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The Quantum-Mechanical Contributions of the Terms Arising from Higher Order Approximations on Gaseous Viscosity and Thermal Conductivity.

By Kozo HIROTA, Akira TAKAHASHI and Tatsuya YOSHITOMI.

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I. Introduction. Since the study of Massay and Mohr,(1) gaseous viscosity was often treated and discussed quantum-mechanically by several authors, among whom the senior author(2) is included. However, perfect agreement between theory and experiment has not been obtained, even by the adjustment of the intermolecular potential as tried by Massay and Buckingham(3) and Uehling and Hellund.(3) Such result may be due to two following reasons. Firstly the effect due to ternary collisions, the role of which becomes conspicious at low temperature, was not taken into account. Secondly they applied viscosity formula of the first order approximation in spite of the suspicion that the contributions arising from the higher order ones may not be neglected. In the works published by the senior writer the same formula was also adopted. Then it will be the next step to know quantitatively to what degree these two effect contribute quantum-mechanically, before we carry on the detailed treatment, e.g., introduction of some complicated model.

It is the aim of the present paper to clarify the first effect on viscosity on one hand and, applying its basic numerical value, to the thermal conductivity which has never been studied quantum-mechanically on the other. Helium which will show probably most marked effect was adopted as the object of the research by use of two models, i. e. that of rigid elastic sphere and that of Slator's potential.

II. Theoretical Formula. i) *Viscosity:* According to the rigorous theory of Chapman and Enskog, the gaseous viscosity η is expressible with respect to every types of the adopted model by the formula :(4)

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(1) H. S. Massay and C B.C. Mohr, *Proc. Roy. Soc.* A **141,** (1933) 434.

(2) H. Hirota, *Bull Chem. Soc. Japan,* **19,** (1944) 109.

(3) H. S. Massay and R. A. Buckingham, *Proc. Roy. Soc.,* A **168,** (1938) 378; **169,** (1939) 304; E. A. Uehling and E. J. Hellund. *Phys. Rev.,* **54,** (1938) **479.**

(4) Chapman and Cowling, "Mathematical Theory of Non-uniform Gases," Cambridge (1939).

$$\eta = \frac{5}{8}\frac{kT}{\Omega^{(2)}(2)}\,(1+\varepsilon_1+\varepsilon_2+\cdots\cdots\cdots) \qquad 1)$$

Small terms ε_i's arising from the higher order approximations and will be called i-th order approximation terms. The first and second approximation-terms are expressed, respectively, by use of the usual notation which is the same as the previous papers (Cf. Chapman and Cowling, ibid.) as:

$$\varepsilon_1 = b_{12}^2 \Big/ \begin{vmatrix} b_{11} & b_{21} \\ b_{12} & b_{22} \end{vmatrix}, \qquad 2\,a)$$

and

$$\varepsilon_2 = b_{11} \begin{vmatrix} b_{21} & b_{22} \\ b_{31} & b_{32} \end{vmatrix}^2 \Big/ \begin{vmatrix} b_{11} & b_{21} \\ b_{12} & b_{23} \end{vmatrix} \begin{vmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{52} & b_{33} \end{vmatrix}, \qquad 2\,b)$$

where $b_{11} = 4\Omega^{(2)}(2)$, $b_{12} = b_{21} = 7\Omega^{(2)}(2)-2\Omega^{(2)}(3)$,

$$b_{22} = \frac{301}{12}\Omega^{(2)}(2)-7\Omega^{(2)}(3)+\Omega^{(2)}(4)$$

$$b_{13} = b_{31} = \frac{63}{8}\Omega^{(2)}(2)-\frac{9}{2}\Omega^{(2)}(3)+\frac{1}{2}\Omega^{(2)}(4),$$

$$b_{23} = b_{32} = \frac{1365}{32}\Omega^{(2)}(2)-\frac{321}{10}\Omega^{(2)}(3)+\frac{25}{8}\Omega^{(2)}(4)-\frac{1}{4}\Omega^{(2)}(5),$$

$$b_{33} = \frac{25137}{256}\Omega^{(2)}(2)-\frac{1755}{32}\Omega^{(2)}(3)+\frac{381}{32}\Omega^{(2)}(4)-\frac{9}{8}\Omega^{(2)}(5)$$

$$+\frac{1}{16}\Omega^{(2)}(6)+\frac{1}{2}\Omega^{(4)}(4),$$

$$\Omega^{(l)}(r) = \sqrt{\pi}\int_0^\infty e^{-V^2}\,V^{2r+2}\phi^{(l)}dV,$$

$$\phi^{(l)} = \frac{v}{2\pi}Q_\eta^{(l)}(v), \qquad V = \sqrt{\frac{M}{2kT}}\,v.$$

(M: mass of a colliding particle; v: its velocity.)

$Q_\eta^{(l)}$ has the dimension of square of length and $Q_\eta^{(2)}$ corresponds to the so-called viscosity "cross-section" of rigid elastic sphere. Classical quantity of $Q_\eta^{(l)}$, which will be hereafter denoted as $Q_{\eta_0}^{(l)}$, is given by $\frac{\pi}{2}r_0^2\left[2-\frac{1}{l+1}(1+(-1)^l)\right]$ $(l = 1, 2\cdots\cdot)$, r_0 denoting the molecular diameter. Thus $Q_{\eta,0}^{(2)}$ and $Q_{\eta,0}^{(4)}$, which are concerned in the present paper, equal to $\frac{2}{3}\pi r_0^2$ and $\frac{4\pi}{5}r_0^2$, repsectively. Quantum-mechanically, $Q_\eta^{(l)}$ depends upon the velocity of colliding particles (v), so it will be denoted as $Q_\eta^{(l)}(v)$, if necessary. $Q_\eta^{(l)}(v)$ and $Q_\eta^{(4)}(v)$ are given by the following formula in the cases of the similar collisions:

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(5) Chapman and Cowling, ibid., p. 169.

$$Q_{\eta}^{(2)}(v) = \frac{4\pi}{k^2} \sum_n \left\{ \sin \delta_n \frac{4n^3+6n^2-2n-2}{(2n+1)(2n+3)} \right.$$
$$\left. - \cos(\delta_n - \delta_{n-2}) \sin \delta_n \sin \delta_{n-2} \frac{2(n+1)(n+2)}{2n+3} \right\}, \qquad \text{3 a)}$$

and
$$Q_{\eta}^{(4)}(v) = \frac{4\pi}{k^2} \sum_n \left\{ (2n+1) \sin^2 \delta_n - \frac{1}{2n+1} \left[\frac{n^2(n-1)^2}{2n-1} \sin^2 \delta_{n-2} \right. \right.$$
$$+ \frac{(4n^3+6n^2-1)}{(2n-1)(2n+3)} \sin^2 \delta_n + \frac{(n+1)^2(n+2)^2}{(2n+3)^2} \sin^2 \delta_{n+2}$$
$$+ \frac{(4n^3+6n^2-1)(n+1)n}{(2n-1)^2(2n+3)} \sin \delta_n \sin \delta_{n+2} \cos(\delta_{n+2} - \delta_n)$$
$$+ \frac{(4n^3+6n^3-1)(n+1)(n+2)}{(2n-1)^2(2n+3)^2} \sin \delta_n \sin \delta_{n+2} \cos(\delta_{n+2} - \delta_n)$$
$$\left. \left. + \frac{n(n-1)(n+1)(n+2)}{(2n-1)(2n+3)} \sin \delta_{n-2} \sin \delta_{n+2} \cos(\delta_{n+2} - \delta_{n-2}) \right] \right\} \qquad \text{3 b)}$$

where $k = \frac{\pi M v}{h}$ and δ_n is the phases of n-th waves. In the former paper δ_n has been calculated extensively in case of rigid elastic sphere models, and $Q_{\eta}^{(2)}$ of this model was shown to vary in such a way that it becomes larger as the velosity is decreased. This tendency is concordant qualitatively with the experimental results of the temperature effect on viscosity, though yet insufficient quantitatively.

The terms of higher order approximation are calculated by Chapman in cace of rigid elastic sphere model; i. e., $\varepsilon_1 = 0.01485$, $\varepsilon_2 = 0.00103$, $\varepsilon_3 = 0.00012$ ($\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = 0.01600$). As these terms are small and independent upon temperature, it may be considered that no serious change will occur in the arguement as usually done, even if they are neglected. However, it cannot be admitted quantum-mechanically that these terms are practically independent upon temperatures. Such conclusion gives us the reason to carry on the present research which tries to clarify the degree of contribution of the terms.

ii) *Thermal conductivity*: The gaseous thermal conductivity is given(*), using the similar notation as Eq. (1), by

$$\lambda = \frac{25}{16} C_v \frac{kT}{\Omega^{(2)}(2)} (1 + \varepsilon_1' + \varepsilon_2' + \cdots\cdots); \qquad \text{4)}$$

here C_v denotes the molecular specific heat at constant volume and ε_i' the i-th order approximation term; ε_1' is shown as,

$$\varepsilon_1' = a_{12}^2 / (a_{11} a_{22} - a_{12}^2) \qquad \text{5)}$$

(*) Cf. Chapman and Cowling, p. 169.

where $a_{11} = b_{11}$, $a_{12} = b_{12}$ and $a_{22} = b_{22} = \frac{35}{24} b_{11}$.

