STUDIES IN THE PHYSICAL CHEMISTRY OF DETONATION AND RELATED TOPICS

by

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Introduction

The well-established physical theory of detonation specifies the properties of the infinite plane detonation wave in terms of the thermochemistry of the detonation reaction and the equation of state of the detonation products, (see, for example, Taylor, 1952). Thus physical chemistry has two roles in the discussion of the plane detonation wave, the provision of thermochemical information and the determination of the equation of state. This theory deals however with an ideal case, in which rate processes have no effect; in the real wave, complicated rate processes have to be taken into account. Here again physical chemistry has information to supply in the fields of chemical kinetics and rates of energy transfer. The present thesis deals with contributions to physical chemistry in the fields of thermochemistry, equation of state and intermolecular forces, chemical kinetics and energy transfer.

Thermochemistry

There are two methods of obtaining thermochemical information: one is to determine the required quantity experimentally, the other is to deduce it theoretically. This thesis includes work of both types.

Although the heats of formation of most of the simpler organic substances of interest as possible constituents of explosives have been known for some time, very little information was available about the amine nitrates. The preparation of these substances and the determination of their heats of combustion by conventional methods is described in paper (1).

The correlation of heats of formation with molecular structure allows the prediction of heats of formation simply from a knowledge of structure. Such prediction is useful in evaluating the probable properties of compounds not yet made or not readily available. One method of carrying out this correlation is by expressing the heat of formation as the sum of a set of bond energy terms, and investigations of several aspects of this are reported here. The effect of temperature on the additivity of bond energy terms is examined in paper (2) and it is shown that even in hydrocarbons at $0^{\circ}K$ there are deviations from additivity which are intimately concerned with molecular structure and which persist even when differences in vibrational zero-point energy are allowed for. These differences explain various discrepancies in estimates of the "resonance energy" of aromatic compounds, as is shown in paper (3).

The amount by which a compound whose structure cannot be expressed by a single valence bond diagram is more stable than the sum of the bond energy terms of the most stable single structure is known as the "resonance energy". This "resonance stabilisation"

may be of the aromatic type, or it may be "covalent-ionic", in which the stabilisation is due to the possibility of charge transfer from one atom to another. This effect has been held to be responsible for the stability of compounds of type A-B, compared with the mean of A-A and B-B, and is the basis of Pauling's electronegativity scale (Pauling 1944). The logical basis of this argument seemed doubtful, and it is carefully examined in paper (4), the results of which have since been largely confirmed (Hurley 1953). It is shown that even if ionic structures are left out of account, a molecule A-B is still more stable than the mean of A-A and B-B because of reduced internuclear repulsions. This suggests that the electronegativity scale may be more directly connected with nuclear charge than its original derivation indicated, and shows that the usual picture of covalent-ionic resonance, taking into account only the valence electrons, is probably not valid.

The correlation of molecular structure and thermochemistry in terms of bond properties is reviewed in paper (5), and discussed more extensively in a book (6). Although some of this book is a review of previously published work, much of Chapters 1 and 6 is a new discussion of the logical status of the representation of molecular properties as bond properties, which is at least partly original. Further, Chapter 10 is devoted to the deduction from thermochemistry of a wide variety of bond energy terms, giving perhaps the most comprehensive list in the literature. Some of the discussion of numerical values is now outdated, however, and a second edition is at present with the printer.

Equation of State and Intermolecular Forces

In the calculation of the properties of the detonation wave, a knowledge of the equation of state of the detonation products is required. The products of the detonation of solid or liquid explosives consist of a mixture of gases well above their critical temperatures and at a density of well over 1 g./cm.^{3} Under these circumstances the intermolecular repulsive forces, which have relatively little effect in determining the thermodynamic properties of gases at ordinary densities, are probably very important. Accordingly an examination of these forces was undertaken: a review is given in paper (7). Michel's deduction that at even quite moderate pressures there is an increase in the electronic kinetic energy of a gas was used as the basis of an attempt to predict intermolecular energy as a function of density or pressure, at first rather crudely in paper (8) and later by calculating the energy of a molecule in a box as a function of box size (paper 9). In the course of this work a proof of the validity of the virial theorem in this connection was given (paper 10) and it was recognised for the first time (paper 11) that a very wide class of approximate molecular wave functions gave values of the kinetic and potential energy which satisfied the virial theorem.

The calculated dependence of molecular energy on density was sufficiently similar to that deduced for explosive products from other considerations for it to be used as the basis of a simple cell model equation of state for detonation products (paper 12). This gave satisfactory results for the detonation of pentaerythritol

tetranitrate. More sophisticated cell models have subsequently been adopted by several authors for the equation of state of detonation products.

In the course of work on energy transfer (see later) the validity of the simple mixture laws for the second virial coefficient of gas mixtures was in question. A novel apparatus for the study of the compressibility of gases at ordinary pressures was designed (paper 13), and the second virial coefficient of mixtures of carbon dioxide with helium, hydrogen, argon, nitrogen, oxygen and carbon monoxide was determined (papers 13 and 14). These results, which were in close agreement with such fragmentary information as was available in the literature, showed that in these systems the empirical combining rules for force constants did not give correctly the temperature dependence of the second virial coefficient of the mixtures. This work, however, had to be stopped before very extensive information could be obtained.

Chemical Kinetics

The mode of decomposition of organic explosive substances, though perhaps not directly relevant to their detonation, is of importance in connection both with their stability and their deflagration. The decomposition of organic nitrates has been widely studied, and is usually considered to involve the splitting of the $O-NO_2$ bond. It seemed that an analagous $C-NO_2$ splitting might occur in nitrocompounds, and an investigation of the thermal decomposition of some simple nitroparaffins was undertaken to

discover if this were so (papers 15 and 16). When this work was started there was only one previous reported investigation, in which was postulated the unlikely initial step of $CH_3NO_2 \rightarrow CH_3NO + O$. The product analysis given in paper (15) suggested that C-N bond fission was much more likely, and it was noted in addition that the activation energy was close to $D(CH_3 - NO_2)$. This reaction has since been the subject of further study by other workers. The kinetic constants obtained by the present author have been confirmed, but some analytical results on the products at slightly higher temperatures suggest that the initial step may be an intramolecular rearrangement. (Hillenbrand and Kilpatrick, 1953) It has also been suggested that the reaction is a chain reaction. (Gray, Yoffe and Roselaar, 1955) In paper (16) it was suggested that the decomposition of nitroethane and nitropropane went by an initial intramolecular rearrangement to produce the olefin and nitrous acid. This reaction has also been further studied, and it has been suggested that this reaction is also a chain reaction, (Gray, Yoffe and Roselaar, 1955) but the present author's interpretation of it has been confirmed (Wilde, 1956).

In the decomposition of both the organic nitrates and nitro-compounds, it is probable that oxidations by nitrogen dioxide produced from the $-NO_2$ grouping play an important part. This has led to a study of gas ~~phox~~ phase oxidations using this reagent, in particular, arising directly out of the work on nitroethane and nitropropane, the oxidation of ethylene and of propylene (papers 17 and 18 respectively). The overall kinetics of these reactions

were shown to be third order, and the activation energies are in line with those expected from other work.

Distinct from these problems in classical kinetics is the discussion of the mechanism of the propagation of the detonation wave. It has been suggested that compressional heating in the shock front in liquid nitroglycerine is sufficient to cause homogeneous thermal decomposition of the nitroglycerine in the time available in the detonation zone. However, for heterogeneous explosives, and for explosives in which the detonation velocity is lower and the shock front less intense, this mechanism cannot apply and some form of local heating, or temperature fluctuation, must be invoked. It has been suggested that gas spaces (bubbles in liquid explosives and intergranular spaces in solid explosives) form the required hot spots by compressional heating. Until recently the chief evidence for this has been the direct demonstration of the importance of bubbles by Bowden and his colleagues, (see, for example, Bowden and Yoffe, 1952) and the fact that increase of external pressure desensitizes explosives. However, if compressional heating in gas spaces is important, substitution of an inert gas for air in the spaces, with consequent increase in the temperature attained on compression, should effect improvement in the propagation of detonation in marginal circumstances. This effect has been demonstrated (paper 19). It is very difficult to produce any other explanation of the effect, and this observation is, therefore, quite significant in the field.

Energy Transfer

In the times associated with detonation reactions (microseconds) it is questionable whether energy is partitioned among all degrees of freedom. In particular, it seems likely that appreciable disequilibrium of vibrational energy might exist. It could be argued, however, that at the temperatures involved, translational-vibrational energy exchange could occur at almost every collision, because of increase in collision efficiency of energy transfer with increasing temperature. To check this it is necessary to know the temperature dependence of energy transfer rates: simple theory suggests that this should be quite large, on the other hand this does not appear to be borne out experimentally (see, for example, Arnold, McCoubrey and Ubbelohde, 1957). In view of the approximations usually made in applying the theory, it was decided to make as exact calculations as possible for a simple system, methane (papers 20 and 21). It was found that the calculated temperature dependence was still much greater than the experimental results indicated. This was confirmed in a new experimental determination of the relaxation time of methane, at lower temperatures than had previously been studied (paper 22). This work is still continuing, and is at present directed to comparison between theoretical and experimental values for the relaxation time in CD_4.

In the theoretical discussion of energy transfer it is necessary to know the force field governing molecular encounters.

In view of the large effect of some foreign gases in altering the relaxation time of carbon dioxide, a study of the second virial coefficients of mixtures of carbon dioxide and other gases was undertaken. This is mentioned in Section 2 of the thesis.

Notes on Authorship

In papers 1, 2, 6 - 9 and 13 - 22, the author of the present thesis originated the work and was either the sole or the senior author. In papers 10 - 12, the present author originated the work but the other author was equally senior and contributed roughly equally to its content. In papers 3, 4 and 5 the present author was the junior author but in paper 4 he had a considerable part in originating the work.

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392. *The Preparation and Heats of Combustion of Some Amine Nitrates.*

By T. L. Cottrell and J. E. Gill.

The nitrates of mono-, di-, and tri-methylamine, mono-, di-, and tri-ethylamine, ethanolamine, glycine, aniline, and benzylamine have been prepared, and their heats of combustion determined. The heats of solution of mono- and tri-methylamine nitrates in water have also been determined.

The object of the present work was to prepare a series of amine nitrates and examine the effect of alteration of structure on a variety of their physical properties. Unfortunately the work was not completed, and only the heat of combustion of all the salts prepared was determined, as well as the heat of solution of two of them in water.

Early work on amine nitrates is due to Franchimont (*Rec. Trav. chim.*, 1883, **2**, 329), van Romburgh (*ibid.*, 1886, **5**, 246), and Walden (cf. *Chem. Centr.*, 1914, I, 1800). More recently, Willis (*Trans. Faraday Soc.*, 1947, **43**, 97) has prepared the nitrates of a number of cyclic bases, and determined their heats of combustion, but only one of the compounds investigated by him, aniline nitrate, has been studied by us.

Experimental.

Preparation of Amine Nitrates.—An aqueous solution of the base was neutralised with 70% nitric acid, the water removed by distillation *in vacuo*, alone and with alcohol, and the product recrystallised from absolute alcohol. M. p.s and analyses are given in Table I. The m. p.s are several degrees higher than those previously recorded, probably because many of the salts are very hygroscopic. No further comment is necessary, except for ethanolamine nitrate, which was prepared by Gabriel (*Ber.*, 1888, **21**, 2668) by saturating an aqueous solution of vinylamine with nitric acid, whereas we found that this precaution to prevent formation of the nitric ester is unnecessary, and that the pure nitrate can be formed if the temperature is kept below 10° during addition of nitric acid to an aqueous solution of ethanolamine. Aniline nitrate, for which we obtain a slightly different heat of combustion from that recorded by Willis (*loc. cit.*), was prepared as above, and a separate sample was prepared by treatment of aqueous aniline hydrochloride with silver nitrate solution, the final product being tested for absence of Ag^+ and Cl^-. Both samples gave the same heat of combustion.

Table I.

Nitrate.	M. p.	Found : N, %.	Calc. : N, %.
Methylamine	110·5—111·5°	29·9; 29·8	29·8
Dimethylamine	75·5— 76·5	26·0; 25·8	25·9
Trimethylamine	155 —156	22·9; 23·0	22·9
Ethylamine	Syrup	25·8; 25·9	25·9
Diethylamine	104 —105	20·5; 20·8	20·6
Triethylamine	113 —114	17·2; 17·1	17·1
Ethanolamine	52 — 53	22·6; 22·4	22·6
Glycine	145 —147 (d.)	20·3; 20·4	20·3
Aniline	(d.) ~182—184	17·6; 17·7	17·95
Benzylamine	137·5—138·5	16·4; 16·4	16·5

Heats of Combustion.—The heats of combustion were determined by using a Griffin-Sutton bomb calorimeter (*J. Sci. Instr.*, 1933, **10**, 286), temperature changes being measured on a B.S.S. 791 mercury-in-glass thermometer. The water equivalent of the system was found by the combustion of benzoic acid, obtained from the Bureau of Analysed Samples, Ltd., its heat of combustion at constant volume being taken as 6324 cals./g. in air.

Whenever possible the sample was made into a pellet, but some of the compounds examined did not give a firm pellet. In these cases the sample was weighed directly into the silica crucible in which it was held when in the bomb. The bomb was filled with oxygen to a pressure of 25 atmospheres. The ignition of the sample was facilitated by means of a paper fuse, hung over the platinum ignition wire so as to dip into the sample. For the fuse Whatman's No. 41 filter paper, dried at 110°, was used and a correction was applied for its known heat of combustion.

All the determinations were corrected for the heat of formation of oxides of nitrogen. This correction was generally very small, about −7 calories per g. of sample used.

The results obtained are given in Table II. An approximate figure for the standard deviation of the mean of duplicate determinations calculated from the differences between duplicates is ±8 calories.

This of course does not take into account systematic errors of the determination or errors due to impurities in the sample, which, in view of the great hygroscopicity of the compounds, may be slightly greater than those usually experienced in this type of calorimetric work.

The temperature at which the determinations were carried out was about 16°.

From the observed heats of combustion, the heats of formation of the salts from the elements in their standard states at 298·16° K. were calculated, the values for the heats of formation of water and carbon dioxide given by Wagman, Kilpatrick, Taylor, Pitzer, and Rossini (*J. Res. Nat. Bur. Stand.*, 1945, **34**, 143) being used.

TABLE II.

Nitrate.	Heat of combustion, const. vol., water liq.; cals./g.	Heat of combustion, const. press., kcals./mole (mean).	Heat of formation, kcals./mole.
Methylamine (s)	2336, 2320	218·4	80·6
Dimethylamine (s)	3527, 3553	382·4	79·0
Trimethylamine (s)	4514, 4504	550·7	73·1
Ethylamine	3462, 3472	374·5	86·9
Diethylamine (s)	5055, 5038	687·4	98·7
Triethylamine (s)	6162, 6173	1013·6	97·3
Ethanolamine (s)	2614, 2613	323·8	137·6
Glycine (s)	1604, 1592	219·5	173·6
Aniline (s)	5080, 5104, 5098, 5095	795·1	42·5
Benzylamine (s)	5538, 5542	942·7	57·2

The heats quoted are $-\Delta H$ values.

Heats of Solution (with Dr. N. F. H. BRIGHT).—The heats of solution of mono- and tri-methylamine nitrate in water were determined by using an adiabatic calorimeter adapted from a design of Miles and Bullock (unpublished work). The following results were obtained :

	Q (soln.) (kcals./mole) in x moles of water.	x.
Methylamine nitrate	−5·33	846
	−5·28	506
	−5·31	313
Trimethylamine nitrate	−5·61	1248
	−5·54	635
	−5·56	429

These determinations were carried out at 29°. The heat of solution at infinite dilution, $-\Delta H^{\infty}_{29°}$, may be estimated to be −5·3 kcals./mole for methylamine nitrate and −5·6 for trimethylamine nitrate.

DISCUSSION.

Willis (*loc. cit.*) gives the heat of combusion of aniline nitrate as 787·9 ± 0·7 kcals./mole, which does not agree very closely with our value of 795·1 kcals. The standard deviation of our result is about ±1·2 kcals., and the difference between the results is 7·2 kcals., or 0·9%. It is difficult to explain the discrepancy, but it may be that the lower result was due to the presence of a small amount of moisture in the sample.

It is possible to combine our value of the heat of formation of methylamine nitrate with its heat of solution, the heat of formation of the nitrate ion in solution, and the heats of solution and ionisation of methylamine, to arrive at a value for the heat of combustion of gaseous methylamine of 262·0 ± 1·5 kcals./mole (subsidiary data from " Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand., 1948). Bichowsky and Rossini (" The Thermochemistry of the Chemical Substances," New York, 1936) quote 258·1 and 261·4 kcals./mole. Our result is in good agreement with the higher of these, suggesting that it is the more reliable.

The analyses and combustions were carried out by the Analytical Department of Imperial Chemical Industries Limited, Nobel Division.

IMPERIAL CHEMICAL INDUSTRIES LTD., NOBEL DIVISION,
RESEARCH DEPARTMENT, STEVENSTON, AYRSHIRE.

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295. *Binding Energies in Hydrocarbons.*

By T. L. Cottrell.

The energy of a molecule at ordinary temperatures may be regarded as being composed of its chemical binding energy, its zero-point vibrational energy, and its heat content relative to the molecule at 0° K. The last two quantities have been subtracted from the total energy of several typical hydrocarbons, to give an estimate of the total binding energy. This has been split into "binding-energy terms" per bond, and it is found that the replacement of conventional bond-energy terms by "binding-energy terms" has little effect on discussions involving them. In particular, estimates of resonance energy and steric strain are almost unchanged. It is noteworthy that the binding energy of *cyclo*hexane is less than that calculated on the basis of "binding-energy terms"; it is shown that this indication of the relative instability of *cyclo*-hexane, which is not indicated by conventional bond-energy terms, is in agreement with other evidence.

It is well known that conventional bond-energy terms include the vibrational, rotational, and translational energies of the molecule, as well as the chemical binding energy. Pauling ("The Nature of the Chemical Bond," New York, 1940, p. 54) has stated that there is no "appreciable disadvantage" in this, and Mulliken, Reike, and Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 41) have expressed the opinion that errors introduced into calculation of conjugation energies by omitting to correct ΔH values for thermal energy and zero-point vibrational energy probably cancel, but suggested that it would be desirable to verify this. On the other hand, the importance of the

zero-point vibrational energy correction was pointed out by Zahn as early as 1934 (*J. Chem. Physics*, **2**, 671), but at that time insufficient experimental evidence was available for a satisfactory discussion of the effect. It has also been suggested that non-additivity of bond-energies in the paraffins (cf. Rossini, *Chem. Reviews*, 1940, **27**, 1) is partly due to differences in the zero-point energies of isomers (Deitz, *J. Chem. Physics*, 1935, **3**, 58; Wolkenstein, *Compt. rend.* (*Doklady*) *Acad. Sci. U.R.S.S.*, 1946, **51**, 213). Again, it has been suggested by Dewar (*Trans. Faraday Soc.*, 1946, **42**, 767) that the discrepancy between the resonance energy of benzene, as obtained from heat of hydrogenation data and from comparison of the heat of formation calculated on the basis of bond energies with that observed from combustion data, results from a systematic difference between the internal kinetic energy of open-chain and cyclic compounds. It has been shown (Cottrell and Sutton, *J. Chem. Physics*, 1947, **15**, 685; cf. also Wheland, "The Theory of Resonance," New York, 1944, Ch. 3) that the discrepancy discussed by Dewar is not, in fact, due to the causes he mentions, but it certainly seems true that there is likely to be some difference in internal kinetic energy between open-chain and cyclic compounds, and also between isomers in the same series.

Zahn (*loc. cit.*) and Dewar (*loc. cit.*) have both argued that there are no theoretical reasons for expecting internal kinetic energy to be an additive bond property. This is not altogether true. Vibrations which involve the relative motions of one light atom and one heavier one, typically C–H vibrations, are fairly independent of the vibrations of the rest of the molecule. Hydrogen frequencies contribute largely to the zero-point energy, and it might therefore be expected that that quantity would depend roughly on the number of C–H bonds present, and thus be, in hydrocarbons at least, very approximately, an additive bond property. The heat content, on the other hand, being concerned with translational and rotational motion as well as vibrational, and its vibrational component being chiefly dependent on the low-frequency skeletal vibrations, is not likely to be an additive property of the bonds, but to depend on the shape of the molecule. It should be remembered that the zero-point energy is about ten times as great as the heat content.

Many data have recently been obtained on the thermodynamic properties of hydrocarbons by workers on the American Petroleum Institute Research Project No. 44 ("Tables of Selected Properties of Hydrocarbons"), and it seemed of interest to make use of them in an examination of the effect of internal kinetic energy on the additivity of bond energies, resonance, and steric strain.

Data used.—All data refer to the compounds in the ideal gas state. Heats of formation from the elements in their standard states at 298·1° K. and 0° K., and values of the heat content $H^0_{298\cdot1} - H^0_0$, have been taken from A.P.I. 44 data (*op. cit.*) for all the compounds considered with the exception of *cyclo*propane and *cyclo*butane, which are not covered by that investigation. The heat of formation of *cyclo*propane is from Rossini ("The Chemical Background to Engine Research", 1943, Ch. 2, quoted by Skinner, *Trans. Faraday Soc.*, 1945, **41**, 645), and its thermodynamic properties have been calculated from spectroscopic data by Linnett (*J. Chem. Physics*, 1938, **6**, 692) and by Kistiakowsky and Rice (*ibid.*, 1940, **8**, 610), using the molecular dimensions given by Pauling and Brockway's electron-diffraction study (*J. Amer. Chem. Soc.*, 1937, **59**, 1223). The third law entropy has been shown by Ruehrwein and Powell (*ibid.*, 1946, **68**, 1066) to agree with that calculated from molecular data. Since this work, a new electron-diffraction study of *cyclo*propane has been made by Bastiansen and Hassel (*Tids. Kjemi Berg.*, 1946, **6**, 71), giving slightly altered molecular dimensions. The thermodynamic properties have therefore been recalculated, using the new values for the molecular dimensions, and the frequency assignment, which is that used by Kistiakowsky and Rice (*loc. cit.*) as modified by Smith (*Physical Rev.*, 1941, **59**, 924), quoted by Herzberg ("Infra Red and Raman Spectra of Polyatomic Molecules", New York, 1945, p. 352). These changes make little difference to the results, which at 298·16° K. are: $S = 56\cdot85$ e. u., $H^0 - H^0_0 = 2740$ cals., $C_p = 13\cdot48$ cals./deg. Ruehrwein and Powell (*loc. cit.*) give 56·75 for the calorimetric entropy at 298·16° K.; these values for the thermodynamic functions therefore appear to be reliable. No sufficiently accurate determination of the heat of formation of *cyclo*butane is available; its thermodynamic properties have been calculated from molecular data (Cottrell, *Trans. Faraday Soc.*, in the press).

The zero-point energies have been obtained on the harmonic oscillator approximation, *i.e.*, Zpt. $E = \frac{1}{2}\sum_i \boldsymbol{h}\nu_i = 0\cdot001429\ \Sigma\nu_i(\text{cm.}^{-1})$ kcals./mole. An estimate of the magnitude of the effect of anharmonicity may be obtained by considering the zero-point energy of water. The fundamental frequencies of the H_2O molecule as quoted by Herzberg (*op. cit.*, p. 281) are 1595·0, 3651·7, and 3755·8 (cm.$^{-1}$), giving a zero-point energy of 12·86 kcals./mole. Darling and Dennison (quoted by Herzberg, *op. cit.*) have obtained the anharmonic constants, and the true

zero-point energy estimated by these authors is $4631{\cdot}2_5$ cm.$^{-1}$ or 13·24 kcals./mole. The error due to neglect of anharmonicity is thus about 3%. Though the absolute values of zero-point energies may be out by this amount, the figures are probably quite useful for comparative purposes, since it seems reasonable to assume that *differences* in anharmonicities in molecules containing the same type of bonds will be much less than this.

A pleasing confirmation of the view that *differences* in errors in zero-point energies are very small comes from the work of Ingold and his collaborators on the spectra of benzene and its deuterated derivatives (cf. Ingold, Septième Conseil de Chimie Solvay, "Isotopes in the Spectroscopy of Polyatomic Molecules with Special Reference to the Benzene Molecule"). Consideration of the isotope effect on the position of the electronic origin of the transition $A_{1g} \rightarrow B_{2u}$ for benzene and hexadeuterobenzene shows that the electronic origin of hexadeuterobenzene lies 200 cm.$^{-1}$ further out towards the far ultra-violet than that of benzene. The energy of an electronic transition is not simply the difference between the electronic energies of the states concerned; it is this plus the difference in zero-point energies. The electronic energy is, to a high degree of approximation, unaltered by isotopic substitution; the difference between the electronic origins must therefore be due to differences in zero-point energies. For benzene and hexadeuterobenzene complete sets of vibration frequencies have been given for both electronic states, and the zero-point energies calculated on the harmonic oscillator approximation. The calculated isotopic shift of the electronic origin is 208 cm.$^{-1}$, in very good agreement with the observed shift of 200 cm.$^{-1}$. This agreement, is, however, rather better than might be expected, considering the errors to which some of the frequencies are liable.

The vibrational frequencies used to obtain the zero-point energies have been taken from the assignments quoted by Herzberg (*op. cit.*) except as discussed below. For propane, for which Herzberg does not quote a complete assignment, that due to Pitzer (*J. Chem. Physics*, 1944, **12**, 310) was used. For *n*-butane, *n*-pentane, and *n*-hexane the frequencies have been estimated according to Pitzer (*Ind. Eng. Chem.*, 1944, **36**, 829; *J. Chem. Physics*, 1940, **8**, 711). The frequencies for *iso*butane and *neo*pentane are from Pitzer and Kilpatrick (*Chem. Reviews*, 1946, **39**, 435). It is of interest to compare them with those given by Wolkenstein (*loc. cit.*). The sums of the frequencies, not including those due to torsional oscillation, as obtained from the results of the American and Russian workers are given below, to the nearest 100 wave-numbers.

	Pitzer.	Wolkenstein.		Pitzer.	Wolkenstein.
n-Butane	55,800	55,400	*n*-Pentane	68,000	67,400
*iso*Butane	55,500	54,900	*neo*Pentane	66,800	67,000

The agreement is reasonably good, but the difference is sufficiently great to render doubtful the significance of the last two figures to which Wolkenstein quotes zero-point energies. We have added an arbitrary 200 wave-numbers for each torsional oscillation. The assignment for 2 : 2-dimethylbutane is due to Kilpatrick and Pitzer (*J. Amer. Chem. Soc.*, 1946, **68**, 1070). For ethylene, propylene, *cis*-but-2-ene, *trans*-but-2-ene, and *iso*butene, the assignments are due to Kilpatrick and Pitzer (*J. Res. Nat. Bur. Stand.*, 1947, **38**, 191), and that for but-1-ene is due to Aston *et al.* (*J. Chem. Physics*, 1946, **14**, 74). These assignments for ethylene and propylene have been preferred to those given by Rasmussen and Brattain (*ibid.*, 1947, **15**, 120), for consistency with the A.P.I. results. For *cyclo*hexane the assignment is due to Beckett, Pitzer, and Spitzer (*J. Amer. Chem. Soc.*, 1947, **69**, 2488); for *cyclo*pentane, that of Kilpatrick, Pitzer, and Spitzer (*ibid.*, p. 2483); and for aromatic compounds, those of Pitzer and Scott (*ibid.*, 1943, **65**, 805). That for *cyclo*butane is due to Wilson (*J. Chem. Physics*, 1943, **11**, 369). In *cyclo*pentane, the effect of the degree of freedom concerned with "rotation" of the puckering round the ring has been neglected, and in *cyclo*hexane the effect of anharmonicity in the low-frequency vibrations has also been neglected.

For some of the larger molecules the assignments have involved the use of averaged hydrogen frequencies (for details see the references given). This procedure may be justified to some extent by the agreement between the observed and the calculated thermodynamic properties, and by the way in which the zero-point energies obtained by using averaged frequencies fit in with those of molecules for which all the frequencies have been observed. The correctness of the assumption of averaged values for the C–H stretching vibration cannot readily be checked by the agreement of the calculated with the observed thermodynamic properties, because its contribution to these is small, but it seems unlikely that the averaged value can be wrong by more than 50 cm.$^{-1}$, which would only make a difference of 0·14 kcal. per CH_2 group. In the following discussion significance will not in general be attached to zero-point energy differences as small as this.

The values of the heats of atomisation of the elements in their standard states are those given by Coates and Sutton (*J.*, in the press): for carbon 125·1 kcals./g.-atom at 0° K., 126·3 kcals. at 298·16° K.; for hydrogen, 51·24 kcals./g.-atom at 0° K., 51·71 at 298·16° K.

The values of the fundamental constants quoted by Wagman, Kilpatrick, Taylor, Pitzer, and Rossini (*J. Res. Nat. Bur. Stand.*, 1945, **34**, 143) are used. These are the same as those used in the compilation of the "Tables of Selected Values of Properties of Hydrocarbons".

Heat Contents.—Before discussing the effect of considering binding energy only, it is of interest, in view of Dewar's speculations (*loc. cit.*), to note the values of the heat content of some hydrocarbons. In Table I are set out (in kcals./mole) values of $H^0_{298\cdot16} - H^0_0$ for a number of compounds.

TABLE I.

No. of C atoms.	*n*-Paraffins.	Branched-chain paraffins.	*cyclo*-Paraffins.	1- Mono-olefins.	Aromatics.
1	2·40	—	—	—	—
2	2·86	—	—	2·53	—
3	3·51	—	2·74	3·26	—
4	4·65	4·28 (*iso*butane)	3·24	4·22	—
5	5·67	5·03 (*neo*pentane)	3·60	5·36	—
6	6·99	5·94 (2 : 2-dimethyl-butane)	4·24	6·38	3·40

The heat contents of the *cyclo*paraffins are systematically less than those of the *n*-paraffins, and the heat contents of branched-chain paraffins are also less than those of the isomeric *n*-paraffins. This effect is the expected one. The results for the olefins show that, in general, the heat content of *cyclo*paraffins is less than that of open-chain hydrocarbons with the same number of atoms. This raises an interesting point in connection with *cyclo*hexane. It has been pointed out (Cottrell and Sutton, *loc. cit.*) that bond energies obtained from *n*-paraffins at 298·16° K. give the heat of formation of *cyclo*hexane exactly. Without apportioning energy between the C–C and C–H bonds, we can make an equivalent statement by pointing out that at 298·16° K. the increment per CH_2 group to the heat of formation from the elements in their standard states of *n*-paraffins is 4·926 kcals., and, if bond energies are additive, that the heat of formation of *cyclo*hexane should be $6 \times 4\cdot926$ or 29·56 kcals., in good agreement with the observed value of $29\cdot43 \pm 0\cdot19$ kcals. At 0° K. the constant increment per CH_2 group in the *n*-paraffins is 3·673 kcals., and on the basis the heat of formation of *cyclo*hexane should be 22·04 kcals., whereas it is in fact 20·01 kcals. Thus *cyclo*hexane is less stable per CH_2 group, and therefore, presumably per bond, than *n*-hexane at 0° K. The chemical significance of this difference will be discussed when we consider the binding energies themselves.

Zero-point Energies.—The zero point energies of the compounds considered are given in Table II. One general result is seen from the table: the zero-point energy of branched-chain

TABLE II.

