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TABLE I.*

| NAME | INCREMENT OF SURFACE TENSION PER MOLE/LITER OF SOLUTE $\Delta\sigma/\Delta C$ σ in dynes/cm | LOG OF SOLUBILITY RATIO IN WATER- ETHANOL SYSTEM LOG N/N_0 |
|------------------------------|--|---|
| α Alanine | +0.58 | |
| β Alanine | +0.77 | -2.856 |
| Glycine | +0.92 | -3.139 |
| α Aminocaproic acid | -23 | -1.414 |
| ϵ Aminocaproic acid | -0.25 | -2.972 |
| α Aminobutyric acid | -0.41 | |
| β Aminobutyric acid | +0.05 | |

* Taken from Pappenheimer, Lepie and Wyman, J. Am. Chem. Soc. 58, 1851 (1936); Cohn, McMeekin, Edsall, and Weare, J. Am. Chem. Soc. 56, 2270 (1934); 57, 626 (1935); 58, 2173 (1936).

surface tension without dipole for glycine will be about the same or little larger than that of alanine. Thus the difference of 1.32 for glycine between the theoretical and experimental values may be due to the positive adsorption tendency of the molecules without the dipole, and this value may be considered quite reasonable. Thus we may consider that the theory of surface tension of the dipolar ions based on the image force idea explains the experimental facts quite satisfactorily.

In conclusion the writer wishes to thank Dr. H. A. Erikson for his kind encouragement.

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Thermodynamic Functions for Molecules Having Restricted Internal Rotations

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The partition function is considered for molecules having restricted internal rotations, and expressions are obtained which are reasonably accurate for most actual molecules. Tables are presented which list the contributions of a single restricted rotational degree of freedom to the entropy, energy, free energy, and heat capacity.

THE presence of a potential barrier of about 3000 cal./mole restricting rotation about the single bond in ethane, which was shown to exist by Kemp and Pitzer² and confirmed by Howard,³ suggests that the internal rotations of a large number of molecules may be appreciably hindered. It is therefore desirable that as general and simple a procedure as possible be developed for calculating the thermodynamic functions of these molecules. Assuming a reasonable shape of restricting potential, the pertinent theory will be briefly discussed and tables presented, which make possible easy and quite accurate calculations of the complete rotational contribution to the entropy, energy, and heat capacity of almost any molecule. The moments of inertia and potential barriers must, of course, be known, unless the calculation is to be reversed, and one or more of these quantities derived from thermodynamic data.

In a second paper the method here developed will be applied to a number of molecules.

Little is known concerning the exact shape of the restricting potentials, except that they must be the same qualitatively as that expressed by $\frac{1}{2}v(1 - \cos n\phi)$ where v is the height and n the number of potential maxima. This, moreover, is the only form for which the mathematics has been even partially developed, and must, consequently, be adopted. For low barriers the exact shape should make little difference, while for higher barriers the shape near the minimum is the important element so that, although a somewhat incorrect height may need to be used, the thermodynamic functions should be quite accurate.

It is, of course, necessary to use approximate methods if results of general applicability are desired. In the case of high potential barriers, when the restricted rotation becomes essentially a torsional oscillation, the method commonly used with vibrating molecules is applicable. The entropy (or other thermodynamic quantity) is

¹ Shell Research Fellow, Academic Year 1936-37.

² Kemp and Pitzer, J. Chem. Phys. 4, 749 (1936); J. Am. Chem. Soc. 59, 276 (1937).

³ Howard, Phys. Rev. 51, 53 (1937).

TABLE I. $(S_f - S)$ cal./deg. mole.