Theoretically, it is convenient to discuss thermal conductivity by a quantity f defined by

$$f = \lambda / (\eta \cdot C_v) . \qquad 4\text{ a)}$$

As C_v is constant in case of rigid elastic sphere model, and with respect to the same model, $\varepsilon_1' = 0.02273$, $\varepsilon_2' = 0.00209$ and $\varepsilon_3' = 0.00031$ ($\varepsilon_1' + \varepsilon_2' + \varepsilon_3' = 0.02513$) for all temperatures classically. Thus f_1 equals to $2.5 \frac{1+\varepsilon_1'}{1+\varepsilon_1}$, according to the formulas (1) and (3), and the higher order approximation gives us also practically the similar constant value (2.5), because the factor $(1+\varepsilon_1') / (1+\varepsilon_1)$ neaaly equals to one, (in case of the above model, 1.00885). Though the conclusion holds well at ordinary temperatures, it was denied at low temperatures at least for helium by Eucken and later by Weber⁽⁶⁾; 2.51 at 2.73° K, 2.23 at 81° K and 2.02 at 21° K.⁽†⁾

It will be interesting to investigate the quantal contribution on f as well as viscosity itself. In the present paper it was tried only by means of the same simplest model as done in the study of viscosity, though more difinite conclusion may be obtained, if some other specific model be adopted.

iii) *Terms determined in this paper*: Three terms ε_1, ε_2 and ε_1' were determined actually because procedure of the further approximation is very difficult numerically. The conclusion will, however, be nearly sufficient for the object of study even at this stage of approximation. Because the values here obtained are found to be comparable order of magnitude with the classical ones and their temperature dependencies are not so large, the contribution of the further terms thus being negligibly small.

III. Calculation and Discussion of ε_1 and ε_1' in Case of Rigid Elastic Sphere Model. i) *Assumptions and Calculations*: It was assumed that the diameter of helium was 2.0 A or 2.1 A, similary as in the former papers.⁽²⁾ Though the basic numerical results of Bessel function of half-integers ($J_{\nu+\frac{1}{2}}(x)$) already obtained were utilized as much as possible, it was obliged newly to perform trouble calculations complimentarily and also to take more figures down one or two places in order to determine $\Omega^{(l)}(\alpha)$ ($\alpha = 2, 3, 4 \ldots, 7$) accurately. Integration of the latter values was performed graphically, so their ranges of error occurred in the final values

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(6) A Eucken, *Phys. Zeits.*, **14**, (1913) 324; Weber, *Ann. der Physik*, **54**, (1918) 325, 437, 481; **82**, (1927) 479.

(†) Cf. course other molecules, which have the internal degrees of freedom, lower values may be expected as suggested by Eucken. Such discussion will be omitted in the present treatment.

were not clear (ambiguous figures were shown by a small style in the table).

The obtained ε_1 and ε_1' values together with $\frac{b_{22}}{b_{11}}$, $\frac{b_{12}}{b_{11}}$ etc., are shown in table 2. The constants used consistently in the present series of papers are shown in table 1.

Table 1. Universal Constants Employed in the Present Series of the Research. (by K. Shiba)

Planck's Constant (h)	6.624×10^{-27} erg. sec
Temperature of the Ice Point	273.16° K
Joul's Constant	4.1858×10^{7} erg. cal.
Avogadro's Number	6.023×10^{-7}
Boltzmann's Constant (k)	1.3804×10^{-16} erg. deg.$^{-1}$

ii) *Discussions*: As shown in the table 2, the lower is the temperature, the smaller is ε_1, it increases asymptotically to the classically to the classical values as the temperature rises. Such temperature dependency of viscosity conforms with the tendency due to the quantal effect on "cross-section", though the degree of the improvement by the term ε_1 is not so large.

The variation due to molecular radius (Cf. the result of r_0 2.0 and 2.1 A) seems also to be small. The theoretical viscosity was redetermined by multiplying the first approximation term by the factor $1+\varepsilon_1$ (assuming molecular radius $r_0=2.1$ A, in which case the coincidence of theory and experiment was the better in lower temperatures). The comparison, which is given by table 3, denotes that the introduction of the second approximation terms do not fulfil our object yet to obtain the perfect agreement between theory and experiment.

Nextly the term $(1+\varepsilon_1')/(1+\varepsilon_1)$ tablated in the last column of table 2 will be discussed. It is nearly constant from 89° to 1090° K and also practically equal to the classical one. So for every monoatomic molecules, f will be 2 53, so far as the rigid elastic sphere model is concerned. Thus even if the contribution and quantal correction of the term $\frac{1+\varepsilon_1'}{1+\varepsilon_1}$ are taken into consideration, there is practically few improvement in the divergency from the experimental values. Therefore the result on the thermal conductivity also suggests it to be necessary that some new way of attack is to be tried.

Table 2. Numerical Results for the Helium Gas.

Radius of Helium	Temp. (°K)	b_{12}/b_{11} $(=a_{12}/a_{11})$	b_{22}/b_{11} $(=a_{22}/a_{11}=35/24)$	ε_1	ε_1'	$\frac{1+\varepsilon_1'}{1+\varepsilon_1}$
2.0 Å	15	-0.13_1	4.2	0.004_6	0.007_1	1.002_5
	88.5	-0.20_7	4.2	0.010_3	0.016	1.006
	273.1	-0.21_7	4.2_5	0.011_2	0.018	1.006
	680	-0.23_2	4.2_5	0.012_8	0.020	1.007
	1090	-0.24_6	4.2_5	0.0144	0.022	1.007
2.1 Å	273	-0.21_8	4.2_6	0.0114	0.017	1.006
Classical Case	For all temp.	-0.25 $(=-1/4)$	4.27 $(=205/48)$	0.01485	0.02273	1.008

Table 3. Gaseous Viscosity of Helium. $\eta(\times 10^6)$

Temp. (°K)	η(Obs)	η(Calc.) First Approx.		Second Approx.		Classical*
		r=2.1 A	2.0	2.1	2.0	——
15.0	29.5	30.5	32.5	30.8	32.9	46
88.8	91.8	93.4	101.8	94.4	102.9	110
273.1	187.0	177.9	194.9	180.0	197.3	193
680	343.6	294.6	323.2	298.4	326.7	313
1090	471.3	378.8	415.8	384.3	420.5	386

* Atomic radius was adopted properly, so as to obtain the perfect coincidence of at 373° K.

IV. Calculations and Discussions of ε_2. The second approximation term ε_2 was then calculated only at 15° and 273.1° K, due to the complicated procedure of its calculation, especially due to the occurrence of the term $Q_\eta^4(v)$ included in $\Omega_i^{(4)}(v)$ or in b_{33}. $'Q_i^{(4)}(v)$ given by Eq. (3 b) was calculated and ratios of these to $Q_{\eta,0}^{(4)}$ are tabulated against kr_0 in table 4.

Table 4. $Q_\eta^{(4)} / Q_{\eta,0}^{(4)}$

kr_0	0.5	1	1.5	2	3	4	5	10
$Q_\eta^{(4)} / Q_{\eta,0}^{(4)}$	7.37	5.61	3.45	2.19	1.80	1.65	1.67	1.68

The final results obtained were shown in table 5 with those of classical ones.

Table 5. The Second Approximation Term ε_2.

Method of Calculation	Temperature	b_{13}/b_{11}	b_{23}/b_{11}	b_{33}/b_{11}	ε_2
Quantal Method	15° K	0.0038	−0.721	8.55	0.00009
	273.1	−0.0024	−1.093	8.67	0.00077
Classical Method	Indep. on Temp.	−0.03125 (−1/32)	−1.273 (163/128)	11.61 (11889/1024)	0.00103

It is found that quantum-mechanical value of ε_2 at ordinary temperature is of the same order as classical one at 273° K, while it becomes smaller at lower temperatures. However, their absolute values being small as compared with the second approximation term ε_1, it may almost be negligible for the usual discussions.

V. Calculations and Discussions for Some Special Model. Judging from the above results, it will be interesting to calculate ε_1 and ε_1' in such a case where some model of molecular interaction nearer to the actual molecule than the rigid elastic sphere is introduced.

