visible, and only a slight yellow color due to the tail of the ultraviolet absorption. The presence of the metal in two valence states in the same molecule thus produces an enormous intensification in absorption, presumably due to a charge transfer mechanism. Similar behavior has been observed in Cu(II)–Cl–Cu(I) complexes but to a much lesser degree.[11,12] Evidently the presence of a sulfide between the Cu(II) and Cu(I) in (I) facilitates the electron transfer greatly.

Comparison of Mercaptans.—Mixing of Cu(II) with several other thiols also produced a violet-colored complex, but not every mercaptan worked. Thioglycolic acid, β-mercaptoethylamine and α,β-dimercaptosuccinic acid formed violet solutions, β-mercaptopropionic acid and cysteine did not. With thioglycolic acid, spectra and polarographic measurements also were recorded. The color intensity was weaker in this case, and the peak at 520 mμ not nearly as strong as in Fig. 4. Correspondingly in the polarographic titration, i_d for the RSH wave followed a course very similar to that for thiomalic acid shown in Fig. 3. However, in contrast to Fig. 3, the Cu(II) wave appeared immediately after the disappearance of the RSH one. Clearly Cu(II)[RS-Cu(I)]$_4$ is a much weaker complex, *i.e.*, its dissociation is much greater, when RS is thioglycolic acid instead of thiomalic. Likewise the complex with β-mercaptoethylamine must also be much weaker for its absorption peak, although at 520 mμ, was much lower than that for thiomalic acid. Thus it is clear that copper forms mixed valence complexes with a variety of thiols and that these complexes are characterized by much more intense absorption spectra than are customarily found in cupric or cuprous complexes.

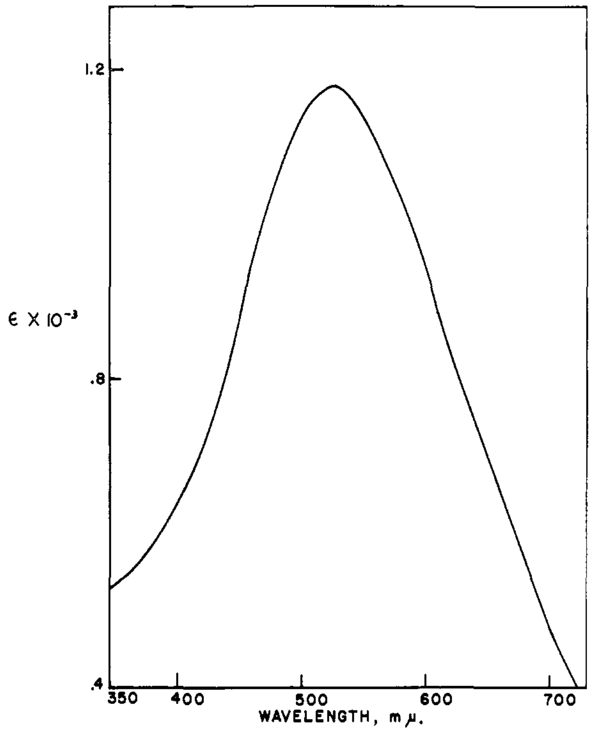

Fig. 4.—Absorption spectrum of the violet complex, Cu(II)[Cu(I)SR]$_4$: Cu(II) total concentration, 0.0010 *M;* thiomalic acid, 0.0016 *M.* In acetate buffer, under nitrogen, at *p*H 5.8, 25°.

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EVANSTON, ILLINOIS

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

Osmotic Pressure, Protein Solutions and Active Transport. II[1]

BY TERRELL L. HILL

RECEIVED DECEMBER 6, 1957

This paper discusses some of the statistical thermodynamic relations between two solutions separated by a membrane with properties such that two species, though present on both sides of the membrane, are not in equilibrium across the membrane while the remaining species are in equilibrium. This situation might arise, for example, in so-called "active transport" across biological membranes (the two non-equilibrium species in this case might be two small ions or one small ion and one protein molecule). The osmotic pressure and activity coefficient ratios are given particular attention. A special case is treated by a modification of the method of Donnan and also by the McMillan–Mayer method.