| V/RT | $10^{-36}n^2/IV$ | | | | | | | | |
|------|------------------|------|------|------|------|------|------|------|------|
| | 0 | 1 | 2 | 4 | 8 | 16 | 32 | 64 | 128 |
| 0.0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.5 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| 1.0 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.11 | 0.11 | 0.10 | 0.09 |
| 2.0 | 0.42 | 0.41 | 0.41 | 0.41 | 0.40 | 0.38 | 0.36 | 0.29 | 0.21 |
| 3.0 | 0.79 | 0.77 | 0.76 | 0.75 | 0.74 | 0.68 | 0.62 | 0.47 | |
| 4.0 | 1.13 | 1.11 | 1.10 | 1.08 | 1.05 | 0.97 | 0.84 | 0.61 | |
| 5.0 | 1.42 | 1.39 | 1.37 | 1.35 | 1.29 | 1.18 | 0.98 | | |
| 6.0 | 1.66 | 1.62 | 1.60 | 1.57 | 1.49 | 1.34 | 1.08 | | |
| 7.0 | 1.87 | 1.82 | 1.79 | 1.74 | 1.63 | 1.44 | 1.12 | | |
| 8.0 | 2.04 | 1.98 | 1.95 | 1.88 | 1.74 | 1.50 | 1.12 | | |
| 9.0 | 2.19 | 2.11 | 2.07 | 1.98 | 1.81 | 1.54 | | | |
| 10.0 | 2.32 | 2.21 | 2.16 | 2.06 | 1.86 | 1.55 | | | |
| 12.0 | 2.53 | 2.37 | 2.32 | 2.17 | 1.91 | 1.53 | | | |
| 14.0 | 2.69 | 2.51 | 2.42 | 2.23 | 1.91 | 1.46 | | | |
| 16.0 | 2.83 | 2.63 | 2.50 | 2.27 | 1.89 | 1.36 | | | |

TABLE II. $(F - F_f)/T$.

| V/RT | $10^{-36}n^2/IV$ | | | | | | | | |
|------|------------------|------|------|------|------|------|------|------|------|
| | 0 | 1 | 2 | 4 | 8 | 16 | 32 | 64 | 128 |
| 0.0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.5 | 0.47 | 0.40 | 0.38 | 0.36 | 0.32 | 0.29 | 0.23 | 0.16 | 0.08 |
| 1.0 | 0.87 | 0.77 | 0.73 | 0.68 | 0.61 | 0.53 | 0.42 | 0.28 | 0.12 |
| 2.0 | 1.52 | 1.35 | 1.28 | 1.18 | 1.04 | 0.86 | 0.63 | 0.35 | 0.11 |
| 3.0 | 1.98 | 1.73 | 1.63 | 1.49 | 1.29 | 1.03 | 0.70 | 0.32 | |
| 4.0 | 2.33 | 1.99 | 1.85 | 1.67 | 1.43 | 1.10 | 0.70 | 0.26 | |
| 5.0 | 2.60 | 2.18 | 2.00 | 1.78 | 1.50 | 1.11 | 0.65 | | |
| 6.0 | 2.81 | 2.30 | 2.10 | 1.85 | 1.52 | 1.08 | 0.58 | | |
| 7.0 | 2.98 | 2.39 | 2.16 | 1.88 | 1.51 | 1.03 | 0.49 | | |
| 8.0 | 3.13 | 2.45 | 2.20 | 1.89 | 1.48 | 0.96 | 0.38 | | |
| 9.0 | 3.26 | 2.50 | 2.22 | 1.89 | 1.45 | 0.88 | | | |
| 10.0 | 3.38 | 2.53 | 2.24 | 1.88 | 1.40 | 0.82 | | | |
| 12.0 | 3.57 | 2.57 | 2.23 | 1.83 | 1.31 | 0.69 | | | |
| 14.0 | 3.72 | 2.59 | 2.21 | 1.76 | 1.20 | 0.57 | | | |
| 16.0 | 3.86 | 2.59 | 2.18 | 1.68 | 1.08 | 0.43 | | | |

taken as the sum of the translational and rotational entropies of the rigid molecule, and the entropies due to vibration, torsional or otherwise. With very high potentials one may use the harmonic oscillator or Einstein functions in which:

$$h\nu/kT = \theta/T = (nh/2\pi kT)(v/2I)^{\frac{1}{2}} \\ = 4.463(n/T)(V/10^{40}I)^{\frac{1}{2}},$$

where I is the reduced moment of inertia (I_1I_2/I_1+I_2), n the number of potential maxima, v the height of the potential maxima in ergs/molecule, and V , the same in cal./mole. For moderately high potentials it is preferable to use the values obtained with the above potential function itself.