Massay and Buckingham(3) calculated the viscosity at low temperatures by use of 1.3 times of Slator's potential(7): i.e.,

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(7) On the reason of the factor 1.3, Cf. *Proc. Roy. Soc.* A **169**, (1939) 204.

$$V(r) = 7.7 \times 10^{-10} \exp (r/0.217 - 1.47 \times 10^{-12} r^6) \text{ erg},$$

r being the distance between the centres of helium atoms, and found that the agreement at temperatures above 15° K is quite good though the calculated values are slightly too large, while below 15° K the agreement becomes less satisfactory and the discrepancy is in the opposite sence; Exper. value was 12.67×10^{-6}, while calc. value 10.7×10^{-6} at 4.23° K.(8)

The present authors used their δ_n values and calculated ε_1 and ε_1' at 4.23° K and tested if the above descrepancy might be decreased. The result is, $a_{12}/a_{11} = b_{12}/b_{11} = 0.73$, $b_{22}/b_{11} = 4.1$, $a_{22}/a_{11} = 2.6$, so $\varepsilon_1 = 0.001$ and $\varepsilon_1' = 0.002$ by Eqs. (2 a) and (4); that is by use of the present model, the terms of the second order approximation ε_1 and ε_1' are also positive and very small, if compared with the classical values (0.014 and 0.227, respectively). Therefore, there occurred few improvement in viscosity as compared with that of the rigid elastic sphere model. (Cf. table 2.), so that the discrepancy of 20% cannot be almost diminished.

One way of settling the above difficulty is to obey the conclusion that it is necessary to find some suitable potential function as asserted by Massay and Buckingham; Hellund really suggested(9) that the intermolecular potential of helium determined emperically from the data of viscosity is fairly more complicated than that of Slator. However it will be rather reasonable that the effect due to ternary collison becomes more important, especially for the viscosity at lower temperatures. Simple calculation showed us that the reasoning is plausible.

Summary

The quantum-mechanical contribution of the terms arising from higher order approximation on viscosity and thermal conductivity has been calculated by use of the rigorous formula of Chapman and Enskog. The contributions are found in both properties to be so slight that it may be negligible with respect to both models adopted (rigid elastic sphere and Slator's potential).

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(8) Theoretical value calculated by us was 10.4×10^{-6}. The difference will be ascribed to the error arising from the numerical integration.

(9) E. J. Hellund, *Phys. Rev.*, **58**, (1940) 278.

A New Micro-Estimation Method of Amino-Group.

By Tokuro SODA and Hiroshi TERAYAMA.

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Introduction. Several method have already been published for the estimation of amino-group, the Van Slyke's method, however, is used most popularly.(1) That method, as is well known, needs a special apparatus for the measurement of nitrogen liberated by the reaction of amino-group with nitrous acid. The apparatus is somewhat complicated, and requires some skill in the treatment.

A new micro-estimation method of amino-group will be described in the following. The method consists of the same principle as that of the Van Slyke's but measures the residual nitrogen (non-amino nitrogen) instead of the liberated one, so no costly and complicated appratus is necessary. It is also possible to practise in a scale of micro-analysis.

At first the total nitrogen is determined by micro-Kjeldahl method in a definite quantity of the sample and then the residual nitrogen of the same sample, which is not reacted with nitrous acid.(2) The value of amino nitrogen is calculated as the difference of the total and the residual nitrogen thus obtained.

It was our chief problem how to deal with the excess of nitrous acid, its decomposition products and the secondary combined nitrogen (nitro, nitroso and ester) during the deamination reaction. The nitrous acid is decomposed and driven away with air stream(3) under the reduced pressure as quickly as possible after the deamination reaction.

The remaining nitrous acid is oxidized to nitric acid by hydrogen peroxide, which is then driven off by the vacuum distillation.(4)

At last a trace of the nitric acid is decomposed by ferrous sulphate. A proper amount of potassium permanganate solution is added before the vacuum distillation for the purpose of preventing the formation of ammonia. If there is any chloride compound, an unpleasant action will occur during the treatment with the permanganate. A method has been deviced to avoid this action.

Experimental. At first the total nitrogen contained in a definit

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(1) Van Slyke, *J. Biol. Chem.*, **7** (1910) 34; **9** (1911) 185; **10** (1911) 15
12 (1912) 275; **16** (1915) 281.

(2) Scott and West, *Ind. Eng. Chem., Analyt. Ed.*, **9** (1937) 50.

(3) Gomberg, Ber, (1903) 3281.

(4) Cambier et Leroux, *Compt. rend.*, **195** (1932) 1280.

quantity of the sample is estimated by the usual micro-Kjeldahl method. Then the residual nitrogen is determined by means of the deamination in the following manner.

The concentration of the sample solution is made so as it contains 0.2–0.6 mg. nitrogen per cubic centimeter. The sample solution (1–3 c.c.) is transfered into a Kjeldahl digestion flask, add 0.7 c.c. of 30% sodium nitrite solution and 0.35 c.c. of the potassium iodide solution. The latter is made by dissolving 4 grams potassium iodide in 2 c.c. of water and diluting to 100 c.c. by adding the glacial acetic acid. The reaction proceeds at room temperature, or at constant temperature if necessary, under continuous shaking· The relation between the temperature and the reaction time is shown in the following table.

Temperature (°C.)	15	20	25	30
Time (min.)	6-7	5–6	4-5	3.5–4

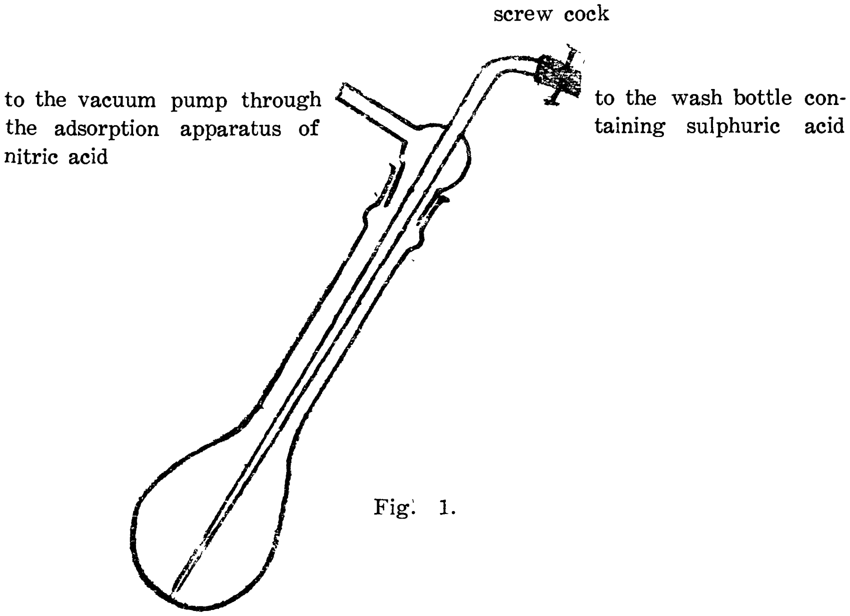

Fig. 1.

As soon as the deamination reaction is over, the flask is connected to the vacuum distillation apparatus as shown in Fig. 1. The bubbling, causing from the decomposition of the nitrous acid, ceases in about four minutes at room temperature. Then the air washed with the concentrated sulphuric acid is passed about one minute. Two drops of 35% hydrogen peroxide solution and one c.c. of 50% sulphuric acid are added, and the vacuum distilation is undertaken again. The air washed with sulphuric acid is passed cautiously during first one minute to change the remaining nitrous acid to nitric acid. The flask is, then, immersed in the warm water of 50°C. till its neck, and distilled in vacuum about 15 or 20 minutes. At last the air is passed slowly until the sodium sulphate crystallizes out, which takes about 2 minutes.

The residual hydrogen peroxide must be driven off completely by distillation. It is not necessary, however, to remove the hydrogen peroxide so completely if there is no substance which is easily converted into nitro- or nitroso-compounds. If the sample contains much substances which are easily converted into nitro- or nitroso compounds, such as tyrosin, tryptphan or phenylalanin etc., the treatment with potassium permanganate is necessary during the nitric acid distillation to prevent the reduction of the secondary combined nitrogen in these compounds into ammonia. Namely, after the above mentioned operations one c.c. of 50% sulphuric acid is added to resolute the sodium sulphate crystals once more, and then 0,5 normal potassium permanganate solution is added drop by drop with the aid of measuring pipette. At first, the dropped permanganate solution is instantly decoloured but after some time tne faint violet colour remains. After this state has been reached where the colour reamins unchanged during one minute, two or three times more permanganate solution is added.

Now the flask is again connected to the vacuum pump, and the temperature raises steadily from 50°C. to 100°C. A slow air stream is passed at the beginning, to prevent the bumping, and then distilled under high vacuum; the temperature reachs to 100°C. in 7 to 8 minutes. During the last one minute, a sufficient air is passed cautiously. Then one drop of hydrogen peroxide solution and one c.c. of distillation water are added, shaken well, and the vacuum distillation is resumed at 100°C. during some minutes. By these treatments the nitric acid is removed almost entirely. In the course of distillation the flask is shaken moderately and the air is passed adequately both at the beginning and the ending of the distillation.