I. Introduction

In an earlier paper[2] we used the McMillan–Mayer solution theory to discuss the pressure difference across a membrane when one species of ion, though present on both sides, has different electrochemical potentials on the two sides of the membrane, either (1) because the species cannot pass through the membrane or (2) because the membrane does work (active transport) to maintain the electrochemical potential difference. Each solution was assumed to be in an equilibrium state though the solutions are not in complete equilibrium with each other. Since the discussion concerned statistical thermodynamic properties of the solutions only, we could ignore the (possibly non-equilibrium) processes occurring in the membrane itself.

In the present paper we extend the theory to the case of two ionic species with different electrochemical potentials on the two sides. Systems of this type are undoubtedly very important in active

(1) This investigation was supported by a research grant from the Heart Institute, Public Health Service.

(2) T. L. Hill, THIS JOURNAL, **78**, 4281 (1956). Hereafter denoted by I.

transport (*e.g.*, two ions, or one protein and one ion).

II. General Theory

The notation is the same as in I. The argument parallels that of I, so that a number of details can be omitted. We take $z_1 \neq z_1^*$, $z_2 \neq z_2^*$ but $z_3 = z_3^*$, etc. That is, species 1 and 2 are the two "non-equilibrium" species. Let $\mathbf{z} = z_1, z_2, z_3^*, \ldots$ and $\mathbf{z}^* = z_1^*, z_2^*, z_3^*, \ldots$. We find from eq. I-1[3]

$$\frac{\Pi}{kT} = \sum_{i,j \geq 0} b_{ij}(\mathbf{z}^*) x_1^i x_2^j \qquad (1)$$

where

$$x_i = \frac{\gamma_i}{\gamma_i^*}\rho_i - \rho_i^* \quad i = 1, 2 \qquad (2)$$

and

$$\begin{aligned} b_{00} &= 0 \\ 1!\,0!\,Vb_{10} &= Z_{10} = V,\ b_{10} = 1 \\ 0!\,1!\,Vb_{01} &= Z_{01} = V,\ b_{01} = 1 \\ 2!\,0!\,Vb_{20} &= Z_{20} - Z_{10}^2 \\ 1!\,1!\,Vb_{11} &= Z_{11} - Z_{10}Z_{01} \\ 0!\,2!\,Vb_{02} &= Z_{02} - Z_{01}^2 \\ 3!\,0!\,Vb_{30} &= Z_{30} - 3Z_{10}Z_{20} + 2Z_{10}^3 \\ 2!\,1!\,Vb_{21} &= Z_{21} - 2Z_{10}Z_{11} - Z_{20}Z_{01} + 2Z_{10}^2 Z_{01} \end{aligned} \qquad (3)$$

etc. The configuration integrals Z_{ij} are defined by

$$Z_{ij}(\mathbf{z}^*) = \int \exp\left[-\frac{w_{ij}(\mathbf{z}^*)}{kT}\right] \mathrm{d}(1_1)\,\mathrm{d}(2_1)\ldots\mathrm{d}(\mathrm{i}_1)\,\mathrm{d}(1_2)\ldots\mathrm{d}(\mathrm{j}_2) \qquad (4)$$

where $w_{ij}(\mathbf{z}^*)$ is the potential of the average force for a set of i molecules of species 1 and j molecules of species 2 in the $\mathbf{z}^*$ solution.

If we define

$$\xi_i = \rho_i - \frac{\gamma_i^*}{\gamma_i}\rho_i^* \quad i = 1, 2 \qquad (5)$$

we can also express Π in the form of a generalized virial expansion[2,3]

$$\frac{\Pi}{kT} = \sum_{i,j \geq 0} B_{ij}(\mathbf{z}^*) \xi_1^i \xi_2^j \qquad (6)$$

where the virial coefficients B_{ij} are given by

$$\begin{aligned} B_{00} &= 0,\ B_{10} = B_{01} = 1 \\ B_{20} &= -b_{20},\ B_{11} = -b_{11},\ B_{02} = -b_{02} \\ B_{30} &= 4b_{20}^2 - 2b_{30} \\ B_{21} &= 4b_{20}b_{11} + b_{11}^2 - 2b_{21} \end{aligned} \qquad (7)$$

etc.

