

Effect of Limiting Summation over Vibrational Levels on Calculations of Thermodynamic Properties

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Citation: *The Journal of Chemical Physics* **17**, 347 (1949); doi: 10.1063/1.1747254

View online: <http://dx.doi.org/10.1063/1.1747254>

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reasonably replace m^* by the molecular mass m , and at least as a rough approximation we may suppose that δ is for all liquids the same fraction $bv^{1/3}$ of the mean molecular distance. Making these substitutions we get for comparison with experiment:

$$\eta = b \frac{(2\pi mkT)^{1/3}}{v^{1/3}} e^{\Delta E_a / \beta RT}. \quad (4)$$

Equations (1) and (4) were compared with the experimental data for 67 liquids. The quantity h in Eq. (1) was treated as an adjustable empirical constant. A least squares solution with respect to $\log \eta$ gave the following values for the parameters: $\alpha = 2.84$, $h = 1.41 \times 10^{-26}$ erg sec., $\beta = 3.26$, $b = 0.075$. The value found for α does not differ greatly from the value 2.45 obtained by Eyring and collaborators by restraining h to be Planck's constant. The value found for b does not seem inconsistent with its interpretation as the fraction of the mean molecular distance to be ascribed to the activated complex, although the interpretation of the length δ is not so clear in the case of a flowing liquid as in the case of a chemical reaction, where it may be related to a feature of the in principle calculable potential energy hypersurface.

The root mean square deviations of the common logarithm of η as calculated for the 67 liquids by Eqs. (1) and (4) were 0.250 and 0.189, respectively. The precision with which these equations represent the experimental data is accordingly not great. In view of the complexity of the liquid state and the consequent obscurity that surrounds the quantities δ and ΔF_a , one may hesitate to ascribe much significance to the fact that Eq. (4) represents the data appreciably better than does Eq. (1); but it is satisfying that, of the two equations, the one whose form does not suggest that viscosity is a quantum phenomenon and whose derivation seems the more nearly understandable, does represent the data at least as well as the other.

¹ Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), pp. 491-493.

² E. Brunner, "The thermodynamic properties of activated complexes," *J. Chem. Phys.* **17**, 347 (1949).

Effect of Limiting Summation over Vibrational Levels on Calculations of Thermodynamic Properties

HAROLD W. WOOLLEY

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January 3, 1949

A NUMBER of laboratories are engaged in computing thermodynamic functions for simple polyatomic molecules by direct summation over the vibrational levels. The writer has had occasion to inquire as to the error introduced by stopping such summations at too low a total vibrational energy. The result for the simple case of harmonic oscillators may be of interest to readers contemplating such calculations.

For a single harmonic oscillator, the summation over all levels gives $Q_H = (1 - e^{-hc\omega/kT})^{-1}$, and if levels above W wave numbers are omitted, the partition function as calculated will be $Q = Q_H(1 - e^{-hcW/kT})$. In an actual computation, one might be tempted to assume that essentially the same relative error would be introduced in the case of a polyatomic molecule by stopping the summation when the combined energy of its several assumed harmonic oscillators has reached the value W . While such a relation between errors could be expected if the summation included all levels for which the energy of each component oscillator was less than W , actual summations would scarcely be carried out with such an irregular total energy of cut-off. With a uniform energy of cut-off, the situation is somewhat less favorable.

The proper estimate may be made readily by noting that the summations are made over the points of a hyperlattice,

using only points in the positive domain of v_i 's, limited by the

hyperplane $E = \sum_{i=1}^n \omega_i v_i$. The number of modes of vibration is

n , so that each component of any degenerate frequency is to be counted. The portion of hyperspace thus bounded has the "volume" $V = \frac{E^n}{n! \prod_i \omega_i}$, so that the number of states between