The quantum mechanics of the one dimensional restricted rotator has been discussed by Nielsen.⁴ The wave equation in this case is easily transformed into Mathieu's differential equation:

$$M'' + [\alpha + 16q \cos 2x]M = 0, \quad (1)$$

where $q = \pi^2 I v / n^2 h^2$ and $E - v/2 = n^2 h^2 \alpha / 32 \pi^2 I$.

The single value condition requires, in general, solutions for which the characteristic values α are not known; however, it can be shown that the characteristic values for these solutions must lie in regions which are closely enough bounded so as to allow a reasonably accurate

partition function to be calculated. It is convenient to take the ratio of this function to the partition function of the free rotator, since this ratio depends on only two variables (V/RT) and (n^2/IV). By means of numerical sums the above partition function ratio and its first two temperature derivatives were calculated for a range of values of each of the two variables. (These calculations were actually made for the case $n=2$ and $I_1 = \infty$, $I_2 = I$, which involves only the ordinary Mathieu functions, for which some characteristic values have been tabulated by Ince⁵ and Goldstein⁶ and others were calculated as needed. The results, however, are quite accurately applicable to the general case, as stated above.) The results thus obtained for the quantities $(S_f - S)$, $(F - F_f)/T$, H/T and C are listed in Tables I, II, III and IV. The absolute values of S and F/T are given by the equations:

$$S = R(-0.767 + \frac{1}{2} \ln T + \frac{1}{2} \ln I \times 10^{40} - \ln n) \\ - (S_f - S), \quad (2)$$

$$-F/T = R(-1.267 + \frac{1}{2} \ln T + \frac{1}{2} \ln I \times 10^{40} \\ - \ln n) - (F - F_f)/T, \quad (3)$$

where n is the symmetry number of the free rotator which will ordinarily be the same as the n in the potential function. If there are n potential minima, at least approximately equal, yet the molecule is not identical in the various equilibrium positions, an approximate treatment may be obtained with the n 's not the same. A

⁴ Nielsen, Phys. Rev. **40**, 445 (1932). See also Pauling, Phys. Rev. **36**, 430 (1930); Teller and Wiegert, *Nachr. Ges. Wiss. Göttingen. Math. physik. Klasse.* (1933) p. 218.

⁵ Ince, Proc. Roy. Soc. Edinburgh, **46**, 316 (1925-26).

⁶ Goldstein, Trans. Camb. Phil. Soc. **23**, 303 (1927).

case of this sort, *n*-butane, will be discussed in the following paper.

As the potential barrier becomes lower the uncertainty in the above treatment becomes greater, since the molecule spends an increasing fraction of the time in configurations appreciably different from the equilibrium one. In order to investigate this situation a study will be made of the limiting high temperature (or large moment of inertia) form of the partition function:

$$Q = \frac{1}{h^m} \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \int_{\alpha_1}^{\beta_1} \dots \int_{\alpha_m}^{\beta_m} e^{-1/kT(K.E. + \Phi)} \times dq_1 \dots dq_m dp_1 \dots dp_m, \quad (4)$$

where *K.E.* and Φ are the kinetic and potential energies, respectively, *m* the number of rotational degrees of freedom, and α_i, β_i the range of the *i*th angular coordinate. Edinoff and Aston⁷ have shown that this form gives a very satisfactory approximation in the case of free rotation, while for small barriers the degree of approximation may be estimated by noting the variation of the functions in Tables I to IV with (n^2/IV), holding (*V/RT*) constant. The first column ($n^2/IV=0$) was calculated with the aid of this limiting function as is explained below. Using the results of Edinoff and Aston⁷ who discussed the integration with respect to the

momenta, one obtains:

$$Qr = \frac{(2\pi kT)^{m/2}}{h^m} \int_{\alpha_1}^{\beta_1} \dots \int_{\alpha_m}^{\beta_m} [A]^{\frac{1}{2}} \times e^{-\Phi/kT} dq_1 \dots dq_m, \quad (5)$$

where [*A*] is the determinant of

$$2K.E. = \sum_{i,j=1}^m A_{ij} \dot{q}_i \dot{q}_j$$

and Φ may be expressed:

$$\Phi = \sum_{i=4}^m \frac{1}{2} v_i (1 - \cos n_i q_i).$$

It may be noted at this point that the limits of integration of all internal coordinates will be 0 and 2π and that by substituting $q_1' = n_1 q_1$ the *n*'s may be removed except possibly for the factor [*A*]^{1/2}. For many molecules one may take

$$[A] = \sin^2 q_1 \prod_{i=1}^m I_i$$

in which the *I*'s are all constants, moments of inertia. This gives:

$$Qr = \frac{(2^9 \pi^7 k^3 T^3 I_1 I_2 I_3)^{\frac{1}{2}}}{h^3} \prod_{i=4}^m \left(\frac{(2\pi k T I_i)^{\frac{1}{2}}}{h} \times \int_0^{2\pi} e^{-(v_i/kT)(1-\cos x)} dx \right). \quad (6)$$

TABLE III. *H/T*.

| <i>V/RT</i> | $10^{-36} n^2/IV$ | | | | | | | | |
|-------------|-------------------|------|------|------|------|------|------|------|------|
| | 0 | 1 | 2 | 4 | 8 | 16 | 32 | 64 | 128 |
| 0.0 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 |
| 0.5 | 1.43 | 1.36 | 1.34 | 1.32 | 1.28 | 1.25 | 1.19 | 1.12 | 1.04 |
| 1.0 | 1.74 | 1.64 | 1.60 | 1.55 | 1.48 | 1.41 | 1.30 | 1.17 | 1.02 |
| 2.0 | 2.09 | 1.93 | 1.86 | 1.76 | 1.63 | 1.47 | 1.26 | 1.05 | 0.89 |
| 3.0 | 2.18 | 1.95 | 1.86 | 1.73 | 1.54 | 1.34 | 1.07 | 0.84 | |
| 4.0 | 2.19 | 1.87 | 1.74 | 1.58 | 1.37 | 1.12 | 0.85 | 0.64 | |
| 5.0 | 2.17 | 1.78 | 1.62 | 1.42 | 1.20 | 0.92 | 0.66 | | |
| 6.0 | 2.14 | 1.67 | 1.49 | 1.27 | 1.02 | 0.73 | 0.49 | | |
| 7.0 | 2.10 | 1.56 | 1.36 | 1.13 | 0.87 | 0.58 | 0.36 | | |
| 8.0 | 2.08 | 1.46 | 1.24 | 1.00 | 0.73 | 0.45 | 0.25 | | |
| 9.0 | 2.06 | 1.38 | 1.14 | 0.90 | 0.63 | 0.33 | | | |
| 10.0 | 2.05 | 1.31 | 1.07 | 0.81 | 0.53 | 0.26 | | | |
| 12.0 | 2.03 | 1.19 | 0.90 | 0.65 | 0.39 | 0.15 | | | |
| 14.0 | 2.02 | 1.07 | 0.78 | 0.52 | 0.28 | 0.10 | | | |
| 16.0 | 2.02 | 0.95 | 0.67 | 0.40 | 0.18 | 0.06 | | | |

⁷ Edinoff and Aston, *J. Chem. Phys.* 3, 379 (1935).

TABLE IV. *C*.