We now wish to derive more practical expansions in powers of $\rho_1 - \rho_1^*$ and $\rho_2 - \rho_2^*$. Following the procedure in I, we find first

$$\frac{\gamma_1^*}{\gamma_1} = \sum_{i,j \geq 0} X_{ij}(\mathbf{z}^*) \xi_1^i \xi_2^j \qquad (8)$$

$$\frac{\gamma_2^*}{\gamma_2} = \sum_{i,j \geq 0} Y_{ij}(\mathbf{z}^*) \xi_1^i \xi_2^j \qquad (9)$$

where

$$\begin{aligned} X_{00} &= 1,\ X_{10} = 2b_{20},\ X_{01} = b_{11} \\ X_{20} &= -4b_{20}^2 + 3b_{30} \\ X_{11} &= -2b_{20}b_{11} - b_{11}^2 + 2b_{21} \\ X_{02} &= -2b_{02}b_{11} + b_{12} \end{aligned} \qquad (10)$$

etc., and

$$\begin{aligned} Y_{00} &= 1,\ Y_{10} = b_{11},\ Y_{01} = 2b_{02} \\ Y_{20} &= -2b_{20}b_{11} + b_{21} \\ Y_{11} &= -2b_{02}b_{11} - b_{11}^2 + 2b_{12} \\ Y_{02} &= -4b_{02}^2 + 3b_{03} \end{aligned} \qquad (11)$$

We multiply eq. 8 by $-\rho_1^*$, add ρ_1 to both of the equation, and obtain

$$\rho_1^* = (1 + X_{10}\rho_1^*)\xi_1 + X_{01}\rho_1^*\xi_2 + X_{20}\rho_1^*\xi_1^2 + X_{11}\rho_1^*\xi_1\xi_2 + X_{02}\rho_1^*\xi_2^2 + \ldots \qquad (12)$$

Similarly

$$\rho_2 - \rho_2^* = Y_{10}\rho_2^*\xi_1 + (1 + Y_{01}\rho_2^*)\xi_2 + Y_{20}\rho_2^*\xi_1^2 + Y_{11}\rho_2^*\xi_1\xi_2 + Y_{02}\rho_2^*\xi_2^2 + \ldots \qquad (13)$$

The inverses of eq. 12 and 13 are

$$\xi_1 = \sum_{i,j \geq 0} C_{ij}(\mathbf{z}^*) \eta_1^i \eta_2^j \qquad (14)$$

$$\xi_2 = \sum_{i,j \geq 0} D_{ij}(\mathbf{z}^*) \eta_1^i \eta_2^j \qquad (15)$$

where

$$\eta_1 = \rho_1 - \rho_1^*,\ \eta_2 = \rho_2 - \rho_2^* \qquad (16)$$

$$\begin{aligned} C_{00} &= D_{00} = 0 \\ C_{10} &= -(1 + 2b_{02}\rho_2^*)/R \\ C_{01} &= b_{11}\rho_1^*/R \\ D_{10} &= b_{11}\rho_2^*/R \\ D_{01} &= -(1 + 2b_{20}\rho_1^*)/R \end{aligned} \qquad (17)$$

etc., and

$$R = b_{11}^2\rho_1^*\rho_2^* - (1 + 2b_{20}\rho_1^*)(1 + 2b_{02}\rho_2^*) \qquad (18)$$

Expressions for higher C_{ij}'s and D_{ij}'s are easy to derive but are algebraically complicated, so we omit them here.

Finally, substitution of eq. 14 and 15 into eq. 6, 8 and 9 leads to

$$\frac{\Pi}{kT} = \frac{[b_{11}\rho_2^* - (1 + 2b_{02}\rho_2^*)](\rho_1 - \rho_1^*)}{R} + \frac{[b_{11}\rho_1^* - (1 + 2b_{20}\rho_1^*)](\rho_2 - \rho_2^*)}{R} + \ldots \qquad (19)$$

$$\frac{\gamma_1^*}{\gamma_1} = 1 + \frac{[b_{11}^2\rho_2^* - 2b_{20}(1 + 2b_{02}\rho_2^*)](\rho_1 - \rho_1^*)}{R} - \frac{b_{11}(\rho_2 - \rho_2^*)}{R} + \ldots \qquad (20)$$

$$\frac{\gamma_2^*}{\gamma_2} = 1 - \frac{b_{11}(\rho_1 - \rho_1^*)}{R} + \frac{[b_{11}^2\rho_1^* - 2b_{02}(1 + 2b_{20}\rho_1^*)](\rho_2 - \rho_2^*)}{R} + \ldots \qquad (21)$$

plus rather unwieldy higher terms.