Paraffins.		*cyclo*Paraffins.		Olefins.		Aromatics.	
Compound.	Zero-pt. energy (k.cals.).	Compound.	Zero-pt. energy (kcals.).	Compound.	Zero-pt. energy (kcals.).	Compound.	Zero-pt. energy (kcals.).
Methane	27·1	*cyclo*Propane	49·1	Ethylene	30·5	Benzene	61·7
Ethane	45·2	*cyclo*Butane	67·3	Propylene	48·4	Toluene	78·5
Propane	63·0	*cyclo*Pentane	86·0	But-1-ene	66·1	*o*-Xylene	96·0
n-Butane	80·6	*cyclo*Hexane	104·5	*cis*-But-2-ene	65·9	*m*-Xylene	95·2
*iso*Butane	80·2	—	—	*trans*-But-2-ene	65·6	*p*-Xylene	95·5
n-Pentane	98·5	—	—	*iso*Butene	65·5	—	—
*neo*Pentane	96·8	—	—	—	—	—	—
n-Hexane	116·2	—	—	—	—	—	—
2 : 2-Dimethyl-butane	114·5	—	—	—	—	—	—

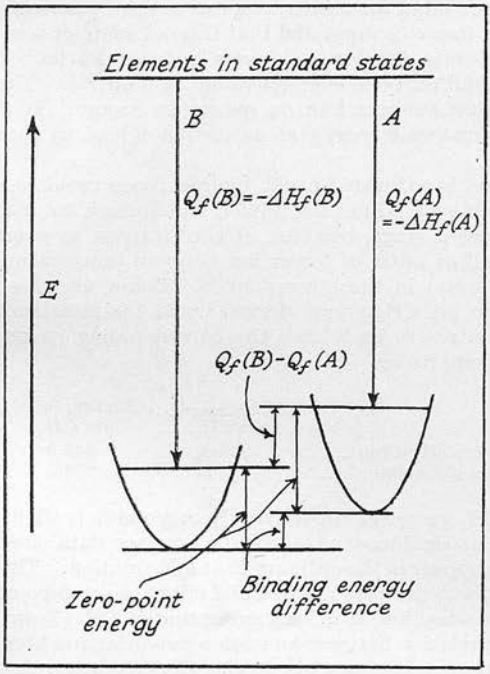
isomers is less than that of unbranched compounds. Thus part of the "Rossini effect" of the increased stability of branched-chain hydrocarbons is due to zero-point energy differences. In no case, however, does the zero-point energy account for as much as half the discrepancy. The

TABLE III.

Compound (A).	Compound (B).	$Qf_{0°K.}$ (B) − $Qf_{0°K.}$ (A) (kcals.).	Zpt. E (A) − Zpt. E (B).	Percentage of effect due to zero-point energy.
n-Butane	*iso*Butane	1·27	0·4	31
n-Pentane	*neo*Pentane	4·03	1·7	42
n-Hexane	2 : 2-Dimethyl-butane	3·63	1·7	47
But-1-ene	*cis*-But-2-ene	1·36	0·2	15
,, ...	*trans*-But-2-ene	2·64	0·5	19
,, ...	*iso*Butene	3·49	0·6	17

comparison is set out in Table III, and in the form of a schematic energy level diagram in the figure. In the first colums the *n*-compound used as reference is given, and in the second, the branched-chain compound to be compared with it. In the third column the difference in heats of formation at 0° K. is given. The notation used is that $Qf_{T°K.}$ represents the heat *evolved* when the compound concerned is formed from its elements in their standard states at T° K. The symbol $AQf_{T°K.}$ refers to the heat of formation from atoms. In the fourth column the zero-point energy difference is given; in the last, the percentage of the effect which can be accounted for by the zero-point energies. Although little exact quantitative significance can be attached to these figures, they do show that an appreciable part of the effect is accounted for. Wolkenstein (*loc. cit.*) gives similar results for butane and pentane, but his estimate of the proportion of the Rossini effect accounted for differs from that given here.

Schematic representation of energy levels in hydrocarbons (cf. Table III).



It is noteworthy that the increment in zero-point energy per CH_2 group is approximately constant: in the *n*-paraffin series to *n*-hexane, it is 18·1, 17·8, 17·6, 17·9, 17·7 kcals. It is of interest that the *cyclo*paraffins and the mono-olefins, both of which have the general formula C_nH_{2n}, have very nearly the same zero-point energies; they differ only by about 1·5% for $n = 3$ and $n = 4$.

Binding-energy Terms.—To obtain binding-energy terms, the same procedure is followed as was used by Coates and Sutton (*loc. cit.*) for bond-energy terms. They are given relative to atomic carbon in the ^3P state.

(*a*) C–C and C–H. We have the following figures (in kcals.) for the *n*-paraffins:

	$AQf_{0°K.}$.	Binding energy.	Binding-energy terms (Sum).		$AQf_{0°K.}$.	Binding energy.	Binding-energy terms (Sum).
Methane	346·1	373·2	370·6	*n*-Butane	1036·1	1116·7	1117·3
Ethane	574·2	619·4	619·5	*n*-Pentane	1267·7	1366·2	1366·2
Propane	804·7	867·7	868·4	*n*-Hexane	1498·9	1615·1	1615·1

From the figures in the second column the binding energies (C–C) = 63·6 kcals., (C–H) = 92·65 kcals. are deduced. The total binding energies calculated by using them are given in the third column; apart from that of methane, the binding energies of the compounds are given satisfactorily by using these terms.

(*b*) C=C. If the C–C and C–H energies are assumed constant, we have for the C=C energy term: in propylene 103·2, in but-1-ene 102·9, and in *cis*-but-2-ene 104·1. In the higher 1-olefins, the C=C term is very nearly the same as that in propylene. Using these binding energy terms, we may discuss resonance energies in aromatic compounds and " steric strain ".

Resonance Energies of Aromatic Compounds.—We have the following data:

	$AQf_{0°K.}$	Binding energy.	Sum of binding-energy terms.		Resonance energy.	
			(*a*).	(*b*).	(*a*).	(*b*.
Benzene	1034·0	1095·7	1056·3	1059·0	39·4	36·7
Toluene	1268·1	1346·6	1305·2	1310·6	41·4	36·0
o-Xylene	1502·1	1598·1	1554·1	1561·3	44·0	36·8
m-Xylene	1502·3	1597·5	1554·1	1561·3	43·4	36·2
p-Xylene	1502·1	1597·6	1554·1	1561·3	43·5	36·3

In the colums headed (*a*) are listed the sums of the binding energy terms with $E(C{=}C)$ given the value for the double bond in 1-mono-olefins. In those headed (*b*) corrections have been applied for "substitution effect", as described by Cottrell and Sutton (*loc. cit.*). Where binding energies were not available for the relevant olefins, it was assumed that about one-third of the substitution effect was due to zero-point energy differences (cf. Table III). In these circumstances no great significance is to be attached to the actual figures quoted: they serve merely to indicate that the use of binding energies instead of bond energies in discussing resonance in aromatic compounds makes no difference to the trend of the results, and leaves the "resonance energies" almost unchanged numerically. Deitz (*loc. cit.*) suggested that if bond energies were corrected for zero-point energies and in addition a cross interaction between hydrogens attached to the same carbon was taken into account, the resultant bond energies would be additive. The surprising result emerged from this treatment that benzene had no resonance energy. It is obvious from the above that consideration of zero-point energy alone does not lead to that result.

Steric Strain.—A full discussion of steric strain in saturated cyclic hydrocarbons requires a more detailed examination than is at present possible (cf. Kilpatrick, Pitzer, and Spitzer, *loc. cit.*; also Pitzer, *Science*, 1945, **101**, 672). At the present stage, however, it is of interest to point out that consideration of binding energies instead of heats of formation at room temperature makes little difference to an estimate of steric strain in these compounds. Below are given (in kcals./mole) the heats of formation from atoms per CH_2 group of three cyclic hydrocarbons, and the binding energies of the same compounds: in each case the corresponding energy increment for the normal paraffins is given for comparison.

	$AQf(g)_{298·1°K.}$ per CH_2.	Binding energy per CH_2.		$AQf(g)_{298·1°K.}$ per CH_2.	Binding energy per CH_2.
n-Paraffin	234·6	248·9	*cyclo*Pentane	233·4	247·0
*cyclo*Hexane	234·6	248·3	*cyclo*Propane	225·5	238·3

It is seen that the effect on strain energy per CH_2 group in the different compounds is slight. There is, however, one effect which appears to be significant: the binding-energy data show "strain" in *cyclo*hexane, an effect which does not appear in the ordinary heat of formation. This effect, as has been pointed out already, is due mainly to the heat content, and not to the zero-point energy, and is therefore certainly real. In this connection, it is interesting that Walsh (*Trans. Faraday Soc.*, 1946, **42**, 779), who has suggested a relation between ionisation potential and bond order, has noted that the first ionisation potential of *cyclo*hexane occurs considerably below that for ethane, and that *cyclo*hexane begins to absorb at longer wave-lengths than ethane in a comparable pressure range. Ramsay and Sutherland (*Proc. Roy. Soc.*, 1947, *A*, **190**, 245) have calculated the skeletal frequencies of *cyclo*hexane on simple valence force field, and find that the C–C stretching force constant is $3·7 \times 10^5$ dynes/cm., compared with $4·5 \times 10^5$ dynes/cm. in ethane. Partington (unpublished results) has shown that, although values for the activation energy for the thermal decomposition of both ethane and *n*-hexane in the presence of nitric oxide (when reaction chains are inhibited) are approximately equal, and are about 74 kcals., yet that for *cyclo*hexane under similar conditions is 2 kcals. less. The relation of this last observation to the bond energy in *cyclo*hexane is not clear, since the reaction probably does not involve the direct fission of a C–C bond (Staveley, *Proc. Roy. Soc.*, 1937, *A*, **162**, 557) but it does indicate that in some way *cyclo*hexane is less stable than the corresponding normal hydrocarbon.

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Resonance Energies from Thermal Data

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July 3, 1947

IN a recent paper Dewar[1] discussed the discrepancy between the values for resonance energies of benzene derivatives found by the Pauling-Sherman method from heats of combustion and by the Kistiakowsky method from heats of hydrogenation, and suggested that it is due to differences in internal kinetic energy between cyclic and open-chain compounds. In particular, he predicted that the heat of formation of cyclohexane should be greater than that calculated from the bond-energy sum by an amount equal to the difference between the resonance energy of benzene obtained by the two methods.

Recent data show that in fact the heat of formation of cyclohexane is the same as that calculated from bond energies obtained from the normal paraffins. The discrepancy between the two ways of obtaining resonance energies of benzene derivatives proves to be due to the use of incorrect bond-energy values. No special explanation in terms of differences in stability between cyclic and open-chain structures is necessary, since the required bond energies may be derived from open-chain compounds.

The bond energies in the normal paraffins reach constant values with increasing chain length. From Rossini's data[2] for the heats of formation of the paraffins, and values of 126.3 and 51.71 kcal. as the heats of formation per gram atom of carbon and hydrogen, respectively, in their standard states from monatomic gases at 298.1°K[3], the the C−C and C−H bond energies are found to be 60.3 and 87.1_5 kcal. The sum of these bond energies gives the heat of formation of *n*-hexane exactly, and using them we obtain 1407.6 kcal. for the heat of formation of cyclohexane from atoms, which is in very good agreement with the value of 1407.8 obtained from Rossini's data.[4]

With the above C−C and C−H values, that for the C=C energy may be obtained from Rossini's data[5] for the heats of formation of the monoölefin hydrocarbons, which were obtained by combining heats of hydrogenation with specific heat and heat of combustion data. For olefins with the double bond in the 1 position, this tends to a constant value of 101.2 kcal. With these bond energies, the apparent resonance energy of benzene is 41 kcal., in disagreement with hydrogenation result of 36. If, however, the heats of formation of the isomeric olefins are considered, and the other bond energies taken as constant, the C=C energy is found to vary from, for example, 101.3 in 1-henene to 107.2 in 2,3-dimethyl-2-butene. This is, of course, the well-known substitution effect noted by Kistiakowsky,[6] which persists to a considerable extent at 0°K.[7] The hexene in which the double bond most nearly resembles that found in an unsubstituted ring is clearly *cis* 3-hexene, for which the C=C energy is found to be 102.9 kcal. Using this C=C value, we obtain for the resonance energy of benzene 36 kcal. in agreement with the hydrogenation value. Similarly for 0-xylene, two of the C=C bonds may be taken as equivalent to that in 2-methyl-2-butene, and the third as equivalent to that in *cis* 3-hexene, which reduces the derived resonance energy by 12 kcal. to 34. Again, with Rossini's value for the heat of combustion of styrene,[8] and appropriate C=C energies obtained from non-cyclic compounds as before, the resonance energy of styrene obtained by the two methods agrees. That it is legitimate to consider the double bond in a ring structure as similar to a *corresponding* double bond in an olefin is shown by the fact that the heat of hydrogenation of non-cyclic compounds of the type CHR=CHR (*cis*) is the same as that of cyclohexene.

We should point out that while for convenience we have assumed that bond-energy differences are localized in the C=C bond, this is a purely formal treatment; some change may occur in other bond energies.

[1] Trans. Faraday Soc. **42**, 767 (1946).
[2] Prosen and Rossini, J. Research Nat. Bur. Stand. **34**, 263 (1945).
[3] Coates and Sutton, to be published.
[4] Prosen, Johnson, and Rossini, J. Research Nat. Bur. Stand. **37**, 51 (1946).
[5] Prosen and Rossini, J. Research Nat. Bur. Stand. **36**, 269 (1946).
[6] Kistiakowsky *et al.*, J. Am. Chem. Soc. **58**, 137 (1936).
[7] Rossini, Chem. Rev. **27**, 1 (1940).
[8] Prosen and Rossini, J. Research Nat. Bur. Stand. **34**, 59 (1945).

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(4)

Covalency, electrovalency and electronegativity

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With a view to obtaining a clearer understanding of several generalizations concerning bond strength, calculations on a number of model molecules have been made. The Heitler-London-Sugiura treatment has been extended to systems of two nuclei and two electrons in which the nuclear charges are less than or greater than $+1e$, and in which they may or may not be equal. In this way the screening effect of electrons which are not involved in the bond, as in a real molecule, has been roughly simulated. The effect of adding ionic terms and minimizing with respect to them has been studied in a number of cases.

The results obtained help to resolve the apparent contradiction between Pauling's adjacent charge rule and Gordy's rule connecting electronegativities and bond strength. They also suggest that the importance of changes in internuclear repulsion is greater, and that of changes

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in ionic contributions is less, in causing the relative stabilization of molecules with unequal centres, than has previously been supposed. They lead, however, to an expression for this stabilization which is similar in form to that evolved by Pauling, and so provide a new basis for interpreting atomic electronegativities. Finally, they reconcile in large measure the latter relation with Walsh's views concerning bond polarity and bond strength.

Introduction

The usual discussion of the covalent bond is essentially an extrapolation of the Heitler-London treatment for a hydrogen molecule. There are two rather different ways of proceeding. The first is the semi-empirical one of guessing the result of such a treatment for a case where it cannot actually be carried out, deriving therefrom a relation between observable quantities, and then testing and applying this. An example is Pauling's well-known postulate of the arithmetic mean rule (or, more exactly, the geometric mean rule) for predicting the energy of a covalent bond (Pauling 1944). Some theoretical support for it comes from consideration of the exchange integrals for single-electron bonds (Pauling & Sherman 1937); but it is accepted mainly because by applying it, and by making the further postulate that any difference between the predicted and the actual energies is due to increased ionic character, Pauling was able to derive an electronegativity scale with which he could correlate a great many facts. There is no doubt of the usefulness of the electronegativity scale; but this does not necessarily mean that the postulates underlying it are correct, for they may not be an unique basis. Mulliken (1935) has given further support to the existence of such a scale; but in so doing he too assumed the arithmetic mean rule.

The second procedure is to study a model system for which calculations are practicable but which is a reasonable approximation to the real one; and to take the results as a guide to what is actually happening. This is what is done in the present paper.

Calculations have been made on diatomic 'molecules' consisting of two electrons and of two nuclei which have charges varying from less than to more than the proton charge $+1e$, and which may or may not be equal. The object of this is to simulate the imperfect screening of the nucleus by electrons not involved in the bond, such as occurs in a real molecule. It was hoped that in this way some further test might be made of semi-empirical generalizations such as the arithmetic mean or geometric mean rule for covalent bond energies and the electronegativity rule, the adjacent charge rule (Pauling 1944) which states that a bond is weakened by the presence of like formal charges on the two atoms which it joins, and of Gordy's rule that the strength of a bond between two atoms is proportional to the product of their electronegativities (Gordy 1946*a*, *b*). In addition, it seemed desirable to find out what changes occur in a bond, or rather in a series of them, when one atom remains the same but the other is gradually altered.

The model

The combinations of nuclear charge for which calculations have been done are shown in figure 13, the two nuclear charges being designated α and β. Systems such as those with nuclear charges $+1{\cdot}2e$ and $+0{\cdot}8e$, or $+1{\cdot}0e$ and $+1{\cdot}0e$, will be referred to as the $(1{\cdot}2:0{\cdot}8)$ or the $(1{\cdot}0)_2$ molecules.

By first using only Heitler-London functions, it has been possible to study the effect of nuclear charge changes on a purely covalent link, if we accept as the definition thereof a bond described by such functions only.

Because we are interested in dissociation energies, we ought to use the best atomic

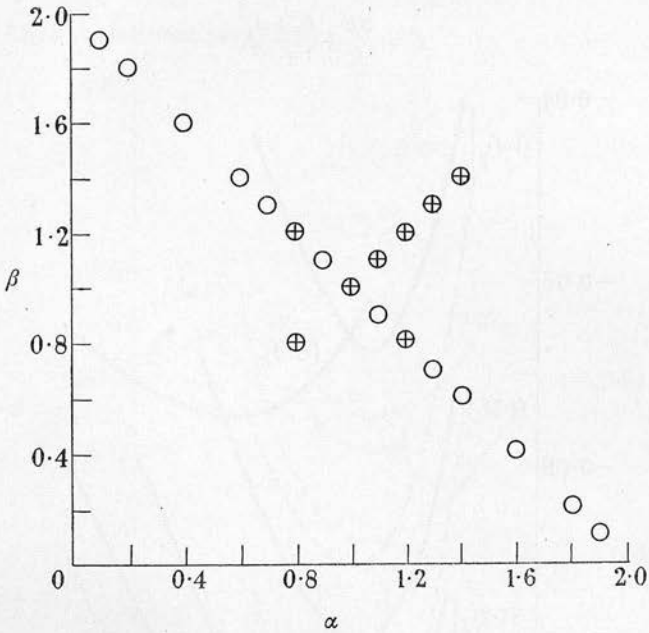

FIGURE 13. Systems studied. ○, covalent structures only; ⊕, covalent and ionic structures.

orbitals appropriate to the bonded and to the dissociated states respectively. While in principle it is possible to use atomic orbitals with varying exponents, to minimize with respect to these at each distance, and then to remove the appropriate energy of the separated atoms, this would greatly increase the difficulty of computation; so we have used unchanged atomic orbitals in the wave functions.

The first step is therefore a first-order perturbation treatment exactly analogous to the Heitler-London-Sugiura treatment of the hydrogen molecule (Heitler & London 1927; Sugiura 1927). 1*s* hydrogen-like atomic orbitals are used for simplicity. The second step is to bring in ionic terms with variable coefficients, much as did Weinbaum (1933), though, again to simplfy the computations, without using a screening constant. Systems for which this has been done are distinguished in figure 13 by crossed circles.

If the two nuclei are A and B, with nuclear charges α and β, and the electrons are numbered 1 and 2, the covalent wave function is

$$\Psi_{\text{cov.}} = N[\psi_A(1)\,\psi_B(2) + \psi_A(2)\,\psi_B(1)],$$

where

$$\psi_A(1) = \left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}} \exp\left[-\alpha r_{A1}\right], \quad \text{etc.},$$

and N is a normalizing factor. The interaction energy between the two atoms is given in the usual way by

$$E = \int \Psi H' \Psi \, d\tau,$$

where H' is the Hamiltonian for the interaction. E takes the form

$$E = \frac{\alpha\beta}{R} + \frac{K+J}{1+S^2},$$

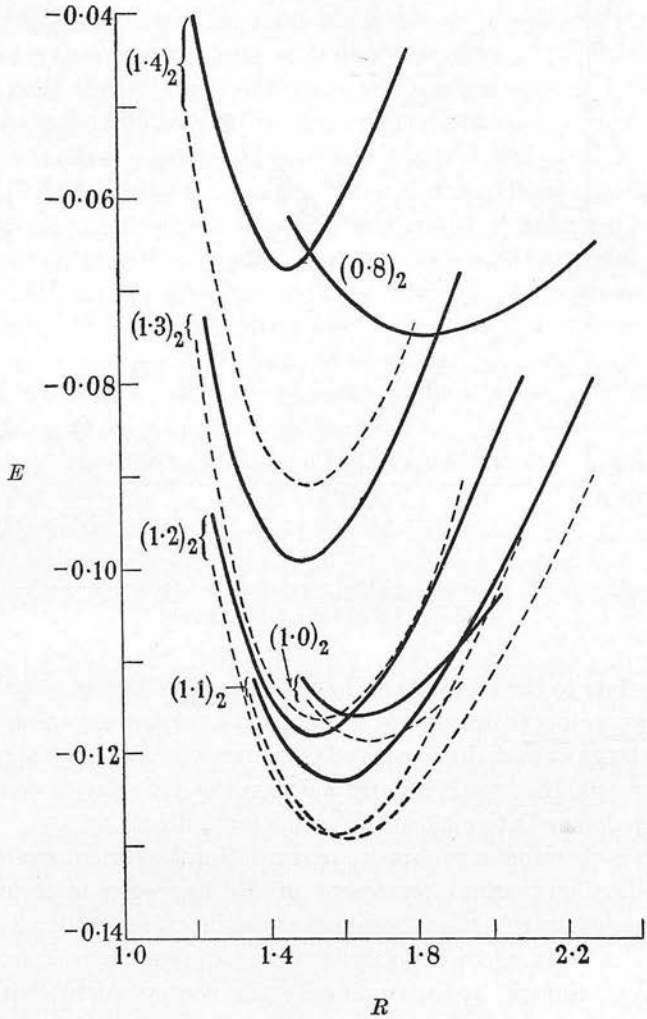

FIGURE 14. Equal centres, energy as a function of R (atomic units).
—— covalent; ----- covalent-ionic.

where R is the internuclear distance, J and K are the Coulomb and exchange integrals, and S is the overlap integral between the atomic functions. $\alpha\beta/R$ is the Coulomb term corresponding to internuclear repulsion. The sign of the second term is negative, thus giving binding. It is obvious that for constant total charge the internuclear repulsion is a maximum for $\alpha = \beta$, and it is reasonable to expect

that the second term will also become smaller with increasing asymmetry of nuclear charge distribution. The properties of a series of bonds for which $\alpha+\beta=$ *constant* will therefore depend upon the relative importance of the two effects.

The ionic wave function is

$$\Psi_{\text{ion}} = a\psi_A(1)\,\psi_A(2)+b\psi_B(1)\,\psi_B(2),$$

where a and b are variational parameters.

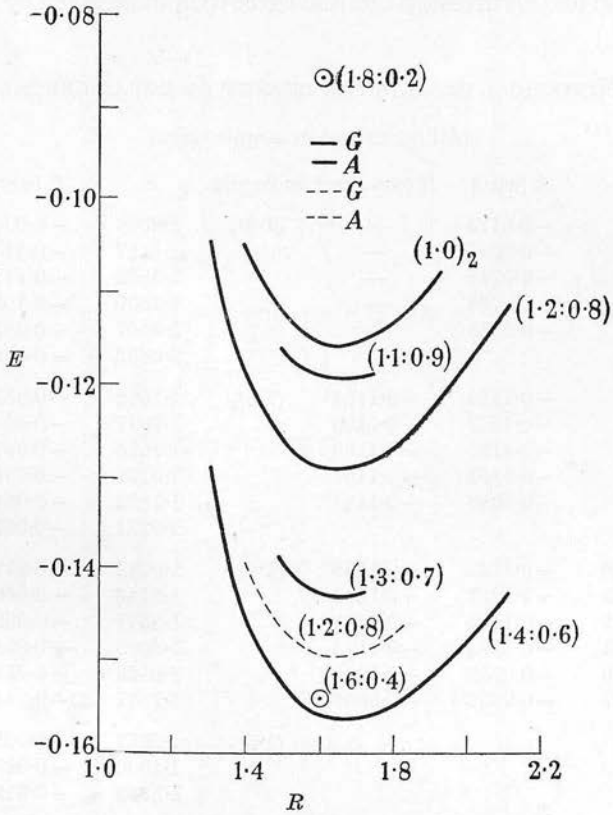

FIGURE 15. Unequal centres, energy against R. —— covalent; ---- covalent-ionic; —— G, —— A } geometric and arithmetic means of $E(1{\cdot}2)_2$ and $E(0{\cdot}8)_2$ taken ----G, ---A } at the minima for covalent and covalent-ionic structures.

The calculations

Details of the calculation of interactions between s electrons have been given by several authors (e.g. Rosen 1931; Hellmann 1935; Coulson & Duncanson 1938; Coulson 1942; Hirschfelder & Linnett 1950). It was found convenient to express the integrals in terms of the functions $A_n(\alpha)$, $B_n(\alpha)$ and $F_n(\alpha)$ used by Rosen (1931). Several corrections to the first paper by this author are given in the second: an additional one is that his equation (44) on p. 265 should read

$$A_n^m(\alpha) = \sum_{\nu=0}^{m} \frac{\alpha^\nu}{2^\nu \nu!} A_{n+\nu}(\alpha).$$

A fresh tabulation of these functions had to be made for this work.

Results and discussion

In tables 14 and 15 the values of interaction energy and interatomic distance are given for equal and unequal centres respectively, figures 14 and 15 show them graphically. Table 16 gives the dissociation energies and equilibrium distances obtained from these curves. The zero of energy is in each case the energy of the separated 'atoms'. The results for the hydrogen molecule itself, which are included, were recalculated for this investigation and agree with those given by Coulson (1937).

TABLE 14. NUMERICAL RESULTS FOR ENERGY OF EQUAL CENTRE MOLECULES

(All quantities in atomic units)

molecule	R	E (cov.)	E (cov.-ion)	molecule	R	E (cov.)	E (cov.-ion)
$(0{\cdot}8)_2$	1·25	−0·0173	—	$(1{\cdot}2)_2$	1·2500	−0·0941	−0·0995
	1·50	−0·0647	—		1·4167	−0·1149	−0·1234
	1·75	−0·0745	—		1·5833	−0·1172	−0·1286
	2·00	−0·0734	—		1·7500	−0·1091	−0·1229
	2·25	−0·0668	—		1·9167	−0·0959	−0·1112
					2·0833	−0·0807	−0·0966
$(1{\cdot}0)_2$	1·5	−0·1127	−0·1144	$(1{\cdot}3)_2$	1·1538	−0·0537	−0·0618
	1·6	−0·1157	−0·1180		1·3077	−0·0887	−0·1010
	1·7	−0·1155	−0·1185		1·4615	−0·0991	−0·1154
	1·8	−0·1131	−0·1169		1·6154	−0·0954	−0·1150
	1·9	−0·1089	−0·1131		1·7692	−0·0842	−0·1059
					1·9231	−0·0696	−0·0923
$(1{\cdot}1)_2$	1·3636	−0·1125	−0·1158	$(1{\cdot}4)_2$	1·0714	+0·0128	−0·0163
	1·5455	−0·1227	−0·1281		1·2143	−0·0405	−0·0574
	1·7273	−0·1194	−0·1268		1·3571	−0·0621	−0·0841
	1·9091	−0·1089	−0·1179		1·5000	−0·0649	−0·0913
	2·0909	−0·0950	−0·1051		1·6429	−0·0573	−0·0867
	2·2727	−0·0802	−0·0906		1·7857	−0·0446	−0·0752
				$(1{\cdot}5)_2$	1·2667	−0·0028	—
					1·4000	−0·0146	—
					1·5333	−0·0126	—

TABLE 16

E (MINIMUM) FOR MOLECULES CONSIDERED

(All quantities in atomic units)

molecule	E (cov.) at R_e		E (cov.-ion) at R_e	
$(0{\cdot}8)_2$	−0·075	$1{\cdot}8_5$	−0·075	$1{\cdot}8_5$
$(1{\cdot}0)_2$	−0·116	$1{\cdot}6_5$	−0·119	$1{\cdot}6_7$
$(1{\cdot}1)_2$	−0·123	$1{\cdot}5_8$	−0·128	$1{\cdot}6_1$
$(1{\cdot}2)_2$	−0·118	$1{\cdot}5_2$	−0·129	$1{\cdot}5_7$
$(1{\cdot}3)_2$	−0·099	$1{\cdot}4_9$	−0·116	$1{\cdot}5_4$
$(1{\cdot}4)_2$	−0·066	$1{\cdot}4_5$	−0·091	$1{\cdot}5_0$
(1·1:0·9)	−0·119	$1{\cdot}6_5$	—	—
(1·2:0·8)	−0·129	$1{\cdot}6_4$	−0·149	$1{\cdot}6_4$
(1·3:0·7)	−0·143	$1{\cdot}6_5$	—	—
(1·4:0·6)	−0·156	$1{\cdot}6_5$	—	—

TABLE 15. NUMERICAL RESULTS FOR ENERGY OF UNEQUAL CENTRE MOLECULES

(All quantities in atomic units)

mol.	$(1{\cdot}0)_2$	(1·1:0·9)	(1·2:0·8)		(1·3:0·7)	(1·4:0·6)	(1·6:0·4)	(1·8:0·2)	(1·9:0·1)
R	E (cov.)	E (cov.)	E (cov.)	E^* (cov.-ion)	E (cov.)	E (cov.)	E (cov.)	E (cov.)	E (cov.)
1·3	—	—	−0·1055	—	—	−0·1298	—	—	—
1·4	−0·1055	—	−0·1193	−0·1405	—	−0·1460	—	—	—
1·5	−0·1126	−0·1164	−0·1262	−0·1466	−0·1396	−0·1525	—	—	—
1·6	−0·1157	−0·1192	−0·1291	−0·1493	−0·1427	−0·1557	−0·1539	−0·0866	−0·0428
1·7	−0·1155	−0·1191	−0·1290	−0·1491	—	−0·1561	—	—	—
1·8	−0·1131	—	−0·1267	−0·1470	—	−0·1547	—	—	—
1·9	−0·1089	—	−0·1227	—	—	−0·1519	—	—	—
2·0	—	—	−0·1176	—	—	−0·1480	—	—	—
2·1	—	—	−0·1118	—	—	−0·1434	—	—	—

* The ionic contribution includes both A^+B^- and A^-B^+. If only A^-B^+ is taken into account, the energy is $-0{\cdot}1464$ at $R = 1{\cdot}6$.

Equal centre molecules

For equal centre molecules E (minimum) is plotted against α, the common nuclear charge, in figure 16. The covalent bond attains maximum strength at about $\alpha = +1{\cdot}12e$ and then rapidly weakens. When ionic terms are included, the maximum comes at about $+1{\cdot}16e$.

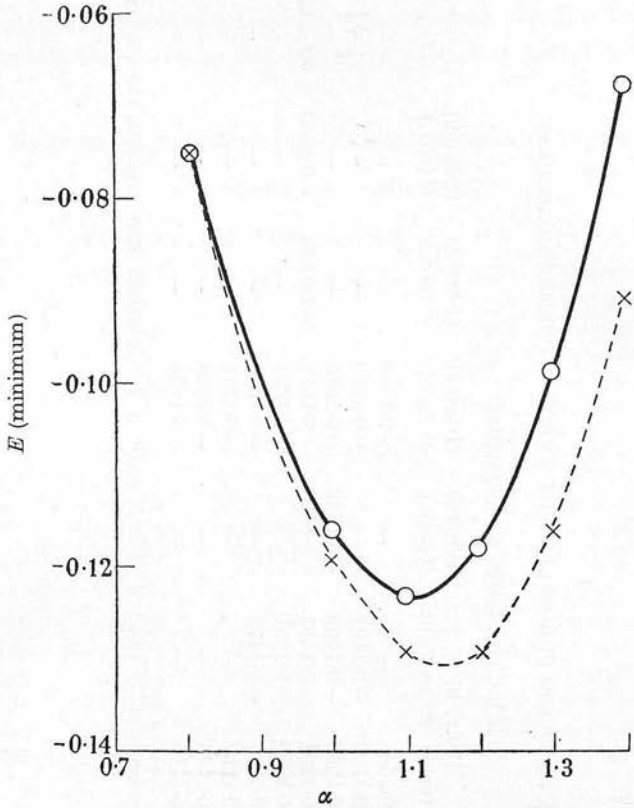

FIGURE 16. Plot of E (minimum) against α for equal centre molecules.
——○—— covalent, ---×--- covalent-ionic.