It is necessary to add two c.c. of concentrated sulphuric acid and one or two drops of 25% ferrous sulphate solution in dilute sulphuric acid in order to detect and to decompose a trace of the remaning nitric acid. If the nitric acid remains still in considerable amount, the colour becomes brown by the addition of ferrous sulphate which soon decolours. In such a case one c.c. of water is added and the vacuum distillation must repeated at 100°C.

If the nitric acid is in a trace, which is proved by the reddish orange colouration, the flask is shaken moderately at 100°C. and under high reduced pressure. A drop of ferrous sulphate solution is added again for the assurance of the elimination of nitric acid. If the presence of nitric acid is not detected, a drop of hydrogen peroxide solution and a small quantity of copper sulphate are added to the mixture.

If there still remains nitric acid, the addition of ferrous sulphate and the vacuum distillation must be repeated untill there remains no nitric acid. After these treatments the usual micro-Kjeldahl process is followed. The residual nitrogen, that is non-amino nitrogen and not reacted with nitrous acid, can thus be measured. The value must be corrected with the result of blanc test.

Notices.

I. *On the Use of Acetic Acid Solution containing 4% Potassium Iodide.* Kendrick and Hanke⁽⁵⁾ improved the original Van Slyke's method of amino-nitrogen determination by use of the acetic acid solution containing 4% potassium iodide instead of the pure glacial acetic atid. We have undertaken the experiments on glycine, alanine, cystine and lactic acid. By use of the pure acetic acid we obtained the results that these substances give considerable amount of residual nitrogen, notwithstanding they contain no residual nitrogen. No such nitrogen, however, was detected when the acetic acid solution containing 4% potassium iodide was used. Only in the case of cystine, 10-20% residual nitrogen is still found. The secondarily generated nitrogen from cystine thus obtained is perhaps ammonia and is already generated in the course of the deamination reaction. The potassium permanganate treatment, therefore, shows no effect as shown in Table 2.

Table 2. Cystine.

Total nitrogen mg.	0.5 N. $KMnO_4$ c.c.	Residual nitrogen mg.	Ratio %
0.0826	0	0.0175	21.2
0.1652	0	0.0284	17.2
0.2913	0	0.0402	13.8
0.2913	0.2	0.0410	14.1
0.2913	0.6	0.0402	13.8

II. *The Removal of Nitrous and Nitric Acid.*

Obviously it is necessary to eliminate completely the surplus nitrous and nitric acid before the Kjeldahl digestion process. It is shown, from the results of experiments, that the reducing agents may not be used to decompose nitrous or nitric acid. For example, paraformaldehyde, hydrogen sulphide, sodium thiosulphate and sulphurous acid generate more or less ammonia. After all, the physical method is used and the ferrous sulphate is used only at the end of the treatment to detect and to decompose a trace of nitric acid.

III. *The Effect of Potassium Permanganate on the Analysis of Tyrosine and Tryptophane etc.*

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(5) Kendrick and Hanke; *J. Biol. Chem.*, **117** (1937) 161.

Some amino-acids which are easily converted into nitro- or nitroso-compounds during the deamination reaction are apt to be reduced by the organic decomposition product and generate ammonia. Such a reaction occurs during the vacuum distillation of nitric acid at 50–100°C., and so the adequate amount of potassium permanganate solution is used to prevent the reduction. Table 3 shows the results of these experiments.

Table 3.

Sample Total nitrogen (mg.)	0.5 N. $KMnO_4$ c c,	Resid. nitrogen mg.	Ratio %
Tyrosine 0.2252	0	0.1590	70.6
	0.6 faint red)	0.0565	25.1
	1.2	0.0136	6.0
	1.5	0.0108	4.8
Tyrosine 0.1126	0	0.0708	62.8
	0.3 (faint red)	0.0348	30.9
	0.6	0.0152	13.5
	0.9	0.0008	0.00
Tyrosine 0.0563	0	0.0236	42
	0.15 (faint red)	——	——
	0.3	0.0132	23.3
	0.45	0.0026	4.4
Tyrosine 0.0282	0	0.0069	24
	0.075 (faint red)	——	——
	0.22	0.0072	25
Tryptophane 0.2608	0	0.2661	102.0
	0.3 (faint red)	0.2268	87.0
	0.9	0.1736	66.5
Tryptophane 0.1300	0	0.1309	100.0
	0.6	0.0866	66.4
Phenylpropionic acid (2.405 mg.)	0	0.0550	
	0.075 (faint red)	——	
	0.15	0.0327	
	0.22	0.0269	
	0.50	0.0126	

IV. *Effect of Potassium Permanganate to the Kjeldahl-digestion.*

The potassium permanganate was already used as an oxidizing agent of the Kjeldahl digestion. Usual amino-acids give theoretical values of nitrogen even under the presence of potassium permenganate. The substances which contain peptid bonds, guanidine groups and halides, however, give somewhat less nitrogen in the presence of potassium permenganate. The results are shown in Table 4.

Tabe 4.

Samples	Nitrogen (Absence of $KMnO_4$) mg.	Nitrogen (Presence of $KMnO_4$) mg.	0.5 N-$KMnO_4$ c.c.	Ratio %
Ammonia	0.4730	0.4728	2.5	100.0
Glycine	0.3928	0.3910	1.0	99.5
Glycyl-glycine	0.6930	0.5974	1.0	86.2
Tryptophane	0.4730	0.4728	2.5	100.5
Tyramine-HCl	0.2547	0.1537	2.0	60.3
Arginine-HCl	0.7624	0.3885	3.0	50.9
Guanidine-H_2CO_3	0.2690	0.1398	1.0	52.0
Glutokyrine	0.3668	0.3510	1.0	90.2

In our method, however, the potassium permanganate treatment is undertaken only during the vacuum distillation at 50–100°C., so the conditions are different. Table 5 show the effect of potassium permanganate treatment in our methods.

Table 5.

Sample	Nitrogen (without $KMnO_4$ treatment) mg.	Nitrogen (with $KMnO_4$ treatment) mg.	0.5 N-$KMnO_4$ c.c.	Ratio %
Arginin-HCl	0.4039	0.4061	1.0	100.5
Glycyl-glycine	0.6300	0.6244	1.0	99.1
Tyramine.HCl	0.2547	0.2294	1.0	90.1
Asparagine	0.6100	0.6105	1.0	100.0

We see that the influence of potassium permanganate is very weak excepting tyramine hydrochloride. On the influence of the chloride the results shown in Table 6 were obtained.

Table 6.

Glycine (N = 0.3942 mg.) added with 1 c.c. of 0.5 N-$KMnO_4$

Sodium chloride mg.	Nitrogen found (In presence of halide) mg.	Ratio %
12	0.3116	79.4
12 (Added few drops of 5% $AgNO_3$	0.3910	99.1
6	0.3683	92.3
6 (Added few drops of 5% $AgNO_3$)	0.3960	100.4
2	0.3872	97.5
0.5	0.3948	100.1

The influence of halide is small, providing its amount is not so great. The addition of a silver salt such as silver nitrate or silver sulphate is proved to be effective to exclude the halide errors. The reason of this effect may be explained by the stability of silver chloride to potassium permanganate.

V *Results of Our Method.*

The results of the new modified micro amino nitrogen estimation method applied to the various amino-acids, proteins and their decomposition products are quite satisfactory as shown in Table 7. The amino nitrogen value of glycine is greater than the theoretical one by 7–8 % when the Van Slyke's method is used, while the present method gives the theoretical value. This method give a smaller error than Van Slyke's one in the case of cystine. When the sample contains much reducing organic substances such as carbohydrates etc., we had better to add the more amount of potassium permanganate than usual.

Table 7.

