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J.C. McLennan D.Sc. F.R.S. & W.G. Plummer Ph.D.

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XCII. *The Crystal Structure of Solid Methane.* By J. C. McLennan, *D.Sc., F.R.S., and* W. G. Plummer, *Ph.D.*

THE structure of the methane molecule has recently become a most interesting subject of discussion among theoretical physicists and chemists. According to some authorities, the results of recent work in the field of Atomic Physics are said to demand a pyramidal structure for the molecule instead of the hitherto universally accepted tetrahedral structure. In much of the literature upon the subject the state of the molecule under consideration is left entirely unspecified.

The present paper deals with an X-ray investigation by the "powder" method of analysis of solid methane at temperatures intermediate between those of liquid air ($-190°$ C.) and liquid hydrogen ($-255°$ C.). It is to be understood, in speaking of *the* molecule, that the *crystal* molecule is implied throughout, and the question of the relationship which it may bear to the chemical molecule will not be discussed here.

Any attempt at a complete determination of structure by the "powder" method alone must necessarily be open to a considerable amount of criticism, but at the present time the growth of single crystals of methane and their maintenance over a period sufficiently long for X-ray examination is not practicable; for this purpose a constant supply of liquid

* Communicated by the Authors.

hydrogen would be required.   Hence, although it may not be permissible to regard the suggested structure as more than an approximation to the true one, the results of this examination definitely prove the existence of a cubic modification for solid methane over the temperature range of these experiments.

Fig. 1.
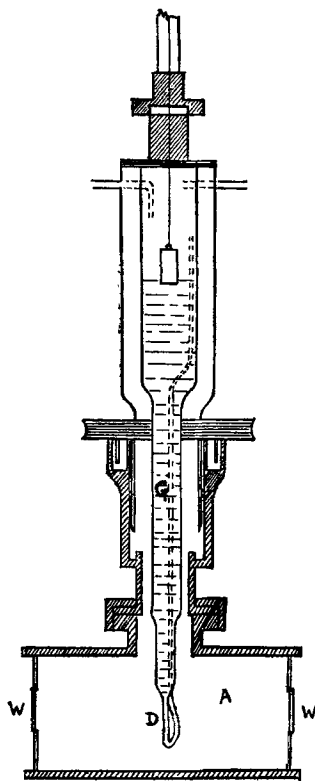
Apparatus.

   A Debye-Scherrer type of camera, which closely resembled that described in a previous paper [1], was employed (fig. 1). After loading the cylindrical film-holder and placing it in the correct position in the camera (already determined by preliminary experiment), the edges of the loose lid were covered with a small quantity of a preparation of petrolatum

and beeswax, and the lid was firmly held in position by means of six clamps. The main chamber A was then evacuated for several hours by means of suitable pumps, a liquid-air trap having been inserted next to the chamber to prevent any mercury-vapour from reaching it. Next, the nickel-silver container G was filled with liquid hydrogen, and an interval of a quarter of an hour allowed for the cooling of the apparatus, after which a small quantity of pure methane was admitted to the main chamber from a side tube (the tap connecting the main chamber with the pumps having, of course, been closed just previously to introducing the methane). The deposition of crystals of solid methane on the outside of the copper capillary tube D could be observed through the window W, and when a layer of the desired thickness had formed, the crystalline powder was irradiated with X-radiation generated by a Shearer tube and suitably filtered to exclude β-lines. The rays passed into the camera through a lead slit 1 mm. wide which formed part of the camera, and was covered on the outside with thin aluminium foil. The exposure varied from 5 to 10 hours, with a current of approximately 6 milliamperes through the tube. Owing to the gradual decrease in thickness of the methane layer during the exposure, it was found advantageous to observe the layer carefully during the first stages, and to admit fresh methane when required. (Incidentally this procedure assisted in producing a more random orientation of crystals than would otherwise have been the case.)

Preparation of Methane.

Owing to the comparative ease with which most substances crystallize at liquid hydrogen temperatures, it is of the utmost importance that the methane employed shall be of the highest possible purity. Every precaution was taken to exclude impurities, and separate X-ray photographs under the same experimental conditions were taken of solid methane prepared by two different methods; the diffraction patterns obtained were apparently identical in the two cases.