Now, Pauling's adjacent charge rule and Gordy's rule (see above) appear to be contradictory, because according to the former increase of the effective nuclear charges should weaken a bond, while according to the latter it should do the opposite. From our results, it seems that this paradox can be resolved; for Gordy's rule appears to hold for equal charges up to about $+1{\cdot}2e$, while Pauling's holds for higher ones.

Unequal-centre molecules

From the figures it will be noted that for molecules with $\alpha+\beta = 2$, but $\alpha \neq \beta$, which may be designated $(A:B)$, the covalent dissociation energy $-E_{\text{cov.}}(A:B)$ is greater than the arithmetic or geometric mean of $-E_{\text{cov.}}(A)_2$ and $-E_{\text{cov.}}(B)_2$. Indeed, in all cases save $(1{\cdot}1:0{\cdot}9)$ it is greater than either of the latter. The wave function used is the simple Heitler-London one, so this stabilization has no reference to the effects of ionic terms: it is characteristic of the purely covalent bonds.

When the effect of ionic terms is considered as it has been for (1·2 : 0·8), further stabilization is found; but when ionic terms are also included in $E(1{\cdot}2)_2$ and $E(0{\cdot}8)_2$, it is found that the further change in energy relative to the arithmetic mean is comparatively small. This is shown by evaluating $\Delta = -E_{AB} - \frac{1}{2}(-E_{AA} - E_{BB})$ as follows:

molecules:	$(1{\cdot}2)_2$	$(0{\cdot}8)_2$	A.M.	(1·2:0·8)	Δ
$-E$ (cov.)	0·118	0·075	0·096	0·129	0·033
$-E$ (cov.-ion.)	0·129	0·075	0·102	0·149	0·047

The value of Δ due to the change in covalent energy alone is 70 % of that found when ionic terms are also included.

In order to show the reason for this stabilization of the purely covalent bond, the second term of the expression for E (p. 52), i.e. $(K+J)/(1+S^2)$, the bonding function, is plotted against R in figure 17. For $(1{\cdot}0)_2$ and (1·2 : 0·8) the curves nearly coincide. When values of the function for $(1{\cdot}0)_2$ and (1·2 : 0·8) are taken at the respective equilibrium distances, they are very nearly equal ($-0{\cdot}725$ and $-0{\cdot}720$ respectively). Furthermore, if similarly the values for $(1{\cdot}2)_2$ and $(0{\cdot}8)_2$ and (1·2 : 0·8) are taken at the equilibrium distances, the arithmetic mean for the first two comes very near the value for the last: the actual values are $-0{\cdot}74$ and $-0{\cdot}72$ respectively; and it may be noted that the discrepancy corresponds to *weaker* binding in (1·2 : 0·8) than in the mean. The stabilization in (1·2 : 0·8), shown by Δ (covalent) must therefore be due to changes in the first term for E, i.e. *to a decrease in nuclear repulsion.*

If we may generalize from the particular case of (1·2 : 0·8) we should expect (*a*) *that the bonding function* $(K+J)/(1+S^2)$ *is constant for all molecules having* $\alpha+\beta =$ *constant*, provided that $(\alpha-\beta)$ is not too large, (*b*) *that* $(K+J)/(1+S^2)$ *for AB is the arithmetic mean of the values for AA and BB.*

From the first rule we should expect that the difference between $E_{\text{cov.}}$ for a molecule with equal centres of charge $\frac{1}{2}(\alpha+\beta)$ and an unsymmetrical one with centres of charge α and β would be:

$$\Delta' = \left(\frac{\alpha+\beta}{2}\right)^2 \frac{1}{R_e} - \frac{\alpha\beta}{R_{AB}} \simeq \left(\frac{\alpha-\beta}{2R^{\frac{1}{2}}}\right)^2. \tag{25}$$

The second step follows because our results for the $\alpha+\beta = 2$ series show R to be substantially constant (figure 14). Since Δ' must therefore be positive, it follows that the nuclear repulsion energy is less in the latter molecule than in the former, and that this stabilization is proportional to $(\alpha-\beta)^2$. This is, indeed, approximately true for when E is plotted against $(\alpha-\beta)^2$ for this series the curve is almost straight up to $\alpha-\beta = 0{\cdot}6$ (see figure 18). Beyond that point the generalization quickly breaks down, and when $\alpha-\beta$ is 1·2, covalency is rapidly ceasing to be important.

From the second rule, if we evaluate

$$\Delta_{AB} = -E_{AB} - \tfrac{1}{2}(-E_{AA} - E_{BB}), \quad \text{where} \quad E_{AB} = \alpha\beta/R_{AB} + C_{AB},$$

$$E_{AA} = \alpha^2/R_{AA} + C_{AA}, \quad E_{BB} = \beta^2/R_{BB} + C_{BB}$$

we find that, since $$C_{AB} = \tfrac{1}{2}(C_{AA}+C_{BB}),$$

$$\Delta_{AB} = \frac{1}{2}\left(\frac{\alpha^2}{R_{AA}}+\frac{\beta^2}{R_{BB}}\right)-\frac{\alpha\beta}{R_{AB}}.$$

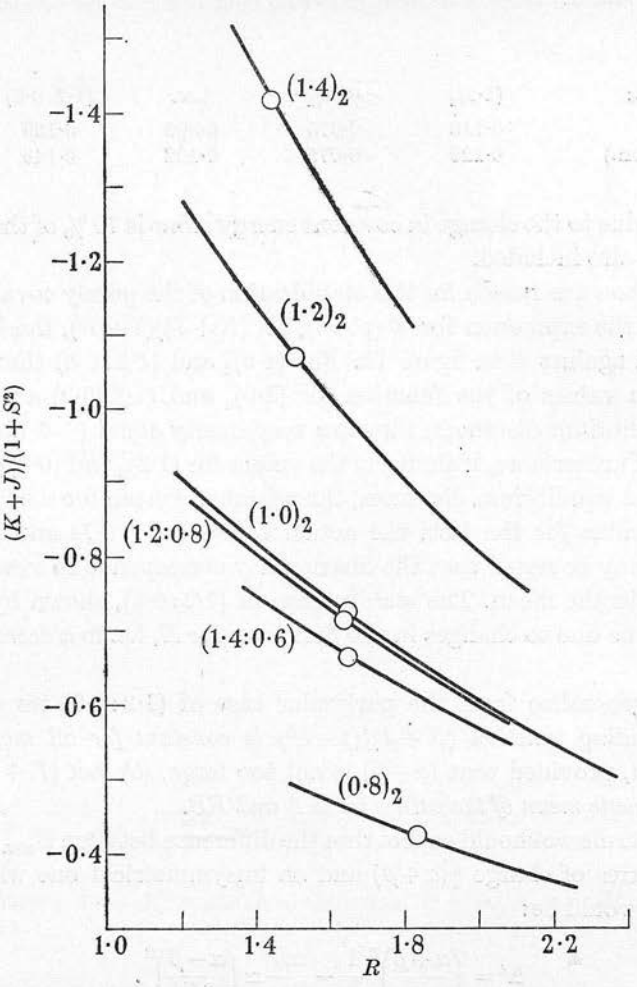

FIGURE 17. Plot of $(K+J)/(1+S^2)$ against R for various systems. ○ indicates equilibrium distance.

If now we assume that $R_{AB} = \sqrt{(R_{AA}R_{BB})}$ (for $(1\cdot2:0\cdot8)$ R is $1\cdot64$ a.u.; the geometric mean is $1\cdot68$ a.u.), it follows that

$$\Delta = \frac{1}{2}\left[\frac{\alpha}{R_{AA}^{\frac{1}{2}}}-\frac{\beta}{R_{BB}^{\frac{1}{2}}}\right]^2. \tag{26}$$

This relation is of the same form as that derived more empirically by Pauling; but it has no reference whatsoever to ionic terms. At present we cannot say whether any similar relation would appear if ionic terms were included, because for lack of time it has not been possible to include them in any unequal-centred molecule save $(1\cdot2:0\cdot8)$. In any case, however, for this molecule what is true for covalent linkage is the major truth for the total linkage.

If we take the expression for Δ' and extend it stochastically, thus:

$$\Delta' = \left[\frac{\alpha}{2R_{AA}^{\frac{1}{2}}} - \frac{\beta}{2R_{BB}^{\frac{1}{2}}}\right]^2 \tag{27}$$

then $\Delta = 2\Delta'$, e.g. for the set $(1{\cdot}2:0{\cdot}8)$, $(1{\cdot}0)_2$, $(1{\cdot}2)_2$ and $(0{\cdot}8)_2$ we find that $\Delta' = 0{\cdot}013_5$ while $\frac{1}{2}\Delta = 0{\cdot}016_5$. If we write $\alpha/\sqrt{(2R_{AA})} = y_A$, $\beta/\sqrt{(2R_{BB})} = y_B$, we can say that in order to obtain the covalent dissociation energy of the molecule with equal

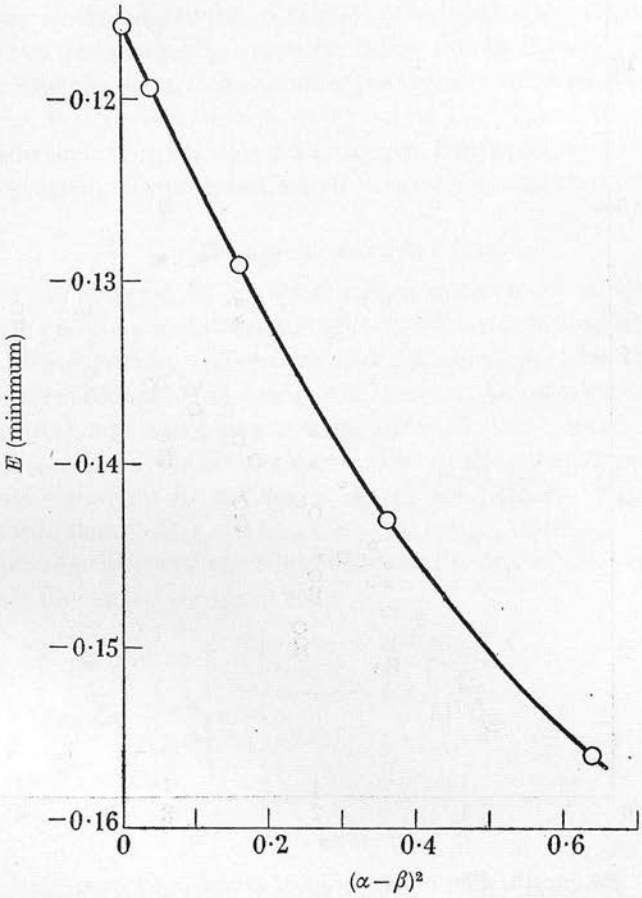

FIGURE 18. Plot of E against $(\alpha-\beta)^2$.

centres $\frac{1}{2}(y_A+y_B)$, $\frac{1}{2}\Delta_{AB}$ is subtracted from $-E_{AB}$, e.g. $-E_{(1{\cdot}2:0{\cdot}8)} = 0{\cdot}1295$ and $\Delta = 0{\cdot}033$; so $-E_{(1{\cdot}0)_2}$ predicted is $0{\cdot}113$, the observed value being $0{\cdot}116$ a.u.

These results for imaginary molecules suggest simple relations that may hold for real ones. In real atoms the electrons not forming the bond do two things. They shield the nucleus more or less effectively, and they give the atom a radius. Gordy (1946*c*) suggested that the effective nuclear charge is approximately $\frac{1}{2}(n+1)e$, where n is the number of valency shell electrons; and that the radius in question may be taken as the observable covalent radius. Incorporating these ideas into our expression for Δ, we should expect that since Δ is actually observed to be expressible

as $(x_A - x_B)^2$, where x_A and x_B are what Pauling calls the electronegativities of A and B, that there would be a linear relation between x and $(n+1)/\sqrt{(2r)}$. Gordy supposed that it is the electrostatic potential at the surface of the atom which determines electronegativity, so he predicted a linear relation between x and $(n+1)/r$. In figure 19 the two functions are plotted against x. Gordy's function

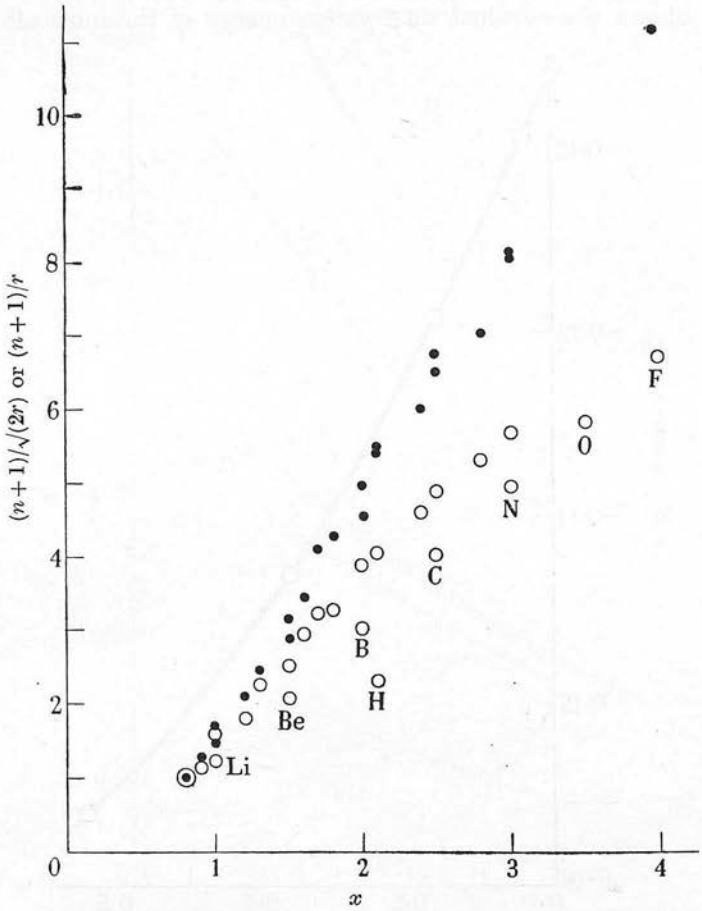

FIGURE 19. Plot of $(n+1)/\sqrt{(2r)}$, ○ and $(n+1)/r$, •, against Pauling's x for the elements up to Br.

groups better about a single line, but ours gives two reasonably straight ones, one of them, for the elements of the first short period, being particularly good. Inasmuch as we know that ionic terms make some contribution to Δ, we cannot expect that a treatment which ignores them will give perfect results; furthermore, the use of $\frac{1}{2}(n+1)e$ to give the effective nuclear charge is an over-simplification. Although, in our view, the reason why Δ is given by a function of the form $(x_A - x_B)^2$ is different from that originally proposed, the name electronegativity for x remains just as apt.

It may be remarked that the geometric mean rule for bond lengths, used in deriving equation (26), is quite well obeyed by actual bonds, provided the radii are not too different. It gives shorter distances than the arithmetic mean rule, and so is rather

similar in its effect to the Schomaker and Stevenson rule (Schomaker & Stevenson 1941) though no theoretical relation between the two can be given. The Heitler-London type of calculation is known not to give good values for internuclear distances; so we have not tried to apply our results to obtaining quantitative relations between this and effective nuclear charges; they may, however, be of qualitative use.

The curvatures found for the potential energy functions may also be of qualitative value: the contrast between those for the $(1{\cdot}4)_2$ and $(0{\cdot}8)_2$ molecules is very striking.

The equivalent electronegativities for some of the 'atoms' used in our calculations have been derived from our expression for Δ, by taking R values from figure 14, expressing Δ in electron volts, and assuming that atom 1·0 has the electronegativity of hydrogen, viz. 2·1. The results are $x(0{\cdot}8) = 1{\cdot}44$ (beryllium, 1·5); $x(1{\cdot}2) = 2{\cdot}85$; $x(1{\cdot}3) = 3{\cdot}17$ (nitrogen, 3·0), $x(1{\cdot}4) = 3{\cdot}53$ (oxygen, 3·5); $x(1{\cdot}6) = 4{\cdot}15$ (fluorine, 4·0). These have no exact significance, but help to illustrate the range of the calculations.

Variation of one atom in a bond

Walsh (1947) has adduced an empirical rule that the more polar a bond is, the weaker it is, *ceteris paribus*: and it was thought that this was in conflict with Pauling's rule about electronegativity differences and stabilization. The two rules refer, however, to different things. If by 'strength' is meant dissociation energy, then the first rule states that, e.g. if in a pair AB one atom, B (the more electronegative of the two) is kept the same while the environment of the other is varied so that its electronegativity decreases in the series A, A', etc., then $-E_{AB} > -E_{A'B}$. The second rule states that $-E_{AB} + \frac{1}{2}(E_{AA} + E_{BB}) < -E_{A'B} + \frac{1}{2}(E_{A'A'} + E_{BB})$. Because E_{AA} and $E_{A'A'}$ can be different, there is not necessarily any conflict between the two statements, as is illustrated by figure 20.

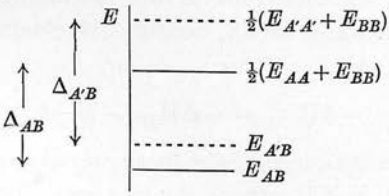

FIGURE 20

The present results show that for the $(0{\cdot}9:1{\cdot}1)$ and the $(1{\cdot}1)_2$ molecules, the dissociation energies are $-0{\cdot}119$ and $-0{\cdot}123$; so that in this case the more polar bond is the weaker; but whereas the stabilization of $(1{\cdot}1)_2$ relative to the arithmetic mean is necessarily zero, that of the $(0{\cdot}9:1{\cdot}1)$ molecule is 0·007. For $(0{\cdot}8:1{\cdot}2)$ compared with $(1{\cdot}2)_2$, the dissociation energies are 0·129 and 0·118 respectively; so the more polar bond is now the stronger and, again, whereas Δ for the latter is necessarily zero, for the former it is 0·033. For the pair $(0{\cdot}7:1{\cdot}3)$ and $(1{\cdot}3)_2$ the more polar bond is much the stronger (0·143 against 0·099).

A related point arises in the discussion by Baughan, Evans & Polanyi (1941) of the behaviour of the R—X bond in alkyl halides, as a function of increasing polarity. They sought to explain why, the more polar the molecule is, the less is the dissociation energy for the process $R\text{—}X \rightarrow R + X$. This again might appear to conflict with

Pauling's rule; but these authors suggested that there was a relation between the importance of polar structures R^+X^- in hybridization with R—X, and the stabilization of the free radical R; and that the latter has more effect in reducing the dissociation energy than the former has in increasing it.

In our treatment, no equivalent of stabilization of the radical R appears; so we only find, for (1·2 : 0·8) and more polar molecules, that the dissociation energy increases with polarity. Now, Pauling's rule would be concerned with the reaction:

$$R\text{—}R + X\text{—}X \rightarrow 2R\text{—}X - \Delta\mathrm{H}$$

and would require that if this be compared with another one

$$R'\text{—}R' + X\text{—}X \rightarrow 2R'\text{—}X - \Delta'\mathrm{H},$$

where R' is less electronegative than R so $R'X$ is more polar than RX, then

$$-(\Delta'\mathrm{H} - \Delta\mathrm{H}) > 0.$$

If $\Delta'\mathrm{H}$ and $\Delta\mathrm{H}$ be expressed in terms of the several dissociation processes into which the reactions can be analyzed, then

$$-(\Delta'\mathrm{H} - \Delta\mathrm{H}) = \Delta\mathrm{H}_{R'R'} - \Delta\mathrm{H}_{RR} - 2(\Delta\mathrm{H}_{R'X} - \Delta\mathrm{H}_{RX}).$$

If $-\Delta\mathrm{H}_{R'X}$ is increased relative to $-\Delta\mathrm{H}_{RX}$ by the greater polarity of $R'X$, but is reduced by greater radical stabilization, we may write:

$$-\Delta\mathrm{H}_{R'X} = -\Delta\mathrm{H}_{RX} + p - r.$$

But $-\Delta\mathrm{H}_{R'R'}$ will be decreased relative to $-\Delta\mathrm{H}_{RR}$ by $2r$: it will also be changed by the effect of the different nuclear charges on the bond itself. The sign of the latter term, b, will depend upon whether Gordy's rule or Pauling's adjacent charge rule is operative: the former is the more likely, because the electronegativities of R and R' are probably low enough, so

$$-\Delta\mathrm{H}_{R'R'} = -\Delta\mathrm{H}_{RR} - 2r - b.$$

Therefore $-(\Delta'\mathrm{H}\text{—}\Delta\mathrm{H}) = 2p + b$; so if the foregoing assumptions about p and b are correct, $-(\Delta'\mathrm{H}\text{—}\Delta\mathrm{H}) > 0$, and Pauling's electronegativity rule is obeyed. If, however, the electronegativity of R is so high that the adjacent charge rule is operative for $R'R'$ relative to RR, b will be negative. Our results indicate that p would probably be positive; but until more points on the energy surface (figure 13) have been obtained, this is not certain, so there is some doubt as to whether Pauling's rule would apply in this range.

Limitations of the treatment

The quantitative shortcomings of simple Heitler-London-Sugiura calculations are well-known and have already been stressed in this discussion. Apart from such technical troubles, there is a major difficulty of principle in correlating our results with reality, which arises from our very simple way of simulating the screening effect of electrons that are not forming the bond.

We have assumed that the effective nuclear charge of either atom is the same for the bonding electrons and for the other nucleus. At a sufficient distance, however,

the effective nuclear charge of an atom with one electron removed is obviously $+1e$. Were this always in fact the effective nuclear charge at the second nucleus, our treatment and our conclusions would be largely irrelevant. There could be no stabilization by change of internuclear repulsion, nor by change of our covalent bonding function: it could then occur only through change of contribution by ionic terms.

The truth most probably lies between these two extreme views. The repulsion of one atom by the other should not be treated simply as a force between point charges: it is not the field *at* the second nucleus which alone is relevant. Atoms have extent; and even though the effective radius of the screening clouds of non-bonding electrons may be less than the internuclear distance, the interatomic repulsion energy is not necessarily e^2/R. To the extent that the interaction between these electron clouds is not to be treated as that between two charged spheres, distance R apart, our treatment will be nearer the truth.

It is difficult to devise or apply tests which would decide which extreme view is nearer the truth; and a rigorous theoretical treatment is perhaps not yet practicable. It has, however, at least been possible to show explicitly what happens on one of these views, and to show furthermore that in general form the results agree reasonably well with reality. They provide not only an alternative but in some respects a more consistent explanation of the phenomena considered.

The authors wish to express their gratitude to Dr William Moffitt for valuable criticisms and suggestions, and also to Imperial Chemical Industries Ltd., Nobel Division, for enabling one of us (T.L.C.) to carry out this work.

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Note: references in the text to electron diffraction work are quoted from Allen & Sutton (1950) if not given separately.

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THE INTERPRETATION OF BOND PROPERTIES

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It is our aim in this Review to discuss some recent attempts to interpret variations in length and strength of bonds. The extent of the subject—which includes in principle the whole of structural chemistry—makes it impossible for us to do more than consider a few of what appear to be the most interesting suggestions which have been advanced. In particular, we shall not discuss recent treatments of the structure of metals and intermetallic compounds by valence-bond methods.[1]

Before discussing the interpretation of these quantities, it is desirable to examine what they are and how they are obtained. There is no ambiguity, other than that involved in the method of observation, in the determination of bond length. The same is not true of bond strength.

Bond energies are quantities which may be assigned so that their sum in a molecule gives its heat of formation from separated atoms.[2–4] E. T. Butler and M. Polanyi [5] prefer to call them "bond energy terms" and reserve bond energy for the dissociation energy of a bond. For molecules for which an unambiguous valence bond structure may be written, the energy is regarded as an additive bond property, and the component terms as constants. It has been noted [5] that additivity is not evidence for a constant heat of formation of the bonds concerned. Consider two kinds of bonds formed, for example, by carbon with two different atoms X and Y. Whatever the variation in the energies of the C–X and C–Y bonds with the position of the C atom, no deviation from the additivity rule would result, so long as the variations are equal for both kinds of bond.

It has been pointed out by various authors [6–9] that heats of formation at ordinary temperatures include vibrational, rotational, and translational energy as well as chemical binding energy, and that although there is some theoretical justification for considering that the last of these is an additive bond property, the others are unlikely to be. The question has been quantitatively discussed for hydrocarbons by T. L. Cottrell,[10] who concludes

[1] L. Pauling, *J. Amer. Chem. Soc.*, 1947, **69**, 542.
[2] K. Fajans, *Ber.*, 1920, **53**, 643; 1922, **55**, 2826.
[3] L. Pauling, "The Nature of the Chemical Bond", Cornell, 1940.
[4] N. V. Sidgwick, "The Covalent Link in Chemistry", Cornell, 1933.
[5] *Trans. Faraday Soc.*, 1943, **39**, 19.
[6] V. Dietz, *J. Chem. Physics*, 1935, **3**, 58. [7] R. Serber, *ibid.*, p. 81.
[8] M. J. S. Dewar, *Trans. Faraday Soc.*, 1946, **42**, 767.
[9] M. V. Wolkenstein, *Compt. rend.* (*Doklady*), *Acad. Sci. U.R.S.S.*, 1946, **51**, 213.
[10] *J.*, in the press.

that bond energies obtained conventionally may be used instead of " binding energy terms ", without introducing serious error. Tables of bond energies have been given by Sidgwick,[4] Pauling,[3] and, more recently, by G. E. Coates and L. E. Sutton,[11] and by Y. K. Syrkin.[12]

The bond energy of a diatomic molecule is the same as its dissociation energy if the atoms are produced in their ground states ; or may readily be derived from it if the state of excitation of the atoms produced is known. In molecules such as H_2O, NH_3, CH_4, where there is only one type of bond, the bond energy is obtained by dividing the heat of formation from atoms by the number of bonds. The bond energy need not be the same as, and in general differs slightly from, the dissociation energy of a bond in the molecule. This is because the energy of dissociation of a bond in a polyatomic molecule includes the energy of reorganisation of the radicals formed. There is the further difficulty in carbon compounds that the latent heat of sublimation of carbon to the valence state is not accurately known. This comes into the bond energy obtained from the heat of formation of the compound, but not into the dissociation energy.[13] The same is true of nitrogen compounds.

For a molecule in which there is more than one type of bond, it is necessary to know the energies of all types but one from other data, and to obtain the remaining bond energy as the residuum. This leads to rather large differences in the energy of the " same " bond in different molecules because the total environmental effects causing deviations from additivity in the bond energies as a whole are lumped into an effect on the one bond considered last. If allowance is to be made for the effects of differences in environment on the individual bonds in a molecule, it is necessary to make an assumption of the type which we wish to test about the effect of distortion, on at least one sort of bond, and then to see if this leads to self-consistent conclusions. For example, for organic compounds, it is necessary to assume a relationship between the energy and length of the CH bond, since all CH bonds are not the same and the CH bond in methane is the only bond in any organic compound whose energy may be determined unambiguously.

The observed variation of length of the CH bond is from $1{\cdot}059_7$ A. in acetylene to $1{\cdot}093_6$ A. in methane.[14] At first sight the question to be answered appears to be : " How much does the CH bond energy change from acetylene to methane ? " This question is not only unanswerable but meaningless. We have defined bond energy as the quantity of energy which must be assigned to each bond so that the sum gives the heat of formation of the molecule. It is not an observable property of a bond but a conveniently chosen part of the energy of a molecule. The question is more properly put : " How much of the difference between the energies of formation of methane and acetylene should be attributed to the fact that the CH bond is shorter in acetylene than in methane, in order to

[11] *J.*, in the press.
[12] *J. Phys. Chem. Russia*, 1943, **17**, 347.
[13] L. H. Long and R. G. W. Norrish, *Proc. Roy. Soc.*, 1946, *A*, **187**, 337.
[14] G. Herzberg, " Infra Red and Raman Spectra ", New York, 1945, Chap. IV.

arrive at a scheme of bond energies which fits in as well as possible with other bond properties ?"

The simplest answer is to regard the CH bond energy as constant because the change in length is small compared with changes in length of other bonds. J. J. Fox and A. E. Martin [15] have assumed that the energy difference between two CH bonds of differing length is given by $\Delta E = \frac{1}{2}k(\Delta r)^2$, where k is the mean of the CH force constant in methane and acetylene, and Δr is the difference in length. This is only about 0·5 kcal./mole, so they consider it negligible. Their procedure is unsound because the difference of the equilibrium bond lengths in the two compounds indicates that there is some difference in bond character and also that we are dealing with separate potential energy minima between which there need not be any simple relation. Nevertheless W. Gordy,[16] assuming the constancy of the CH bond energy, has shown that CO, CC, and CN links obey a simple relationship of the form $E = lr^{-2} + m$, where l and m are constants.

H. A. Skinner,[17] on the other hand, starts with the general assumption that short bonds are stronger than long bonds, and therefore that the variation in length of CH is important. To allow for this, he took the point corresponding to CH in methane and that to "ideal covalent" CH, of length equal to the sum of the covalent radii of C and H (the latter from H_2), and of energy the arithmetic mean of the latent heat of sublimation of carbon and the H–H bond energy, drew a straight line between the two, and extrapolated linearly to shorter bond lengths. This arbitrary procedure gives reasonably smooth energy–length curves for derived bond energies for CC, CO, CN, CCl, and CS bonds, of the form Er^n = constant, with $n = 3$—4. The numerical results are quite sensitive to the energy–length relationship assumed for the CH bond, but they all show energy varying with length more rapidly than was supposed for CH.

We may compare the OH bond. The OH distance in the OH radical is 0·971 A.,[18] in water 0·958 A.[14] (these are r_e values). The OH bond energy in the radical is $\sim$100 kcals.,[19] in water 110·4 kcals.[17] The straight line joining these points on an energy–length graph has a much steeper slope than that joining either to "ideal covalent" OH, which also suggests that for the CH bond Skinner has underestimated the variation of energy with length.

We have stated that our aim in arriving at corrected bond energies should be to produce a scheme which fits in as well as possible with other bond properties. If the latter can be satisfactorily inter-related, then the bond energies should be chosen to fit in with such a scheme; *e.g.*, if both force constant and dissociation energy of a bond increase, then we should consider that the bond energy increases too. We may now consider the

[15] *J.*, 1938, 2106.

[16] *J. Chem. Physics*, 1947, **15**, 305.

[17] *Trans. Faraday Soc.*, 1945, **41**, 645.

[18] G. Herzberg, "Molecular Spectra and Molecular Structure", New York, 1939, Chap. VIII.

[19] R. J. Dwyer and O. Oldenburg, *J. Chem. Physics*, 1944, **12**, 351.

CH bond in that light. In the compounds CH, CH_4, C_2H_4, C_2H_2 we know the CH distances, the force constants, and the dissociation energies; and the type of orbital hybridisation has been considered theoretically.[20] The properties of CH in these molecules are set out in Table I.[21]

TABLE I

Properties of CH *bonds*

Molecule.	Hybridisation.	r_0(CH), A.	k(CH), dynes/cm. × 10^5.	D(CH), kcals.
CH	p	1·131[14]	4·3*	80[18]
CH_4	sp^3	1·094[14]	5·0[22]	102[23]
C_2H_4	sp^2	1·071[14]†	5·1[22]	100[24]
C_2H_2	sp	1·059[14]	5·9[22]	104,[23] 121[25]

* From the value for the vibration frequency given by Herzberg [18] (cf. J. W. Linnett [26]).