Samples	0.5 N-$KMnO_4$ c.c.	Total-N mg.	Resid N mg.	Amino-N mg.	Ratio %	Reference %
Glycine	0	0.2664	−0.0006	0.2670	100.2	100 (calc.) Van Slyke 107
Alanine	0	0.6253	0.0007	0.6246	99.9	
Cystine	0	0.2913	0.0402	0.2511	86.2	V.S. 108-14
(Table 2)	0.6	0.2913	0.0402	0.2511	86.2	
Tyrosine	0	0.1126	0.0703	0.0418	37.1	
(Table 3)	0.3	0.1126	0.0348	0.0778	69.1	
	0.9	0.1126	−0.0008	0.1134	100.7	
Asparagine	0	0.6100	0.2911	0.3118	51.3	50 (Calc.)
Tryptophane	0	0.4789	0.4557	0.0232	4.8	50 (Calc.)
	1.5	0.4789	0.3684	0.1105	33.7	
	2.0	0.4789	0.2640	0.2145	44.8	V.S. 40-60
Threonine (d. l-)	0	0.1701	0.0088	0.1613	94.9	
	0.32	0.1701	0.0011	0.1690	99.4	
Histidine-HCl	0	0.4164	0.2762	0.1402	33.9	33.3 (Calc.)
	0.3 (+Ag)	0.4164	0.2807	0.1357	32.6	
	0.5 (+Ag)	0.4164	0.2587	0.1577	37.9	
Arginine-HCl	0	0.7624	0.5665	0.1959	25.6	25 (Calc.)
	1.0	0.3946	0.2931	0.1015	25.7	
	1.0	0.1973	0.1395	0.0578	29.3	
Ammonia	0	0.3600	0.2783	0.0817	22.7	
Urea	0	0.4002	0.3395	0.0607	15.1	V.S. 7-8
	0.2	0.4002	0.3175	0.0823	20.5	
Guanidine 1/2 H_2CO_3	0	0.2706	0.2496	0.0210	7.8	
Tyramine-HCl	0	0.2547	0.1583	0.0964	37.9	
	0.45	0.2547	0.0938	0.1609	63.2	
	1.35	0.2547	0.0302	0.2245	88.2	
Tyrosine	1.0	0.0704	0.0005	0.0699	99.3	
Tyrosine + d-Glucose	1.0	0.0704	0.0055	0.0649	92 2	

Table 7.—(*Continued*)

Samples	0.5 N-$KMnO_4$ c.c.	Total-N mg.	Resid-N mg.	Amino-N mg.	Ratio %	Reference %
Tyrosine + Arginine-HCl	0.9	0.1095 0.3840	0.2909	0.2026	41.1	41.7 (Calc.)
	0.45	0.0555 0.1946	0.1462	0.1039	41.5	
	0.15	0.0555 0.1946	0.1522	0.0979	40.1	
Tyrosine + Arginine-HCl + d-Glucose (1.5 mg)	1.0	0.0352 0.0324	0.0242	0.0434	64.2	64.0 (Calc.)
Tyrosine + Arginine-HCl + Glycine	0	0.0938 0.1748 0.2457	0.0278	0.4855	94.5	95.2 (Calc.)
	0.55		0.0215	0.4928	95.8	
Tyrosine + Arginine-HCl + Glycine	0.3	0.0563	0.0786	0.5376	87.2	88.0 (Calc.)
	0.7	0.0987	0.0755	0.5467	87.8	
	1.0	0.4612	0.6778	0.5384	87.4	
Tyrosine + Histine-HCl	1.0	0.1205	0.1487	0.1815	54.7	
	2.0	0.2080	0.1362	0.1923	58.6	57.6
Phenyl-propionic acid	0	0.0000	0.0550			
	0.15	0.0000	0.0327			
	0.22	0.0000	0.0269			
Glycyl glycine	0	0.0139	0.2925	0.3214	52.3	(Calc. 50)
	0.28	0.6139	0.2925	0.4214	52.3	V.S. 60–65
	1.0	0.6139	0.2662	0.3477	56.6	
Glutokyrine (6)	0	0.3668	0.2624	0.1044	28.4	V.S. 29–30
	0.21	0.3668	0.2598	0.1070	29.2	
	0.60	0.3668	0.2616	0.1052	28.8	
Peptone	0	0.3577	0.2075	0.2302	38.5	V.S. 39.6
	0.21	0.4021	0.2416	0.1662	39.9	
	0.40	0.4021	0.2359	0.1662	41.3	
Casein (hydrolysed)	0	0.4160	0.1059	0.3101	74.5	
	0.3	0.4160	0.0807	0.3353	80.6	
	0.9	0.4160	0.0807	0.3353	80.6	
Casein	0	0.5568	0.5695	0.0127	-2.3	Lysine
	0.6	0.5368	0.5162	0.0206	3.7	amino N=3.2
	1.2	0.2734	0.2671	0.0113	4.1	
Gelatine	0	0.6289	0.6008	0.0281	4.5	Lysine amino N=3.2
	0.3	0.6289	0.5988	0.0301	4.8	
	0.6	0.6289	0.5810	0.0479	7.6	
Serum (horse)	0.4	0.2351	0.2187	0.0164	7.0	

$$\left[\text{Ratio} = \frac{\text{Amino N.}}{\text{Tot. N.}} \times 100\right]$$

Laboratory of Biochemistry, Faculty of Science.
Imperial University of Tokyo.

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(6) Grassman, *Biochem. Z.*, **269** (1934) 211; **284** (1936) 177.

On the Determination of Copper by the Polarographic Method.

By Shigeru OHASHI.

(Received October 6, 1947.)

For the determination of copper by the polarographic method various kinds of the regulating solutions were recommended, up to the present time, by a large number of investigators.

The earlier investigation of Shikata⁽¹⁾ was of a preliminary nature. Maassen⁽²⁾ reported the polarograph to be very useful for the determination of copper in steel and Hohn⁽³⁾ in his monograph described an outline for copper determination in brass and metal alloys. Suchy⁽⁴⁾ used the dropping mercury electrode for simultaneous estimation of copper, bismuth, lead and cadmium, and Stout⁽⁵⁾ suggested a procedure for polarographic estimation of copper. Reed and Cumming⁽⁶⁾ reported the determination of copper in plant materials and Lingane and Kerlinger⁽⁷⁾ discussed the polarographic wave of copper in their investigation on the determination of nickel and cobalt.

The regulating solutions recommended by these investigators are shown in Table 1. In these electoryte ferric iron is reduced at a potential more positive than the calomel zero, and hence its diffusion current interferes with the waves of copper and the others when iron is present in large excess.

Table 1.

Regulating solution	Author
Sodium Nitrate (Grundlösung A)	H. Hohn
Ammoniacal Solution of Ammonium Chloride (Grundlösung C)	H. Hohn
Sodium Potassium Tartrate	K. Suchy
Sodium Citrate	J. F. Reed
Potassium Chloride-Pyridine	J. J. Lingane

For this reason copper must be determined after the elimination of ferric iron from the solution. This may be done usually by adding an

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(1) M. Shikata, I. Tachi and N. Hozaki, *Bull. Agr. Chem. Soc. Japan*, **3** (1927), 883.

(2) G. Maassen, *Angew. Chem.*, **50** (1937), 375.

(3) H. Hohn, "Chemische Analysen mit dem polarographen", 84, Berlin (1937).

(4) K. Suchy, *Collection*, **3** (1911), 354.

(5) P. R. Stout, J. Levy and L. C. Williams, *Collection* **10** (1938), 129.

(6) J. F. Reed and R. W. Cummings, *Ind. Eng. Chem., Anal. Ed.*, **13** (1941), 124.

(7) J. J. Lingane and N. Kerlinger, *ibid.*, **13** (1941), 77.

excess of ammonium hydroxide to the boiling solution and filtering, or by reducing with hydroxylamine to ferrous iron that deposits at a more negative potential than ferric iron and copper. On the other hand after copper is seperated from iron by extraction with dithizone, then it can be determined by the use of the regulating solutions described above.

The writer discovered a new regulating solution for the determination of copper in the presence of large amounts of ferric iron, the following solution being used.

Sodium Potassium Tartrate	1 mol
Sodium Hydroxide	1 normal

By means of this electrolyte, ferric iron deposits at a more negative potential than copper, probably owing to the complex formation. Therefore, the copper that accompanies with large amounts of iron can be determined without interference of the latter and the time used for the analytical procedure can be reduced.

As an example the polarographic wave of copper in the presence of large amounts of iron is shown in Fig. 1. In this case the concentrations of copper and iron are 50 γ and 100 mg per 10 cc. respectively, the ratio of iron to copper being 2000 : 1 ; the copper wave is distinctly observed. Moreover, since in this regulating solution the solubility of oxygen is very small, the sensitivity of galvanometer can be raised to 1/2 or more without removing the oxygen by passing of hydrogen or nitrogen gas.

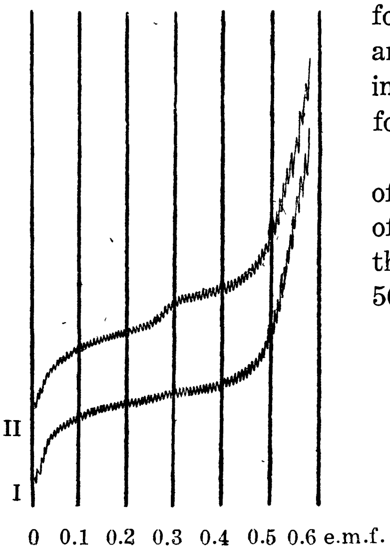

Fig. 1.

Curve I. Wave due to 100 mg of iron in 10 cc of regulating solution.
Curve II. Wave due to 50γ of cooper and 100 mg of iron in 10 cc. of regulating solution. Sensitivity 1/2.

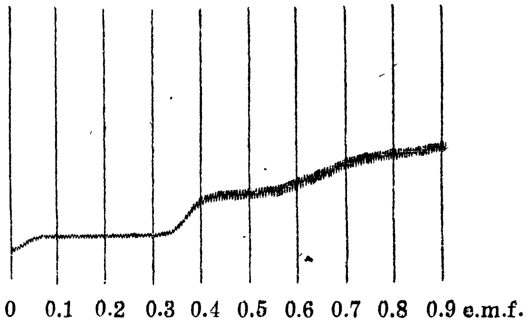

Fig. 2.