It is also useful to express eq. 19–21 (including contributions from quadratic terms omitted in these equations) in the form of expansions in powers of ρ_1, ρ_1^*, ρ_2 and ρ_2^*. We find

$$\frac{\Pi}{kT} = (\rho_1 - \rho_1^*) + (\rho_2 - \rho_2^*) - b_{20}(\rho_1 - \rho_1^*)(\rho_1 + \rho_1^*) - b_{02}(\rho_2 - \rho_2^*)(\rho_2 + \rho_2^*) - b_{11}(\rho_1\rho_2 - \rho_1^*\rho_2^*) + \ldots \qquad (22)$$

$$\frac{\gamma_1^*}{\gamma_1} = 1 + 2b_{20}(\rho_1 - \rho_1^*) + b_{11}(\rho_2 - \rho_2^*) + [(3b_{30} - 4b_{20}^2)\rho_1 - 3b_{30}\rho_1^* + (b_{21} - b_{11}^2)\rho_2 - b_{21}\rho_2^*](\rho_1 - \rho_1^*) + [(b_{21} - 2b_{11}b_{20})\rho_1 - b_{21}\rho_1^* + (b_{12} - 2b_{11}b_{02})\rho_2 - b_{12}\rho_2^*](\rho_2 - \rho_2^*) + \ldots \qquad (23)$$

$$\frac{\gamma_2^*}{\gamma_2} = 1 + b_{11}(\rho_1 - \rho_1^*) + 2b_{02}(\rho_2 - \rho_2^*) + [(b_{21} - 2b_{11}b_{20})\rho_1 - b_{21}\rho_1^* + (b_{12} - 2b_{11}b_{02})\rho_2 - b_{12}\rho_2^*](\rho_1 - \rho_1^*) + ([b_{12} - b_{11}^2)\rho_1 - b_{12}\rho_1^* + (3b_{03} - 4b_{02}^2)\rho_2 - 3b_{03}\rho_2^*](\rho_2 - \rho_2^*) + \ldots \qquad (24)$$

The $b_{ij}(\mathbf{z}^*)$ in these equations are, of course, themselves functions of ρ_1^* and ρ_2^*.

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(3) See also W. G. McMillan and J. E. Mayer, *J. Chem. Phys.*, **13**, 276 (1945).

The above discussion of the situation when there are *two* non-equilibrium species has an important application when there is only *one* non-equilibrium species, as in I. If we let $z_2 \rightarrow z_2^*$, species 2 becomes an "equilibrium" species. In this case, "species 2" can refer to any one of the equilibrium species in I, say species k. Since species 1 is now the only non-equilibrium species, we drop the subscript 1. Then if we put $\xi_2 = 0$ in eq. 9, we have an expression for ρ_k/ρ_k^*, the ratio of the concentrations of the equilibrium species k on the two sides of the membrane. That is

$$\frac{\gamma_k^*}{\gamma_k} = \frac{\rho_k}{\rho_k^*} = 1 + b_{11}\xi + (b_{21} - 2b_{20}b_{11})\xi^2 + \ldots \quad (25)$$

where $b_{ij}(\mathbf{z}^*)$ involves, through eq. 3, a set of i molecules of the non-equilibrium species and j molecules of species k, in the $\mathbf{z}^*$ solution of I. Using eq. I-17 to change variables from ξ to $\rho - \rho^*$, we find

$$\frac{\rho_k}{\rho_k^*} = 1 + \frac{b_{11}(\rho - \rho^*)}{1 + 2b_{20}\rho^*} + \frac{[b_{21} - 2b_{20}b_{11} + \rho^*(2b_{21}b_{20} - 3b_{11}b_{30})](\rho - \rho^*)^2}{(1 + 2b_{20}\rho^*)^3} + \ldots \quad (26)$$