† This value, quoted by Herzberg,[14] is due to W. S. Gallaway and E. F. Barker,[27] and presumably must be regarded as superseding earlier values still frequently quoted. An uncertainty of ± 0·01 has been assigned to the length by F. Halverson.[28] Linnett [26] has estimated the length as 1·088 from the force constant.

These variations do not appear to have any simple inter-relation. As mentioned in the footnote to the table, the estimate of the CH length in ethylene from the force constant is in disagreement with the experimental value, although apart from this the length changes smoothly with force constant; and the dissociation energies do not show a regular trend. Thus it is not certain whether one should make the bond energy change or not.

Discussion of bond strength may be concerned with bond energies, force constants, or dissociation energies. Because of the difficulties mentioned above, the bond energy is not a wholly satisfactory measure of it. The force constant is often used for bonds in simple molecules, such as the CH bonds mentioned above, where an unambiguous assessment of bond energy is not possible. On the other hand, there are many more molecules for which we have thermochemical data than for which it is possible to make the assignment of the fundamental vibration frequencies necessary for the derivation of force constants. Moreover, many force constants depend markedly on the type of force field assumed.[29] There is no entirely satisfactory relationship between force constant and energy, although some

[20] Cf. C. A. Coulson, *Quart. Reviews*, 1947, **1**, 144.
[21] Cf. A. D. Walsh, Faraday Society Discussion, 1947, "The Labile Molecule".
[22] G. Herzberg, "Infra Red and Raman Spectra", New York, 1945, Chap. II.
[23] E. W. Steacie, "Atomic and Free Radical Reactions", New York, 1946, Chap. III.
[24] K. J. Laidler, *J. Chem. Physics*, 1947, **15**, 712.
[25] R. Cherton, *Bull. Soc. roy. Sci. Liége*, 1942, **11**, 203.
[26] *Trans. Faraday Soc.*, 1945, **41**, 223.
[27] *J. Chem. Physics*, 1942, **10**, 88.
[28] *Rev. Mod. Physics*, 1947, **19**, 87.
[29] J. W. Linnett, *Quart. Reviews*, 1947, **1**, 73.

regularities have been found.[30] The use of dissociation energies is limited because of the possible effect of radical reorganisation energy.

We have now discussed the property of the bond which we hope to correlate with its length, and incidentally we have given the form of the correlation, *viz.*, the longer the bond the weaker. Instead of directly correlating length with strength, it is more illuminating to consider the interpretation of changes in each from a more theoretical standpoint. There are three obvious factors which have to be taken into account: the multiplicity, *i.e.*, whether the bond is single, double, or triple, the polarity, and the type of orbital hybridisation involved. We shall consider these separately.

(1) *Bond Multiplicity and Bond Order.*—The realisation, brought about by the application of quantum mechanics to problems of molecular structure, that bonds are not necessarily pure single, double, or triple, but might have intermediate characteristics, made it necessary to devise some more elastic type of description for a bond than that permitted by the simple valency picture, and the term bond order thus came into use.

For bonds which might be between single and double, an early approach was to relate empirically "double-bond character" to bond length, using a knowledge of the lengths of "pure" bonds and of those bonds where an easy assessment of "double-bond character" seemed possible, and thence to estimate the latter in other cases. If only the Kekulé forms of benzene are considered, each bond has 50% "double bond character", and in graphite the bonds have 33% "double bond character".[3] Thus, with the values for ethane and ethylene, there are four points through which a smooth curve may be drawn. More recently, Pauling [1] has extended the idea by defining "bond number" as the number of shared electron pairs involved in the bond, and has drawn a smooth curve of bond number against length through the points for ethane, ethylene,* and acetylene. This is fitted by a logarithmic relation involving only one constant. However, the point for a bond of order 1·5 does not give the bond distance in benzene. Pauling therefore makes the assumption that resonance shortens the bond, and gives a correction factor for use with resonating structures. In connection with later discussion it is of interest to note that, without this resonance correction, the bond number in benzene is required to be 1·64 to make the relation hold. Pauling has applied it in a discussion of internuclear distances and bond numbers in metals which, however, we shall not consider further. "Indices de liaison", corresponding to Pauling's bond numbers, have been calculated for many molecules by Daudel *et al.*[31-33]

[30] Cf. J. W. Linnett, *Trans. Faraday Soc.*, 1940, **36**, 1123; 1942, **38**, 1.
[31] P. Daudel, R. Daudel, R. Jaques, and M. Jean, *Rev. sci.*, 1946, **84**, 489.
[32] C. A. Coulson, P. Daudel, and R. Daudel, *ibid.*, 1947, **85**, 29.
[33] C. A. Coulson and W. E. Moffitt, in course of publication.

* Pauling takes 1·330 A. as the C–C length in ethylene. The more recent value of 1·353 A. given by Gallaway and Barker [27] does not fit the form of the curve so well.

Pauling's definition of bond order has been criticised by W. G. Penney.[34] If the bond in benzene has 50% double-bond character, and if we seek, as we reasonably might, to make "character" indicate all the properties of a bond, including its energy, then we would expect the heat of formation of benzene to be given by the sum of the bond energies of six C–H bonds, three C–C bonds, and three C=C bonds. In fact, of course, the heat of formation of benzene is greater because of resonance energy. Thus the bond order in benzene would be better expressed by a number somewhere between 1·5 and 2·0.

Penney's other criticism is based on the effect of including the three Dewar structures on the resonance energy of benzene. We consider that, after the formation of a ring of single C–C bonds and the C–H bonds, benzene may be regarded as a hexagonal structure of univalent atoms. L. Pauling and G. W. Wheland [35] have shown that, if only the two Kekulé structures (I) and (II) are taken into account, the wave function and

exchange energy are given by

$$\Psi = 0{\cdot}632(\psi_{\mathrm{I}} + \psi_{\mathrm{II}})\,; \quad W = 2{\cdot}40J$$

where J is the exchange integral. If the full canonical set (I)—(V) is taken into account, the wave function and energy become

$$\Psi = 0{\cdot}410(\psi_{\mathrm{I}} + \psi_{\mathrm{II}}) + 0{\cdot}178(\psi_{\mathrm{III}} + \psi_{\mathrm{IV}} + \psi_{\mathrm{V}})\,; \quad W = 2{\cdot}61J$$

This inclusion improves the energy by about 9%. But if the excited structures (III)—(V) are taken into account in obtaining the bond order as defined by Pauling, it is found that the order drops from 1·5 to 1·46.

Penney therefore proposed another definition. It is assumed that all electron orbits are equivalent and that the energy of the most stable state of the system can be calculated as a function of J, the appropriate exchange integral. There are assumed to be k equivalent pairs of neighbouring orbits, so the average energy per pair is W/k. According to the electron-pairing approximation, within a pair the coefficient of the exchange integral is $+1$, while it is $-\frac{1}{2}$ between two electrons not belonging to the same pair.[36, 37] The actual linkage of the system can be expressed as p (the bond order) times a single bond plus $(1 - p)$ times "no bond", and this is equated to the calculated energy thus :

$$W/k = p(J) + (1 - p)(-\tfrac{1}{2}J)$$

whence

$$p = \tfrac{1}{3}(1 + 2W/kJ)$$

Penney's definition of bond order is based on spin theory : we quote the above equivalent, but less fundamental derivation, for simplicity.

For benzene, structures (I)—(V) being taken into account, p is 0·623.

[34] *Proc. Roy. Soc.*, 1937, *A*, **158**, 306. [35] *J. Chem. Physics*, 1933, **1**, 362.
[36] Cf. J. H. Van Vleck and A. Sherman, *Rev. Mod. Physics*, 1935, **7**, 167.
[37] Cf. L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics", New York, 1935, Chap. XIII.

The total bond order is therefore 1·623. Penney has shown that his bond orders give a reasonably good value for the energy of other aromatic compounds, and Fox and Martin [15] have pointed out that Penney's order for benzene fits fairly well on an energy–order curve drawn through points for bonds of order 0, 1, 2, 3. It also gives a smooth order–length curve, including the point for a bond of order 3, the CC distance in ethylene being taken to be 1·33 A.

Coulson has treated bonds of fractional order by the method of molecular orbitals, and has given a definition of bond order in terms of the coefficients used in building up molecular orbitals by the linear combination of atomic orbitals (L.C.A.O.).[38, 39, 20] The order of a bond is, as before, considered to be the sum of two parts, one of magnitude unity, corresponding to the single localised σ bond between two atoms, and the other part, p, contributed by the mobile electrons. For ethylene, p is 1, and the total bond order is 2; for acetylene, the total bond order is 3. p in a conjugated system is evaluated as follows. If a given electron occupies a molecular orbital represented by

$$\Psi = a_1\psi_1 + a_2\psi_2 + \ldots + a_n\psi_n$$

where

$$a_1^2 + a_2^2 + \ldots + a_n^2 = 1$$

and where the ψ's are atomic orbitals, its contribution to the mobile order of a bond between atoms R and S is $a_R a_S$. More generally, if the a's are complex, p_{RS}, the contribution of one mobile electron to the order of the bond R–S, is given by $p_{RS} = \frac{1}{2}(a_R a_S^* + a_R^* a_S)$. The total mobile bond order is the sum of contributions p_{RS} from each mobile electron present. On this basis, the total bond order in benzene is 1·667.

Coulson derives the relation between p_{RS} and β_{RS}, the resonance integral, and the total resonance energy of the system. Using J. E. Lennard-Jones's [40] identification of 2β with the difference in energy between a pure double bond and a pure single bond, $E_d - E_s$, each corrected for compression or extension to the length of the actual bond (usually by Hooke's law), the energy of a bond of mobile order p is shown to be $pE_d + (1-p)E_s$. There appears to be some confusion in the literature about this. Gordy [16] uses the above relation without correction for compression and extension, and even Coulson seems to have done so at times.[32] For benzene, the bond energies considered appropriate by T. L. Cottrell and L. E. Sutton [41] being used, the C–C energy is 85·3 kcals. if compression and extension are taken into account, and 88·6 kcals. otherwise. The actual value is 87·6 kcals., but the significance of this test is doubtful, because, as Penney [34] has pointed out, the value of the latent heat of sublimation affects the relative as well as the absolute values in this case. Further, since the interpretation of the resonance integral is not certain, it would in any case be unwise to attach too much importance to small differences.

[38] C. A. Coulson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 413.
[39] J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.*, 1939, **35**, 811.
[40] *Proc. Roy. Soc.*, 1937, *A*, **158**, 280.
[41] *J. Chem. Physics*, 1947, **15**, 685.

Another difficulty is that if, for C–C bonds, the energy is plotted against the order for the points 0, 1, 2, 3, the curve is concave towards the order axis.[11, 15] If the compressional and stretching effects are neglected, Coulson's relation (see above) gives a straight-line plot between total order 1 and 2, while if these effects are taken into account, the curve is convex to the order axis. There are two possible reasons for this discrepancy. First, as we have already pointed out, the uncertainty in the interpretation of β means that the relationship between order and energy on the M.O. approximation is not rigorous. Secondly, it is not obvious that the curve representing bonds which are intermediate between single and triple should pass through the point corresponding to a double bond.

For NN bonds, the empirical energy–order curve is convex to the order axis, while for CN bonds the plot is nearly linear.

Using the above interpretation of p, and a Hooke's law allowance for compressional and extensional effects, Coulson [38] obtains for the length, R of a bond

$$R = R_s - (R_s - R_d)\left[1 + \frac{k_s}{k_d}\left(\frac{1-p}{p}\right)\right]^{-1}$$

where k_s/k_d is the ratio of the force constants of a single and a double bond. Pauling [3] has given the same relation, putting $k_s/k_d = 1/3$, and with x, the " double-bond character ", in place of p. In fact, the ratio of k(CC) in ethane to that in ethylene is more nearly 1/2 than 1/3 [29], and Coulson has given reasons for believing that the fraction here applicable is even greater. Thus Pauling's value of the term $k_s(1-p)/k_d p$ is about correct, although his value of 0·5 for x in benzene is low compared with the bond order. From an empirical curve of length against order, using as fixed points ethane, graphite, benzene, ethylene, and acetylene, the value 0·765 for k_s/k_d is obtained. Coulson [38] has calculated the order of the links in several conjugated hydrocarbons, and has determined the lengths from the curve, good agreement with the observed results being obtained.

C. A. Coulson [42] has calculated mobile bond orders in systems containing the carbonyl group, and H. C. Longuet-Higgins and Coulson [43] have done the same for some heterocyclic molecules containing nitrogen. These authors [44] have also given a formal discussion of the application of the molecular orbital method to conjugated systems and the calculation of bond orders and related properties. In connection with the calculations on the carbonyl group, it is worth emphasising that the mobile bond order as defined by Coulson is the *covalent* bond order, and, because of the partial ionic character of the bond, $p < 1$ for pure C=O. Coulson gives for C=O, $p = 0{\cdot}895$. A more exact treatment of the CO link in carboxyl and amide groups has been given by K. Wirtz,[45] who finds that taking into account compressional and stretching energy makes some difference to the bond order and a considerable difference to the estimated value of the resonance integral. Calculations involving heteronuclear systems are less reliable than those for homonuclear systems, because the resonance integrals are

[42] *Trans. Faraday Soc.*, 1946, **42**, 106.
[43] *Ibid.*, 1947, **43**, 87.
[44] *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.
[45] *Z. Naturforsch.*, 1947, **2**, *a*, 264.

no longer equivalent for all the links, and no satisfactory interpretation of the Coulomb integrals has been given.

The assumption that the bonds in ethane, ethylene, and acetylene are pure single, double, and triple bonds depends upon the view that the CH bonds are completely localised. R. S. Mulliken, C. A. Rieke, and W. G. Brown [46] (hereafter denoted by M.R.B.) have concluded that this is not quite true and have considered the extent to which "hyperconjugation" takes place.[20, 47] Briefly, in ethane, for example, the CH_3 group is considered to act as an electron donor to the C–C link, since it is possible to construct molecular orbitals for CH_3 of the required symmetry. This means that the C–C link in ethane has a contribution from mobile electrons, making its bond order greater than unity. M.R.B. have calculated bond orders in a number of compounds which give a smooth curve when plotted against length, except that the formal single bond of systems C—C≡C is shorter than indicated by the curve. This agrees with a suggestion of L. Pauling, H. D. Springall, and K. J. Palmer [48] that bonds with much s character in the σ bond are shorter than usual. Bond orders given by this method have been found by Gordy [16] to fit a relationship of the form $N = aR^{-2} + b$, where N is the order and R the length of the bond. A plot of N against R^{-2} gives a good straight line for CC, NN, and OO bonds.

Many other empirical relationships connecting order—or multiplicity—with length and energy have been suggested.[49–52] In view of the relatively small alterations in length for large alterations in order, it is hardly surprising that it is possible to get agreement between the observed and the calculated lengths with a variety of functional forms of the relationship. The accuracy of some of the predictions is not as good as might be desired. For example, Lagemann [50] obtains an equation and constants which predicts lengths of 1·50, 1·36, and 1·31 A. for the CC links in ethane, benzene, and ethylene, respectively, compared with the experimental values of 1·55,[53] 1·40,[54] and 1·353 A.[27] There is no general agreement on what is to be regarded as the order of a bond. Lagemann and Gordy use M.R.B. bond orders; Kavanau considers that his equation fits the Coulson bond order best. Better results are always obtained for the prediction of lengths than of energies.

A. D. Walsh [55] has criticised previous definitions of bond order as being oversimplified, and has suggested that it should be possible to obtain an experimental measure of a suitably defined bond order. The bond order

[46] *J. Amer. Chem. Soc.*, 1941, **63**, 41.
[47] C. L. Deasy, *Chem. Reviews*, 1945, **36**, 145.
[48] *J. Amer. Chem. Soc.*, 1939, **61**, 927.
[49] J. L. Kavanau, *J. Chem. Physics*, 1944, **12**, 467; 1947, **15**, 77; *J. Amer. Chem. Soc.*, 1947, **69**, 1827.
[50] R. T. Lagemann, *J. Chem. Physics*, 1946, **14**, 743.
[51] H. J. Bernstein, *ibid.*, 1947, **15**, 284, 339, 688.
[52] R. Cherton, *Bull. Soc. chim. Belg.*, 1943, **52**, 26.
[53] L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 1223.
[54] J. H. Archer, C. Finbak, and O. Hassel, *Tids. Kjemi Berg.*, 1942, **2**, 33.
[55] *Trans. Faraday Soc.*, 1946, **42**, 779.

is defined as the "summed total electronic energy per bond". The ionisation potential of the electrons concerned in the bond is considered to be a measure of this, in a manner which will be clarified by an example: ethylene has two π electrons, the ionisation potential for one π electron in ethylene is 10·45 v.,* so the mobile bond order is proportional to 20·90 v. Acetylene has four π electrons, each of ionisation potential 11·35 v., giving a mobile order of 45·40 v. Ionisation, in fact, is used as a perturbation to discover how tightly an electron is bound. Benzene has four π electrons with an ionisation potential 9·19 v. and two at 11·7 v.; the mobile order therefore corresponds to $\frac{1}{6}(4 \times 9{\cdot}19 + 2 \times 11{\cdot}7) = 10{\cdot}03$ v. σ electrons have an ionisation potential of 12·0 v. The total bond order is obtained by adding this to the mobile bond order. The results are scaled to ethylene having a mobile bond order of 1, or total bond order 2. This scheme shows that the π bond in ethylene is only 0·87 as strong as the σ bond, and that the mobile bond order in acetylene is more than twice that in ethylene. This is surprising, since bond energies show that the second π bond in acetylene is not so strong as the first. Environmental factors are automatically taken into account; for example, the bond order in tetramethylethylene is different from that in ethylene. There is a smooth relation between length and order, and a straight line is obtained by plotting a selected set of values for CC force constants against order. A fairly smooth curve is obtained from a plot of bond order against bond energy, although here some of the energies are obtained from an empirical energy–length curve. One interesting result of this approach is that the bond order of *cyclo*hexane is rather less than the bond order in ethane, a conclusion which is indicated by other evidence.[10]

We conclude this section with Table II, comparing the various bond orders given for some C–C bonds.

TABLE II

C–C *Bond orders*

Bond in:	Pauling.	Penney.	Coulson.	M.R.B.	Walsh.
Ethane	1	1	1	1·12	1·07
Ethylene	2	2	2	2·12	2·00
Acetylene	3	3	3	3	3·10
Benzene	1·5	1·623	1·667	1·667	1·51
Graphite	1·33	1·45	1·53	1·53	1·3
Formal C=C in butadiene	1·81	1·911	1·894	1·945	1·91
Formal C–C in butadiene	1·18	1·333	1·447	1·325	1·175

It is worth pointing out that all these definitions of order are concerned with *covalent* bonds only, as is to be expected since the idea grew from multiplicity of carbon–carbon bonds. An extension of the idea to include ionic bonds by W. Gordy [56] will be discussed in the section on polarity.

[56] *Physical Rev.*, 1946, **69**, 130; *J. Chem. Physics*, 1946, **14**, 305.

* The ionisation potentials quoted in this review are all taken from Walsh's papers.

(2) *Polarity.*—Pauling [3] has suggested that bonds are stabilised by covalent–ionic resonance, and that therefore the energy of a bond A–B is greater than the arithmetical, or more properly the geometrical, mean of the A–A and B–B energies. That this is not the whole story is shown by the following results for the calculated energy of the hydrogen molecule: pure covalent, 3·76 e.v.; covalent–ionic hybrid, 4·00 e.v.; variation treatment with no reference to covalent or ionic structures, 4·70 e.v.; observed, 4·72 e.v.[57, 58, 59] Furthermore, as A. Burawoy [60] has remarked, there are bonds where a large contribution from the ionic form might be expected, but where stabilisation is not found. Nevertheless, Pauling's generalisation seems to apply in many cases.

E. Warhurst [61] has considered the effect of covalent–ionic resonance on lengths and force constants. His calculations are not rigorous—they involve neglect of the non-orthogonality integral—and are inconclusive so far as they bear on bond lengths. He has, however, given a successful treatment of the decrease of vibration frequency, which occurs when certain gases are liquefied or dissolved in non-ionising solvents, by considering the effect of alteration of the dielectric constant of the medium on the energy of the ionic form. Ionic character in diatomic molecules has also been treated by F. T. Wall,[62] who shows that if the wave function is written $\Psi = \psi_c + a\psi_i$, a^2 is given by the relation

$$a^2 = (H_{cc} - W)/(H_{ii} - W)$$

where the subscripts c and i refer to covalent and ionic forms, and H_{cc} and H_{ii} are integrals of the type $\int \psi_c H \psi_c \mathrm{d}\tau$ and therefore represent the energies of the covalent and ionic forms respectively. E. C. Baughan, M. G. Evans, and M. Polanyi [63] derived a for a series of CH_3–X compounds from the dipole moment, and thence calculated the resonance energy, obtaining values agreeing very roughly with those derived from Pauling's geometric mean rule.

On the basis that stabilisation in bonds between unlike atoms is due to ionic contributions, Pauling [3] derived a scale of "electronegativity" values for the elements from thermochemical data. R. S. Mulliken [64, 65] showed that "electronegativities" are related to the average of the ionisation potential and electron affinity of the atom, and W. Gordy [66] has related them to the effective nuclear charge of the atom and its covalent radius. Bond dipole moments are roughly proportional to the electronegativity difference between the linked atoms.[67] C. P. Smyth [68] observed that some moments, notably those for carbon attached to large atoms such as sulphur

[57] C. A. Coulson, *Trans. Faraday Soc.*, 1937, **33**, 1479.
[58] S. Weinbaum, *J. Chem. Physics*, 1933, **1**, 593.
[59] H. M. James and A. S. Coolidge, *ibid.*, p. 825
[60] *Trans. Faraday Soc.*, 1943, **39**, 79.
[61] *Ibid.*, 1944, **40**, 26.
[62] *J. Amer. Chem. Soc.*, 1939, **61**, 1051.
[63] *Trans. Faraday Soc.*, 1941, **37**, 377.
[64] *J. Chem. Physics*, 1934, **2**, 782.
[65] *Ibid.*, 1935, **3**, 573.
[66] *Physical Rev.*, 1946, **69**, 604.
[67] J. G. Malone, *J. Chem. Physics*, 1933, **1**, 197.
[68] *J. Physical Chem.*, 1937, **41**, 209; *J. Amer. Chem. Soc.*, 1938, **60**, 183; 1941, **63**, 57.

or iodine, are larger than expected; he remarked that the reason why better results are given for small atoms may be their smaller polarisability.

In the discussions mentioned, with the exception of Mulliken's,[65] it has been assumed that the dipole moment is due solely to contributions from ionic forms. This assumption is unjustified, as has been shown by Mulliken, and in more detail by C. A. Coulson.[69] Analysis using the L.C.A.O. molecular orbital approximation shows that there are four terms in the expression for the dipole moment of a bond.* The first is that arising from the formal charge effect. The second is the "homopolar dipole", *i.e.*, that due to the asymmetry of the electron distribution relative to the bond given by Heitler–London type of terms even when the component atomic functions are symmetric about their nuclei: this may be quite large if the atoms differ much in size. The third term is the "atomic dipole", *i.e.*, that due to the asymmetry of the atomic orbitals about their nuclei, which is large if we are dealing with a hybridised orbital.

The fourth term represents the secondary dipole moment which may be induced in any non-bonding electrons. This is unlikely to be important unless a "lone pair" is present; when also it may be that orbital hybridisation will cause these to have a moment of the "atomic dipole" type. The moment of the covalent form may be large: Coulson [69] has calculated that for the CH bond the "pure covalent" structure has a moment 1·97 D. (C^+H^-), whereas the ionic form has a moment 1·53 D. (C^-H^+). The overall moment is calculated to be 0·40 D. (C^+H^-). To assume that moments are due only to ionic forms may therefore introduce serious error.

It is, however, worth considering the relation of electronegativity to other bond properties. V. Schomaker and D. P. Stevenson [70] have suggested the relation

$$r_{AB} = r_A + r_B + \beta(x_A - x_B)$$

for the length r_{AB} of a bond between atoms A and B, where r_A and r_B are the covalent radii in A., x_A and x_B are the electronegativities, and $\beta = 0{\cdot}09$ for single bonds. The rule has also been used for double bonds.[71, 72] It is not altogether satisfactory. For example, the Sn–Cl distances in $SnMe_3Cl$, $SnMe_2Cl_2$, $SnMeCl_3$, and $SnCl_4$ are 2·37, 2·34, 2·32, and 2·30 A., respectively.[73] The sum of the covalent radii of Sn and Cl is 2·39 A.; the Schomaker–Stevenson rule gives 2·28 A. For $AsCl_3$ and $AsMe_2Cl$ the As–Cl distances are 2·16 and 2·18 A.,[73] the sum of the covalent radii is 2·20 A., and the Schomaker–Stevenson rule gives 2·11 A.

Gordy [56] has suggested that the force constant of a bond depends on

[69] *Trans. Faraday Soc.*, 1942, **38**, 433.
[70] *J. Amer. Chem. Soc.*, 1941, **63**, 37.
[71] G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J.*, 1945, 146.
[72] W. Gordy, *J. Chem. Physics*, 1947, **15**, 81.
[73] H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, 1944, **40**, 164.

* $\mu = Q_bR - 4eabS(R/2 - x_{ab}/S) + 2e(a^2x_{aa} - b^2x_{bb}) + \mu_s$ where Q_b is the formal electronic charge on nucleus B, R is the internuclear distance, a and b are the coefficients of ϕ_a and ϕ_b (the atomic orbitals combined to give the molecular orbital), S is the overlap integral $\int\phi_a\phi_b d\tau$, and x_{ab}, x_{aa}, and x_{bb} are given by $\int x\phi_a\phi_b d\tau$, $\int x\phi_a^2 d\tau$, and $\int(R - x)\phi_b^2 d\tau$; x is the distance measured from A.

the *product* of the electronegativities of the atoms, and is given fairly accurately by

$$k = aN(x_A x_B / r^2_{AB})^{3/4} + b$$

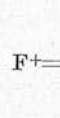
a and b are constants (equal to 1·67 and 0·30 respectively if lengths are in A. and the force constants in dynes/cm. $\times 10^{-5}$) which are the same for all bonds; N is the bond order, defined as the effective number of covalent *or ionic* linkages involved. For covalent linkages the bond order used is that defined by M.R.B.,[46] which may be non-integral; but bonds with partial ionic character are considered integral, *e.g.*, HCl as single, C=O as double. It does not always work, however; one reason for this may be that there is no method of including changes of electronegativity due to environmental effects. The CH bond in aldehydes, for example, has a very low force constant,[26] which is not predicted. A. D. Walsh [74] discusses other exceptions to Gordy's rule in a forthcoming paper.

Walsh [75] has suggested that in a given bond, *ceteris paribus*, the force constant and bond energy decrease and the length increases with increasing polarity. The statement seems in contradiction to Pauling's rule for bond energies and to the Schomaker–Stevenson rule for bond lengths. This is not necessarily so. The last two rules compare a bond between atoms A and B with one between atoms C and D. The second of them states that if the electronegativity difference between A and B is greater than that between C and D the AB bond will be shorter than $r_A + r_B$ (the sum of the covalent radii) by an amount greater than that by which the CD bond is shorter than $r_C + r_D$; the first applies *mutatis mutandis* to strengths. On the other hand, Walsh's rule is that, if environmental factors in polyatomic molecules X and Y both containing a bond AB cause the polarity of the bond to be greater in X than in Y, then its length will be greater, and its strength less, in X than in Y. It is conceivable that decrease in electronegativity of atom A, if initially $x_B > x_A$, may reduce the *covalent* strength of AB, so that although the ionic–covalent resonance may be increased, the total bond energy may nevertheless decrease. Similar considerations apply to the length. Walsh's rule would then be compatible with the idea of covalent–ionic resonance. Walsh, on the other hand, has suggested that the internuclear distances of the covalent and ionic forms are too different to allow resonance.

We now consider some of the evidence bearing on this rule. Skinner and Sutton [73] have shown that substitution of Cl for methyl in the methyltin chlorides reduces the Sn–Cl distance. A similar shortening of the M–Hal link on further halogen substitution is shown by fluorinated methanes, chlorinated silanes, brominated silanes, methyltin bromides, methyltin iodides, methylarsenic chlorides, and methylchloroamines.[73] Such substitution might be expected to reduce the polarity of the M–Hal link. Dipole-moment data [76] show that this drop in polarity does occur in the chlorosilanes and chloromethanes. This seems to be evidence for Walsh's

[74] *J.*, in the press.
[75] *Trans. Faraday Soc.*, 1947, **43**, 60.
[76] Cf. L. O. Brockway and I. E. Coop, *ibid.*, 1938, **34**, 1429.

rule, though there is no evidence in most instances to show whether the energies increase as the bonds shorten ; furthermore, there are other possible descriptions of the effect. L. O. Brockway and H. O. Jenkins [77] ascribe the shortening in tetrafluoromethane to structures such as (I), so that the decrease in polarity is incidental to the strengthening due to increased multiplicity. Skinner and Sutton [73] suggest that substitution of a less by a more electronegative outer grouping increases the electronegativity of the central atom and hence decreases its effective radius—a suggestion which is in agreement with Gordy's [66] expression for electronegativity—and that successive substitutions of halogen decrease the radius of the central atom. The halogen atoms will be enlarged by their negative charges ; but it is likely that the charge on each atom will be less the more such atoms there are, and thus this enlargement will decrease progressively.



(I.)

The evidence for the effect of polarity on the strengths of less ambiguously single bonds is suggestive rather than rigorous. For example, the experimental data allow us to be fairly arbitrary in our choice of CH bond energies ; and little is known with certainty about its polarity. According to Coulson,[69] the polarity is about the same in almost all CH bonds, but his calculations are more reliable for CH in methane than in other compounds. Thus any discussion of the effect of polarity on the CH link must be very tentative.

The application of the polarity rule to multiple bonds is obscured by the possibility of change of multiplicity. The —C≡N and C=O links are both polar, with the negative end of the dipole at the nitrogen and the oxygen atom. We would expect therefore, that substitution of Cl for H in these compounds, if it did not alter multiplicity, would reduce the polarity and increase the strength of the bonds. Some experimental data are given in Table III.

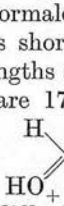
TABLE III

Molecule.	CN length.	CN force constant.	Molecule.	CO length.	CO force constant.
HCN	1·157[14]	17·9[22]	H_2CO	1·21[79]	12·0[81]
ClCN	1·15[78]	16·7[22]	Cl_2CO	1·18[80]	12·14[81]

The CN force constant in ClCN is less than in HCN. This is not in accordance with the rule. Instead, it indicates that $Cl^+{=}C{=}N^-$ is an important structure, a view supported by the shortening of the C–Cl bond to 1·64 A. On the other hand, carbonyl chloride shows the expected polarity

[77] *J. Amer. Chem. Soc.*, 1936, **58**, 2036.
[78] C. H. Townes, A. N. Holden, and F. R. Merritt, *Physical Rev.*, 1947, **71**, 64.
[79] D. P. Stevenson, J. E. LuValle, and V. Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 2508.
[80] V. Schomaker, private communication.
[81] C. R. Bailey and J. B. Hale, *Phil. Mag.*, 1938, **25**, 98.

effect: there is no important contribution from $Cl^{+}{=}CCl{-}O^{-}$,* the C–Cl length being 1·74 A.[80] Walsh's explanation is that the importance of $Cl_2C{-}O^{-}$ is reduced compared with $Cl_2C{=}O$; Schomaker's is that $Cl^{-}CCl{\equiv}O^{+}$ is important.