Wave due to 1 mg of copper in 8 cc of regulating solution. Sensitivity 1/20.

In this electrolyte copper shows two waves very similar to the double waves obtained in Hohn's Grundlösung C, with half-wave potentials of −0.55 and −0.81 v. vs. the normal calomel electrode (see Fig. 2). The first wave is due to the reduction of the cupric complex to the cuprous complex, and the second to the reduction of the cuprous complex to the metal. The first wave appears in the range of about 0.08 v. along the voltage axis (although the width of the wave varies in accordance with the concentration of metal). The linear spread of the second wave is about 0.15 v with a not steep slope and hence this electrode reaction is so-called irreversible one. Therefore, the second one may not be used and the first wave that has a steep slope and is a reversible one may be used for the quantitative estimation.

To prove that this copper wave can be used for the quantitative analysis, the writer took the polarograms of copper in various concentrations. The results given in Fig. 3 shows that the height of wave is proportional to the concentration of copper in the solution (at about 10^{-8} normal).

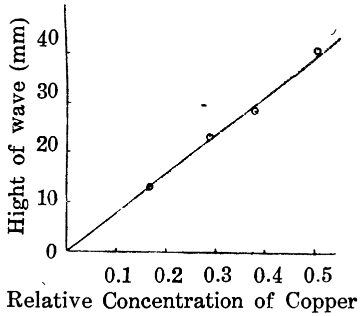

Fig. 3.
Sensitivity 1/20.

Bismuth deposits at —0.7 v. and its reducing wave is not steep. Cadmium gives a steep, reversible wave at —0.8 v., but when copper is present the determination of cadmium and bismuth is impossible in this regulating solution because the cadmium wave is not separated from the second wave of copper and bismuth wave. The reducing wave of ferric iron begins at —1.1 v. and its reaction is irreversible one. As antimony (trivalent) deposits at —1.1 v. too, it is duplicated with iron wave. Zinc deposits electrolytically at —1.4 v., but its diffusion current tends to appear irregularly and shows the slight maximum. Nickel, cobalt and arsenic give the irreversible wave from about —1.2 v. and tinn does not reduced electrolytically before —1.7 v.

It may be concluded that the copper can be determined by the use of its first wave, even in the presence of the many other above-mentioned heavy metals are present. Lead must be removed, because it gives the duplicated wave with copper.

Summary.

A new method for the determination of copper with the dropping mercury electrode was studied and the following regulating solution was used: 1 mol sodium potassium tartrate and 1 normal sodium bydroxide. By this method copper can be determined in the presence of large ammounts of iron.

The writer expresses his hearty thanks to Prof. Kenjiro Kimura and Dr. Kazuo Kuroda for their kind guidance in the course of this study.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

On the Configuration of Chain Molecules. I.
Normal Paraffine.

By Keizô SUZUKI.

(Received October 8, 1947)

1. Introduction. The problem of configurations of chain molecules is the fundamental groundwork of the physics of chain molecules.

Quite concrete answers are given by studies through X-ray diffraction etc. in the cases when the molecule has only one regular configuration as in crystals. But in the cases of many configurations the problem becomes complicated.

The first quantitative treatment was developed by W. Kuhn, who took up the long chain molecule of n-paraffine type and calulated the relative position of the both ends of the chain.(1) Assuming the constant length a of the elements of the chain, the C–C bonds, the constant angle α of any two concecutive bonds, and the completely free rotation round the axis of any bond, he found the distance r of the both ends of the chain:

$$\langle r^2\rangle = a^2\{n(1+c)/(1-c) - 2c(1-c^n)/(1-c)^2\}, \qquad (1)$$

where n is the number of elements, c is $\langle\cos\alpha\rangle$, and $<>$ means average.

His third assumption, the free rotation, is not satisfied by the real molecule, For the recent physico-chemical studies told us that the real molecule has no free rotation but the more or less hindered rotation at the ordinary temperature.

The stretched forms of the n-paraffine molecule are more stabile than the contracted and curled forms. So $\langle r^2\rangle$ must be larger than Kuhn's value, which is true only in the limiting case of high temperature.

We shall give a solution for the case of hindered rotation.

2. The molecule of normal paraffine. The series of n vectors, $a_0, a_1, a_2, \ldots, \ldots, a_i, \ldots, a_{n-1}$, represents one of the many configurations of a_n n-membered chain molecule, $C_{n+1}H_{2n+3}$, where a_i represents the i th element of the chain (Fig. 1). The four valencies of the carbon atom of paraffine have the tetrahedral symmetry:

$$\widehat{a_{i-1}a_i} = \alpha_i = \text{const.} = \cos^{-1}(1/3) \fallingdotseq 71^\circ.$$

a_{i+1} rotate round a_i holding the angle α constant. And let the rotation angle φ_i be π when $a_{i+1} // a_{i-1}$ (Fig. 2).

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(1) W. Kuhn, *Kolloid Z.*, 68 (1934), 2.

Kuhn assumed the uniform distribution probability for the whole range of φ_i: $\langle \cos \varphi_i \rangle = 0$, $\langle \sin \varphi_i \rangle = 0$. We take up the none-uniform case. In paraffine the distribution is dominant in the 'trans' configuration ($\varphi = \pi$), therefore $\langle \cos \varphi_i) \rangle < 0$. But the probability is symmetrical as regard to the positive φ_i and negative φ_i, therefore $\langle \sin \varphi_i \rangle = 0$.

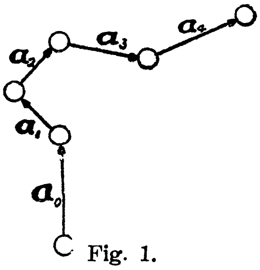

Fig. 1.
Vector representation of a molecule.

If the mean values of $\cos \widehat{a_j a_k}$ are known for all the sets of j and k, they can describe several mean properties of the chain.

Let ρ_i be $\widehat{a_0 a_i}$, and let us calculate $\langle \cos \rho_i \rangle$.

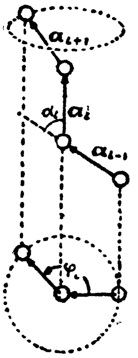

Fig. 2.
Bond angle α_i and rotation angle φ_i.

3. The problem of correlated random paths on the spherical surface. For a while put the magnitude of a_i out of consideration, and consider the direction only. And a_i is represented as a point A_i on the sphere of unit radius (Fig. 3). The tracing of a congiguration of the molecule from one end to other end is converted as follows.

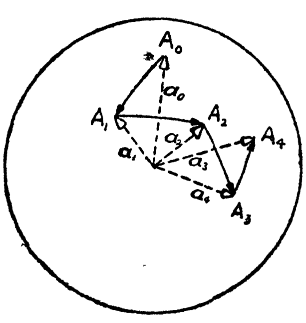

Fig. 3.
Spherical random paths. (Formation)

A moving point on the unit sphere initially situated at the point A_0 travels step by step through the series of points, A_1, A_2, ..., A_i, ... α_i is the width of the ith path $\widehat{A_{i-1}A_i}$, φ_i is the angle between the ith path and the $i+1$th path, and ρ_i is the distance $\widehat{A_0 A_i}$ (Fig. 4).

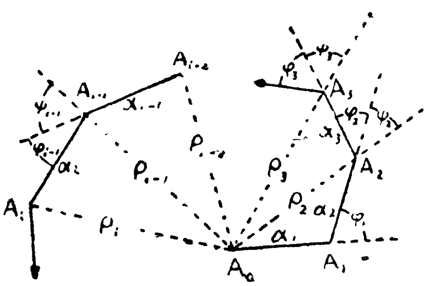

Fig. 4.
Spherical random paths. (Analysis)

We solve the problem under three assumptions: (2)

1. the width of the paths is constant. $\cos \alpha_i = c$,
2. the direction of the ith path is correlated only with the $i-1$th path,
3. $\langle \sin \varphi_i \rangle = 0$, $\langle \cos \varphi_i \rangle = b$.

The first corresponds the constant bond angle, the second means that a_i has direct correlation with a_{i-2} but without a_{i-3}, a_{i-4} etc., and the third describes the correlation of a_i with a_{i-2}.