E and $E + dE$ is $dV = \frac{E^{n-1} dE}{(n-1)! \prod_i \omega_i}$. The summation over states above $E = W$ is then given approximately by

$$\frac{1}{(n-1)! \prod_i \omega_i} \int_W^\infty e^{-hcE/kT} E^{n-1} dE = \prod_i \left(\frac{kT}{hc\omega_i} \right) \cdot e^{-y} \sum_{m=0}^{n-1} \frac{1}{m!} y^m,$$

where $y = hcW/kT$. With Q_H representing the result of complete summation for all levels of the oscillators, the partition function actually obtained using levels only up to $E = W$ will be

$$Q = Q_H(1 - \rho e^{-y}),$$

where $\rho = \sum_{m=0}^{n-1} \frac{1}{m!} y^m$. In regard to calculations for very high

temperatures ($y \ll 1$), it is of interest that ρ , the multiplier of e^{-y} , is composed of the early terms of the power series development for e^y . For the moderate temperatures for which calculations are made, e^{-y} is made small by making y of the order of magnitude of a sizeable integer. Under these conditions ρ becomes a considerable magnitude.

The approximate effect on the thermodynamic functions due to neglect of high levels is readily expressed in terms of the effect for a single oscillator. For the single harmonic oscillator with levels cut off at W wave numbers, the error would be

$$\Delta(-F^0/RT)_1 = \ln(1 - e^{-y}) \approx -e^{-y},$$

where $y = hcW/kT$,

$$\Delta(H^0/RT)_1 = -ye^{-y}/(1 - e^{-y}),$$

and

$$\Delta(C_p^0/R)_1 = -y^2 e^{-y}/(1 - e^{-y})^2.$$

For a system of n modes of vibration with levels cut off at W wave numbers

$$\Delta(-F^0/RT)_n = \Delta(-F^0/RT)_1 \cdot \rho$$

$$\Delta(H^0/RT)_n = \Delta(H^0/RT)_1 \cdot \left(\frac{1 - e^{-y}}{1 - \rho e^{-y}} \right) \frac{y^{n-1}}{(n-1)!}$$

and

$$\Delta(C_p^0/R)_n = \Delta(C_p^0/R)_1 \cdot \left(\frac{1 - e^{-y}}{1 - \rho e^{-y}} \right)^2 \left[\frac{y^{n-1}}{(n-1)!} - \frac{y^{n-2}}{(n-2)!} \right],$$

approximately, for $n > 1$.

In Table I, a few rough values are given to compare the

TABLE I. Effect of cut-off on thermodynamic functions for harmonic oscillators (for one and for four vibrational modes).

| Boltzmann factor e^{-y} | $\Delta(-F^0/RT)_n$ | | Ratio |
|------------------------------|---------------------|-----------|-------|
| | ($n=1$) | ($n=4$) | |
| 10^{-4} | 0.0001 | 0.0183 | 183 |
| 10^{-5} | 0.00001 | 0.0033 | 333 |
| 10^{-6} | 0.000001 | 0.00055 | 550 |
| e^{-y} | $\Delta(H^0/RT)_n$ | | Ratio |
| | ($n=1$) | ($n=4$) | |
| 10^{-4} | 0.0009 | 0.12 | 133 |
| 10^{-5} | 0.000115 | 0.029 | 255 |
| 10^{-6} | 0.000014 | 0.0061 | 440 |
| e^{-y} | $\Delta(C_p^0/R)_n$ | | Ratio |
| | ($n=1$) | ($n=4$) | |
| 10^{-4} | 0.0085 | 0.77 | 91 |
| 10^{-5} | 0.0013 | 0.25 | 189 |
| 10^{-6} | 0.00019 | 0.07 | 344 |

cut-off error for a molecule with four vibrational degrees of freedom ($n=4$) with that for a single degree of freedom

($n=1$). The four degrees of freedom might, for example, be for two non-degenerate vibrations and one doubly degenerate vibration. It is seen that for the molecule with four vibrational modes, the summation would have to extend above the point where the Boltzmann factor is 10^{-6} in order to avoid introducing an error in C_p^0 as large as $0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, because of the presence of a multiplying factor in excess of 300. The situation would be modified appreciably in the case where effects of anharmonicity were included, so that the present results do not apply quantitatively for that case.

In conclusion, it should be noted that the multiplying factors for the errors increase very rapidly in passing to molecules with a larger number of atoms.

