, if these results were not first-order but complete in themselves, one could conclude that the actual potential function of a hydrogen bridge is different from the assumed potential function. If the actual potential function of the O-H molecule has less curvature than the Morse potential in the region $r > r_0$, then the discrepancy can be explained without drop-

ping the basic assumption concerning the addition of two O-H potentials.

Attention should be paid to the second point in the interpretation of experimental spectra. The present theory predicts that the fundamental vibration spectrum of a hydrogen bridge should consist of a pair of bands of comparable intensity whose separation increases rapidly with decreasing bridge length.

A more complete discussion of the theory including treatments of the transverse vibration frequencies, of the unusual widths of the absorption bands, and of the isotope expansion of hydrogen bridges will be given in a later issue of this journal.

* This paper is abstracted from a portion of a thesis submitted in partial satisfaction of the requirements for the Ph.D. degree in physics at the University of California at Los Angeles.

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Errata: The Intrinsic Viscosities and Diffusion Constants of Flexible Macromolecules in Solution

[*J. Chem. Phys.* **16**, 565 (1948)]

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IN this article, the effect of the hydrodynamic interaction of the segments of a polymer chain on the intrinsic viscosity was determined by a function $\varphi(x)$, satisfying the following integral equation:

$$\varphi(x) = f(x) - \lambda \int_{-1}^{+1} \frac{\varphi(t)}{(|x-t|)^{1/2}} dt$$

with

$$\int_{-1}^{+1} f(x) dx = 0, \quad (A1)$$

where λ is proportional to the square root of the degree of polymerization. By a justified inversion of order of integration, the last member of this equation was expressed in the form

$$\int_{-1}^{+1} \frac{\varphi(t)}{(|x-t|)^{1/2}} dt = \frac{1}{\pi^{1/2}} \int_{-\infty}^{+\infty} g(x, \beta) d\beta, \quad (A5)$$

where $g(x, \beta)$ satisfies the following differential equation:

$$\frac{\partial^2 g}{\partial x^2} - \beta^2 g = -2\beta^2 \varphi. \quad (A6)$$

We wish to call attention to the fact that the solution of (A6)

$$g(x, \beta) = 2 \sum_{k=-\infty}^{+\infty} \frac{\beta^2 \varphi_k}{\pi^2 k^2 + \beta^4} e^{i\pi k x}$$

presented in (A8) and (A9) is incomplete. To it must be added a linear combination of the solutions $e^{-\beta^2 x}$ and $e^{\beta^2 x}$ of the homogeneous equation in order that (A5) be actually satisfied. When this is done, the analytical solution of (A1) proves to be impracticable.

A numerical solution of (A1) will therefore be undertaken in the near future for the purpose of correcting the function $F(x)$ of Eq. (22) and the constant $\lim_{x \rightarrow \infty} x F(x)$ of Eq. (23). The only impor-

tant change in the results presented in the paper, which is anticipated, is a correction in the numerical value of this constant. It is hoped that this correction will produce improved agreement between the values of the end-to-end distance of a flexible coil calculated from the intrinsic viscosity and from turbidity and sedimentation constant. It should be pointed out that the results

presented for the translational diffusion constant and semimentation constant of flexible coils remain exact and require no correction.

A similar incompleteness in the solution of the corresponding integral equation for rod-like macromolecules¹ exists and requires correction by numerical integration. However, the analytical solution of the equation, constructed for rods in this paper, becomes asymptotically exact for large degrees of polymerization or large ratios of length to radius. Therefore, the asymptotic results for long rods remain correct here as well as in the paper of Kirkwood and Auer² on the viscoelastic properties of rod-like macromolecules.

The authors are indebted to Dr. Bruno Zimm for calling their attention to the necessity for the corrections which are discussed here.

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A Relation Between the Activation Energy for Viscous Flow and the Lennard-Jones (12, 6) Potential Parameter, ϵ/k

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THE temperature dependence of the viscosity (η) of a liquid is best represented by the energy of activation for viscous flow, ΔE_{vis} , which is defined as¹

$$\Delta E_{vis} = R \frac{d \ln \eta}{d(1/T)},$$

where T is the absolute temperature and R is the molar gas constant. (ΔE_{vis} is obtained experimentally from determinations of η at different temperatures, T .)