Calculation of $\langle \cos \rho_i \rangle$ is as follows:

$$\cos \rho_1 = \cos \alpha_1 ,$$

at the spherical triangle $A_0 A_1 A_2$

$$\cos\rho_2 = \cos\alpha_1 \cos\alpha_2 - \sin\alpha_1 \sin\alpha_2 \cos\varphi_1 ,$$

and generally at the triangle $A_0 A_{i-1} A_i$

$$\cos\rho_i = \cos\rho_{i-1}\cos\alpha_i - \sin\rho_{i-1}\sin\alpha_i \cos(\varphi_{i-1}+\psi_{i-1})$$

where ψ_i is the angle between $\vec{\rho_i}$ and $\vec{\alpha_i}$. We can rewrite the last factor

$$\cos(\varphi_{i-1}+\psi_{i-1}) = \cos\varphi_{i-1}\cos\psi_{i-1} - \sin\varphi_{i-1}\sin\psi_{i-1} .$$

And at the triangle $A_0 A_{i-1} A_{i-2}$

$$\cos\rho_{i-2} = \cos\alpha_{i-1}\cos\rho_{i-1} + \sin\alpha_{i-1}\sin\rho_{i-1}\cos\psi_{i-1} .$$

Then from those three equations

$$\cos\rho_i = \cos\rho_{i-1}\cos\alpha_i - \sin\rho_{i-1}\sin\alpha_i\{\cos\varphi_{i-1}(\cos\rho_{i-2} - \cos\alpha_{i-1}\cos\rho_{i-1})/\sin\alpha_{i-1}\sin\rho_{i-1} - \sin\varphi_{i-1}\sin\psi_{i-1}\} .$$

Taking average under the three assumptions (2) we get the recurrence formula,

$$\langle\cos\rho_i\rangle = c(1+b)\langle\cos\rho_{i-1}\rangle - b\langle\cos\rho_{i-2}\rangle , \qquad (3)$$

with the initial conditions,

$$\langle\cos\rho_1\rangle = c,$$
$$\langle\cos\rho_2\rangle = c^2-(1-c^2)b .$$

Solution of the formula (3) is

$$\langle\cos\rho_i\rangle = C_3 s_3^i + C_4 s_4^i , \qquad (4)$$

where s_3, s_4 are the two roots of the equation

$$s^2 - c(1+b)s + b = 0 , \qquad (4\,a)$$

and C_3, C_4 are determined by the initial conditions:

$$C_3 = (c-s_4)\,/\,(s_3-s_4) , \quad C_4 = (c-s_3)\,/\,(s_4-s_3) . \qquad (4\,b)$$

An analogous derivation can be executed starting from A_j instead of A_0, giving

$$\langle\cos\rho_{jk}\rangle = \langle\cos\rho_{k-j}\rangle ,$$

in which ρ_{jk} is $\overset{\frown}{A_j A_k}$.

4. The dipole momont of paraffine substituted at the both ends. The molecul $X(CH_2)_n Y$ is now under consideration. X and Y are substitutes groups with dipole moments μ_0 and μ_n in equal directions to a_0 and a_n respectively (Fig. 5.). The apparent dipolement μ must be

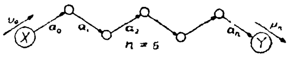

Fig. 5.
The molcule $X(CH_2)_n Y$

$$\mu^2 = (\vec{\mu_0}+\vec{\mu_n})^2 = \mu_0^2 + \mu_n^2 + 2\mu_0\mu_n\cos\rho_n$$

for each configuration. The mean value over all the configurations is observable and given theoretically as

$$\langle\mu^2\rangle = \mu_0^2 + \mu_n^2 + 2\mu_0\mu_n(C_8 s_8^n + C_4 s_4^n) . \qquad (6)$$

If X = Y, $\mu_0 = -\mu_n$. So we have

$$\langle\mu^2\rangle = 2\mu_0^2(1-C_3s_3^n-C_4s_4^n)\,. \tag{7}$$

The value of the equation are plotted on Fig. 6 and compared with the observed value of $Br(CH_2)_nBr$.(2) The indented theoretical values express quite well the tendency of the observed values. The old theoretical values of the free rotation model can give only a very poor coincidence (shown in the figure as $b=0$). The repulsive interaction of two dipoles diminishes the observed μ for molecules of the shorter chains. The nnmerical value of b seems to be about $-1/2$ at the ordinary temperature.

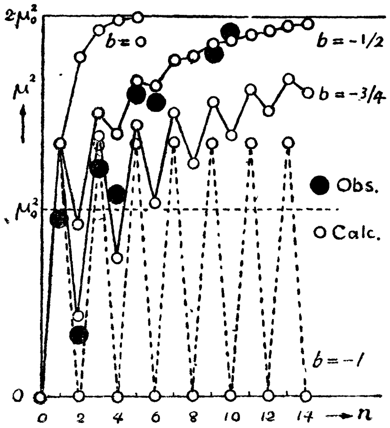

Fig. 6.
Dipole moment μ of $X(CH_2)_nX$

5. The distance of the both ends. The distance of the both ends of the molecule with n bonds, r, is obtained as follows: for any configuration,

$$r = \left|\sum_{i=0}^{n-1} a_i\right|, \quad |a_i| = a,$$

$$r^2 = (\sum a_i \sum a_i) = \sum_{i=0}^{n-1}(a_i a_i) + \sum_{k=1}^{n-1}\sum_{j=0}^{k-1}(a_j a_k),$$

where ( ) is the scalar product of vectors:

$$(a_i a_i) = a^2,$$

$$(a_j a_k) = a^2\cos\rho_{jk}\,.$$

Then we average r^2 over all the configurations, knowing that $\langle\cos\rho_{jk}\rangle$ is the function of $k-j$ only as seen in (6):

$$\langle r^2\rangle = a^2 n + 2a^2\sum_{i=1}^{n-1}(n-i)\langle\cos\rho_i\rangle^x. \tag{8}$$

Putting (5) in (8) we finally

$$\langle r^2\rangle = a^2\{n(1+c)(1-b)/(1-c)(1+b) - 2C_3s_3(1-s_3^n)(1-s_3)^{-2} - 2C_4s_4(1-s_4^n)(1-s_4)^{-2}\}\,. \tag{9}$$

For large n (9) gives $\langle r^2\rangle$ proportional to n:

$$\langle r^2\rangle \cong a^2 n(1+c)(1-b)/(1-c)(1+b)\,, \tag{9a}$$

and for $b=-1$ (9) gives the length of the most stretched chain:

$$r^2 = a^2n^2(1+c)/2 \qquad \text{for even } n\,, \tag{9b}$$

$$r^2 = a^2n^2(1+c)/2 + a^2(1-c)/2 \qquad \text{for odd } n\,, \tag{9c}$$

Of course the equation (9) includes the Kuhn's formula (1) as a special

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(2) C. P. Smyth, *J. Amer. Chem. Soc.* 53 (1931), 2988; 54 (1932), 2261.

case $b = 0$. Kubo's ingeneous intramolecular statistics in his first paper⁽³⁾ does not include this result, for his generalised theory cannot yet describe the doubly correlated chain rigorously.

The theoretical values are shown in Fig. 7. $\langle r^2 \rangle$ must be about three times larger than the Kuhn's value, for b is not 0 but about $-1/2$ at the ordinary temperature.

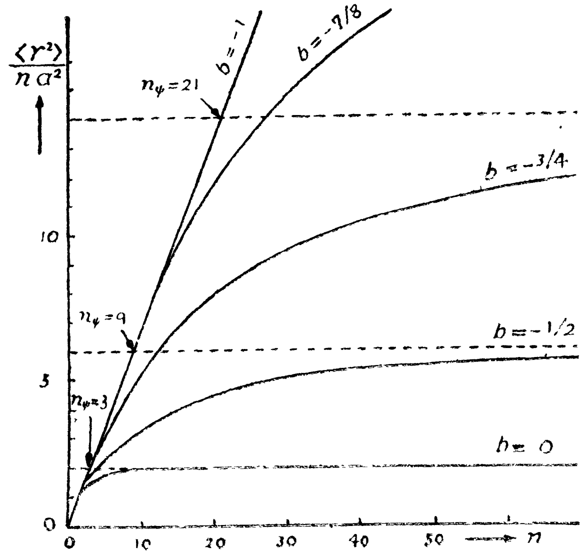

Fig. 7.

Apparent length r and Pseudosegment n_ψ of $C_{n+1}H_{2n+3}$

6. The moment of inertia. The moment of inertia about the axis (parallel to the Y axis) passing through the centre of, I_Y, is a significant quantity concerning the viscosity of the solution of the molecules.⁽⁴⁾ We define the quantity I as

$$I = \sum_{p=0}^{n} m \, | r_p - R |^2 , \tag{10}$$

where r_p and R are the radius vectors of the p th atom and the centre of mass, m is the mass of the atom and subsequent atoms, CH_2 in paraffine. Then

$$3 \langle I_Y \rangle = 2 \langle I \rangle . \tag{11}$$

I is obtained as follows: for any configuration

$$r_p = r_0 + \sum_{i=0}^{p-1} a_i ,$$

$$R = \sum_{p=0}^{n} r_p / (n+1) = r_0 + \sum_{i=0}^{n-1} (n-i) \, a_i / (n+1) ,$$

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(3) R. Kubo, *J. Phys. Soc. Japan*, 2 (1947), 47: In the recent meeting of the physical society of Japan at Sept. 9, 1947 Kubo read the expansion of his theory to the doubly correlated chain and gave the approximating formulae of $\langle r^2 \rangle$ etc. for large n.