This equation allows a computation of ρ_k/ρ_k^* without introducing the membrane potential (compare eq. I-34 and I-39). The expansion in powers of ρ and ρ^* is

$$\frac{\rho_k}{\rho_k^*} = 1 + b_{11}(\rho - \rho^*) + (\rho - \rho^*)[(b_{21} - 2b_{20}b_{11})\rho - b_{21}\rho^*] + \ldots \quad (27)$$

III. The Donnan Method

The discussion in Sec. II is quite general. Here we consider a special case, and treat it by a modification of the method of Donnan.[4] Let the $\mathbf{z}^*$ side (the "outside") of the system contain an electrolyte solution, the jth species ($j = 3,4,\ldots$) of which has a valence q_j and a concentration ρ_j^*. Two non-equilibrium species (subscripts 1 and 2) are also present at concentrations ρ_1^* and ρ_2^*, and with valences q_1 and q_2. On the other side ($\mathbf{z}$ or "inside") of the membrane, the jth species of electrolyte (in equilibrium across the membrane) has a concentration ρ_j, while the non-equilibrium species have concentrations ρ_1 and ρ_2. The membrane potential is ψ. The outside solution is assumed dilute enough to follow the Debye–Hückel theory. In order to ensure that the inside solution also is sufficiently dilute for the Debye–Hückel theory to be applicable, we use expansions in powers of ρ_1 and ρ_2 (as well as ρ_1^*, ρ_2^* and α, defined below), and retain linear terms only. All ions are considered hard spheres of diameter a and are immersed in a continuous medium of dielectric constant D.

On equating inside and outside electrochemical potentials for the jth species, we have

$$\rho_j\gamma_j(\text{in})e^{q_j\epsilon\psi/kT} = \rho_j^*\gamma_j(\text{out}) \quad j = 3, 4, \ldots \quad (28)$$

where

$$\ln \gamma_j(\text{out}) = -\frac{q_j^2\epsilon^2\kappa}{2DkT(1 + \kappa a)} + v\sum_{s \geq 1} \rho_s^* \quad (29)$$

$$\ln \gamma_j(\text{in}) = -\frac{q_j^2\epsilon^2\kappa_{\text{in}}}{2DkT(1 + \kappa_{\text{in}}a)} + v\sum_{s \geq 1} \rho_s \quad (30)$$

and

$$\kappa^2 = \frac{4\pi\epsilon^2 \sum_{s \geq 1} \rho_s^* q_s^2}{DkT}$$

$$\kappa_{\text{in}}^2 = \frac{4\pi\epsilon^2 \sum_{s \geq 1} \rho_s q_s^2}{DkT}$$

$v = 4\pi a^3/3$
ϵ = protonic charge

If we write ρ_j and ψ in the form

$$\rho_j = \rho_j^* + a_{1j}(\rho_1 - \rho_1^*) + a_{2j}(\rho_2 - \rho_2^*) + \ldots \quad j = 3, 4, \ldots \quad (31)$$

$$\epsilon\psi/kT = A_1(\rho_1 - \rho_1^*) + A_2(\rho_2 - \rho_2^*) + \ldots \quad (32)$$

and substitute eq. 29–32 in eq. 28, we find, after the necessary expansions, and on comparing ρ_j from eq. 28 with ρ_j in eq. 31, that

$$a_{ij} = -q_jA_i\rho_j^* + \frac{q_j^2\beta(q_1^2 + \Sigma^{(i)})\rho_j^*}{4\Sigma_2} - v S_i\rho_j^* \quad i = 1, 2 \quad (33)$$

where

$$\beta = \frac{\alpha}{(1 + \kappa_0 a)^2}$$

$$\alpha = \epsilon^2\kappa_0/DkT$$

$$\kappa_0^2 = 4\pi\epsilon^2\Sigma_2/DkT$$

$$\Sigma_n = \sum_{s \geq 3} \rho_j^* q_j^n$$

$$\Sigma^{(i)} = \sum_{s \geq 3} a_{is}q_s^2$$

$$S_i = 1 + \sum_{s \geq 3} a_{is}$$

Next we sum eq. 33 over $j \geqslant 3$ (a) as it stands, (b) after multiplication by q_j and (c) after multiplication by q_j^2. These summations lead, for each value of i, and with the aid of the neutrality conditions, to three linear equations in A_i, $\Sigma^{(i)}$ and S_i. On solving these equations we find, except for terms of negligible order