In the first method methane was prepared by dropping a mixture of equal parts of methyl iodide and 95 per cent. methyl alcohol from a stoppered bottle into a large quantity of freshly-prepared zinc-copper couple. The gas, after being passed over another zinc-copper couple, was collected over distilled water and afterwards passed through tubes containing phosphorus pentoxide. Spectroscopic examination showed the gas to be free from nitrogen and possible iodide

impurity, and the only bands in evidence were those associated with the elements carbon and hydrogen.

The second method of preparation was from aluminium carbide and water. The flask, delivery tube, etc., were evacuated before commencing the reaction in order to save the trouble of displacing air in the apparatus. The gas was collected over distilled water and purified by bubbling it slowly through a solution of potassium dichromate and concentrated sulphuric acid. It was then passed through a caustic potash tube and two tubes containing phosphorus pentoxide. The final product was subjected to spectroscopic examination, and no bands other than those characteristic of carbon and hydrogen and CH compounds were observed.

After each exposure the communicating tap between the pumps and the main chamber was closed, and the frozen methane upon the capillary tube was allowed to warm up slowly until it reached the gaseous state. Samples of this methane were then examined spectroscopically for impurities, and the absence of nitrogen and oxygen bands indicated that air had not leaked into the chamber during the course of the experiment. This point was capable of further verification on development of the X-ray film, upon which no " powder " lines for those elements were observed.

Crystallographic Information.

The melting and boiling points of methane are given in the International Critical Tables[2] as $-184°$ C. and $-161°·4$ C., respectively. In 1912 W. Wahl[3] found that pure methane crystallized very readily when cooled with liquid air under exhaust, and that the growth structures were always developed according to the hexahedron, and closely resembled those of ammonium chloride. The more rapid the crystallization, the finer were the resulting growth structures. The crystals were found to be isotropic ; the molecule must therefore possess the four trigonal axes of symmetry characteristic of the cubic system, and consequently the valency directions must be assumed to make equal angles with one another. This argument applies also to the cubic forms of carbon tetrachloride, carbon tetrabromide, carbon tetraiodide, and tetramethylmethane.

Each of these compounds shows a low-temperature doubly-refracting modification ; similarly for methane at very low (liquid hydrogen) temperatures Wahl[4] observed an enantiotropic transition into a doubly-refracting form.

Experimental Results.

For seven of the eight " powder " photographs obtained for solid methane the freezing agent employed was liquid hydrogen ; in the case of the remaining one liquid air under reduced pressure was used. Apart from slight displacements of the lines attributable to differences in thickness of the various layers, the X-ray patterns were apparently the same in all cases, and were typical of the cubic modification. Variation of the experimental conditions so as to favour the formation of the doubly-refracting modification observed by Wahl produced no change in the photographs. This is rather surprising, but the probable explanation is that, owing to inefficient heat insulation, a not inconsiderable temperature gradient existed between the inside of the copper capillary tube in contact with the liquid hydrogen and the exterior layers of crystals frozen upon the outside of this tube which were being photographed.

Four of the exposures were made with characteristic zinc K radiation and the remaining four with iron K_α-rays. The photographs obtained with the latter radiation were not so clear as those made with the zinc rays on account of the higher dispersion, and consequently broader lines, but the experimental spacings are in close agreement in the two cases. (Compare Tables I. and II. with Tables III. and IV.)

Table I. shows the derivation of the experimental spacings from measurements of the lines upon a typical " powder " photograph of solid methane (prepared in this case from methyl iodide and irradiated with zinc rays). As a very thick layer of methane was employed, the lines due to the copper of the capillary tube were scarcely visible, and have been excluded from the table. The approximate intensities of reflexion are indicated by the customary symbols : V.S., M., etc. The theoretical spacings in column 4, which correspond to the planes opposite them in column 5, have been calculated upon the assumption of a unit cube of edge 6·35 Å.

In order that more precise values of the longest spacings which occur might be obtained, together with a more accurate representation of the relative intensities of reflexion from the various planes, a very thin layer of solid methane was exposed (also to zinc radiation), for a shorter period ; the resulting spacings are given in Table II. In consequence of the reduced exposure, only four lines (in addition

TABLE I.—Methane Frozen with Liquid Hydrogen.