The carbonyl link is of particular interest, because Walsh [83] has, in a series of compounds, attributed thereto polarities obtained from the ionisation potential of the non-bonding $p\pi$ electrons on the oxygen atom. This is the energy difference between the ground state and the ion: to regard it as exclusively concerned with the ground state of the molecule is therefore somewhat arbitrary. Furthermore, a theoretical discussion by W. E. Moffitt [84] of the electronic configuration of simple compounds containing CO shows that it is not strictly correct to attribute variations in the ionisation potential to change in the carbonyl group alone. A possible example of this difficulty is that the ionisation potentials of carbon dioxide and carbon oxysulphide are 13·73 and $\sim$12 v., the difference being almost 40% of the total variation for all compounds considered. This indicates, according to Walsh, a considerable difference in polarity in the carbonyl links, whereas the CO lengths are almost the same in each compound—1·163 [14] and 1·161 A.,[85] respectively. Again, the ionisation potential of formic acid is 11·3 and that of formaldehyde is 10·8 v., which should mean that the bond in formic acid is shorter and stronger than that in formaldehyde, whereas in fact the lengths are 1·24 [86] and 1·21 A.,[79] respectively, and the vibration frequencies are 1740 cm.$^{-1}$ and 1750 cm.$^{-1}$.[87] These facts agree with the view that  is an important structure.

It appears that it is more difficult than was expected to disentangle polarity effects.

(3) *Orbital Hybridisation.*—Hybridisation is important in the discussion of bond properties apart from its contribution to stereochemistry, because it affects the overlap of the bonding orbitals, and thus the extent and density of the electron cloud between the nuclei, which is responsible for the bond being formed. Energy is required to form hybridised orbitals from atomic orbitals, because to do so involves moving electrons further from the nucleus; but this can be more than offset by the energy of forming the bond.

We intend to discuss here only hybridisation of s and p orbitals. CH bonds are particularly suitable in this connection, because changes in the property of the bond are likely to be due mainly to changes in the carbon atom. We have shown (Table I) that as we pass from methane to acetylene

[82] L. O. Brockway, L. Pauling, and J. Y. Beach, *J. Amer. Chem. Soc.*, 1935, **57**, 2693.

[83] *Trans. Faraday Soc.*, 1946, **42**, 56; 1947, **43**, 158. [84] To be published.

[85] T. W. Dakin, W. E. Good, and D. K. Coles, *Physical Rev.*, 1947, **71**, 640.

[86] J. Karle and L. O. Brockway, *J. Amer. Chem. Soc.*, 1944, **66**, 574.

[87] G. Herzberg, "Infra Red and Raman Spectra", New York, 1945, Chap. III.

* An earlier electron-diffraction study [82] gave CO in carbonyl chloride as 1·28 A., and a large contribution from this structure was assumed to explain the result.

the CH length decreases and the force constant increases. Most authors consider that at the same time the *s* character increases.[20] Approximate calculations by L. Pauling and J. Sherman [88] showed that tetrahedral * or sp^3 orbitals give the maximum projection along the bond axis and therefore presumably the maximum strength of bond. The facts therefore seem in disagreement with the theory.

Walsh [21] has enunciated the principle : " the more *s* character in a carbon valency, the more electronegative is the carbon atom in that valency ". He has combined this with the two rules that the strength of a bond increases with the product of the electronegativities of the bound atoms, and that increase in polarity causes a decrease in the strength of a bond to explain the order of strengths in CH bonds.

The question may be looked at as follows : *s* character brings the overlap zone nearer the carbon atom—thus incidentally altering the homopolar moment—and, because an *s* orbital has no directional properties, the charge cloud becomes more diffuse. Thus in a volume element on or near the line joining the nuclei, the electron density is reduced, and the screening of the nucleus thereby becomes less, with the result that the carbon atom behaves as if it were more positive. To take account of this in the description of the bond, we should have to adjust the ionic terms in the electron-pair approximation, or alter the relative magnitudes of the coefficients of the atomic orbitals in the L.C.A.O. molecular orbital approximation, in such a way as to increase the proportion of electron round the carbon. In the particular case of the CH link, it may be that, although increase of *s* character decreases the overlap, the loss in strength may be outweighed by additional stabilisation due to resonance with ionic structures.[91]

J. Duchesne [92] has suggested that substitution of a more for a less electronegative group on carbon increases the electronegativity of the carbon with respect to other groupings attached to it, causing these bonds to have more *s* character and therefore the bond to the electronegative group more *p* character. His evidence is from the CH force constants of certain methyl compounds, derived from their Raman spectra in the liquid state. Considering the changes in vibration frequency which often occur in passing from the liquid to the vapour, this evidence is not completely satisfactory. Walsh [21] has extended the application of the idea. It provides an explanation of the weakness of secondary CH bonds, but as T. L. Cottrell and R. E. Richards [93] have pointed out, there seem to be cases where it does not apply. For example, since carbon is more electronegative than hydrogen, we would expect that the CH links in ethylene

[88] *J. Amer. Chem. Soc.*, 1937, **59**, 1450. [89] *Ibid.*, 1931, **53**, 1367.
[90] *Ann. Reports*, 1940, **37**, 67.
[91] Cf. E. Warhurst, Faraday Society Discussion, 1947, " The Labile Molecule ".
[92] *Nature*, 1947, **159**, 62.
[93] Faraday Society Discussion, 1947, " The Labile Molecule ".

* Pauling [89] pointed out in 1931 that it is also possible to form tetrahedral orbitals which give strong bonds from *s*, *p*, and *d* orbitals. Sutton [90] has suggested that these might occur in tetrahedral silicon compounds, such as SiF_4, possibly accounting for the shortness of the link.

would have more s character than sp^2, and that the HCH angle would be greater than 120°. In fact it is 119° 55′.[27]

It is, however, not clear why an electronegative group should desire to have more p character in its bond with carbon beyond sp^3, because sp^3 orbitals have the greatest projection along the bond axis. On the other hand, if sp^3 hybridisation had not occurred completely, it is easy to see that such effects might be appreciable.

Conclusions.—In planning this Review we intended to consider how far there has been given a consistent interpretation of variations in bond lengths and strengths. Such an interpretation would appear to require simultaneous consideration of the effects of multiplicity, polarity, and orbital hybridisation. This, in fact, has hardly been attempted in the literature, probably because it is extremely difficult either to apply the necessary theoretical treatment or to analyse the data in such a way as to distinguish with certainty the effects of these factors. A rigorous treatment would doubtless short-circuit these terms, but they are the concepts with which it has been found useful to work. All we have been able to do within the limits available has been to follow a sectional treatment, though we have tried to indicate the inter-relations between the concepts. Our opinion is that this inter-relation needs to be carried a good deal further.

At present the subject abounds in hypotheses which have a limited success but which are *ad hoc* and probably not unique. To say this is no disparagement of the advances which have been made, nor to deny the importance of the striking changes which have taken place in structural chemistry in the past twenty years.

In addition to the general unification of the whole subject indicated above, further work on the effect of orbital hybridisation and of polarity seems to be particularly desirable.

In conclusion, we wish to express our thanks to Mr. W. E. Moffitt for many valuable discussions.

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Reference (6) is the book

"The Strengths of Chemical Bonds"

which is separately bound.

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INTERMOLECULAR REPULSIVE FORCES

INTERMOLECULAR REPULSIVE FORCES

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The theoretical and experimental evidence on intermolecular repulsive forces is summarized and discussed. It is shown that at close range an inverse power law is inadequate to represent the repulsive potential, whereas an exponential fits the results tolerably well. Information about the equilibrium properties of gases at ordinary temperatures and pressures is almost irrelevant to the discussion of intermolecular forces and the discussion of matter at high density is obscured by the need to take into account many-body forces, so that the study of high-energy elastic collisions gives most information about the repulsive potential. Valuable empirical information may, however, be obtained from the study of matter at very high pressure, using new techniques of measurement.

Molecular interactions, in the absence of chemical reactions, are usually considered in terms of relatively long-range attractive forces and of short-range repulsive forces. Under normal conditions in gases the attractive forces are of most importance in determining the equilibrium properties, but at high pressures and temperatures repulsive forces become important: indeed, even at quite low temperatures and pressures up to six or seven hundred Amagat it is possible to treat the equation of state of nitrogen and argon by considering attractive forces as perturbations on the repulsive forces.[1] This paper reviews some of our knowledge of these repulsive forces.

There are two theoretical ways of discussing intermolecular forces: the direct calculation of the potential between a pair of molecules, and the calculation of the energy of a molecular model when constraints, chosen to represent the average effect of the environment, are applied. The results are discussed in the following sections, and thereafter the experimental evidence is considered.

DIRECT CALCULATION OF INTERMOLECULAR INTERACTION

The simplest system to discuss is the $^3\Sigma$ state of the hydrogen molecule; the energy, which is accurately known,[2, 3] depends approximately exponentially on internuclear distance. If an expression for the energy as an inverse power of the distance is fitted to the results, the repulsive index n varies nearly linearly with distance, from about 2 at 1 Å to about 5 at 2 Å.

The more complicated interaction between helium atoms has been treated approximately in various ways:[4-7] all the results for energy against distance fit an exponential with the same exponent ($-2{\cdot}4/a_0$), although the absolute magnitude appears to be less certain. Neon has also been treated,[8] though the errors here may be greater.

Direct calculation for two hydrogen molecules[9] gave a minimum potential similar to that calculated from viscosity data using the Lennard-Jones 12:6 potential,[10] although the theoretical potential was appreciably less steep than the empirical at short distances.

Calculation of the potential for more complicated molecules is not at present feasible: the information about simpler systems must be extrapolated to more complicated ones. One method of taking account of the theoretical information is to use an exponential rather than an inverse power for the repulsive term in an empirical potential function.[11-13] A difficulty arises in the application of simple formulae to polyatomic molecules. Here the main interactions are probably between the peripheral atoms, so that the form of the interaction as a function of the intermolecular distance may well be different from that required to fit monatomic gases. Chloroform, for example, deviates little from the principle of corresponding states [14] but when molecular centres are over 4 Å apart, the chlorine nuclei may be about 1 Å apart. Thus the expected potential, as a function of intermolecular distance, will be steeper than that associated with monatomic gases. The point was noted by Hamann, McManamey and Pearse [15] who used an expression for the potential due to a spherical shell, each element of which has a potential given by the inverse power law,[16] to derive the intermolecular potential. They found little improvement in the fit to experimental virial coefficient data. However, the correct potential to use on this approximation is rather the potential between two uniform spherical shells each element of which interacts with each element of the other, according to a known potential function.[17]

In this approximation, one should not use for the peripheral atoms repulsive potentials obtained empirically from the bulk properties of the monatomic gases, because they are known to be inadequate at short range. The method was applied to the repulsive potential between methane molecules, assuming the repulsion between the peripheral atoms to lie between that calculated for hydrogen and for helium.[17] The resulting potential was fitted to an exponential, and used to calculate the vibrational relaxation time of methane.

Accurate discussion of polyatomic molecules is complicated by the loss of even approximate spherical symmetry in the close-range encounters during which repulsive forces predominate. Averaging is adequate for bulk properties,[9] but more questionable for close approaches.

At greater density, interaction between two molecules only is less relevant, and one must either treat many-body interactions explicitly or treat the interaction of a molecule with its environment described by an averaged potential. Little progress has been made with the former programme; the latter is discussed in the next section.

MODEL CALCULATION OF MOLECULE-ENVIRONMENT INTERACTION

Cell theories of liquids and gases at high pressures have aroused much interest recently, rather from the point of view of the combinatorial problem than from that of the intermolecular potential.[18-23] A different approach to the cell model in which the interaction between molecule and environment is directly calculated arose from a phenomenological treatment of the energy of compressed gases by Michels and his colleagues.[24, 25] Applying the virial theorem to a substance at pressure p and volume v,

$$\Delta\overline{T} = 3\Delta(pv) - \Delta E,$$

where E is the total energy and $\overline{T}$ the average kinetic energy of electrons and nuclei.[26] $\Delta(pv)$ can be measured and $\Delta\overline{T}$ calculated in this way for the compression of some simple gases up to 3000 atm, showed a large increase amounting to 5 kcal mole^{-1} for nitrogen. This kinetic energy must be electronic and is thus an indication of the effect of pressure in distorting the electron distribution. It was therefore suggested [25] that at high densities the effect of environment on a molecule might be calculated by replacing it by the impenetrable wall of a small sphere of radius r_0. From the virial theorem [25, 27] the average kinetic energy of electrons and nuclei is

$$T = -r_0 \frac{\partial E}{\partial r_0} - E.$$

Comparison of the kinetic energy calculated in this way with the experimental values should check the validity of this approach. De Groot and ten Seldam,[28] extending earlier work [24] discussed the hydrogen atom in a spherical box in terms of the radius of the box, and found that the change in kinetic energy on compression was similar to that found experimentally. Such calculations have been made for helium,[29] argon,[30] and the hydrogen molecule-ion.[31] In the last, results were obtained to 10^6 atm, to throw some light on the behaviour of gases at very high pressures.

For molecular volumes less than 60 Å^3, the energy-volume curve calculated in this way for the hydrogen molecule-ion is approximated by an inverse square,[32] which implies an inverse sixth power of distance. This confirms the view that the inverse power most suitable at long range is too high for short range. Further, the inverse sixth power is becoming too steep at volumes less than 25 Å^3. Thus the evidence suggests that for close approach, the potential varies with quite low powers of r.

EXPERIMENTAL EVIDENCE

EQUATION OF STATE OF GASES

At low pressures the equation of state of gases is insensitive to the repulsive force. For example, the second virial coefficient of methane can be represented equally well by two Morse functions,[33] in which the exponents in the one differ from those in the other by a factor of 2. Hamann *et al.*[15, 34, 35] have tried to use virial coefficient data to discuss the shape of the potential, but were not able to to reach very firm conclusions, except that the Lennard-Jones function does not fit polyatomic molecules very well.

The equation of state for gases at very high densities and temperatures above the critical is expected to depend significantly on intermolecular repulsive forces. Gaseous products from condensed detonating explosives are formed at densities between 1 and 2 g cm^{-3} and temperatures of a few thousand °K. The hydrodynamic theory of detonation [36] relates the thermodynamic properties of the system, including the equation of state of the products, to the properties of the detonation wave: that is, to the detonation pressure, temperature, density, streaming velocity and wave velocity. Until recently only the last of these could be measured, and it was at one time thought that comparison of observed detonation velocities with the calculated would allow the determination of the equation of state.[37, 38] This, however, is not so,[39, 40] the problem not being determinate. Moreover, the calculated velocity is insensitive to the form of equation used; for example an equation of the form $pv = \boldsymbol{R}Tf(v)$, which implies $(\partial E/\partial V)_T \equiv 0$ has been successfully used in calculating the velocity of detonation of a wide range of explosives,[37, 41] although the assumed form is probably incorrect. On the other hand, good agreement with experiment for a high-energy explosive has also been obtained with an equation which may exaggerate intermolecular repulsive forces.[32]

A possibility of progress stems from the recent measurement at the Los Alamos laboratory of a second detonation wave property, the detonation pressure (Chapman-Jouguet pressure).[42] This should allow closer definition of the equation of state, and hence of intermolecular forces, but the results so far published [43] are concerned only with the determination of the parameters in the Kistiakowsky-Wilson equation of state which cannot be readily interpreted in terms of intermolecular forces and does not even fit the data. However, the Lennard-Jones and Devonshire equation of state is being similarly examined: the results have still (May, 1956) to be published.

Measurement of the temperature would be more useful in determining intermolecular repulsive forces, because this quantity is most sensitive to the assumptions made. For example, an equation making no allowance for repulsive forces reproduces the detonation velocity against density curve for penta-erythritol

tetranitrate fairly well with no adjustable parameters,[41, 36] and predicts that the temperature at the Chapman-Jouguet point should increase with density. On the other hand, the equation based on the molecule-in-a-box calculation reproduces the detonation velocity curve better than the other equation, though with one adjustable parameter, and predicts that the temperature should decrease with increasing density.[32] This is because much of the energy liberated is used in overcoming intermolecular forces at high density. The relevant figures are given in table 1, where the sensitiveness of the temperature is clearly shown.

TABLE 1.—DETONATION OF PENTA-ERYTHRITOL TETRANITRATE

loading density gcm^{-3}	velocity (obs.) m/sec	velocity calc. (*a*)	velocity calc. (*b*)	temp. calc. (*a*) °K	temp. calc. (*b*) °K	pressure calc. (*a*) atm	pressure calc. (*b*) atm
1·727	8,360	9,500*	8,200	5,500	1,950	$2{\cdot}20 \times 10^5$*	$2{\cdot}85 \times 10^5$
1·40	7,000	7,600	7,010	5,290	2,630	1·61	1·86
1·00	5,520	5,560	5,530	5,150	3,650	0·74	0·88
0·75	4,700	4,520	4,760	5,060	4,060	0·42	0·53
0·40	3,710	3,350	3,660	4,990	4,525	0·15	0·19

(*a*) $pv = RTf(v)$,[41, 36] (*b*) $E \propto 1/v^2$.[32] * extrapolated.

EQUATION OF STATE OF LIQUIDS

For liquids the statistical problems are so difficult that it is doubtful whether any important evidence about intermolecular repulsive forces can be derived.

EQUATION OF STATE OF SOLIDS

There are two approaches to deducing intermolecular forces from information on solids. One is to accept the observed structure of the solid, and calculate from the experimental data on interatomic distances and sublimation energy the values of the parameters in an assumed force function, checking the results with those obtained for the gas. An investigation of the values of the indices in the double reciprocal potential for a large number of face-centred cubic crystals [44] showed a wide variation from substance to substance, the repulsive index ranging from -6 to -12, and the attractive from -2 to -6. Corner [45] has determined the intermolecular potentials in neon and argon in this way, and obtained slightly better agreement with an exponential than with a reciprocal repulsion term.

A more fundamental approach is to deduce the most stable crystal lattice from the theory and compare with experiment. It has been shown [46, 47] that the lattice energy arising from pure London forces is less for hexagonal than for cubic close-packing; the conclusion is not upset by the addition of central exchange forces.[48] However, apart from helium, the rare gases adopt cubic close-packing. Four explanations have been suggested:

(i) zero-point vibrational energy,

(ii) thermal vibrational energy,

(iii) the potential is additive but of a different shape,

(iv) the potential is not strictly additive.

The third possibility was considered by Kihara and Koba,[49] who suggested that the actual potential well is much wider than that given by the 12 : 6 law,[50] but a wider potential gives disagreement in other respects. All the possibilities except the last have been eliminated by the work of Barron and Domb.[51] Thus, in order to obtain exact information about intermolecular potentials from crystals, account has to be taken of many-body interactions.

However, it ought to be possible to deduce some semi-empirical information about repulsive forces from the equation of state of solids at very high pressures. For example, Guggenheimer [52] has shown that Bridgman's high pressure data lead to an exponential repulsion. The available experimental information for such studies has recently been increased by the measurement of the Hugoniot for metals up to 4×10^5 atm, using the shock wave from explosives.[53]

TRANSPORT PROPERTIES

In the theory of transport properties the coefficients are expressed in terms of integrals which involve the dynamics of molecular collisions and hence the intermolecular potential. Detailed analysis of the viscosity results for helium, compared with other evidence, gives results in accord with those obtained theoretically.[54] Hirschfelder and his colleagues [10, 55] have used the transport properties to derive the values of the parameters in the Lennard-Jones potential for various gases, the agreement with those from second virial coefficients not being very close, because the two properties depend on different parts of the potential. More recently, an exponential repulsive term has been used in discussing transport properties.[56-58] For spherical molecules, good agreement between transport properties and second virial coefficients is obtained, but results are less satisfactory for polyatomic molecules.

HIGH-VELOCITY ELASTIC COLLISIONS

Study of the scattering of high-velocity atoms by room temperature atoms is the only theoretically straightforward method for deducing interactions at close range. In matter at high temperatures and pressures many-body interactions must be considered, whereas in this process only two atoms are involved. Unfortunately it has been applied to very few systems. For helium-helium interactions,[59] the scattering results, together with viscosity results, can be fitted by a potential function including an exponential repulsion with an exponent the same as that obtained theoretically.[4, 7]

INELASTIC COLLISIONS

Calculation of the probability of energy transfer from external to internal modes during a molecular encounter requires knowledge of the potential in the highly repulsive region. Experimental results have usually been interpreted on the Landau-Teller theory,[60] in which an exponential repulsion is assumed. It has been stated [54] that values of the exponent obtained in this way agree with those obtained in other ways, but further examination suggests that the Landau-Teller theory requires a steeper repulsive potential than that indicated theoretically.[17] Using energy transfer to determine the potential has been suggested [61] but the theory is not sufficiently far advanced for this to be a practicable programme.

DISCUSSION

Twenty years ago, London presented a paper on " The general theory of molecular forces " to a Faraday Society discussion.[11] In it the form of the long-range attractive forces was established, but little information was available about repulsion which, on the basis of the work of Slater [4] and Bleick and Mayer,[8] London took to be exponential. The present examination of our knowledge of the repulsive potential does not take us much further than London was able to go, though the range of evidence on which we can draw is much greater.

The conclusion that the repulsive potential for monatomic gases is best represented by an exponential has been confirmed, both theoretically and experimentally, and it is clear that an inverse power is inadequate at distances of one or two Ångstroms. The expected superiority of the exponential repulsion is not

demonstrated by the results on gases at fairly low pressures, either in the virial coefficients or in the transport properties, from which one may conclude that the detailed form of the repulsive potential is not yet relevant in the average collision at normal temperatures and pressures. In matter at high density the detailed form is important, but the situation is obscured by the need to take account of many-body interactions, and it is possible that a more empirical approach, involving the interaction of a molecule with its averaged environment, may be valuable. The repulsive potential may be most accurately mapped by studying high velocity collisions, but this can only be done in face of considerable experimental difficulty for elastic collisions, and theoretical difficulty for inelastic collisions.

It seems likely that advance will come from further experimental observation, either of the bulk properties of matter under more extreme conditions, as in the work with explosives, or in the extension of the collision experiments to a wider range of substances.

[1] Zwanzig, *J. Chem. Physics*, 1954, **22**, 1420.
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Electronic Kinetic Energy in Gases at High Pressures

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May 31, 1950

APPLICATION of the virial theorem to a substance of volume V and pressure p gives

$$\Delta\bar{T}=3\Delta(pV)-\Delta U, \tag{1}$$

where $\bar{T}$ is the average kinetic energy of electrons and nuclei and U is the total energy.[1] Michels *et al.*[2] have used this result to calculate changes in average kinetic energy brought about by compression of gases; $\Delta(pV)$ was directly measured and ΔU was calculated from the observed P-V-T relationships. $\Delta\bar{T}$ was found to increase with pressure, and it was pointed out that this must be due to an increase in electronic kinetic energy. It was shown that a change of the correct order of magnitude in electronic kinetic energy could be demonstrated by solving the wave equation for the hydrogen atom with the boundary condition that $\Psi=0$ at $r=r_0$.[2,3] It is of interest to try to interpret these results on a molecular basis, particularly because such an interpretation may enable one to discuss the effects of pressures greater than those used by Michels (3×10^3 atmos.).

Slater[4] has pointed out that, for a diatomic molecule,

$$\bar{T}=-E-R(dE/dR), \tag{2}$$

where E is the electronic energy, as a function of the internuclear distance R. This shows that as the nuclei are moved closer together than the equilibrium distance, there is a sharp rise in kinetic energy, and a relatively flat rise in total energy. Thus, if the compression of a gas composed of diatomic molecules could be regarded as pushing the nuclei a little closer together, the qualitative explanation of the effect is clear. The large effect of compression on the kinetic energy is very striking, but it is notable that a compression which increases the kinetic energy by an amount as great as the dissociation energy of the molecule leads to only a small increase in total energy. Using the $E(R)$ function and constants given by Linnett,[5] we may use (2) to calculate how E and $\bar{T}$ vary with R for nitrogen:

$R(A)$	E(kcal./mole)	ΔT(kcal./mole)
1.094	0.00	0.00
1.092	0.01	6.9
1.050	3.45	172.

The force required to bring about a given change in R and hence in $\bar{T}$ can thus be obtained from spectroscopic data; moreover, the corresponding pressure required can be obtained from Michels' experimental work. From this force and pressure the "effective area" of the molecule can be calculated. This "effective area" should be about the same as that of the van der Waals sphere, but close agreement is not to be expected: Michels' results on the hydrogen atom suggest that the area might be greater. The results for nitrogen are of the correct order, and their approximate constancy with increasing pressure suggests that this viewpoint is justifiable. They are as follows:

$\Delta\bar{T}$(kcal.)	1	2	3	4	5	6
Area (A^2)	143	151	152	149	145	142.

The "effective area" seems to be decreasing at high pressures; thus $\Delta\bar{T}$ calculated from it for still higher pressures is likely to be an upper limit. In nitrogen at 10^5 atmospheres, for example, 180 kcal. is an upper limit to the change in kinetic energy, and 4 kcal. to the change in energy. Dissociation should take place at about 10^6 atmospheres.

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MOLECULAR ENERGY AT HIGH PRESSURE

MOLECULAR ENERGY AT HIGH PRESSURE

By T. L. Cottrell

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The effect of molecular interaction at high pressure has been discussed using the approximation that a molecule enclosed by its neighbours may be considered to be in a box with an infinitely steep potential wall. The calculation has been carried out by the variation method for the hydrogen molecule-ion in a spheroidal box, and the results have been compared with earlier calculations on the hydrogen atom in a spherical box, with a cruder calculation for diatomic molecules, and with experimental results on other gases. The approximation apparently gives results of the correct order of magnitude, but tends to exaggerate the effect of pressure.

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1. Introduction.—It has been remarked by Michels and de Groot [1] that at high densities molecular collisions must result in considerable distortion of the distribution of the electrons and nuclei. Exact calculation is not possible, but they suggest the approximation of considering a molecule enclosed by its neighbours, whose influence is replaced by the wall of a small sphere of radius r_0. In particular, they point out that using the virial theorem the kinetic energy of electrons and nuclei is given by

$$\overline{T} = - r_0 \frac{\partial E}{\partial r_0} - E,$$

where E is the total energy. This result provides a method of comparing the calculations with experiment. Application of the virial theorem to a substance of pressure p and volume V gives [2]

$$\Delta \overline{T} = 3\Delta(pV) - \Delta E.$$

$\Delta(pV)$ can be measured directly and ΔE calculated from the observed P—V—T relationships. At the low pressures at which exact measurements can be made the kinetic energy is a sensitive indication of the distortion of the electronic distribution.[2]

de Groot and ten Seldam [3] have treated the hydrogen atom in a spherical box, with results for the change in kinetic energy on compression which are of the same order of magnitude as found experimentally for various gases at pressures up to 3,000 atm. This system contains only one nucleus, which is kept at the centre of the box, and thus an essential feature of molecules, the possibility of relative motion of the nuclei, is omitted.

The hydrogen molecule-ion H_2^+ is the only molecular system for which the calculation is feasible without labour quite unjustified by the crudity of the method of representing molecular interactions. We therefore consider the energy of the ground state of the hydrogen molecule-ion in a box with infinitely steep potential walls. A spherical box is only convenient when the system has spherical symmetry, and a spheroidal box was therefore chosen as being more appropriate and more amenable to treatment.

[1] Michels and de Groot, *Physica*, 1950, **16**, 183.
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2. The Hydrogen Molecule-Ion in a Spheroidal Box.—H_2^+ is in a spheroidal box with the nuclei at the foci. The co-ordinates of the electron are prolate spheroidals, ξ, η, ϕ. If the internuclear distance is ρ, and the distances from the electron to the two nuclei are r_A and r_B, the potential energy, in atomic units, is given by

$$\left.\begin{aligned} V &= -\frac{1}{r_A}-\frac{1}{r_B}+\frac{1}{\rho} = -\frac{4}{\rho}\frac{\xi}{(\xi^2-\eta^2)}+\frac{1}{\rho}; \quad 0 \leqslant \xi \leqslant \xi_0 \\ &= \infty; \qquad\qquad\qquad\qquad\qquad\qquad \xi_0 \leqslant \xi < \infty \end{aligned}\right\}$$

The surface $\xi = \xi_0$ is a prolate spheroid, and we are interested in the solution within this surface. The variation method has been used for the molecule-ion in free space by James,[4] and very good results were obtained with the function

$$e^{-\delta\xi}(1 + c\eta^2),$$

where δ and c are variational parameters. This gives $D_e = 2{\cdot}772$ eV, in error by only 0·005 eV. The variation method, using a similar trial function, has been adopted here. Since, in our case, the wave function for $\xi > \xi_0$ is zero, a function for the region inside the box must be zero for $\xi = \xi_0$, and thus the following function was adopted :

$$\psi = e^{-\delta\xi}(1 + 0{\cdot}5\,\eta^2)(\xi_0 - \xi).$$

δ is the only variational parameter, but the value 0·5 for the coefficient of η^2 gives satisfactory results for the energy at large ξ_0. The value of E for the region inside the box was obtained by minimizing with respect to δ the integral

$$\int\psi H\psi\,\mathrm{d}\tau \Big/ \int\psi^2\,\mathrm{d}\tau; \quad 0 \leqslant \xi \leqslant \xi_0; \quad -1 \leqslant \eta \leqslant +1,$$

and of $\overline{T}$ and $\overline{V}$ from

$$\int\psi_0 T\psi_0\,\mathrm{d}\tau \Big/ \int\psi_0^2\,\mathrm{d}\tau \quad \text{and} \quad \int\psi_0 V\psi_0\,\mathrm{d}\tau \Big/ \int\psi_0^2\,\mathrm{d}\tau$$

respectively, where ψ_0 is obtained from the previous minimization.

Here
$$\begin{aligned} H &= T + V, \\ T &= -\tfrac{1}{2}\nabla^2, \\ V &= -r_A^{-1} - r_B^{-1} + \rho^{-1} \text{ in atomic units.} \end{aligned}$$

Now it can be shown that for the approximate wave function under consideration,

$$\overline{T} = \frac{f(\delta, \xi_0)}{\rho^2}; \quad \overline{V} = \frac{g(\delta, \xi_0)}{\rho}.$$

Hence
$$2\overline{T} = -\rho\frac{\partial\overline{T}}{\partial\rho}; \quad \overline{V} = -\rho\frac{\partial\overline{V}}{\partial\rho};$$

and since
$$E = \overline{T} + \overline{V},$$
$$\overline{T} = -E - \rho\frac{\partial E}{\partial\rho},$$

a result analogous to that found for molecules in free space by Slater.[5]

The minimization was carried out for $\rho = 1{\cdot}6 - (0{\cdot}2) - 2{\cdot}4$ and $\xi_0 = 2 - (1) - 8$, with the results given in Table I. The best value of δ was obtained to four decimals because, although the total energy is not sensitive to δ near the minimum, the kinetic energy is.