Ewell and Eyring² have shown that

$$\Delta E_{vis} = \frac{\Delta E_{vap}}{n},$$

where ΔE_{vap} is the molar energy of vaporization, and n is a constant. For liquids whose molecules have spherically, or approximately spherically, symmetrical force fields, $n=3$.

Also¹

$$\Delta E_{vap} = \Delta H_e - RT_b,$$

where ΔH_e is the latent heat of evaporation at the boiling point, T_b .

By using the Lennard-Jones (12-6) model for the intermolecular potential, it can be shown^{3,4} that, for nonpolar liquids with spherically symmetrical molecules,

$$\Delta H_e \approx 14.9\epsilon/k \text{ cal mole}^{-1}$$

and

$$T_b \approx \frac{\epsilon/k}{1.39}$$

where ϵ is the maximum energy of attraction between two molecules and k is Boltzmann's constant.

Thus,

$$\begin{aligned} \Delta E_{vis} &= \frac{1}{n}(\Delta H_e - RT_b) \\ &\approx \frac{1}{3} \left(14.9 - \frac{R}{1.39} \right) \epsilon/k \\ &\approx 4.5\epsilon/k \text{ cal mole}^{-1}. \end{aligned}$$

This applies, of course, only to normal liquids which have nonpolar, symmetrical molecules and whose intermolecular force field is well represented by the Lennard-Jones model.

In Table I, experimental values⁵ of ΔE_{vis} are compared with values calculated from the above relation using tabulated values⁵

TABLE I. Comparison of calculated and experimental values of ΔE_{vis} .

Liquid:	A	N ₂	O ₂	CO	CH ₄
(i) ϵ/k (viscosity)	124	91.46	113.2	110.3	136.5
(ii) ϵ/k (virial)	119.5	95.9	117.5	95.33	142.7
ΔE_{vis} (using (i))	558	412	509	496	615
ΔE_{vis} (using (ii))	538	431	510	429	643
ΔE_{vis} (experimental)	516	449	398	466	719

of ϵ/k (obtained from (i) gas viscosity data, and (ii) second virial coefficients). ΔE_{vis} is given in cal mole⁻¹ and ϵ/k in degrees absolute.

The discrepancy in the case of oxygen is large, and may be attributed² to its paramagnetic properties which make $n=3.5$ rather than 3.0 in the Ewell-Eyring expression. In general, more satisfactory results are obtained by using values of the intermolecular force constant ϵ/k determined from second virial coefficients of gases. The agreement between experimental and calculated values of ΔE_{vis} is satisfactory if the approximations made in obtaining the relation given above are taken into account.

Since ϵ/k is derivable from the temperature dependence of the gas viscosity, it seems that there is some connection between the temperature dependence of the viscosity of the vapor and that of the liquid, notwithstanding the fact that viscous resistance has not the same origin in gases and liquids.

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Stabilization of Free Radicals from the Decomposition of Hydrazoic Acid*

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IT has been reported by Rice and Frearno¹ that a blue solid may be frozen out at 77°K from the vapor phase decomposition of HN₃. The color was attributed to the NH radical. On warming to 148°K it instantaneously changed to a white solid which at room temperature analyzed for (NH)_n with a mass spectrum corresponding to NH₄N₃.

In the present work HN₃ vapor was decomposed by an electric discharge and the products frozen out in different experiments at 4° and at 77°K in an optical cell.² The infrared spectrum of the blue solid showed that it contained a substantial portion of undecomposed HN₃. Deposition of HN₃ at 77°K without passage through a discharge gave a clear colorless glass which on warming to 148°K became polycrystalline. Thus, the disappearance of the blue color in this system accompanies the crystallization of the HN₃. After passage through a discharge the low-temperature infrared spectrum of the blue material showed the presence of NH₄N₃, identification being made by comparison with a known sample of NH₄N₃. The intensities of the NH₄N₃ bands were the same on warming above the 148°K transition temperature.

Bands were also observed at 3500 Å and 6500 Å, the latter being responsible for the blue color. The NH radical in the vapor is known to have a sharp Q branch at 3360 Å; the NH₂ radical has a broad band system whose center is at approximately 6300 Å.³ It appears likely that the bands resulting from the HN₃ decomposition are due to these two radicals.

The absorption in the infrared regions of NH stretching and bending vibrations was very intense, and no bands other than those assignable to NH₄N₃ or HN₃ were observed. No absorption was observed corresponding to the N-N stretching mode of N₂H₄. No fine structure could be detected in the 3500 Å and