| <i>V/RT</i> | $10^{-36} n^2/IV$ | | | | | | | | |
|-------------|-------------------|------|------|------|------|------|------|------|------|
| | 0 | 1 | 2 | 4 | 8 | 16 | 32 | 64 | 128 |
| 0.0 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 |
| 0.5 | 1.06 | 1.06 | 1.06 | 1.06 | 1.06 | 1.06 | 1.06 | 1.05 | 1.04 |
| 1.0 | 1.22 | 1.22 | 1.21 | 1.21 | 1.21 | 1.20 | 1.19 | 1.17 | 1.14 |
| 2.0 | 1.69 | 1.68 | 1.68 | 1.67 | 1.65 | 1.61 | 1.54 | 1.43 | 1.22 |
| 3.0 | 2.10 | 2.08 | 2.07 | 2.05 | 2.01 | 1.91 | 1.73 | 1.47 | |
| 4.0 | 2.29 | 2.27 | 2.25 | 2.21 | 2.13 | 1.98 | 1.73 | 1.34 | |
| 5.0 | 2.33 | 2.30 | 2.27 | 2.23 | 2.12 | 1.89 | 1.56 | | |
| 6.0 | 2.32 | 2.26 | 2.22 | 2.16 | 2.01 | 1.70 | 1.31 | | |
| 7.0 | 2.27 | 2.19 | 2.12 | 2.05 | 1.85 | 1.52 | 1.09 | | |
| 8.0 | 2.22 | 2.11 | 2.04 | 1.92 | 1.68 | 1.34 | 0.91 | | |
| 9.0 | 2.18 | 2.05 | 1.94 | 1.80 | 1.53 | 1.19 | | | |
| 10.0 | 2.15 | 1.99 | 1.86 | 1.68 | 1.39 | 1.03 | | | |
| 12.0 | 2.11 | 1.89 | 1.73 | 1.45 | 1.15 | 0.77 | | | |
| 14.0 | 2.08 | 1.81 | 1.61 | 1.24 | 0.93 | 0.55 | | | |
| 16.0 | 2.06 | 1.75 | 1.51 | 1.06 | 0.72 | 0.34 | | | |

In (6) the first factor pertains to the free rotation of the molecule as a whole while each of the other factors pertain to an internal rotation with restricting potential v_i . The integral in the latter factors has been evaluated by suitable expansions for various values of (v/kT) , the results being used to obtain the contribution of a single degree of freedom to the functions $(S_f - S)$, $(F - F_f)/T$, H/T and C as listed in the first columns of Tables I, II, III and IV, respectively. It is apparent from Eq. (6) that for this group of molecules, the treatment of the entropy as a sum of independent contributions is valid for all magnitudes of restricting potential.

Where this treatment is not exact, it is, nevertheless, a good approximation, particularly for high potential barriers. This can be seen from Eq. (5) in which the principal contribution to the integral will be from configurations for which Φ is small. Therefore, if $[A]$ varies only slowly with the coordinates, it can be removed from the integral and given the value corresponding to the configuration of minimum potential. The partition function will be most in error under this procedure in the case of free rotation, when, however, an exact value for the integral in Eq. (5) can often be obtained.^{7, 8} Thus an upper limit can be set to this error for all values of the potential. For the temperature derivatives of the partition function no such simple relationship holds; however, an analysis of their behavior with a continuous and slowly varying $[A]$ indicates that the limiting error in $-F/T$ will apply in order of magnitude at least to the other thermodynamic functions. Fortunately in most actual molecules the limiting error in $-F/T$ will probably be small, of the order of 0.1 cal./deg. mole. If the uncertainty of this method is too great the proper procedure

appears to be the further analysis of Eq. (5) for the individual molecule or type of molecules at hand.

The accuracy of the data in Tables I to IV is about 0.02 cal./deg. mole except for certain portions of Table IV which may contain values erroneous by 0.05 cal./deg. mole. However, considering the arbitrary form of the potential function and the approximate methods involved in application to actual molecules, the results obtained with the aid of these tables cannot ordinarily be considered significant beyond 0.1 cal./deg. mole. It should also be emphasized that this treatment will fail at very low temperatures.

As a summary, the methods of calculating thermodynamic quantities for molecules having restricted internal rotations will be briefly reviewed.

1. If (V/RT) is of the order of one or greater, the desired function is calculated for the rigid molecule and to this is added contributions from the various oscillational degrees of freedom. Unless (V/RT) is very large the contributions from torsional oscillations should be calculated from Eqs. (2) and (3) and Tables I to IV.

2. If (V/RT) is fairly large (greater than about three) this result may be considered accurate; however, if (V/RT) is smaller the result may be somewhat in error. An upper limit to the error in $-F/T$ may be found by comparing the result obtained by this method for a hypothetical molecule having free rotation, with the accurate value for that molecule.^{7, 8} The limiting error thus obtained for $-F/T$ applies approximately for S , H/T and C .

3. For very small values of (V/RT) it is preferable to obtain S or $-F/T$ by applying a small correction taken from Table I or II to the value calculated for the freely rotating molecule.

⁸ Kassel, J. Chem. Phys. 4, 276 (1936); 4, 435 (1936).