(4) H. Kramers, *J. Chem. Phys.*, 14 (1946), 415; P. Debye, ibid., 636.

$$\mathbf{r}_p-\mathbf{R} = \left\{ \sum_{i=0}^{p-1} (1+i)\, \mathbf{a}_i - \sum_{i=p}^{n-1})n-i)\, \mathbf{a}_i \right\} / (n+1) ,$$

$$\sum_{p=0}^{n} (\mathbf{r}_p-\mathbf{R})^2 = \left\{ \sum_{i=0}^{n-1} (1+i)\,(n-i)\,(\mathbf{a}_i \mathbf{a}_i) + 2 \sum_{k=1}^{n-1} \sum_{j=0}^{k-1} (1+j)(n-k)(\mathbf{a}_j \mathbf{a}_k) \right\} / (n+1).$$

Meaning over all the configurations we have

$$\langle I \rangle = wa^2 \{ n\,(n+1)\,(n+2) + 2 \sum_{i=1}^{n-1} (n-i)(n-i+1)(n-i+2) \langle \cos \rho_i \rangle \} / 6(n+1) . \tag{12}$$

Using (5) it leads to

$$\langle I \rangle = m\, a^2 [n(n+1)\,(n+2) + 2 \sum C \{ (n+1)\, n\, (n-1)\, s\, (1-s)^{-1} \\ -(n-1) n s^2 (1-s)^{-2} + (n-1) s^3 (1-s)^{-3} - (1-s^{n-1}) s^4 (1-s)^{-4} \}] / 6(n+1), \tag{13}$$

where $\sum$ is summed up for s_3 and s_4, C_3 and C_4. $\langle I \rangle / ma^2 n^2$ plotted against n gives a similar curve to that of $\langle r^2 \rangle$. For large n (13) becomes

$$\langle I \rangle \cong ma^2 n^2 (1+c)\,(1-b) / 6(1-c)\,(1+b) = \langle r^2 \rangle\, mn/6. \tag{14}$$

Combinating (14) with (11) we find

$$\langle I_T \rangle \cong \langle r^2 \rangle\, mn/9 . \tag{15}$$

The equation can be derived much more generally. If b is not -1 and n is so large that (8) is approximately rewritten that

$$\langle r^2 \rangle \cong na^2 (1 + 2 \sum \langle \cos \rho_i \rangle) ,$$

then (12) is also approximately rewritten that

$$\langle I \rangle \cong ma^2 n^2 (1 + 2 \sum \langle \cos \rho_i \rangle) / 6 .$$

Therefore one obtains (14) and (15).

7. The relation between $\langle \cos \varphi \rangle$ and temperature. We have carried out mathematical treatment. Now some physical discussions will be made on the mathematical results.

The distribution of rotational isomers round the bond-axis is somewhat complicated. Our results, however, find out that the mean value of cosine of rotation angle φ can describe such physical quantities as $\langle r^2 \rangle$, $\langle \mu^2 \rangle$ and $\langle I \rangle$ rigorously. Our formulae are derived without approximation under three conditions (2), which are probably satisfied by real molecules to a sufficient extent.

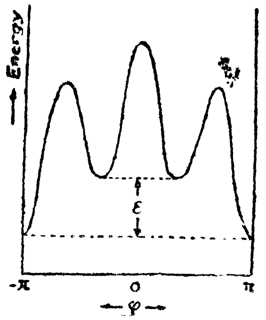

Fig. 8.

The potential curve round the bond-axis shown in Fig. 8 with three peaks and three valleys.(5) Separating into quantum states q we can estimate the distribution probability w_q for each state and $\langle \cos \varphi \rangle$ will be given by $\sum_q w_q \cos \varphi_q$.

But a preliminary estimation is tried here. Only three states at the bottoms of the valleys are regarded as the principal states and others are neglected, for the molecules,

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(5) Mizushima and colaborators, series of papers on "internal rotation" in *Sci. Papers Inst. Phys. Chem. Research* (Tokyo).

in fact, takes chiefly the three states, which are called t, g, and g' respectively corresponding $\varphi = \pi$, $\pi/3$, and $-\pi/3$. The energy of g state is equal to that of g' state and higher that t state. Let ε be the difference. Then the distribution probability w_q are given by the Boltzmann's statistics:

$$w_t = 1/\{1+2\exp(-\varepsilon/kT)\}\,.$$

$$w_g = w_{g'} = \exp(-\varepsilon/kT)/\{1+2\exp(-\varepsilon/kT)\}\,, \qquad (16\,\mathrm{b})$$

where k is the Boltzmann's constant and T is the absolute temperature. Then

$$b = \langle\cos\varphi\rangle = \sum w\cos\varphi = \{-1+\exp(-\varepsilon/kT)\}/\{1+2\exp(-\varepsilon/kT)\}\,. \qquad (17)$$

When T is infinity, b is 0 and the quantities $\langle r^2\rangle$ etc. shows equal values to those of Kuhn's free rotation model. When T is 0, b is -1, and the molecule takes the most stretched form, so $\langle r^2\rangle$ and $\langle I\rangle$ become the largest. With the elevation of temperature b increases and $\langle r^2\rangle$ and $\langle I\rangle$ become smaller and $\langle\mu\rangle$ larger.

ε must be about 1 kilocalorie per mole, if b is $-1/2$ at the ordinary temperature as seen in Fig. 6.

8. Pseudosegment. In Fig. 7 the value $\langle r^2\rangle/a^2n$ for small n is on the line $b = -1$, which shows the most stretched form, and the value for large n approach the horizontal line asymptotically.

Let n_ψ be the abscissa of the cross point of the two lines. The equation of two lines are

$$\langle r^2\rangle\,/\,a^2n = n(1+c)\,/\,2 \qquad \text{for } b = -1, \qquad (9\,\mathrm{b})\ (18)$$

$$\langle r^2\rangle\,/\,a^2n = (1+c)(1-b)\,/\,(1-c)(1+b) \quad \text{for } n = \infty. \qquad (9\,\mathrm{a})\ (19)$$

So we get n_ψ equating the two formulae:

$$n_\psi = 2(1+c)(1-b)\,/\,(1-c)(1+b). \qquad (20)$$

n_ψ is the function of b and accordingly of T.

We divide the n-membered chain every n_ψ element. The number of divided parts n' is

$$n' = n/n_\psi\,. \qquad (21)$$

If each part is stretched forth, the ordinate of the cross point gives its length a':

$$a' = an_\psi\{(1+c)\,/\,2\}^{1/2}. \qquad (22)$$

Here the chain is transformed into a chain with n' members of length a'. If the direction of each member is independent of any other members, the distance r between the both ends is given as a special case of (8) in which $\langle\cos\rho_i\rangle = 0$:

$$\langle r^2\rangle = n'a'^2 \qquad (23)$$

Putting (21), (22) in (23) we have

$$\langle r^2\rangle = na^2 n_\psi(1+c)/2 .$$

The use of the value of n_ψ (20) gives

$$\langle r^2\rangle = na^2(1+c)(1-b)/(1-c)(1+b) .$$

It is the formula for the transformed chain without approximation, but is the same as the approximate formula (19) for the original chain.

We can use the transformed chain, in which the part composed of n_ψ elements moves independently of other parts, instead of the original one, in which every element moves depending on other elements.

This transformation simplifies the theory from the problem of Markoff's chain to that of independent variables. However it is only a model which can give the equal value of $\langle r^2\rangle$, and there is no groups of n_ψ elements moving together as a unit, but every element moves as a unit. Therefore n_ψ is named 'psedosegment'.

In theories of chain molecules the assumption of a certain magnitude of segment moving together as a unit may coincide with some experiments, but this coincidence cannot prove the assumption to be real. In this case above told the adoptation of n_ψ as a unit will succeed in dealing with quantities concerning $\langle r^2\rangle$, but may fail in dealing with other quantities. In fact the psendosegment similarly calculated for $\langle I\rangle$ is twice large as that for $\langle r^2\rangle$.

9. Summary. W. Kuhn's free rotation model for the problems on the configuration of long chain molecules must be seriously revised according to the recent progress of the physics of the molecular structure. We explain that several physical properties of chain molecules like paraffine can be expressed as the functions of the mean value of cosine of rotation angle.

One of the mathematical results, the series of the calculated values of dipole moment of $X(CH_2)_nX$, wins a fine coincidence with the experiment and shows the propriety of this theory.

We give the moment of inertia and the distance of the both ends of the chain molecule with its temperature dependence. These values are given also subject to an assumption of existence of segments, which are named here 'psedosegments' because of their apparent and false existence.

Masaoka-cho, Toyokawa, Aichi pref., Japan.