Zinc X-radiation, $\lambda K_{a_1 a_2} = 1\cdot434$ Å.   Copper filter.
Copper capillary tube.   Exposure : $8\frac{1}{2}$ hr.
Correction for the thickness of the layer $= - 0\cdot12$ cm.
Radius of the circular camera $= 3\cdot52$ cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
5·165 W. to M.	42° 03½′	1·070	1·075	135
4·805 W.	39 06¼	1·137	1·123	440
4·44 M.	36 09	1·215	1·222	{ 115 and 333
4·155 M.	33 48⅓	1·289	1·296	224
3·70 M.	30 08½	1·428	1·420	240
3·595 V.W.	29 15	1·468	1·456	133
3·30 V.W. to W.	26 51½	1·587	1·588	400
......	......	......	1·835*	222
2·715 V.S.	22 06	1·905	1·914	113
2·295 V.S.	18 38	2·244	2·246	220
1·65 M.	13 26	3·09	3·18	200
1·395 V.S.	11 21¼	3·64	3·67	111

* The presence of a reflexion from this plane cannot be established owing to a line from the copper capillary tube at a point corresponding to 1·801 Å.

TABLE II.—Methane Frozen with Liquid Hydrogen.

Zinc X-radiation, $\lambda K_{a_1 a_2} = 1\cdot434$ Å.   Copper filter.
Copper capillary tube.   Exposure : $7\frac{1}{4}$ hr.
Correction for the thickness of the layer $= - 0\cdot07$ cm.
Radius of the circular camera $= 3\cdot52$ cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
2·705 M. to S.	22° 01′	1·913	1·914	113
2·30 V.S.	18 43	2·235	2·246	220
1·62 M.	13 11	3·144	3·176	200
1·39 V.S.	11 19	3·655	3·667	111

to those given by the copper tube, which have been omitted from the table), were sufficiently intense to be measurable ; in this case the methane was prepared from aluminium carbide.

The spacings resulting from the measurement of two other films are derived in Tables III. and IV.; the remaining photographs have also been measured, and give, within the limits of experimental error, similar values.

TABLE III.—Methane Frozen with Liquid Air under Reduced Pressure.

Iron X-radiation, $\lambda K_{\alpha_1 \alpha_2} = 1.934$ Å.
Copper capillary tube.   Exposure: 6 hr.
Correction for the thickness of the layer $= -0.16$ cm.
Radius of the circular camera $= 3.52$ cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
4·64 W. to M.	37° 45½′	1·58	1·588	400
3·71 W. to M.	30 12	1·92	1·914	113
3·12 W. to M.	25 24	2·25	2·246	220
2·25 W.	18 19	3·08	3·176	200
1·88 M.	15 18	3·66	3·667	111

TABLE IV.—Methane Frozen with Liquid Hydrogen.

Iron X-radiation, $\lambda K_{\alpha_1 \alpha_2} = 1.934$ Å.   Manganese filter.
Copper capillary tube.   Exposure: 5½ hr.
Correction for the thickness of the layer $= -0.09$ cm.
Radius of the circular camera $= 3.52$ cm.

Corrected distance of line from centre of film (cm.).	Glancing angle.	Experimental spacing. Å.	Theoretical spacing. Å.	Indices of corresponding plane.
3·74 M.	30° 27′	1·91	1·914	113
3·11 M.	25 19	2·26	2·246	220
2·24 M.	18 13½	3·09*	3·176	200
1·89 M. to S.	15 23	3·65	3·667	111

* This line was particularly broad, and difficult to measure accurately.

Returning to Table I., the experimental spacings in column 3 are seen to be in very close agreement with those calculated for a face-centred cubic cell of edge 6·35 Å., which are given in column 4. Within the range of spacings shown, the only irregularity is the indefiniteness as to whether there is a reflexion from the (222) plane corresponding to 1·835 Å.; if such a reflexion exists, it is indistinguishable in the photographs from a line corresponding to 1·801 Å., for which the copper capillary tube is

responsible.   (It was intended to settle this point by making an exposure with a capillary tube of some suitable metal other than copper.)   Further, all planes which do not satisfy the condition for a face-centred lattice are absent.   The density of liquid methane at approximately its boiling-point has been given as $0\cdot415$ gm./c.c.[5], and if this be used as an approximation to the density of the solid, then :

$$\text{No. of molecules per unit cell} = n = \frac{0\cdot415(6\cdot35)^3}{16\cdot03 \cdot 1\cdot649} = 4\cdot02 ;$$

that is, there are four molecules per unit cell.   There are no abnormal spacings except those demanded by a face-centred lattice, hence all the following space-groups have to be considered :

$$T^2, \ T_h^3, \ T_d^2, \ O^3, \ O_h^5.$$

If the further assumption is made that all the carbon atoms are crystallographically identical, and that all the hydrogen atoms are identical in this sense, only two of these, T^2 and T_d^2 give four equivalent positions for the carbon atoms and sixteen equivalent positions for the hydrogens [6].   In either case the four carbons in the positions of fourfold symmetry without any degrees of freedom will have coordinates :

$$000, \ 0\tfrac{1}{2}\tfrac{1}{2}, \ \tfrac{1}{2}0\tfrac{1}{2}, \ \tfrac{1}{2}\tfrac{1}{2}0 ;$$

the carbons themselves having symmetry T in the case of the space-group T^2, and T_d for the space-group T_d^2.   The sixteen hydrogens in positions of 16-fold symmetry with one degree of freedom u will have coordinates :