$$A_i = \frac{q_i}{\Sigma_2} + \frac{\beta\Sigma_3}{4\Sigma_2^2}\left(q_i^2 - q_i\frac{\Sigma_3}{\Sigma_2}\right) \quad i = 1, 2 \quad (34)$$

$$\frac{a_{ij}}{\rho_j^*} = -v - \frac{q_iq_j}{\Sigma_2} + \frac{\beta}{4\Sigma_2}\left(q_i^2 - q_i\frac{\Sigma_3}{\Sigma_2}\right)\left(q_1^2 - q_j\frac{\Sigma_3}{\Sigma_2}\right) \quad \begin{matrix} i = 1, 2 \\ j = 3, 4, \ldots \end{matrix} \quad (35)$$

Now, since (eq. 31)

$$\frac{\rho_j}{\rho_j^*} = \frac{\gamma_j^*}{\gamma_j} = 1 + \frac{a_{1j}}{\rho_j^*}(\rho_1 - \rho_1^*) + \frac{a_{2j}}{\rho_j^*}(\rho_2 - \rho_2^*) + \ldots \quad (36)$$

and since all ions have the same size a, we see, on comparing eq. 23, 24 and 36, that

$$2b_{20} = \frac{a_{1j}}{\rho_j^*}(q_j \longrightarrow q_1) \quad (37)$$

$$b_{11} = \frac{a_{2j}}{\rho_j^*}(q_j \longrightarrow q_1) = \frac{a_{1j}}{\rho_j^*}(q_j \longrightarrow q_2) \quad (38)$$

$$2b_{02} = \frac{a_{2j}}{\rho_j^*}(q_j \longrightarrow q_2) \quad (39)$$

Hence, from eq. 35

$$2b_{20} = -v - \frac{q_1^2}{\Sigma_2} + \frac{\beta}{4\Sigma_2}\left(q_1^2 - q_1\frac{\Sigma_3}{\Sigma_2}\right)^2 \quad (40)$$

$$b_{11} = -v - \frac{q_1q_2}{\Sigma_2} + \frac{\beta}{4\Sigma_2}\left(q_1^2 - q_1\frac{\Sigma_3}{\Sigma_2}\right)\left(q_2^2 - q_2\frac{\Sigma_3}{\Sigma_2}\right) \quad (41)$$

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(4) Compare T. L. Hill, *J. Phys. Chem.*, **61**, 548 (1957). We follow the procedure in this paper.

$$2b_{02} = -v - \frac{q_2^2}{\Sigma_2} + \frac{\beta}{4\Sigma_2}\left(q_2^2 - q_2\frac{\Sigma_3}{\Sigma_2}\right)^2 \quad (42)$$

Note that β, Σ_2 and Σ_3 depend on properties of the equilibrium ions only, species 3, 4, ...

In summary: eq. 32 and 34 give the membrane potential; eq. 23, 24 and 40–42 give the activity coefficient ratios for the non-equilibrium species; and eq. 22 and 40–42 give the osmotic pressures.

IV. The McMillan–Mayer Method

We consider the same special case as in Sec. III. The basic equations for the osmotic pressure and activity coefficient ratios are eq. 19–21 and 22–24 where, here, the b_{ij}'s are to be calculated directly from eq. 3 and 4. If we use for w_{ij} the potential in eq. 54 of reference 4, we find for b_{20}, b_{11} and b_{02} equations with the same formal appearance as eq. 40–42, but with Σ_2, Σ_3 and β replaced by Σ_2', Σ_3' and β', respectively, where

$$\beta' = \frac{\alpha'}{(1 + \kappa a)^2}$$

$$\alpha' = \epsilon^2\kappa/DkT$$

$$\Sigma_n' = \sum_{s \geq 1} \rho_s^* q_s^n$$

and κ has already been defined (following eq. 30). In other words, the "outside electrolyte" here includes the non-equilibrium ions as well as the equilibrium ions.