Salt Effects on Ionic Equilibria

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January 11, 1949

ABOUT three months ago, we submitted a paper concerning the effects of salts on the rates of ionic reactions in aqueous solution for publication in this journal. In this paper we demonstrated that for a reaction between ions of like sign, the specific rate does not depend upon the ionic strength of the solution. It does depend upon the concentrations and characters of the ions of sign opposite to that of the reactants.

As a logical consequence of this fact, we could expect to find that an equilibrium between ions of the same sign would also be independent of the ionic strength. We now announce that this has been experimentally proved to be so.

The equilibrium studied is $\text{Fe}^{+++} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{++} + \text{H}^+$, in dilute perchloric acid solution (about $0.002M$). The absorption spectra of Fe^{+++} and of FeOH^{++} are sufficiently different in the region $\lambda=3500\text{\AA}$ to $\lambda=2500\text{\AA}$ so that concentration changes can easily be observed even at high dilution (about $3 \times 10^{-4}M$ in iron), by the use of a quartz spectrophotometer. It was found that the addition of NaClO_4 and $\text{La}(\text{ClO}_4)_3$ produced identical shifts of equilibrium for identical normalities and that the addition of NaClO_4 produced a much greater change than did the addition of $\text{La}(\text{ClO}_4)_3$ of such an amount as to result in the same ionic strength. The lanthanum solution in each case was about $0.003M$. In every experiment the shift was such as to cause an increase in the Fe^{+++} concentration.

It is obvious that if these experiments are independently verified, it will be necessary to restudy the Debye-Hückel approach to the calculation of the activity coefficients of ions. The details of these experiments will be submitted for publication soon.

Note on the Coefficient of the Term $\Pi \beta_k^{n_k}$ in the Cluster Integral b_l in Mayer's Condensation Theory

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January 5, 1949

THE cluster integral b_l in Mayer's Condensation Theory is the integral over the configuration space of l particles of a sum of products of functions f_{ij} between the particles i and j .¹ It can be analyzed into a sum of products of irreducible integrals β_k 's, where β_k is defined as the integral over the configuration space of $k+1$ particles, multiplied by a normal-

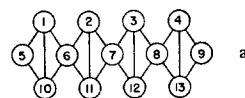
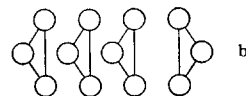


FIG. 1.



ization factor.² Thus b_l can be written as follows:

$$b_l = \frac{1}{l!} \sum_s K_s \prod_k (\beta_k)^{n_k} \quad (1)$$

$$\sum_k n_k = l - 1,$$

in which n_k is the power with which β_k occurs in the term b_l , and K_s is the coefficient to be determined. Using a physical picture of "bolting the frames," Mayer and Harrison obtained the following result,³

$$K_s = \frac{1}{l^{2-n}} \frac{l!}{\prod_k (k!)^{n_k} n_k!} \quad (2)$$

The meaning of n will be given later. The following derivation of Eq. (2) is essentially based upon the idea of Mayer and Harrison, but it does get rid of "frames," "bolts," "washers," etc. and is therefore quite simple.

A singly connected cluster can be transformed into a number of more-than-singly connected clusters by removing one molecule away from the former. (The terms "singly connected cluster" and "more-than-singly connected cluster" have been clearly defined in Mayer and Mayer's book.⁴) Thus, by taking molecule 8 away from Fig. 1a, the singly connected cluster is changed into four more-than-singly connected clusters (Fig. 1b), and by taking molecule 5 away from Fig. 2a, the singly connected cluster is changed into five more-than-singly connected clusters (Fig. 2b). Let n be the total number of more-than-singly connected clusters formed from a singly connected cluster of l molecules. Then

$$\sum n_k = n. \quad (3)$$

Let L_s be the number of ways of placing the numbered molecules into the more-than-singly connected clusters, and M_s be the number of ways of joining together these clusters to form a singly connected cluster. Since there are l ways of removing one molecule, K_s in Eq. (1) becomes

$$K_s = (1/l) L_s M_s. \quad (4)$$

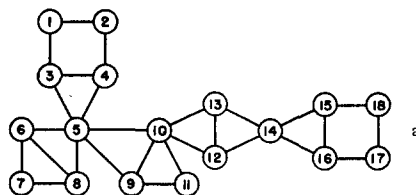


FIG. 2.