$u,$	$u,$	$u;$	$u,$	$\bar{u},$	$\bar{u};$	$\bar{u},$	$u,$	$\bar{u};$	$\bar{u},$	$\bar{u},$	$u;$
$u,$	$u+\tfrac{1}{2},$	$u+\tfrac{1}{2};$	$u,$	$\tfrac{1}{2}-u,$	$\tfrac{1}{2}-u;$	$\bar{u},$	$u+\tfrac{1}{2},$	$\tfrac{1}{2}-u;$	$\bar{u},$	$\tfrac{1}{2}-u,$	$u+\tfrac{1}{2};$
$u+\tfrac{1}{2},$	$u,$	$u+\tfrac{1}{2};$	$u+\tfrac{1}{2},$	$\bar{u},$	$\tfrac{1}{2}-u;$	$\tfrac{1}{2}-u,$	$u,$	$\tfrac{1}{2}-u;$	$\tfrac{1}{2}-u,$	$\bar{u},$	$u+\tfrac{1}{2};$
$u+\tfrac{1}{2},$	$u+\tfrac{1}{2},$	$u;$	$u+\tfrac{1}{2},$	$\tfrac{1}{2}-u,$	$\bar{u};$	$\tfrac{1}{2}-u,$	$u+\tfrac{1}{2},$	$\bar{u};$	$\tfrac{1}{2}-u,$	$\tfrac{1}{2}-u,$	$u.$

If the space-group T^2 is under consideration, the symmetry of the hydrogen atom itself will be C_3; but if the correct space-group is T_d^2 this symmetry will be C_{3v}.

The next step is to calculate the resulting theoretical intensities for the various values of the parameter u, and to ascertain which particular value of u gives the best agreement with the observed intensities.   This work has been summarized in Table V., which shows the intensities of the various planes relative to the standard value 15 arbitrarily chosen for the (111) plane.   The formula employed was

$$\text{Intensity} \propto Q . Z . S^2,$$

where S is the structure factor, which depends upon the

TABLE V.

Intensities Calculated for Various Values of the Parameter u.

Plane.	Q factor.	Z.	Intensity relative to that of the (111) plane, taken as 15.							Experimental intensity.
			$u=0.$	$u=0.1.$	$u=0.13.$	$u=0.15.$	$u=0.18.$	$u=0.2.$	$u=0.22.$	
440	$2\frac{3}{4}$	12	2·1	2·3	3·9	3·1	1·6	1·7	0·3	W.
115 & 333	$2\frac{1}{2}$	{24 & 3}	6·3	1·8	3·1	4·2	4·8	4·3	4·5	M.
224	$2\frac{1}{2}$	24	4·7	2·6	3·2	3·4	3·7	4·6	6·7	M.
240	3	{12 or 24}	2·8 or 5·7	1·5 or 3·0	2·0 or 4·1	2·7 or 5·3	2·9 or 5·9	1·4 or 2·8	0·6 or 1·2	M.
133	3	24	5·7	3·6	6·0	7·6	7·3	5·4	5·2	V.W.
400	$3\frac{1}{2}$	6	1·7	0·2	0·1	0·2	1·0	1·8	0·2	V.W. to W.
222	5	8	3·2	2·1	2·7	2·9	1·8	1·0	0·6	—
113	$5\frac{3}{4}$	24	11	4·5	4·4	4·6	6·3	8·2	9·6	V.S.
220	$8\frac{1}{2}$	12	8·1	4·8	5·2	6·3	9·6	12	1·2	V.S.
200	$17\frac{1}{2}$	6	8·3	6·2	5·0	3·5	2·1	1·3	0·8	M.
111	$23\frac{3}{4}$	8	15	15	15	15	15	15	15	V.S.

geometrical positions of the atoms and on their scattering-powers. As a first approximation, the latter were taken as proportional to the atomic numbers ($C=6$, $H=1$). The Q factor referred to in column 2 was calculated from

$$Q = \frac{1+\cos^2 2\theta}{2} \cdot \frac{1}{\sin^2 \theta \cdot \cos \theta},$$

where θ is the glancing-angle.