If ρ is small compared with ξ_0, the box may be considered a sphere of

[4] James, *J. Chem. Physics*, 1935, **3**, 9.
[5] Slater, *J. Chem. Physics*, 1933, **1**, 687.

radius $\rho\xi_0/2$, a good approximation for the surface area over the range of interest. Thus the most convenient parameter to characterize the size of box is $\rho\xi_0$. A knowledge of the surface $E(\rho, \rho\xi_0)$, shown in Fig. 1,

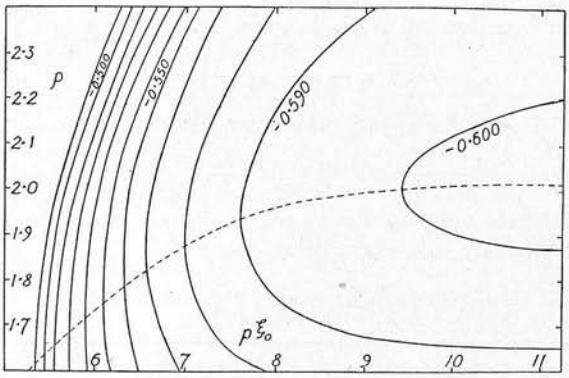

FIG. 1.—The energy surface $E(\rho, \rho\xi_0)$ (atomic units).

provides all the information we require; a section for $\rho\xi_0$ = constant gives the $E(\rho)$ curve for a molecule in that size of box; the minimum of this curve gives the equilibrium internuclear distance, shown by the

TABLE I.—CALCULATION OF δ, E, $\overline{T}$ AT VARIOUS ρ AND ξ_0 (atomic units)

ρ	1·6	1·8	2·0	2·2	2·4
$\xi_0 = 2$					
E	0·554	0·223	0·006	− 0·140	− 0·250
$\xi_0 = 3$					
δ	0·6011	0·6801	0·7604	0·8420	0·9240
E	− 0·4245	− 0·4962	− 0·5356	− 0·5561	− 0·5649
$\overline{T}$	1·1813	0·9702	0·8290	0·7071	0·6215
$\xi_0 = 4$					
δ	0·7136	0·8164	0·9188	1·0188	1·1169
E	− 0·5576	− 0·5829	− 0·5935	− 0·5954	− 0·5921
$\overline{T}$	0·8453	0·7319	0·6483	0·5833	0·5312
$\xi_0 = 5$					
δ	0·8153	0·9292	1·0362	1·1394	1·2408
E	− 0·5802	− 0·5957	− 0·6010	− 0·5999	− 0·5950
$\overline{T}$	0·7610	0·6817	0·6167	0·5633	0·5191
$\xi_0 = 6$					
δ	0·8899	1·0026	1·1101	1·2126	1·3111
E	− 0·5845	− 0·5979	− 0·6021	− 0·6005	− 0·5953
$\overline{T}$	0·7422	0·6705	0·6109	0·5600	0·5163
$\xi_0 = 7$					
δ	0·9393	1·0511	1·1572	1·2592	—
E	− 0·5854	− 0·5983	− 0·6023	− 0·6006	—
$\overline{T}$	0·7373	0·6681	0·6094	0·5595	—
$\xi_0 = 8$					
δ	0·9733	1·0841	1·1896	1·2904	—
E	− 0·5856	− 0·5984	− 0·6023	− 0·6006	—
$\overline{T}$	0·7359	0·6675	0·6093	0·5592	—

dashed line in Fig. 1, which decreases with decreasing size of box. From the slope of this line we can obtain the force acting on the molecule, from which, together with the area of the box, it is possible to calculate the pressure. The results are shown in Table II.

The kinetic energy may be checked using the virial relation [1]

$$\overline{T} = -E - \rho\xi_0 \frac{dE}{d(\rho\xi_0)}\,; \quad \left(\frac{\partial E}{\partial \rho}\right)_{\rho\xi_0} = 0.$$

It is easily shown that this is equivalent to the relation

$$\overline{T} = -E - \rho\left(\frac{\partial E}{\partial \rho}\right)_{\xi_0}$$

which is satisfied by the approximate wave function used.

$$\frac{dE}{d(\rho\xi_0)} \text{ along the line } \left(\frac{\partial E}{\partial \rho}\right)_{\rho\xi_0} = 0$$

was obtained from the results by numerical methods, and compared with $\overline{T}$ calculated directly, agreement being obtained.

TABLE II.—PROPERTIES OF H_2^+ AT EQUILIBRIUM INTERNUCLEAR DISTANCES

$\rho\xi_0$ (at. units)	P (atm.)	E (at. units)	$\overline{T}$ (at. units)	$\Delta\overline{T}$ (kcal.)
12	~ 0	− 0·6023	0·6023	0
11	$4{\cdot}4 \times 10^2$	− 0·6020	0·6051	1·8
10	$2{\cdot}1 \times 10^3$	− 0·6011	0·6124	6·3
9·2	$5{\cdot}9 \times 10^3$	− 0·5995	0·6237	13·5
8·4	$1{\cdot}5 \times 10^4$	− 0·5963	0·6438	26
7·6	$3{\cdot}8 \times 10^4$	− 0·5897	0·6798	49
6·8	$1{\cdot}0 \times 10^5$	− 0·5753	0·7483	92
6·4	$1{\cdot}7 \times 10^5$	− 0·5633	0·7983	123
6·0	$2{\cdot}8 \times 10^5$	− 0·5454	0·8664	166
5·6	$4{\cdot}6 \times 10^5$	− 0·5199	0·9539	220
5·2	$7{\cdot}8 \times 10^5$	− 0·4827	1·0667	292
5·0	$1{\cdot}0 \times 10^6$	− 0·4580	1·1380	336

3. Comparison with other Calculations.—In Fig. 2 the energy of the hydrogen molecule-ion as a function of $\rho\xi_0/2$ is compared with that of the hydrogen atom in a box of radius r_0, as a function of r_0, as obtained by de Groot and ten Seldam.[3] The remarkable similarity of the curves shows that the introduction of two centres of force has little effect on the increase of electronic energy due to compression, though at large values of r_0, the curve for the atom is slightly steeper than that for the molecule-ion, indicating that in this range the molecule-ion is rather more stable with respect to the atom than in free space.

An attempt has recently been made [6] to discuss the effect of high pressure using the energy against internuclear distance relationship obtained spectroscopically. The procedure was thence to obtain the kinetic energy as a function of internuclear distance by applying the virial theorem, and as a function of pressure up to 3,000 atm. from the experimental results of Michels *et al.*[2] The spectroscopic curve gave the force for any value of the kinetic energy, and this was combined with the pressure to give the "effective area" of the molecule, which was taken to be constant and used in conjunction with the spectroscopic results to predict the energy at much higher pressures. The "effective area" for nitrogen was found to be 145 Å² at 2,000 atm. The area of the box enclosing the hydrogen molecule-ion at 2,000 atmospheres is 90 Å². The ratio of the squares of the van der Waals radii of nitrogen and hydrogen is 1·9, which is not far from the ratio of these results. This suggests a further comparison.

[6] Cottrell, *J. Chem. Physics*, 1950, **18**, 1117.

For nitrogen as calculated from the $E(r)$ curve in free space, the change in energy on compression becomes as great as the dissociation energy at 10^6 atm.; for the hydrogen molecule-ion in a box this becomes so at 5×10^5 atm. Thus the pressures required to produce comparable changes in energy are of the same order of magnitude. However, for nitrogen a pressure of 10^5 atm. causes a change of 4 kcal. mole^{-1} in the total energy, and 180 kcal. in the kinetic energy; for the molecule-ion the figures are 16 kcal. and 92 kcal. respectively. Thus the change in total energy relative to the change in kinetic energy is rather different in the two calculations.

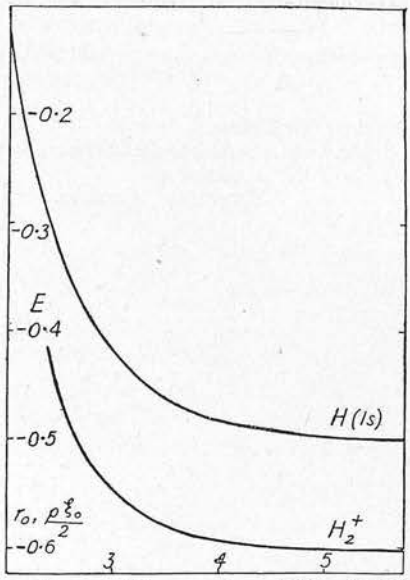

FIG. 2.—The energies of H and H_2^+ as a function of r_0 and $\rho\xi_0/2$ respectively (atomic units).

A way of finding out whether this difference is due to the difference in method is to treat the hydrogen molecule-ion in the same way as for nitrogen. Experimental data are lacking, so in place of a spectroscopic $E(\rho)$ curve, that obtained from the James function is used, and in place of the experimental results on the dependence of kinetic energy on pressure, the results of the calculations for the ion in a box are used. The "effective area" at 2,000 atm. comes out as 200 Å^2 or much greater than the area of the box. At a pressure of 4×10^4 atm. the following results, compared with those for the ion in a box, were obtained:

	E	$\overline{T}$	ρ (atomic units)
$E(\rho)$ curve method .	$-0{\cdot}585$	0·74	1·6
ion in a box . .	$-0{\cdot}589$	0·69	1·93

There is good accord for E, but poor for $\overline{T}$, as before. The two methods therefore do not give the same results. The $E(\rho)$ curve method really assumes that the curve in free space is the locus of the minimum of $E(\rho)$ curves for molecules in compressed gases. Fig. 2 shows that for the box model of a molecule in a compressed gas this is not true. The locus of the minimum is much steeper with respect to ρ than the $E(\rho)$ curve in free space. This is compensated for in the method by the fact that the empirically adjusted "effective area" is greater than the true area of the box. The status of the free space $E(\rho)$ curve method is therefore that of an extrapolation formula, which gives reasonably good results for E.

4. Comparison with Experiment.—The only method of comparison with experiment is to use the results of Michels *et al.* on the increase of kinetic energy with pressure in various gases. The results for $\overline{T}$ at 2,000 atm. are:

2 kcal. mole^{-1} for hydrogen,[7]
5 kcal. mole^{-1} for nitrogen,[2]
6 kcal. mole^{-1} for carbon dioxide,[2]
7 kcal. mole^{-1} for ethylene.[8]

[7] Michels and Goudeket, *Physica*, 1941, **8**, 387.
[8] Michels, de Groot and Geldermans, *Appl. Sci. Res. A*, 1947, **1**, 103.

the present calculations give 6 kcal. mole^{-1} at 2,000 atm. for the hydrogen molecule-ion, a result of the same order of magnitude as those obtained experimentally. If, however, the number of electrons in these molecules is taken into account, and if it is assumed that the valence electrons are chiefly affected, the experimental results give $\overline{T}$ of about 2 kcal. per bond. Thus the calculation appears to exaggerate the effect.

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The Virial Theorem in Quantum Mechanics.

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SUMMARY.

A derivation is given of a form of the virial theorem in quantum mechanics suitable for the discussion of a system of particles in a box.

IF T and V are the kinetic and potential energies of a system, and $\mathbf{r}_i$ is the position vector of the ith particle, the virial theorem in classical mechanics states that

$$-2\overline{\mathrm{T}}=-\overline{\sum_i \mathbf{r}_i \cdot \nabla_i \mathrm{V}}, \qquad (1)$$

where the bars denote time averages, and the R.H.S. is known as the virial. This result has been used in the discussion of equations of state (*cf.* Jeans 1925). In the discussion of the thermal equation of state derived from quantum dynamical principles, de Boer (1949) has used the virial theorem, a procedure which is only justifiable if it can be shown that it holds in quantum mechanics. In view of the recent controversy concerning quantum mechanical equations of state (*cf.* Green 1949, Uhlenbeck and Riddell 1950) it seemed particularly desirable to examine the validity of this assumption.

de Boer justifies the use of the theorem in quantum mechanics by referring to Slater (1933), who concluded that it is valid if the time averages of classical theory are replaced by quantum mechanical averages. A similar conclusion had been reached by Finkelstein (1928). It appears, however, that these proofs apply only to systems where there are no infinite discontinuities of potential, and are thus not applicable to a system in an enclosure where the potential is infinite at the walls. As it is under just these conditions that the theorem is applied in the discussion of equations of state, a further proof is required. The subject has been touched upon again in more recent publications, though only incidentally, and these contributions will be discussed in relation to our treatment.

After some manipulation of the Schrödinger equation, Slater obtains the result

$$\sum_i -\frac{\hbar^2}{2m_i}\sum_j x_j\left(\psi^*\frac{\partial^3\psi}{\partial x_i^2\partial x_j}-\frac{\partial\psi}{\partial x_j}\frac{\partial^2\psi^*}{\partial x_i^2}\right)+\psi^*\left(\sum_j x_j\frac{\partial V}{\partial x_j}\right)\psi=0, \qquad (2)$$

† Communicated by James Taylor.

where the symbols have their obvious significance. To integrate this, use is made of the identity

$$\sum_j x_j\left(\psi^*\frac{\partial^3\psi}{\partial x_i^2\partial x_j}-\frac{\partial\psi}{\partial x_j}\frac{\partial^2\psi^*}{\partial x_i^2}\right)=-2\psi^*\frac{\partial^2\psi}{\partial x_i^2}+\frac{\partial}{\partial x_i}\left[\psi^{*2}\frac{\partial}{\partial x_i}\frac{\sum_j x_j\frac{\partial\psi}{\partial x_j}}{\psi^*}\right]. \quad . \quad . \quad . \quad (3)$$

The second term on the R.H.S. is set equal to zero after integration with respect to x_i, because ψ^{*2} is zero at the limits. It may be seen on performing the differentiation inside the brackets, however, that the term

$$\left[-\sum_j x_j\frac{\partial\psi}{\partial x_j}\cdot\frac{\partial\psi^*}{\partial x_i}\right]_{l_1}^{l_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where l_1 to l_2 is the range of integration, remains, and that this is zero only if $\partial\psi^*/\partial x_i$ vanishes. In free space where the range of integration is $-\infty$ to $+\infty$, the derivative of the wave function vanishes at the limits, but this does not happen when we are concerned with a system inside a box. Here ψ is typically a sine function with a non-vanishing derivative at the limits. This term must be concerned with the virial of the external forces acting on the system by virtue of the walls, and we shall now show that, if a is a parameter defining the scale of the box, the neglected term is equal to $a(\partial\mathrm{E}/\partial a)$, giving the final result

$$2\overline{\mathrm{T}}=-a\frac{\partial\mathrm{E}}{\partial a}+\overline{\sum_i \mathbf{r}_i\,.\,\nabla_i\mathrm{V}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which is the form in which the theorem has, in fact, generally been used.

If $$\mathrm{H}=\mathrm{T}+\mathrm{V}=-\sum_i\frac{\hbar^2}{2m_i}\nabla_i^2+\mathrm{V}(\mathbf{r}_i), \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and the wave equation $\mathrm{H}\psi=\mathrm{E}\psi$ and its complex conjugate hold, it is easy to show, by differentiating with respect to a, *keeping* $\mathbf{r}_i$ *constant*, that

$$\frac{\partial\mathrm{E}}{\partial a}=-\sum_i\frac{\hbar^2}{2m_i}\int\left(\psi^*\nabla_i^2\frac{\partial\psi}{\partial a}-\frac{\partial\psi}{\partial a}\nabla_i^2\psi^*\right)d\tau. \quad . \quad . \quad . \quad (7)$$

In the above, as in all following equations, the volume integral is over the volume of the box for each particle. This volume integral may be transformed into a surface integral using Green's theorem, the surface being that corresponding to the volume through which the $\mathbf{r}_i$ integration is carried. This allows one of the terms to be dropped because ψ^* is zero when any position-vector $\mathbf{r}_i$ terminates on the surface $\mathbf{S}_i$. We obtain

$$\frac{\partial\mathrm{E}}{\partial a}=\sum_i\frac{\hbar^2}{2m_i}\int\left[\int\frac{\partial\psi}{\partial a}(\nabla_i\psi^*)\,.\,d\mathbf{S}_i\right]d\tau_i', \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $d\tau$ has been replaced by $d\mathbf{r}_i \,.\, d\tau_i'$ in the usual convention.

Similarly, starting with the wave equation and proceeding in the same manner as Slater, we obtain

$$-\psi\psi^*\mathbf{r}_j \,.\, \nabla_j \mathrm{V} = \psi^*\mathbf{r}_j \,.\, \nabla_j \left(\sum_i - \frac{\hbar^2}{2m_i}\nabla_i^2\psi\right) - \left(\sum_i - \frac{\hbar^2}{2m_i}\nabla_i^2\psi^*\right)\mathbf{r}_j \,.\, \nabla_j\psi \quad . \quad . \quad . \quad (9)$$

which is equation (2) expressed in vector notation. It can easily be shown by expansion that

$$\sum_j \mathbf{r}_j \,.\, \nabla_j \left(\sum_i - \frac{\hbar^2}{2m_i}\nabla_i^2\psi\right) \equiv \sum_i - \frac{\hbar^2}{2m_i}\nabla_i^2\left(\sum_j \mathbf{r}_j \,.\, \nabla_j\psi\right) - 2\sum_i - \frac{\hbar^2}{2m_i}\nabla_i^2\psi. \quad . \quad . \quad . \quad (10)$$

On substituting in (9) we obtain, after integration throughout the available configuration space,

$$\begin{aligned} -2\overline{\mathrm{T}} + \overline{\sum_j \mathbf{r}_j \,.\, \nabla_j \mathrm{V}} &= -\sum_i - \frac{\hbar^2}{2m_i}\int [\psi^*\nabla_i^2(\sum_j \mathbf{r}_j \,.\, \nabla_j\psi) - (\sum_j \mathbf{r}_j \,.\, \nabla_j\psi)\nabla_i^2\psi^*]\, d\tau \\ &= \sum_i - \frac{\hbar^2}{2m_i}\int [\int (\sum_j \mathbf{r}_j \,.\, \nabla_j\psi)\nabla_i\psi^* \,.\, d\mathbf{S}_i]\, d\tau_i'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11) \end{aligned}$$

If a defines the scale of the box then it may be shown (see Appendix) that $\sum_j \mathbf{r}_j \,.\, \nabla_j\psi = -a(\partial\psi/\partial a)$. Comparing this result with equation (8) we conclude that

$$2\overline{\mathrm{T}} - \overline{\sum_j \mathbf{r}_j \,.\, \nabla_j \mathrm{V}} + a\frac{\partial \mathrm{E}}{\partial a} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which is the form in which the virial theorem is usually used.

Since this work was carried out, it has come to our notice that Price (1950) has derived an expression for the stress tensor at the boundary in a fluid using a similar transformation to a surface integral. By applying Fröhlich's method of boundary perturbations, he obtained a result which can, by combining his equations (25) and (39), be put into the usual form of the virial theorem.

It is true that if the virial in Slater's discussion is regarded as the sum of the virial of the external and internal forces, the result is formally correct, but because of the infinite discontinuity at the walls, the integration of equation (2) throughout infinite space cannot properly be carried out, as has been pointed out by Uhlenbeck and Riddell (1950). These authors attempted to get round this difficulty by considering a smooth though nearly step-like potential at the wall of the box. This does not define the box properly, as pointed out by Green (1950), but it is possible to use Uhlenbeck and Riddell's analytical method together with an infinite

potential wall, to give the correct result. Their method, which has also been applied by Zwanzig (1950) in a similar connection, used a device due to Green (1949) to differentiate the Hamiltonian, but as there seems to be some confusion about the Hermitian character of one of the terms involved, and also because this seems to be a more elegant, if less superficially convincing method, we apply it here.

In Cartesian coordinates the Hamiltonian is

$$\mathrm{H}=\mathrm{T}+\mathrm{V}=-\sum_i \frac{\hbar^2}{2m_i}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right)+\mathrm{V}(x_1 \ldots . z_n). \quad . \quad . \quad (13)$$

We introduce new variables ξ_i, η_i, ζ_i defined by $x_i=a\xi_i$, $y_i=a\eta_i$, $z_i=a\zeta_i$, and differentiate the Hamiltonian with respect to a, *keeping* ξ, η, ζ *constant.* Thus

$$\frac{\partial \mathrm{H}}{\partial a}=\sum_i 2\frac{\hbar^2}{2m_i a^3}\left(\frac{\partial^2}{\partial \xi_i^2}+\frac{\partial^2}{\partial \eta_i^2}+\frac{\partial^2}{\partial \zeta_i^2}\right)+\frac{\partial \mathrm{V}}{\partial a}, \quad . \quad . \quad . \quad . \quad (14)$$

and so

$$a\frac{\partial \mathrm{H}}{\partial a}=-2\mathrm{T}+\sum_i \mathbf{r}_i \,.\, \nabla_i \mathrm{V}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\therefore \quad a\int \psi^* \frac{\partial \mathrm{H}}{\partial a}\psi \, d\tau=-2\overline{\mathrm{T}}+\overline{\sum_i \mathbf{r}_i \,.\, \nabla_i \mathrm{V}}. \quad . \quad . \quad . \quad . \quad (16)$$

By differentiating the Schrödinger equation, and integrating the result, we have

$$\frac{\partial \mathrm{E}}{\partial a}=\int \psi^* \frac{\partial \mathrm{H}}{\partial a}\psi \, d\tau+\int \psi^*(\mathrm{H}-\mathrm{E})\frac{\partial \psi}{\partial a}\, d\tau. \quad . \quad . \quad . \quad . \quad (17)$$

Since $(\partial\psi/\partial a)_{\xi,\eta,\zeta}=0$ at the wall (see Appendix), the second term on the R.H.S. is Hermitian, and so disappears, giving a result which may be combined with (16) to give the virial theorem (12). Green (1950) has stated that when the potential at the wall is infinite, this term is not Hermitian because $\partial\psi/\partial a$ is not zero at the surface. This seems to be due to a confusion about what is kept constant in the partial differentiations. In the present treatment we are concerned with $(\partial\psi/\partial a)_{\xi,\eta,\zeta}$, which is zero at the wall. $(\partial\psi/\partial a)_{x,y,z}$, on the other hand, which we used in the previous treatment, is finite at the wall.

APPENDIX.

Let the equation of the box in rectangular Cartesians be

$$\mathrm{S}(\xi, \eta, \zeta)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where $\xi=x/a$, etc. We can also write

$$\psi(x_i, y_i, z_i, a)\equiv \Psi(\xi_i, \eta_i, \zeta_i, a), \text{ say}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Then provided ξ_i, η_i, ζ_i satisfy (18) for any single i, *i. e.* provided the ith particle is on the surface, Ψ is identically zero.

$$\therefore \quad \left(\frac{\partial \Psi}{\partial a}\right)_{\xi, \eta, \zeta} \equiv 0 \qquad \text{when} \qquad S(\xi_i, \eta_i, \zeta_i)=0. \quad . \quad . \quad (20)$$

But

$$a\frac{\partial \Psi}{\partial a} = \sum_i \left(x_i \frac{\partial \psi}{\partial x_i} + y_i \frac{\partial \psi}{\partial y_i} + z_i \frac{\partial \psi}{\partial z_i}\right) + a\frac{\partial \psi}{\partial a} \equiv \sum_i \mathbf{r}_i \,.\, \nabla_i \psi + a\left(\frac{\partial \psi}{\partial a}\right)_{x, y, z}. \quad . \quad . \quad . \quad (21)$$

The R.H.S. of (21) is, therefore, also zero.

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APPROXIMATE WAVE-FUNCTIONS SATISFYING THE VIRIAL THEOREM

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It is shown that approximate wave-functions for diatomic molecules of the type in which all distances between particles are expressed as a ratio of the distance concerned to the internuclear distance, and which contain parameters λ_k defined by $\partial E/\partial\lambda_k = 0$, give values of the kinetic and potential energy which satisfy the virial theorem.

1. Introduction.—Slater [1] pointed out several years ago that for diatomic molecules the virial theorem requires that the average kinetic and potential energy, $\overline{T}$ and $\overline{V}$, should be related by

$$2\overline{T} + \overline{V} = -R\frac{\mathrm{d}}{\mathrm{d}R}(\overline{T} + \overline{V}). \quad . \quad . \quad . \quad (1.1)$$

Coulson and Bell [2] have shown that this provides a useful check on the goodness of an approximate wave function, and proved that (1.1) was satisfied for all internuclear distances provided that a scale factor, which varies with the internuclear distance, is included in the approximate wave function. Recently the virial theorem has been used to discuss distortion of electronic distribution in gases at high pressures,[3, 4] and in a calculation of the effect of pressure on the hydrogen molecule-ion [5] an approximate wave function of a different class from that considered by Coulson and Bell,[2] which also satisfied the virial theorem, was used. This paper discusses this class of function.

2. Conditions for Satisfying the Virial Theorem.—Consider a system of two nuclei a and b of charges α and β, and n electrons. R is the internuclear distance and x_i, y_i, z_i the Cartesian co-ordinates of the ith electron, with respect to any convenient axes. For simplicity place the origin at a and the x-axis along R. r_{ai}, r_{bi} are the distances of the ith electron from the two nuclei, and the r_{ij} are the interelectronic distances. Let $\psi(x_1 \ldots z_n;\ R;\ \lambda_k)$ be an approximate wave function, where the λ_k are arbitrary parameters whose values are fixed by minimizing E with respect to λ_k. In the following, for convenience, the ψ are considered to be purely real, but the extension to complex functions can readily be supplied. Then

$$\overline{T} = -\tfrac{1}{2}\int \psi \sum_i \nabla_{xi}^2\psi \mathrm{d}\tau_x \Big/ \int \psi^2 \mathrm{d}\tau_x \quad . \quad . \quad . \quad (2.1)$$

$$\overline{V} = \int \psi V \psi \mathrm{d}\tau_x \Big/ \int \psi^2 \mathrm{d}\tau_x \quad . \quad . \quad . \quad . \quad (2.2)$$

where

$$V = -\Big(\sum_i \alpha r_{ai}^{-1} + \sum_i \beta r_{bi}^{-1} - \sum_{i \neq j} r_{ij}^{-1}\Big).$$

Here atomic units are used, and the suffix x means that the co-ordinates involved in the operator are x, y, z; e.g.

$$\mathrm{d}\tau_x = \Pi_i \mathrm{d}x_i \mathrm{d}y_i \mathrm{d}z_i.$$

[1] Slater, *J. Chem. Physics*, 1933, **1**, 687.
[2] Coulson and Bell, *Trans. Faraday Soc.*, 1945, **41**, 141.
[3] Michels and de Groot, *Physica*, 1950, **16**, 183.
[4] Cottrell, *J. Chem. Physics*, 1950, **18**, 1117.
[5] Cottrell, *Trans. Faraday Soc.* (to be submitted shortly).

Evidently
$$\left.\begin{aligned}\overline{T} &= \overline{T}(R, \lambda_k)\\ \overline{V} &= \overline{V}(R, \lambda_k)\\ E &= E(R, \lambda_k).\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (2.3)$$

The virial theorem (1.1) requires
$$2\overline{T} + \overline{V} = -R\frac{\mathrm{d}(\overline{T} + \overline{V})}{\mathrm{d}R} = -R\frac{\mathrm{d}E}{\mathrm{d}R}.$$

Now
$$\frac{\mathrm{d}E}{\mathrm{d}R} = \frac{\partial E}{\partial R} + \sum_k \frac{\partial E}{\partial \lambda_k} \cdot \frac{\mathrm{d}\lambda_k}{\mathrm{d}R}.$$

But
$$\frac{\partial E}{\partial \lambda_k} = 0.$$

Hence the virial theorem requires
$$2\overline{T} + \overline{V} = -R\frac{\partial}{\partial R}(\overline{T} + \overline{V}). \quad . \quad . \quad . \quad (2.4)$$

One obvious way of satisfying (2.4) is to make
$$2\overline{T} = -R\partial\overline{T}/\partial R \quad . \quad . \quad . \quad . \quad (2.5)$$
$$\overline{V} = -R\partial\overline{V}/\partial R \quad . \quad . \quad . \quad . \quad (2.6)$$
separately. This is evidently *sufficient* though it is not *necessary*. From (2.5) and (2.6)
$$\overline{T} = A(\lambda_k)/R^2\,; \quad \overline{V} = B(\lambda_k)/R \quad . \quad . \quad . \quad (2.7)$$
where A and B are arbitrary functions.

Now if
$$\xi = x/R,\ \eta = y/R,\ \zeta = z/R,$$
ψ can always be written
$$\begin{aligned}\psi(x_1 \ldots z_n\,;\ R\,;\ \lambda_k) &\equiv \psi(R\xi_1 \ldots R\zeta_n\,;\ R\,;\ \lambda_k)\\ &\equiv \chi(\xi_1 \ldots \zeta_n\,;\ R\,;\ \lambda_k) \text{ say.}\end{aligned}$$

Then
$$\nabla_x^2\psi = \frac{1}{R^2}\nabla_\xi^2\chi$$

and
$$\mathrm{d}\tau_x = R^{3n}\mathrm{d}\tau_\xi.$$
$$\therefore\ \overline{T} = A/R^2$$

where
$$A \equiv -\tfrac{1}{2}\int\chi\sum_i\nabla_{\xi i}^2\chi\mathrm{d}\tau_\xi \Big/ \int\chi^2\mathrm{d}\tau_\xi. \quad . \quad . \quad . \quad (2.8)$$

Again
$$r_{ai} = R\sqrt{\xi_i^2 + \eta_i^2 + \zeta_i^2},$$
and similarly all distances between electrons and nuclei and all inter-electron distances are expressible in the form
$$r = Rf(\xi, \eta, \zeta).$$

Thus
$$\overline{V} = B/R,$$
$$B \equiv \int\chi V'\chi\mathrm{d}\tau_\xi \Big/ \int\chi^2\mathrm{d}\tau_\xi \quad . \quad . \quad . \quad . \quad (2.9)$$
where $V' = RV$; since $1/R$ may be factored out of V, V' is no longer dependent on R. Thus comparing (2.7), (2.8) and (2.9) it is clear that the virial theorem is satisfied if A and B are independent of R. The most obvious way of satisfying this condition is to make
$$\chi(\xi, \eta, \zeta\,;\ R\,;\ \lambda_k) \equiv R^\gamma F(\xi, \eta, \zeta\,;\ \lambda_k), \quad . \quad . \quad (2.10)$$
where γ is a constant. This means that by taking out a factor R^γ, ψ can be expressed in terms of x/R, y/R, z/R only (and the λ_k). It can easily be shown that (2.10) is equivalent to the following restriction on ψ:
$$x\frac{\partial\psi}{\partial x} + y\frac{\partial\psi}{\partial y} + z\frac{\partial\psi}{\partial z} + R\frac{\partial\psi}{\partial R} = \gamma\psi \quad . \quad . \quad . \quad (2.11)$$
but this would be useful only if (2.10) were hard to test by inspection,

which would not happen often. The factor R^{γ} in (2.10) may be dropped because multiplication of a wave function by a constant factor makes no difference to the results.

We have concluded that a solution based on minimizing E with respect to the parameters λ_k in a wave function $\psi(x_1 \ldots z_n;\ R;\ \lambda_k)$ will satisfy the virial theorem provided ψ is of the form

$$\psi = F\left(\frac{x_1}{R} \ldots \frac{z_n}{R};\ \lambda_k\right). \qquad (2.12)$$

The argument was expressed in terms of rectangular Cartesians (x, y, z); but it evidently holds good in any system, since if x, y, z and R are all increased in the same ratio so also are all other linear co-ordinates. In particular the condition applies in confocal elliptic co-ordinates

$$\xi = \frac{r_a + r_b}{R},\quad \eta = \frac{r_a - r_b}{R},\quad \phi,$$

where it becomes

$$\psi = F(\xi, \eta, \phi;\ \lambda_k).$$

This type of wave function is often used in molecular problems.[6]

It is worth pointing out that if some or all of the λ_k are not varied, but allowed to remain constant, the virial theorem will still be obeyed although of course the energy will be less nearly correct. That this is so may be seen by noting that in the derivation of (2.4) λ_k appears in a term $\frac{\partial E}{\partial \lambda_k} \cdot \frac{d\lambda_k}{dR}$ which was equal to zero because $\partial E/\partial \lambda_k = 0$. This term will also disappear if λ_k is a constant, since then $d\lambda_k/dR = 0$.

3. Comparison with Results of Coulson and Bell.[2]—The present criterion might seem at first sight to be equivalent to that given by Coulson and Bell.[2] However, it can be shown that their procedure yields a solution which satisfies (2.4) but not (2.5) and (2.6). If we write $\overline{T}$ for their $\overline{T}(s, R)$ and $\overline{T}_1$ for their $\overline{T}(1, sR)$ etc., then their equations (7) give

$$\overline{T} = s^2\overline{T}_1;\quad \overline{V} = s\overline{V}_1,$$

and so

$$\frac{\partial \overline{T}}{\partial s} = 2s\overline{T}_1 + s^2R\frac{\partial \overline{T}_1}{\partial(sR)},$$

$$\frac{\partial \overline{T}}{\partial R} = s^3\frac{\partial \overline{T}_1}{\partial(sR)}.$$

Hence

$$s\frac{\partial \overline{T}}{\partial s} = 2\overline{T} + R\frac{\partial \overline{T}}{\partial R}.$$

Consequently

$$R\frac{d\overline{T}}{dR} = R\left(\frac{\partial \overline{T}}{\partial R} + \frac{\partial \overline{T}}{\partial s} \cdot \frac{ds}{dR}\right) = -2\overline{T} + \frac{\partial \overline{T}}{\partial s} \cdot \frac{d(sR)}{dR},$$

so that neither (2.5) nor $R\frac{d\overline{T}}{dR} = -2\overline{T}$ is satisfied. Similarly, neither $R\frac{\partial \overline{V}}{\partial R}$ nor $R\frac{dV}{dR}$ is equal to $-\overline{V}$.