These results, together with eq. 19–21, represent the best available approximation when ρ_1, ρ_2, ρ_1^* and ρ_2^* are not necessarily small quantities. However, if exact (for this model) expansions in powers of ρ_1, ρ_2, ρ_1^* and ρ_2^* are desired, then eq. 22–24 are appropriate and $\Sigma_2' \rightarrow \Sigma_2$, $\Sigma_3' \rightarrow \Sigma_3$ and $\beta' \rightarrow \beta$ (to quadratic terms in the osmotic pressure and linear terms in the activity coefficient ratios). That is, in this case, the McMillan–Mayer method gives the same results as the Donnan method (eq. 40–42).

EUGENE, OREGON

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY OF MARYLAND]

The Vibrational Spectra and Geometrical Configuration of 1,3,5-Hexatriene[1]

BY ELLIS R. LIPPINCOTT, C. EVANS WHITE AND JOHN P. SIBILIA

RECEIVED NOVEMBER 4, 1957

Spectroscopic data for 1,3,5-hexatriene are reported. These include the Raman spectrum of the liquid and the infrared spectrum of the vapor. The spectral data indicate that 1,3,5-hexatriene has the *trans* pseudolinear configuration. An assignment of the vibrational frequencies to the normal modes of vibration is presented.

Introduction

A synthesis of 1,3,5-hexatriene was first reported by Van Romburgh and Van Dorssen,[2] after which a number of other syntheses have been reported.[3] Alder and Von Brachel[4] have postulated a *trans* configuration based upon a Diels–Alder reaction product.

Experimental

A sample of 1,3,5-hexatriene was kindly supplied by Professor G. Forrest Woods of the University of Maryland. It was prepared by the dehydration of 1,3-hexadiene-5-ol and purified by fractional crystallization.[3] Its physical properties were: m.p. −11.7°, b.p. 80°, n^{25}D 1.5035.

The Raman Spectrum.—The Raman spectrum of 1,3,5-hexatriene was obtained with an automatic recording instrument built at the University of Maryland,[5] using 4358 Å. excitation. The source was a "Toronto-type" arc. This consisted of a 30 mm. diameter helical Pyrex tube of four and one-half turns. Its total arc path is nine feet, of which seven and one-half feet effectively radiate the sample. A saturated potassium nitrite solution was used as a filter for the short wave length radiation. Calibration was accomplished by recording an iron arc spectrum. Figure 1 is a trace of one of the resulting Raman curves of 1,3,5-hexatriene. The observed Raman lines are listed in Table III.

The Infrared Spectrum.—The infrared spectrum of liquid 1,3,5-hexatriene has been reported.[3] However, the vapor spectrum has not been reported previously. A Perkin–Elmer Model 12-C single-beam, double-pass spectrometer was used. It was equipped with lithium fluoride, calcium fluoride and sodium chloride prisms. The spectra were run in 10-cm. gas cells at 25 and 35°. The absorption bands are listed in Table II and illustrated in Fig. 2. Figure 2 is a trace of the spectrum using a Beckman IR-4 spectrometer.

TABLE I

THE DISTRIBUTION OF VIBRATION AMONG SPECIES AND SELECTION RULES

trans. C_{2h} Vibr. species	No. of vibrations C	H	Total	Activity
Ag	5	8	13	Raman
Au	2	4	6	Infrared
Bg	1	4	5	Raman
Bu	4	8	12	Infrared
cis C_{2v}				
A_1	5	8	13	Infrared and Raman
A_2	2	4	6	Raman
B_1	4	8	12	Infrared and Raman
B_2	1	4	5	Infrared and Raman

Discussion

The comparative stability of 1,3,5-hexatriene may be postulated as due to resonance. In order to have the maximum amount of resonance stabilization, the molecule must be planar. Of the six possible structures, three have *cis* and three have *trans* configurations. Fisher–Hirschfelder models indicate that five of these structures (2,3,4,5,6 of Fig. 3) cannot be made planar because they are sterically hindered. However, structure 4 cannot be en

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[1] Taken in part from a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Graduate School of the University of Maryland.

[2] Van Romburgh and Van Dorssen, *Verslag Akad. Wetenschappen Amsterdam*, **8**, 565 (1905).

[3] G. F. Woods and L. H. Schwartzman, THIS JOURNAL, **70**, 3394 (1948).

[4] K. Alder and H. Von Brachel, *Ann.*, **608**, 195 (1957).

[5] R. A. Bafford, Master's Thesis, University of Maryland, 1956.