The "Z" number represents the number of cooperating planes, and it will be noted that, in the case of the (240) plane, its value may be 12 or 24, according to whether the space-group is T_2 or T_d^2 respectively ; hence, until the question of the correct space-group is settled, there will be for this plane two possible values for the resulting intensities. The temperature factor was not introduced into the intensity formula, as its effect should be almost negligible at the temperatures used in these experiments.

The particular case of $u=0$ is equivalent to disregarding entirely the scattering effect of the hydrogen atoms ; or, alternatively, to considering that the four valency electrons from the four hydrogen atoms in the CH_4 molecule have joined the four outer electrons belonging to the carbon atom, thus forming a scattering system of eight electrons per molecule, which should be a stable configuration. It is extremely probable that such systems would be very nearly identical for each molecule throughout the structure ; hence each system might be regarded, for the purpose of scattering, as the true structural unit, and might conveniently be supposed to be concentrated at the centre of the carbon nucleus (since it is the same for each molecule). If this be the case, the X-ray results will give no indication of the distance from the centre of the carbon nucleus to the orbit in which the electrons rotate ; it will only be possible to determine the distance from one molecule to the next. A comparison of the experimental and theoretical intensities for the various values of the parameter u in Table V. shows that no value of u gives very good agreement, but $u=0$ apparently gives the nearest correspondence, though the observed reflexion from the (133) plane is too weak. A more encouraging agreement is obtained if, in the calculation of the theoretical intensities, the scattering effect of the hydrogen atoms be neglected ($u=0$), and the factor f given by Ponte [7] for reflecting power of the carbon atom for high-frequency rays (which varies with the spacing) be used instead of the constant factor 6 for the carbon atom. The values of f given in Table VI. are taken from Curve III. of Ponte's

paper, and the square of this factor has been used in the calculation of the theoretical intensities given in column 3 of the table; the Lorentz factor, the geometrical structure factor, and the factor for the number of cooperating planes have also been taken into consideration in this calculation. With the exception of the reflexions from the (111), (200), and (133) planes, which are not sufficiently strong, the observed intensities (taken from Table I.) agree quite well with the corresponding theoretical values. It is only fair to add that the lines corresponding to the (111) and (220) planes in the photographs obtained with zinc radiation (Tables I. and II.)

TABLE VI.

Calculated Intensities using the Ponte Factor.

Plane.	*f.*	Theoretical intensity proportional to :	Observed intensity (from Table I.).
440	1.5	1·0	W.
115 & 333	1·6	3·4	M.
224	1·73	3·0	M.
240	1·90	2·1 or 4·3	M.
133	1·95	4·5	V.W.
400	2·15	1·6	V.W. to W.
222	2·45	4·0	—
113	2·6	15	V.S.
220	3·0	15	V.S.
200	4·05	28	M.
111	4·5	63	V.S.

V.S.=Very strong; S.=Strong; M.=Moderately strong; W.=Weak; V.W. to W.=Very weak to weak; V.W.=Very weak.

are so strong that no further blackening of the film would be detectable, and the next stage would be reversal; this might explain why the (111) reflexion is not stronger in the photographs than that from the (220) plane. However, the comparative weakness of the (200) reflexion still remains unexplained, but in all the photographs the line corresponding to this plane is noticeably broader than the remainder, and this fact cannot very well be taken into account in ordinary eye-estimations of the relative intensities of the lines.

This analysis of intensities would therefore appear to support the idea, to which reference has already been made,

of stable and practically identical scattering systems for each molecule of methane throughout the structure, the molecules being arranged upon a face-centred lattice. It is difficult to interpret in any other way the fact that the most satisfactory agreement of intensities is obtained when $u=0$.

In any case, this investigation confirms the conclusion arrived at by Wahl, by optical methods, that a cubic form of methane really exists, and it disproves the view recently expressed in several papers that the structure of the methane molecule cannot be cubic, but that it must be pyramidal. No evidence of the existence of a pyramidal modification has been found in this work, but its probable existence is not disputed.

The chief arguments put forward in opposition to the existence of a cubic structure for methane have been classified by V. Henri [8] under the following heads :—

(1) The scattering of light by methane (studied by Cabannes).