It appears that Coulson and Bell's method is more general as regards the form of the approximate wave function, but less general as regards the choice of variational parameters.

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An equation of state applicable to gases at densities near that of the solid and temperatures far above the critical

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It is suggested that, at high pressures and temperatures far above the critical, the intermolecular interaction is predominantly repulsive. The effect on a molecule of its neighbours is therefore replaced by an infinitely steep potential well of volume related to the molecular volume. This concept is used to write down the equation of state for such a gas. It is shown that this equation is likely to hold in the range of density and temperature characteristic of the detonation wave in condensed explosives.

The equations of the hydrodynamic theory of detonation are developed in terms of this equation of state, and applied to pentaerythritol tetranitrate. The calculated dependence of detonation velocity on loading density is in very good agreement with experiment; the temperature shows a sharp decrease with increased loading density. This is a consequence of the intermolecular repulsive energy characteristic of the model chosen.

1. Introduction

A very simple model may be used to derive an equation of state which gives an accurate description of highly dilute gases. To describe gases at temperatures near the critical, and in the range of pressure available to laboratory measurements, even quite an elaborate model does not lead to an accurate equation of state. There are indications, however, that at still higher pressures, where the gas has a density in the range usually associated with solids, and provided that the temperature is well above the critical, a simple model is again sufficient for deriving an equation of state. It is the object of this paper to discuss one such model, and to test the resulting equation by using it in the hydrodynamic theory of detonation to describe the gaseous products in the detonation wave of condensed explosives.

Michels, de Boer & Bijl (1937) have shown that in the pressure range in which accurate P-V-T measurements are possible, the kinetic energy of a gas increases with pressure, and have suggested that this is due to an increase in the kinetic energy of the electrons. It is probable that at very high pressures, the total energy will follow the kinetic energy, and intermolecular interaction will result in a corresponding repulsive potential. Michels & de Groot (1950) suggested that this might be calculated for each molecule by replacing its neighbouring molecules by the wall of a small sphere, and calculating the dependence of the energy on the size of the sphere. The problem of the hydrogen atom enclosed in a sphere had been tackled by Michels *et al.* (1937) and by de Groot & ten Seldam (1946); the calculated dependence of kinetic energy on pressure was similar to that found experimentally for various gases. A variation treatment of the energy of the hydrogen molecule-ion in a spheroidal box has been given (Cottrell 1951), which also gives results of the correct order of magnitude for the electronic kinetic energy, and indicates the dependence of molecular energy on density up to high density, although no simple experimental check is available.

Gases at densities covered by this calculation, and at temperatures of several thousand degrees, are obtained as products of the detonation of condensed explosives. In order to use the well-established hydrodynamic theory of detonation to predict the properties of the detonation wave, it is necessary to know the equation of state of the products of the explosive reaction. Alternatively, the observed properties of detonating explosives may be used to give some information about the equation of state. Unfortunately, the information which can be obtained in this way is limited, because the only relevant property which can be measured accurately is the velocity of detonation, and a knowledge of this for different initial densities of explosive is not sufficient to determine the equation of state, but can only be used to fix the values of parameters in an assumed form of equation (Paterson 1948*a*; Jones 1949). Various equations have been suggested (cf. Morris & Thomas 1947; Paterson 1948*b*), most of which give fair agreement with the observed velocity of detonation. They all lead to similar values of the detonation pressure, but the estimated detonation temperatures vary widely. These, in fact, depend on the allowance made for intermolecular repulsive energy, i.e. on $(\partial E/\partial V)_T$. Although equations of the form

$$PV = RTf(V), \tag{1·1}$$

which implies $(\partial E/\partial V)_T \equiv 0$, have been used with some success to predict detonation velocity, it is difficult to justify this assumption theoretically. Further, if an equation of the form

$$PV = RT + f(P) \tag{1·2}$$

be adopted, and $f(P)$ obtained numerically by comparison with the observed dependence of detonation velocity on initial density for pentaerythritol tetranitrate (PETN), a large intermolecular repulsive energy is indicated (Jones 1949). This estimate is shown as a function of volume in figure 1, where it is compared with the calculated dependence of energy on volume for the hydrogen molecule-ion (Cottrell 1951). The close agreement between the two is striking, and confirms that repulsive energy is likely to be of paramount importance at pressures of about 10^5 atm and temperatures of a few thousand degrees. This expectation is also suggested by the form of the experimental curves of internal energy against density for various gases at moderate temperatures (de Boer 1940).

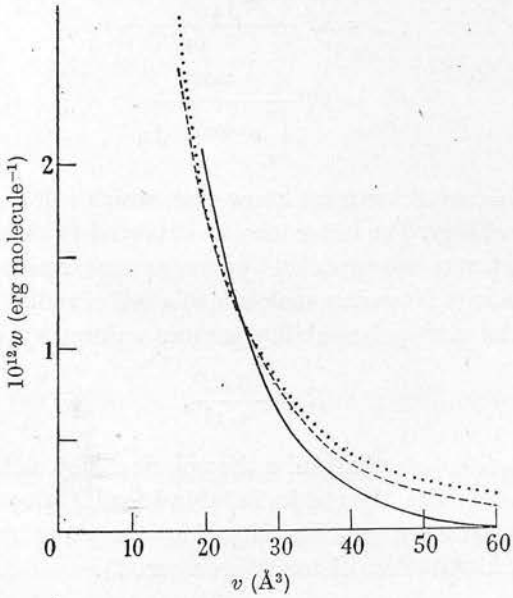

FIGURE 1. Plot of repulsive energy (w) against molecular volume (v). ——, PETN (Jones 1949); ----, H_2^+ (Cottrell 1951); ....., $w = Xv^{-2}$.

A possible model of a gas under conditions where the repulsive energy is most important is one in which the energy of each molecule is calculated as a function of molecular volume, the effect of other molecules being replaced by an infinitely steep potential wall. Thus the programme of calculation is to introduce the distribution laws to the Michels-type model, and to apply the result to hydrodynamic detonation theory.

2. THE MODEL

The model adopted here for a highly compressed gas at high temperature is a cell model. Each molecule is supposed to occupy a cell whose volume is the molecular volume or differs from it only by a constant-packing fraction dependent

on the assumed geometry of the cell, and its energy is calculated as a function of cell volume. Thus the potential energy of the whole assembly, W, is assumed to be just N times the energy of a single molecule in a cell of the appropriate size, i.e.

$$W = Nw(v), \tag{2·1}$$

where v is the molecular volume and N is the number of molecules. The configurational partition function, Ω, is given by

$$\Omega = \frac{1}{N!}\left[\int_0^v \mathrm{e}^{-w(v)/kT}\,\mathrm{d}v\right]^N. \tag{2·2}$$

Now (cf. Fowler & Guggenheim 1939)

$$P = kT\frac{\partial \log \Omega}{\partial Nv} \tag{2·3}$$

$$= kT\frac{\partial \log \int_0^v \mathrm{e}^{-w(v)/kT}\,\mathrm{d}v}{\partial v} \tag{2·4}$$

$$= kT\frac{\mathrm{e}^{-w(v)/kT}}{\int_0^v \mathrm{e}^{-w(v)/kT}\,\mathrm{d}v}. \tag{2·5}$$

In order to use this result, we must know $w(v)$, which will be composed of repulsive and attractive energy. The latter may be expected to be small for this model, an expectation which may be supported by a very approximate calculation, assuming the dispersion energy between a molecule in a cell of radius r and volume v and a bulk medium of the same polarizability per unit volume to be given by

$$E = -\frac{3}{4}\frac{I\alpha^2}{r^6}, \tag{2·6}$$

where I is the ionization potential and α the polarizability. Although this does not hold at the highest densities, the results in table 1 for H_2^+ give an indication of the effect. In these calculations α has been taken from the paper by Bell & Long (1950) for the appropriate internuclear distance (see figure 2).

TABLE 1

v (Å^3)	$-\frac{3}{4}\frac{I\alpha^2}{r^6}$ (attraction) (Å)	repulsive energy (Å)
135	−0·0001	0·0000
104	−0·0001	0·0003
35	−0·0010	0·0126
20	−0·0019	0·0390
11	−0·0037	0·1196

Thus, for the present model, which is to be applied only at high density, the attractive energy may be neglected, and $w(v)$ has merely to have the form shown for the repulsive energy in figure 1. For further calculation it is convenient to use an analytical expression to approximate to the calculated repulsive energy, and

Corrigendum

Proceedings of the Royal Society A. Vol. 213, pp. 216–217.

Since this paper has been printed the authors have realized that the first paragraph of Section 2 is somewhat obscure. In the model used, each molecule occupies a cell of volume v. Its energy will depend upon position within the cell, but this dependence is replaced by dependence on an 'available' volume, which for the ith molecule is v_i, and an upper limit to which is the molecular volume. On this view, the configurational partition function may be approximated by a volume integral as in equation (2·2).

Equation (2·1) should more properly read

$$W = \Sigma_i w(v_i) \tag{2·1}$$

(*Facing p.* 216)

preferably one which will allow the evaluation of the integrals in terms of tabulated functions. It will be seen from figure 1 that for $v < 40$ Å^3 it is a good approximation to put

$$w = Xv^{-2}, \tag{2·7}$$

and this form satisfies the above requirements.

For these hydrogen molecule-ion calculations, the cell volume differs from the volume per molecule by the packing fraction for spheroids, since the energy calculation is for a molecule in a spheroidal box. It is a good approximation to consider the spheroids concerned as spheres, so that the packing fraction is about 0·7,

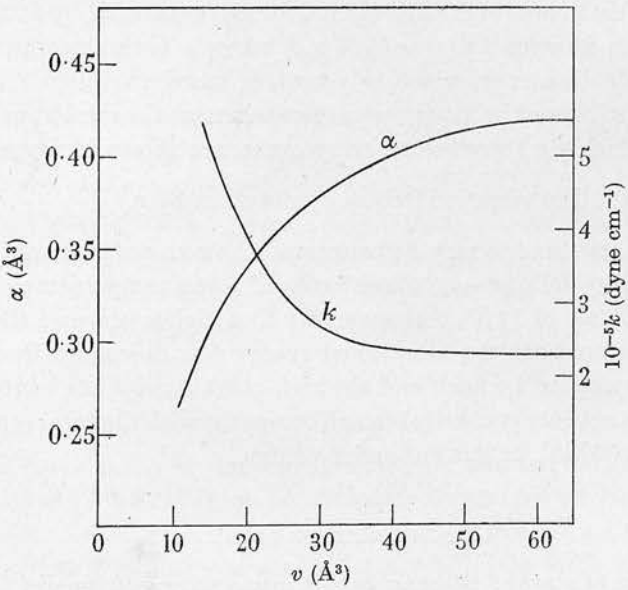

FIGURE 2. Estimated dependence of polarizability α and vibrational force constant k on v for H_+^2.

its precise value depending upon the type of packing. This fraction, or rather its inverse square, may be absorbed in the constant X, and makes no difference to the argument.

We now consider

$$\int_0^v e^{-w/kT}\,dv$$

and put

$$x^2 = w/kT. \tag{2·8}$$

Using (2·7) we have

$$\int_0^v e^{-w/kT} = \left(\frac{X}{kT}\right)^{\frac{1}{2}} \int_x^\infty x^{-2} e^{-x^2}\,dx$$

$$= \left(\frac{X}{kT}\right)^{\frac{1}{2}} \left[x^{-1} e^{-x^2} - 2\int_x^\infty e^{-x^2}\,dx\right], \tag{2·9}$$

and (2·5) becomes

$$Pv = \frac{kT}{[1 - \pi^{\frac{1}{2}} x\, e^{x^2} \operatorname{erfc}(x)]}, \tag{2·10}$$

where $\operatorname{erfc}(x) = 2\pi^{-\frac{1}{2}} \int_x^\infty e^{-t^2}\,dt$, the error function complement. Thus P may be calculated using the tabulated values of the error function. The partition function, on this model, is of the same form as that for the 'smoothed potential' model of a liquid (cf. Fowler & Guggenheim 1939).

A cell model has other consequences which might be mentioned here. For example, a result of the confinement of a molecule in a cell is that its vibration frequency increases above its value in free space. This has two effects: the vibrational energy decreases, while the zero-point energy increases. A calculation for the hydrogen molecule-ion shows that these effects are small. For a given size of box, it is possible to obtain the vibrational force-constant, k, by fitting the energy to the parabolic function $2V(\rho) = k(\rho-\rho_e)^2$, where ρ is the internuclear distance. The energy calculations on which this work is based were made at intervals of 0·2 Å in ρ, and so cannot be fitted very accurately near the minimum to a parabola. The results, which are therefore not very exact, are shown in figure 2, where k is plotted against v. The vibration frequency ν is given by $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, where μ is the reduced mass, and from it may be calculated the zero-point energy, $\frac{1}{2}h\nu$, and the vibrational energy $RTz/(e^z-1)$, where $z \equiv h\nu/kT$. At a temperature of 3000° K and a molecular volume of 14 Å^3, corresponding to a higher pressure than that found normally in detonation, the vibrational energy has decreased from 2·8 kcal, its value in free space, to 1·8 kcal, and the zero-point energy has increased from 4·0 to 6·1 kcal. The net energy change is small compared with the total repulsive energy, which is about 30 kcal, at this molecular volume.

3. Approximate treatment

The equation of state (2·10) may be put into a more convenient form when x is large. We have, from (2·9),

$$N!\,\Omega^{1/N} = \left(\frac{X}{kT}\right)^{\frac{1}{2}} \left[x^{-1}e^{-x^2} - 2\int_x^\infty e^{-x^2}\,dx\right]. \tag{3·1}$$

For x large, we may use the asymptotic expansion of $\int_x^\infty e^{-x^2}\,dx$ and obtain

$$N!\,\Omega^{1/N} = \left(\frac{X}{kT}\right)^{\frac{1}{2}} e^{-x^2}\left(\frac{1}{2x^3} + \frac{3}{4x^5} + \text{etc.}\right). \tag{3·2}$$

Considering only the first term of the expansion, and substituting from (2·8), we have

$$\frac{\partial \log \Omega}{N\,\partial v} = \frac{\partial}{\partial v}\left[\log v^3 - \frac{X}{kTv^2}\right] \tag{3·3}$$

$$= \frac{3}{v} + \frac{2X}{kTv^3}, \tag{3·4}$$

or

$$Pv = 3kT + 2Xv^{-2}. \tag{3·5}$$

The error in P compared with P calculated from (2·10) is expected to be slight only for large x, i.e. for large T and small v. These are, however, just the conditions

under which we shall require to apply the equation. In table 2 a comparison is given between P calculated according to (2·10) and according to (3·5), using the value of X calculated for H_2^+,

$$(X = 7 \times 10^{-58}\,\text{erg cm}^6\,\text{molecule}^{-3} = 3{\cdot}65 \times 10^6\,\text{cal cm}^6\,\text{mole}^{-3})$$

and putting $T = 3000°\,\text{K}$.

TABLE 2. PRESSURE CALCULATED ACCORDING TO EQUATIONS (2·10) AND (3·5) FOR H_2^+ AT 3000° K

		$10^{-10}P$ (dyne cm^{-2})	
v (Å^3)	x	(2·10)	(3·5)
13·70	3·0	62·7	63·4
16·44	2·5	38·2	39·1
20·56	2·0	21·3	22·1
27·41	1·5	10·4	11·3
41·11	1·0	4·2	5·0

For $x > 1$, (3·5) is quite a good approximation, and for H_2^+, $x = 1$ is equivalent to $v = 41{\cdot}11$ Å^3 at 3000° K. The approximation that $w = Xv^{-2}$ is only good for $v < 40$ Å^3, so in the range of applicability of the model (3·5) may be used.

4. APPLICATION TO DETONATING EXPLOSIVES*

The Rankine-Hugoniot equation for a detonation wave may be written

$$\Delta E^{(0)} + \Delta E^{(1)} - Q = \tfrac{1}{2}P(V_0 - V). \tag{4·1}$$

Here, the subscript 0 refers to the original explosive and the unqualified symbols to the equilibrium products; Q is the difference in energies of formation of explosive and products at (T_0, P_0); $\Delta E^{(0)}$ is the change in internal energy of the products in passing from T_0 to T at P_0, i.e. as an ideal gas; $\Delta E^{(1)}$ is the further energy change during compression, at T, from P_0 to P.

Subject to the approximation of § 3, the equation of state proposed is of the general form

$$PV = mnRT + f(V), \tag{4·2}$$

where n is the number of moles in the volume V, R is the gas constant per mole and m is a numerical factor. Then, since

$$\mathrm{d}E = C_v \mathrm{d}T - \frac{f}{V}\mathrm{d}V, \tag{4·3}$$

we conclude at once that

$$\Delta E^{(1)} = \int_V^\infty f \mathrm{d}V / V, \tag{4·4}$$

while of course

$$\Delta E^{(0)} = \int_{T_0}^{T_1} C_v^{(0)}\,\mathrm{d}T, \tag{4·5}$$

$C_v^{(0)}$ being the 'ideal' specific heat, that is, the value computed for the perfect gas state. It will be noticed that, within the range of application of (4·2),

$$\left(\frac{\partial C_v}{\partial V}\right)_T = -\frac{\partial}{\partial T}\left(\frac{f}{V}\right) \equiv 0, \tag{4·6}$$

* For an introduction to detonation theory, see Lewis & von Elbe (1951), or Cole (1948).

so that C_v depends on temperature only. This confirms that (4·2) cannot be expected to apply at low densities, so that (4·4) involves a further approximation. Reference to table 1 shows, however, that this approximation is a good one at practical explosive loading densities.

The Rankine-Hugoniot equation is now

$$\Delta E^{(0)} - Q = \tfrac{1}{2}P(V_0 - V) - \int_V^\infty f \mathrm{d}V/V. \tag{4·7}$$

The left-hand side of (4·7) depends in general on both pressure and temperature, because the equilibrium composition itself does so. If we assume that the state equation (4·2) is independent of the particular composition, and that the equilibria involve no change in the total number of moles, then $\Delta E^{(0)} - Q$ is a function of temperature only. Although this will not be true for all explosives, and in particular cannot hold for explosives like T.N.T. with marked oxygen deficiency, it applies closely to oxygen-balanced or moderately oxygen-negative explosives. For these it is found that $\Delta E^{(0)} - Q$ is closely linear in the temperature over a wide range, so that we may write

$$\Delta E^{(0)} - Q = aT - b, \tag{4·8}$$

where a and b are constants. Equation (4·7) then reduces to

$$P(\lambda V - V_0) = (\lambda - 1) f(V) - 2\int_V^\infty f \mathrm{d}V/V + 2b, \tag{4·9}$$

where λ is defined by

$$\lambda \equiv 1 + \frac{2a}{mnR}. \tag{4·10}$$

Equation (4·9) is the Rankine-Hugoniot equation in terms of P and V. If the slope of the corresponding curve is denoted by $(\mathrm{d}P/\mathrm{d}V)_{\mathrm{RH}}$, the Chapman-Jouguet stability condition is

$$-\left(\frac{\mathrm{d}P}{\mathrm{d}V}\right)_{\mathrm{RH}} = \frac{P}{V_0 - V}, \tag{4·11}$$

which reduces to

$$P = \frac{(V_0 - V)\left[\dfrac{2f(V)}{V} - (\lambda - 1) f'(V)\right]}{(\lambda + 1)V_0 - 2\lambda V}. \tag{4·12}$$

Equations (4·9) and (4·12) provide two simultaneous algebraic equations for V and P, when the form of f is specified.

The equation of state (3·5) applied to the volume V gives

$$PV = 3nRT + 2XV^{-2}, \tag{4·13}$$

where X must be expressed in suitable units, say cal cm^6 g^{-3} if V is the specific volume in cm^3 g^{-1}. The units of n are then mole g^{-1}, and of P, cal cm^{-3} (1 atm = 0·0242 cal cm^{-3}), while R = 1·987 cal mole^{-1} (° K)$^{-1}$. Subject to (4·13), (4·9) becomes

$$P = \frac{2X(\lambda - 2) + 2bV^2}{V^2(\lambda V - V_0)}, \tag{4·14}$$

while (4·12) becomes

$$P = \frac{4X(\lambda - 2)(V_0 - V)}{V^3[2\lambda V - (\lambda + 1)V_0]}. \tag{4·15}$$

Although P may be at once eliminated from these equations, this does not lead to a convenient solution for V. The most convenient procedure is to graph P against V from (4·14) and (4·15) and determine the point of intersection of the two curves. This point is of course also the point of contact on (4·14) of the tangent form (V_0, P_0), so that (4·15) could be dispensed with. However, it helps to define the point of tangency more precisely.

The theory was first applied to PETN at a loading density of 1·5 g/cm³. The products depend almost entirely on the water/gas equilibrium, and to a close approximation, between 1500 and 5000° K,

$$\Delta E^{(0)} - Q = 0{\cdot}364T - 1670\,\text{cal}\,\text{g}^{-1}. \tag{4·16}$$

Consequently, $b = 1670$ cal/g and $\lambda = 4{\cdot}49$, since $n = \frac{11}{316} = 0{\cdot}0348$ mole g^{-1}. X was first given the value $3{\cdot}65 \times 10^6$ cal cm^6 mole^{-3}, suggested by the theory of § 3 above. With the present value of n, this becomes 154 cal cm^6 g^{-3}. After determining the Chapman-Jouguet point (V_1, P_1) as described above, the detonation velocity D was deduced from the equation

$$D = V_0 \sqrt{\frac{P_1}{V_0 - V_1}}. \tag{4·17}$$

The value obtained in this way was 6640 m/s, compared with an experimental velocity of 7420 m/s (Friederich 1933). The theoretical velocity was thus of the right order, but smaller than observed. To bring the two into closer agreement, the constant X had to be increased. When X was set equal to 227 cal cm^6 g^{-3}, an increase of 50 % over the value suggested by the hydrogen molecule-ion, the calculated velocity was 7410 m/s, which effectively coincided with experiment.

This value of X was then used to compute the velocities at 1·727, 1·0 and 0·75 g cm^{-3}. The approximation of § 3 cannot be expected to hold accurately except at the highest densities, and table 3 shows that the velocities are considerably exaggerated at 1·0 and 0·75 g cm^{-3}. Agreement is fairly good at the highest density. It is noteworthy that the temperature shows a marked decrease as the density is raised. This is to be expected, since a larger proportion of the reaction energy is absorbed in overcoming intermolecular repulsions.

Table 3. Detonation velocity (D) as a function of loading density (Δ) for PETN, calculated using (3·5)

Δ (g/cm³)	D/(m/s) calc.	D/(m/s) obs.	$10^5 P_1$(atm.)	T_1(°K)
1·727	8060	8360	3·00	2655
1·50	7410	7420	2·25	3280
1·00	6040	5520	1·10	4420
0·75	5450	4700	0·72	4830

Since it appeared probable that the divergence of theoretical and experimental velocities at the lower densities was due in part at least to the algebraic approximations made in § 3 rather than to the basic assumptions of §§ 1 and 2, it was thought worth while to attempt calculations with the full state equation (2·10). As before we shall first develop the theory in a somewhat general form and afterwards specialize it by introducing equation (2·7).

For 1 g of gas, the equation (2·4) can be written

$$P = nRTg_V, \tag{4·18}$$

where n and R have the same meaning as before, the suffix V denotes a partial differentiation, and $g(V, T)$ is defined by

$$g(V,T) \equiv \log \int_0^V \mathrm{e}^{-W(V)/nRT}\,\mathrm{d}V. \tag{4·19}$$

Then it can readily be shown that

$$\mathrm{d}E = C_V\,\mathrm{d}T + nRT^2 g_{VT}\,\mathrm{d}V. \tag{4·20}$$

If $\Delta E^{(0)}$ and $\Delta E^{(1)}$ are defined as before, then

$$\begin{aligned}\Delta E^{(1)} &= nRT^2 \int_{\rho=\rho_0}^{\rho=\rho} g_{VT}\,\mathrm{d}V \\ &= nRT^2[(g_T)_{P,T} - (g_T)_{P_0,T}].\end{aligned}$$

However, at the low pressure P_0, $W(V)$ is negligible irrespective of the temperature, and $g(V, T)$ therefore reduces to $\log V$, so that $g_T \equiv 0$. Accordingly,

$$\Delta E^{(1)} = nRT^2 g_T, \tag{4·21}$$

and the Rankine-Hugoniot equation is

$$\Delta E^{(0)} - Q = \tfrac{1}{2}P(V_0 - V) - nRT^2 g_T. \tag{4·22}$$

Equation (4·22) is perfectly general.

We now introduce (2·9), that is, assume $W(V) = XV^{-2}$. Then after a little manipulation it can be shown that

$$2Tg_T = Vg_V - 1. \tag{4·23}$$

From (4·18), (4·22) and (4·23), the Rankine-Hugoniot equation then becomes

$$\Delta E^{(0)} - Q = \tfrac{1}{2}nRT - P(V - \tfrac{1}{2}V_0). \tag{4·24}$$

As before, we assume that $\Delta E^{(0)} - Q$ is a function of T only. In the approximate theory it was then possible to eliminate T entirely by means of the equation of state. Now, however, T cannot be readily eliminated, and the Chapman-Jouguet condition is rather complex. The Chapman-Jouguet point on the Rankine-Hugoniot (P, V) curve may, however, be determined graphically by drawing the upward tangent from the initial point (V_0, P_0).

In order to draw the Rankine-Hugoniot curve, let us denote by $A(T)$ the function of T:

$$\frac{nRT}{\Delta E^{(0)} - Q - \tfrac{1}{2}nRT}.$$

Then, from (4·18) and (4·24),

$$\frac{1}{Vg_V} = \left(\frac{V_0}{2V} - 1\right) A(T). \tag{4·25}$$

But, as in (2·10), it can easily be shown that

$$\frac{1}{Vg_V} = 1 - \pi^{\frac{1}{2}} x\,\mathrm{e}^{x^2}\,\mathrm{erfc}\,(x), \tag{4·26}$$

where

$$x \equiv \frac{1}{V}\sqrt{\frac{X}{nRT}}. \tag{4·27}$$

If we denote the function on the right of (4·26) by $B(x)$ the Rankine-Hugoniot equation (4·25) becomes

$$B(x) = \left\{\frac{V_0}{2}\left(\frac{nRT}{X}\right)^{\frac{1}{2}} x - 1\right\} A(T). \tag{4·28}$$

For any given T, the right-hand side represents a straight line in x; the intersection of this line with the curve of $B(x)$ gives x, whence V and finally P can be determined. Thus, starting from a series of values of T, the $(P\text{-}V)$ curve can be mapped out. The graphical procedure enables D and P_1 to be defined with adequate precision. There is rather more uncertainty in T_1, which may be in error by 100°. This could be removed by a numerical calculation, but the additional labour hardly seems justified at the moment.

The method was applied to PETN, with $X = 239\,\mathrm{cal\,cm^6\,g^{-3}}$. This value was slightly larger than before, in order to improve agreement at the highest density, where the approximate theory was most reliable. Table 4 shows the results.

TABLE 4

Δ (g/cm³)	D (calc.) (m/s)	D (obs.) (m/s)	$10^5 P_1$(atm.)	T_1(°K)
1·727	8200	8360	2·85	1950
1·40	7010	7000	1·86	2630
1·00	5530	5520	0·88	3650
0·75	4760	4700	0·53	4060
0·40	3660	3710	0·19	4525

The agreement between calculated and observed velocities is very close over the entire density range. The pressures are appreciably higher than those deduced in earlier calculations by one of us (Paterson 1948*b*), but agree closely with results obtained by Jones (1949) by a different method. He has shown that these pressures are certainly very near the true values. The temperatures fall rapidly as loading density is increased. This conclusion was also reached by Jones, but the effect is more marked in our results. Unfortunately, the experimental determination of the temperature is very difficult, so that although several measurements are available, none is sufficiently reliable to be used with confidence.

A further interesting feature of the solution may be briefly mentioned. It is found that, provided the value of T exceeds a certain minimum T_m, the straight line on the right of (4·28) cuts the curve of $B(x)$ not in one point only but in two. Each provides a point on the Rankine-Hugoniot $(P\text{-}V)$ curve. As T is reduced towards T_m the straight line approaches a position of tangency, and the corresponding points ultimately coincide. It follows that as the state-point moves along the Rankine-Hugoniot curve from high to low V, the temperature falls to a minimum value and then rises again. The minimum is reached at a point not far from the Chapman-Jouguet point but not coincident with it. In the cases examined, the point in question lies to the left of the Chapman-Jouguet point. The physical explanation of this behaviour would seem to be as follows. Under constant-volume conditions the temperature reached corresponds solely to the energy of reaction Q. At higher points on the Rankine-Hugoniot curve, this is supplemented by compression of the element of material in question by preceding elements which have

already passed through the wave. On the other hand, part of the available energy is required to overcome intermolecular repulsions. As the state-point rises along the Rankine-Hugoniot curve, both these quantities of energy increase, while Q remains fixed. At first, the repulsive absorption increases faster than the compressive supply, so that T falls. Ultimately, however, this position is reversed: the supply of energy by compression increases more rapidly with rising density than the intermolecular potential. Beyond this point, T rises again. If an equation of state were used in which internal fields were neglected, the temperature would rise continuously with pressure along the Rankine-Hugoniot curve. This was in fact the case in earlier calculations with such an equation.

A further comparison of the equation with experiment and other theory also comes from work on detonation. Various authors have estimated γ in the adiabatic relation, $PV^\gamma =$ constant, for the expansion of the products of detonation at high pressure. Jones & Miller (1948) have calculated γ for the expansion of the products of detonation of T.N.T., and found $\gamma = 3{\cdot}36$ at the highest density, falling as the density falls. Landau & Staniukovich (1945) and Pokrovskii & Staniukovich (1946) have also concluded that $\gamma \simeq 3$. Now, the limiting form of equation used here,

$$PV = 3RT + 2XV^{-2},$$

becomes, at high density,

$$PV^3 \simeq \text{constant},$$

which is also, under these circumstances, the adiabatic, in agreement with previous work.

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(13)

THE SECOND VIRIAL COEFFICIENT OF GASES AND MIXTURES

THE SECOND VIRIAL COEFFICIENT OF GASES AND MIXTURES

PART 1.—CARBON DIOXIDE + HELIUM MIXTURES

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This paper describes an apparatus for the measurement of the second virial coeffic of gases, vapours, and mixtures at pressures less than 1 atm, with an accuracy of cm^3 mole^{-1}. It differs from the usual " Boyle's apparatus " in that the gas under meas ment is not in contact with mercury. The second virial coefficients of carbon dioxide of an equimolecular mixture of carbon dioxide and helium have been measured at 60 and 90° C.

Little accurate experimental work has been done on the virial coefficients pure gases and vapours at pressures below 1 atm, and even less on mixtur Measurements made in a Boyle's apparatus [2, 3] only have an accuracy of ab 30 cm^3 mole^{-1} and are therefore not suitable for determining interaction coeffici in mixtures when the interaction is small. The determination of interaction efficients by the method of mixtures,[4, 5, 6] which gives much higher accur suffers a disadvantage in common with the Boyle's apparatus in that the gas ur measurement is in contact with mercury. The apparatus described here overco this difficulty.

The accuracy of the apparatus was tested by measuring the second vi coefficient of pure carbon dioxide at 30 and 60° C, the results obtained bein agreement with those obtained at higher pressures.[7, 8] The apparatus was t used for the examination of carbon dioxide + helium mixtures.

EXPERIMENTAL

A series of p, v measurements at a known temperature is obtained by allowing a certain quantity of gas to occupy successively five accurately known volumes, the pressure being measured at each stage.