(2) Its absorption spectrum (examined by Cooley and Dennison).

(3) The emission spectra of the carbon atom (examined by Millikan and Bowen).

(4). The crystal structure of methane derivatives (in particular penta-erythritol, examined by Mark and Weissenberg, and Huggins and Hendricks).

(5) Calculation of the potential energy of the methane molecule (made by Guillemin, and Van Arkel and De Boer).

If it is admitted that methane can exist in two different modifications, it is surely quite impossible to predict which of these forms is assumed for the particular conditions of experiment in cases (1) and (2). In either case the experimental technique is very difficult, and it is even possible that both forms exist together under such conditions. And in case (4) the selection of pentaerythritol as a substance whose structure might be characteristic of that of methane seems rather unfortunate in view of the fact that regular modifications of its more closely-related compounds, carbon tetrachloride, tetrabromide, and tetraiodide, are known to exist, especially as carbon tetrachloride has been shown to possess only a negligible dipole moment. The calculation of the potential energies of the pyramidal and tetrahedral configurations of the methane molecule in case (5) involves the use of the numerical data obtained from the work on the absorption spectrum in (2), and the authors of the two

papers[9,10] dealing with this subject are in disagreement
as to which is the more stable configuration, owing to
differences in original assumptions. With regard to
case (3), it has been shown, by examination of the emission
spectra of the carbon atom, that in neutral carbon the four
valencies are not equal, but that there are two (2, 2) and
two (2, 1) electrons. In methane, however, if the four
electrons belonging to the hydrogen atoms join these four,
and form a stable system of eight (similar to the neon
electron configuration), as the analysis of intensities in this
paper would seem to indicate, this objection to the existence
of a cubic modification is removed. The results of this
investigation therefore leave little doubt that a regular form
of methane does actually exist, and this conclusion is sup-
ported by the recent work of Weissenberg[11], who has
shown from theoretical considerations that for substances of
the type $C\alpha_4$ the occurrence of the electrically symmetrical
molecule is to be expected just as frequently as that of the
pyramidal type.

A complete list of references to papers dealing with this
subject is unnecessary, as excellent lists have already been
prepared by the authors of the following papers :—

K. Lonsdale (*née* Yardley), Phil. Mag. vi. p. 433 (1928).
J. K. Morse, Proc. Nat. Acad. Sci. xiv. (Feb. 1928).

Note.—Though my collaborator has kindly signified that
he wishes my name to be associated with this paper, I desire
to say the details have been practically all worked out by
him. The research is one of a number I planned and
initiated, but the growing pressure of other investigations
precluded my following up the work as closely as I was able
to do in the early stages. I should add that throughout we
had much valuable help from Mr. J. O. Wilhelm in the
liquefaction of air and hydrogen. The investigation is one
of the many made possible with the cryogenic equipment
secured through the help of the Carnegie Corporation, the
National Research Council of Canada, and the University
of Toronto.—J. C. McLennan.

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Physical Laboratory,
   University of Toronto.
   1st January, 1929.

XCIII. *The E.M.F. of Thermal Agitation.   By* E. K. SANDEMAN, *Ph.D., and* L. H. BEDFORD, *M.A.**

A S an incident in a certain investigation carried out for the Laboratories of the International Standard Electric Corporation, some work of J. B. Johnson on the e.m.f. of thermal agitation (Physical Review, vol. xxxii., July 1928, pp 97–109) has been verified. The accuracy of the results is not so great as his, but it is thought that the confirmatory evidence obtained is of value.

A simple precision formula has been derived, which it is believed will prove useful for many practical purposes in calculating quickly and accurately in R.M.S. microvolts the magnitude of noise disturbance which occurs on the grid of the first stage of any amplifier. This formula is admittedly only applicable under certain limiting conditions, but fortunately those limiting conditions are the ones which occur most often in practice. In practice it is usually required to amplify uniformly a given band of frequencies, and the impedance between the grid and filament of the first valve is usually a pure resistance shunted by a capacity, within the pass-band of the system. The truth of this has been verified for audio-frequency systems using good input transformers to the grid of the first stage.

With the above qualifications the noise in microvolts on the grid of the first valve is given by :—

$$N = \frac{J T^{\frac{1}{2}}}{\sqrt{2\pi C}} \sqrt{\tan^{-1} 2\pi RCF_2 - \tan^{-1} 2\pi RCF_1} \quad . \quad (1)$$

(the inverse tangents being expressed in radians),

* Communicated by the Authors.