APPARATUS

VOLUME MEASUREMENT.—The enclosed volume portion of the apparatus is shown in fig. 1. It is immersed in a silicone oil thermostat bath as indicated by the broken line. Except for the Bourdon gauge, the apparatus was constructed in Pyrex glass. The bulbs B, C, D and E were connected to the tube A via taps T_B, T_C, T_D and T_E which are of special design. The volume of bulbs including the bore of the taps was determined prior to assembly of the apparatus by weighing filled with distilled water. A temperature correction was applied to these volumes using a value of $1{\cdot}1 \times 10^{-5}$ for the cubical coefficient of expansion of Pyrex. The taps, in the first series of experiments, were lubricated with Apiezon T grease but it was later found more convenient to use silicone grease.

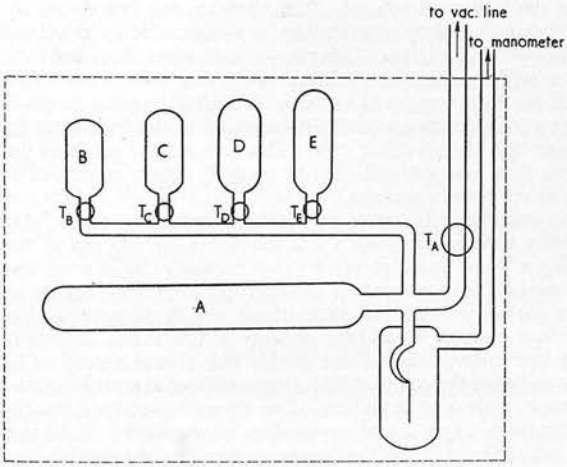

FIG. 1.—Diagram of enclosed volume of apparatus.

The taps were, essentially, mercury-sealed taps with the neck of the tap extending above the level of the oil in the bath. The bottom tubes of the taps were also connected together and brought above the surface. The taps were turned from outside the thermostat bath by Tufnol rods. The bore of taps T_B, T_C, T_D and T_E was 2 mm while that of T_A, the main tap to the vacuum line was 8 mm.

After the assembly of the apparatus, the volume of tube A, the Bourdon gauge sickle and associated tubing was measured by expansion of nitrogen at its Boyle point, into the calibrated bulbs. The volumes of the bulbs were chosen to give approximately equal decrements of pressure.

PRESSURE MEASUREMENT.—The glass Bourdon gauge was used as a null-point detector and the total pressure read on a mercury manometer. The gauge was made from soda glass and was joined to the apparatus through a graded seal. The sensitivity of the gauge was increased, and the need for observing it directly eliminated, by fixing aluminium plates to the fixed and movable portion of the gauge, forming a condenser, the deflection of which was detected using a Fielden P.M.4 Proximity Meter.[9] This arrangement can detect pressure differences of the order of 1μ. The gauge was kept within 0·01 mm of its null-point by admitting or withdrawing nitrogen from the gauge jacket via a needle valve. The gauge jacket was connected to the mercury manometer by a vacuum-jacketed silvered tube. The mercury manometer was of the conventional U-tube type, the one limb being continuously evacuated during pressure measurements. The manometer was made from tubing of 18 mm int. diam. and was enclosed in an air bath controlled to $\pm$ 0·2° C. The difference between the mercury levels was measured with a cathetometer made by the Precision Tool and Instrument Company. Pressure readings taken

by different observers rarely differed by more than 0·002 cm Hg. Pressures were corrected for capillary depression [10] and reduced to cm Hg at 0° C.

The pressure range normally covered was from 76 cm down to 20 cm Hg, so that pressures may be considered known to 1 part in 10,000 at the lowest pressure.

TEMPERATURE CONTROL AND MEASUREMENT.—The calibrated volumes and gauge were immersed in a silicone oil bath, controlled by a Sunvic R.T.1 resistance thermometer controller. Temperature constancy was checked with two Beckman thermometers and was good to within 0·01° C. The actual bath temperature was read on a thermometer checked against an N.P.L. standard.

The temperature of the air thermostat round the manometer was regulated by a Mullard temperature controller, a Stantel thermistor being used as the sensitive detector.

ANCILLARY APPARATUS.—Most of the ancillary apparatus was conventional, consisting of a vacuum line with gas purification trains, storage bulbs, etc., evacuated by an oil pump and mercury vapour pump.

Since the Bourdon gauge will only stand a pressure differential of 2-3 cm Hg, an automatic arrangement was devised for the admission of the balancing gas, nitrogen, to the gauge jacket and manometer simultaneously with the introduction of the gas under measurement to the calibrated volume. The nitrogen was introduced to the apparatus through a capillary and a piece of rubber valve tubing which was opened or closed by the action of a Londex mains relay. This relay opened when the signal from the proximity meter exceeded a predetermined level corresponding to a safe pressure differential. Thus on admission of gas to the enclosed volume, through a fine capillary which acted as a throttle, the signal from the meter gradually increased to the level when the relay opened admitting nitrogen at a slightly faster rate. This restored the gauge to the balance point and the nitrogen flow was cut off. This "on-off" action continued until a suitable pressure was built up in the apparatus.

ANALYSIS OF MIXTURES.—In order to check the accuracy of the method described below of preparing mixtures, provision was made for the analysis of small samples of the mixture using a Pyrex spiral pressure gauge connected to a small freezing trap. A sample of the mixture was isolated in this portion of the apparatus and its pressure measured. The carbon dioxide was then frozen out by immersing the trap in liquid nitrogen, the helium pumped off and the pressure of the carbon dioxide measured. The analyses of any one mixture carried out in this way always agreed to better than 1 % with each other and with the composition calculated from the preparation of the mixture.

PREPARATION OF GASES AND MIXTURES.—The nitrogen used for balancing the Bourdon gauge was drawn from a cylinder of oxygen-free nitrogen (99·9 % nitrogen $\not> 10$ p.p.m. oxygen). The gas used for calibration purposes was drawn from the same cylinder but was passed over phosphoric acid and through two liquid nitrogen freezing traps.

Carbon dioxide was prepared by the addition of sulphuric acid, diluted approximately 1 : 3, to sodium bicarbonate. The carbon dioxide was passed through two wash bottles of bicarbonate solution, through concentrated sulphuric acid and was frozen out in a liquid nitrogen freezing trap. It was then fractionally distilled three times.

Helium was drawn from a British Oxygen Co. cylinder containing $>$ 99·5 % helium. It was passed over phosphoric oxide and through three liquid nitrogen freezing traps.

The mixtures of carbon dioxide and helium which were stored in a 20-l. bulb were prepared as follows. A three-way tap connected the storage bulb to the main vacuum line, and to a small freezing trap. The bulb and freezing trap were initially evacuated and the trap then shut off. Carbon dioxide, to a pressure of approximately 45 cm, was put into the bulb and the pressure accurately measured. The three-way tap was then turned to isolate the bulb from the vacuum line but to put it in contact with the freezing trap, in which the carbon dioxide was condensed by immersing the trap in liquid nitrogen. Meanwhile the carbon dioxide in the manometer and connecting tubing was pumped off. When all the carbon dioxide had condensed, the freezing trap was isolated and the storage bulb opened to allow the introduction of helium, the pressure being again accurately measured. The bulb and freezing trap were now connected and carbon dioxide allowed to evaporate into the bulb. At least 24 h was allowed for mixing before using the mixture, and the first few samples were always discarded.

PROCEDURE

The complete apparatus was first evacuated to a pressure of 0·2 μ or better. Taps T_B, T_C, T_D and T_E to the four bulbs were then closed and the gas under investigation admitted to volume A and the gauge sickle, the pressure being balanced with nitrogen

as described above. When a suitable pressure of gas had been admitted, the main tap T_1 was closed and the tap admitting nitrogen to the gauge jacket also closed. Fine pressure adjustment was made by means of the needle valve. After a suitable length of time for temperature equilibration the pressure of the gas was read on the mercury manometer to 0·001 cm, temperatures and menisci heights being read at the same time. The gas was then allowed to expand slowly into the first bulb, balance of the gauge being maintained as far as possible by withdrawal of nitrogen through the needle valve. Expansion and measurement of pressure at each stage was then continued, this giving five p, v values for each run. From these values the second virial coefficient was calculated by the method described below.

CALCULATION OF RESULTS

It was assumed that the p, v relationship was in the form

$$pv = nRT + nBp, \tag{1}$$

which is true at the pressures employed in this work. Here B is the second virial coefficient and n is the number of moles present, the other symbols having their usual meaning.

In the calibration of the volume of the gauge sickle and associated tubing, nitrogen at its Boyle temperature was used and at this temperature $B = 0$. Successive values of v were known exactly except for an additive constant corresponding to the volume of the gauge, etc. Values of p were obtained from absolute measurement of the pressure and were expected to be subject only to random errors. Then with $B = 0$, (1) becomes

$$p = a/(x + \xi)$$

where $a = nRT$,

x = volume of calibrated bulbs at the corresponding pressure,

ξ = calibration constant for volume of gauge, etc.

On the assumption that errors in p are random and independent of x, the best estimates of a and ξ are found by minimizing

$$\sum[p - a/(x + \xi)]^2$$

with respect to a and ξ. The experimental method and assumptions were validated by testing the resulting residuals, $[p - a/(x + \xi)]$ for randomness. Since the second virial coefficient can be considered to be a co-volume, the analysis used for the calibration runs can also be used for the calculation of virial coefficients. The variance of the virial coefficients obtained as a result of any one run may be obtained in terms of the variance of p.

RESULTS AND DISCUSSION

CALIBRATION OF GAUGE, ETC.

Three gauges in all were used in the series of measurements described here. In each case ten calibration runs were made. The standard deviations of the residuals were less than 2×10^{-3} cm and the 95 % confidence limits of the volume were less than $\pm$ 0·030 cm^3 in all three cases. Since the apparatus holds approximately 0·01 mole of gas at room temperature, this corresponds to $\pm$ 3 cm^3 mole^{-1} in the virial coefficient.

CARBON DIOXIDE

Good straight lines were obtained for the pv against p plots, and the standard deviation of the virial coefficient in any one run was never more than 2·0 cm^3 mole^{-1}. The values obtained are given in table 1, where they are compared with those obtained at higher pressures, the agreement of the mean being to within 3 cm^3 mole^{-1}.

CARBON DIOXIDE + HELIUM MIXTURE

The second virial coefficient B_M, for an equimolecular mixture of carbon dioxide and helium was measured at 30, 60 and 90° C, 12 measurements of B_M being made at each temperature. The means of values are given in table 2 with limits

corresponding to the 95 % confidence limits. Also given are the values of B_{12} the interaction virial coefficient, calculated from the equation,

$$B_M = x_1^2 B_1 + 2x_1x_2B_{12} + x_2^2B_2.$$

Here x_1, x_2; B_1, B_2 are the mole fractions and virial coefficients of components 1 and 2. The values chosen for B_1 and B_2 are also given in the table, and the uncertainty of these values is not taken into account in the limits given for B_{12} (expt.). B_{12} (calc.) is obtained by assuming that the force constants in the Lennard-Jones 6 : 12 potential function are given by $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$ and $\epsilon_{12} = (\epsilon_1\epsilon_2)^{\frac{1}{2}}$. The experimental results agree with the theoretical to within experimental error.

TABLE 1.—VIRIAL COEFFICIENT OF PURE CARBON DIOXIDE

t° C	B (cm³ mole⁻¹)	mean B	literature B [7]	Δ
30	− 122·4			
	− 113·7	− 116·4	− 119·3	+ 2·9
	− 117·6			
	− 111·9			
60	− 99·7			
	− 98·6	− 96·9	− 95·5	− 1·4
	− 92·4			

TABLE 2.—CARBON DIOXIDE + HELIUM MIXTURES, $x_1 = x_2 = 0{\cdot}5$

t° C	B_M (cm³ mole⁻¹)	$B(CO_2)$[7]	B(He)[11]	B_{12} (expt.)	B_{12} (calc.)[a]	B_{12} (calc.)[b]
30	− 16·1 ± 1·7	− 119·3	11·7	21·6 ± 3·4	25·0	21·5
60	− 8·7 ± 1·5	− 95·5	11·5	24·6 ± 3·0	26·0	22·9
90	− 5·3 ± 3·4	− 77·8	11·4	22·6 ± 6·8	26·8	24·3

(*a*) using the force constants given by Hirschfelder,[1]

(*b*) using the force constants quoted by Lunbeck and Boerboom.[12]

The only comparable figure in the literature is that obtained at higher pressure at 30° C by Pfefferle, Goff and Miller [13] for B_M for a mixture containing 50·5 % helium, − 16·2 cm³ mole⁻¹, which agrees excellently with our own value of − 16·1 for the 50 % mixture. It may be concluded that the present apparatus is capable of producing results of the accuracy claimed, and that mixtures of carbon dioxide and helium behave in the region 30-90°C as if their interaction were governed by forces calculated from the empirical combining rules.

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(14)

THE SECOND VIRIAL COEFFICIENT OF GASES AND MIXTURES

PART 2.—MIXTURES OF CARBON DIOXIDE WITH NITROGEN, OXYGEN, CARBON MONOXIDE, ARGON AND HYDROGEN

THE SECOND VIRIAL COEFFICIENTS OF GASES AND MIXTURES

PART 2.—MIXTURES OF CARBON DIOXIDE WITH NITROGEN, OXYGEN, CARBON MONOXIDE, ARGON AND HYDROGEN

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The second virial coefficients of equimolecular mixtures of carbon dioxide with nitrogen, oxygen, carbon monoxide, argon and hydrogen have been measured at 30°, 60° and 90° C. For all these mixtures the derived values of the interaction virial coefficient B_{12} are not very different from those calculated using the empirical combining laws for the force constants in the Lennard-Jones potential, but are appreciably less dependent on temperature.

In calculating the coefficients of interaction between mixtures of non-polar gases, empirical combining laws are used to relate the force constants between unlike molecules to those between like molecules.

$$\sigma_{12} = \tfrac{1}{2}(\sigma_{11} + \sigma_{22}), \tag{1}$$

$$\epsilon_{12} = \epsilon_{11}^{\frac{1}{2}}\epsilon_{22}^{\frac{1}{2}}, \tag{2}$$

where σ and ϵ are the constants in the Lennard-Jones potential function $V = 4\epsilon\{(\sigma/r)^{12} - (\sigma/r)^6\}$ and the subscripts 11 and 22 refer to the pure components, and 12 to the mixture.

There is little experimental evidence of the reliability of these combining laws over a range of temperature. In part 1 [1] an apparatus was described for the measurement of virial coefficients for equimolecular mixtures of carbon dioxide and helium at 30°, 60° and 90° C, the experimental values agreeing with the theoretical values to within experimental error. In the present paper, measurements are reported for mixtures of carbon dioxide with nitrogen, oxygen, carbon monoxide, argon and hydrogen over the same range of temperature.

EXPERIMENTAL

Apparatus and procedure.—The apparatus and procedure were identical with those previously described [1] except for modifications to the mercury manometer. Since it was never necessary to measure pressures less than 10 cm Hg, it was possible to construct the manometer in such a way that the two limbs were co-linear. The limbs were made from Veridia 2 cm diameter precision tubing. A steel scale, graduated in 0·5 mm and calibrated by the N.P.L. was placed along one side of the manometer. The position of the meniscus relative to the scale was measured by interpolation with the micrometer adjustment on the cathetometer. The manometer and scale assembly were adjusted accurately to the vertical and immersed in a silicone oil bath with a plate glass front. The oil was stirred and the temperature was controlled manually by adjusting the current through a small electric bulb placed at the bottom of the bath.

Preparation of gases and mixtures.—The mixtures were prepared and analysed in the way previously described.[1]

Nitrogen was drawn from a cylinder of oxygen-free nitrogen stated to be > 99·5 % nitrogen. It was passed over phosphoric acid and through two liquid-nitrogen traps. Oxygen from a cylinder (> 99·5 % oxygen) was dried over phosphoric acid and distilled several times in liquid nitrogen traps.

Argon (> 99·5 %) was also dried over phosphoric acid and distilled in liquid nitrogen traps.

Carbon monoxide was prepared by the action of concentrated sulphuric acid on formic acid. The gas was passed through sodium hydroxide solution, through concentrated sulphuric acid, over phosphoric acid and through two liquid-nitrogen traps.

Hydrogen was prepared by the action of dilute sulphuric acid on pure arsenic-free zinc, passed through potassium hydroxide, through concentrated sulphuric acid, over phosphoric acid and through two liquid-nitrogen traps.

CALCULATION OF RESULTS

Values of B_M, the second virial coefficient of the mixture, and B_{12}, the interaction coefficient, were derived as described in part 1 [1] from the experimental results. The values of B_{11} and B_{22} required to obtain B_{12} were calculated from the Lennard-Jones potential using the force constants in table 1.[2] The notation and methods used are those given by Hirschfelder, Curtiss and Bird.[2]

TABLE 1

	CO_2	O_2	N_2	CO	A	H_2
ϵ/k	189	118	95·1	100·2	119·8	37·0
σ	4·49	3·46	3·70	3·76	3·405	2·928

RESULTS

Table 2 gives the experimental values of virial coefficients for some of the pure gases. These are normally the mean of at least six measurements, the limits quoted being the 95 % probability limits equal to $2\left\{\frac{(x-\bar{x})^2}{n(n-1)}\right\}^{\frac{1}{2}}$. Comparison with the values calculated from the force constants given in table 1 is also made. The agreement is always within the 95 % probability limit, and the average deviation from the calculated values is less than 2 cm³/mole. These measurements were interspersed with the measurements on the mixtures, and serve as a check on the accuracy of the experimental method.

TABLE 2.—$B(T)$ FOR PURE GASES

	CO_2		O_2		A		H_2	
	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
30°	− 116·4 ± 4·6	− 119·2	− 16·6 ± 5·1	− 14·7	− 13·2 ± 1·8	− 14·9	+ 14·1 ± 1·7	+ 13·8
60°	− 96·7 ± 4·6	− 97·1	− 7·3 ± 2·0	− 9·3	− 9·3 ± 1·3	− 9·7		
90°	− 75·9 ± 4·0	− 79·6	− 2·5 ± 2·3	− 4·9	− 4·3 ± 2·2	− 5·3		

The experimental results of B_M and the B_{12} values derived from them are given in table 3. They are compared with B_{12} values obtained using the force constants given in table 4.

TABLE 3.—B_M AND B_{12} VALUES FOR MIXTURES $x_1 = x_2 = 0{\cdot}5$

mixture	temp. °C	B_{11}	B_{22}	B_M	expt. B_{12}	calc. B_{12}
$CO_2 + O_2$	30	− 119·2	− 14·7	− 52·0 ± 2·6	− 36·8 ± 5·2	− 48·2
	60	− 97·1	− 9·3	− 40·8 ± 2·8	− 28·4 ± 5·6	− 36·8
	90	− 79·6	− 4·9	− 33·9 ± 2·2	− 25·6 ± 4·4	− 27·5
$CO_2 + N_2$	30	− 119·2	− 4·0	− 51·5 ± 3·1	− 41·4 ± 6·2	− 38·4
	60	− 97·1	+ 1·2	− 42·0 ± 2·0	− 36·0 ± 4·0	− 27·7
	90	− 79·6	+ 5·4	− 32·8 ± 1·8	− 28·5 ± 3·6	− 19·2
$CO_2 + CO$	30	− 119·2	− 7·3	− 49·4 ± 2·3	− 34·6 ± 4·6	− 42·5
	60	− 97·1	− 1·6	− 43·0 ± 2·0	− 36·6 ± 4·0	− 31·0
	90	− 79·6	+ 3·0	− 32·0 ± 3·0	− 25·7 ± 6·0	− 22·1
$CO_2 + A$	30	− 119·2	− 14·9	− 49·4 ± 2·3	− 31·8 ± 4·6	− 48·1
	60	− 97·1	− 9·7	− 39·6 ± 2·1	− 25·8 ± 4·2	− 36·6
	90	− 79·6	− 5·3	− 31·0 ± 2·1	− 19·6 ± 4·2	− 27·7
$CO_2 + H_2$	30	− 119·2	+ 13·8	− 26·9 ± 1·9	− 1·0 ± 3·8	+ 3·0
	60	− 97·1	+ 13·9	− 20·6 ± 2·2	+ 0·4 ± 4·4	+ 7·4
	90	− 79·6	+ 14·4	− 16·4 ± 1·6	0·0 ± 3·2	+ 10·8

DISCUSSION

Of the mixtures which have been examined, only values of B_{12} at 30° C for $CO_2 + O_2$, $CO_2 + N_2$ and $CO_2 + H_2$ have been obtained previously. Gorski and Miller [3] obtained values of $-40{\cdot}1$ cm^3 mole^{-1} for $CO_2 + O_2$ and $-39{\cdot}7$ cm^3 mole^{-1} for $CO_2 + N_2$ with both of which our results are in agreement. These values have been recalculated from their experimental results using the same values of B for the pure gases as adopted here.[2] Our value of $-1{\cdot}0$ cm^3 mole^{-1} for $CO_2 + H_2$ at 30° C is in excellent agreement with $-1{\cdot}1$ cm^3 mole^{-1} at 25° C obtained by Michels and Boerboom and quoted by Lunbeck and Boerboom.[4]

TABLE 4.—FORCE CONSTANTS FOR MIXTURES

	ϵ_{12}/k	σ_{12}
$CO_2 + O_2$	149·4	3·975
$CO_2 + N_2$	134·1	4·095
$CO_2 + CO$	137·6	4·125
$CO_2 + A$	150·5	3·948
$CO_2 + H_2$	83·41	3·709

In obtaining the values of B_{12} from the experimental B_M figures, the calculated values of B_{11} and B_{22} were used. This means that the error limits indicated for B_{12} in table 3 are errors arising in the measurement of B_M and do not take into account any errors in B_{11} or B_{22}.

The results show systematic divergences between experimental and calculated values of B_{12}. In all cases the calculated temperature dependence is greater than the observed. The result for helium previously obtained [1] did not show this effect but the temperature dependence of B_{12} calculated for helium is very much less than for the other gases.

From these results it would appear that the empirical combining rules used to obtain the force constants are not fully adequate for the mixtures and temperature range which have been examined.

[1] Cottrell and Hamilton, *Trans. Faraday Soc.*, 1956, **52**, 156.
[2] Hirschfelder, Curtiss and Bird, *Molecular theory of gases and liquids* (New York, 1954).
[3] Gorski and Miller, *J. Amer. Chem. Soc.*, 1953, **75**, 550.
[4] Lunbeck and Boerboom, *Physics*, 1951, **17**, 76.

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THE THERMAL DECOMPOSITION OF NITROMETHANE

THE THERMAL DECOMPOSITION OF NITROMETHANE

By T. L. Cottrell, T. E. Graham and T. J. Reid

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The thermal decomposition of nitromethane has been studied by a static method over the range 380-430° C, and shown to be a homogeneous reaction, of approximately first order at pressures between 200 and 400 mm., with a rate constant given by

$$k = 10^{14.6} \exp(-53{,}600/RT) \text{ sec.}^{-1}.$$

The main products are nitric oxide, methane, carbon monoxide and water, with some carbon dioxide, and small quantities of ethane, ethylene and nitrous oxide. The initial step is considered to be

$$CH_3NO_2 \rightarrow CH_3 + NO_2,$$

followed by a non-chain radical mechanism. The dissociation energy of the C—N bond in nitromethane is thus estimated to be 53 kcal.

By analogy with the behaviour on thermal decomposition of organic nitrates [1, 2, 3] it was thought that a study of the thermal decomposition of the nitroparaffins might give information about the C—N bond strength in these compounds. Preliminary experiments on nitromethane suggested that this view might be correct,[4] and the present paper reports the detailed investigation of the reaction. The only previous kinetic work is that of Taylor and Vesselovsky [5] who studied the thermal decomposition at pressures mainly below 200 mm. over the range 390-420° C. They concluded that the reaction was homogeneous and first order with an activation energy of 61 kcal./mole, and postulated the primary step

$$CH_3NO_2 \rightarrow CH_3NO + O,$$

but did not offer any direct evidence for it. This step does not appear likely on energetic grounds. Moreover, although the reaction was stated to be first order, rate constants calculated from their published values of quarter and half-lives for the reaction show a significant decrease in going from the quarter to the half-life. These considerations suggested that the reaction might well be reinvestigated.

Experimental

Materials.—The nitromethane used in most of the work was obtained from vapour-phase nitration of paraffins, and purified by fractional distillation. Samples of nitromethane prepared by other methods gave the same kinetics. Comparison with the infra-red spectrum of liquid nitromethane given by Smith, Pan and Nielsen [6] was used as a check on purity.

Apparatus.—The apparatus which was constructed throughout of Pyrex glass, was of the usual type for kinetic measurements by the static method. The reaction vessel, 2 in. diam. and of 200 cm.^{3} capacity, was connected by 1·5 mm. capillary tubing to a mercury manometer, and through a three-way tap to a conventional gas line and to a reservoir, trap and Toepler pump for removal of the products for analysis. The capillary tubing was heated with Nichrome wire to prevent condensation, and hot taps were lubricated with Silicone grease.

[1] Appin, Chariton and Todes, *Acta Physicochim.*, 1936, **5**, 655.
[2] Phillips, *Nature*, 1950, **165**, 564.
[3] Adams and Bawn, *Trans. Faraday Soc.*, 1949, **45**, 494.
[4] Cottrell and Reid, *J. Chem. Physics*, 1950, **18**, 1306.
[5] Taylor and Vesselovsky, *J. Physic. Chem.*, 1935, **39**, 1095.
[6] Smith, Pan and Nielsen, *J. Chem. Physics*, 1950, **18**, 706.

The reaction vessel was heated by a horizontal electric furnace, with the winding adjusted to give a constant temperature over a 6-in. range in the middle of the furnace. The temperature was controlled to $\pm 0{\cdot}4°$ C by a Kent temperature recording controller, using the E.M.F. of a chromel-alumel thermocouple whose hot junction was inserted in a pocket in the reaction vessel. Another chromel-alumel couple was arranged with one junction in a pocket in the middle of the vessel and the other at the end, to check temperature uniformity differentially. The couples were standardized at the freezing-points of zinc and tin Because the E.M.F. at a given temperature changed slowly with time frequent restandardizations were carried out.

The nitromethane was freed from dissolved gases by repeated freezing and evaporation in a trap attached near the reaction vessel, into which it was distilled when required. A pressure of 300 mm. could be admitted in 5 sec.

Results

Products.—The infra-red spectrum of the gaseous products at various stages of reaction was examined from 3 to 15μ using a double-beam recording infra-red spectrometer constructed in this Department.[7] The following absorption bands were observed in the products from runs at 414° C. The "cell-band" was

ν (cm.$^{-1}$)	Intensity	Identification
668	medium	CO_2
720	"	CO_2
800, 821	"	C_2H_6
850	v. weak	allene ?
949	weak	C_2H_4
976, 992	weak	?
1285	medium	N_2O
1306	v. strong	CH_4
1340-1380	v. strong	"cell band" ($NaNO_3$) + CH_3NO_2
1580	strong	CH_3NO_2
1906, 1960	medium	NO
2180	medium	CO
2224	strong	N_2O
2349	medium	CO_2
2560	v. weak	?
~3000	medium	CH stretchings

identified as due to sodium nitrate, formed by attack on the rock-salt windows of the cell by nitrogen dioxide, which was present in small quantity.[8] These results were obtained with a pressure of 1 atm. in a 10 cm. cell to ensure absorption from constituents present in low concentration. The complexity of the mixture and the probable effects of pressure broadening did not favour use of the infra-red absorption spectrum for quantitative analysis, but approximate indications of the quantities present were obtained. For a number of runs at 410° C stopped after pressure increases of between 20 % and 60 %, the products included $CH_4 \sim 20$ %, $N_2O \sim 3$-4 %, $C_2H_4 \sim 1$ %, $C_2H_6 \sim 1$-2 %.

The products gaseous at $-78°$ C were analyzed by conventional chemical methods in a Bone and Wheeler apparatus as follows: CO_2 by absorption in 20 % aqueous potassium hydroxide, NO in saturated acidic ferrous sulphate solution, CO and C_2H_4 in freshly prepared ammoniacal cuprous chloride solution. The remainder was combusted with excess oxygen and the resulting CO_2 absorbed. The latter was not equivalent to the decrease in volume on combustion, the difference being taken at first to be H_2. However, the values for CH_4 obtained in this way were rather lower than those obtained by mass-spectrometer and infra-red spectrometer, and it is known that if methane only is present it is more

[7] Brimley, McAuslan, Price and Tetlow, to be published.
[8] Cp. Epshtein, Chirkova and Papulova, quoted by Pollard and Wyatt.[9]
[9] Pollard and Wyatt, *Trans. Faraday Soc.*, 1949, **45**, 760.

reliable to determine it from the combined value of the decrease in volume on combustion and the CO_2 produced.[10] The results obtained thus, assuming no hydrogen, were in good agreement with those obtained by the mass-spectrometer, but it is still possible that a small quantity of hydrogen was present. In the analysis of runs where the amount of reaction was small, the combustion was omitted. The results of analyses of products volatile at $-78°$ C from runs carried out with various initial pressures of nitromethane and at various temperatures are shown in Fig. 1. These establish that essentially the same reaction is under investigation throughout the pressure and temperature range studied. In Fig. 1 are also shown the results of a few analyses carried out using a mass spectrometer, for which we are indebted to Mr. D. L. Nicholson of Billingham Division of I.C.I. Ltd.

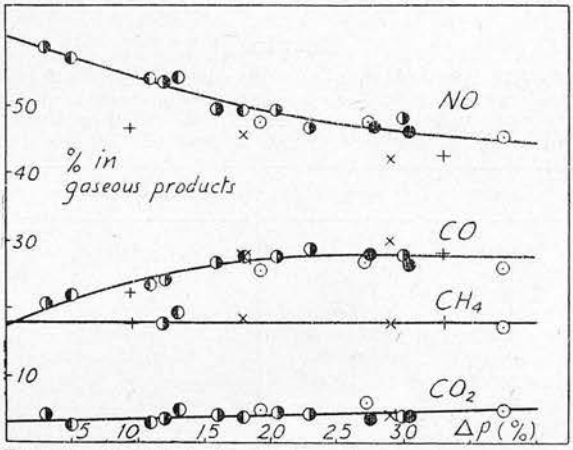

FIG. 1.—Plot of composition of products against percentage pressure change.
◑ 380° C, 400 mm. CH_3NO_2. ◐ 420° C, 400 mm. CH_3NO_2.
○ 380° C, 230 ,, ● 420° C, 230 ,,
× 410° C, 300 mm., chemical.
+ 410° C, 300 mm., mass spectrometer.

The main contents of the trap at $-78°$ C were water and nitromethane. Water was determined by the Karl Fischer method, and found to be approximately equivalent to the oxygen deficiency in the permanent gases. No cyanide or ammonia could be detected when the products were absorbed in water, although a faint smell of hydrocyanic acid was occasionally detected. The presence of small amounts of nitrogen dioxide was detected by the attack on rock-salt previously mentioned, and by liberation of iodine from potassium iodide solution from which air had been removed by repeated freezing and pumping. This was done to avoid formation of nitrogen dioxide from the nitric oxide known to be present. A small quantity of dark-coloured residue was formed in the reaction vessel and in the tubing leading to it, but no analysis of this was attempted.

It is obvious from Fig. 1 that various reactions take place among the products, and that the decomposition of nitromethane itself is best studied from the initial rate of reaction. The initial products were therefore obtained by extrapolation of the curves in Fig. 1, assuming that NO is the only nitrogen-containing product at zero time. The extrapolation is subject to considerable uncertainty, and the following figures for initial volatile products are clearly only semi-quantitative :

Product	*Mole per mole* CH_3NO_2
NO	1·00
CO	0·31
CO_2	0·04
CH_4	0·32
H_2O	0·61
	2·28

[10] Cp. Shepherd, *Anal. Chem.*, 1950, **22**, 881.

The hydrocarbon fraction probably contains some ethane. The remainder unaccounted for is nearly of the formula $(C_nH_{2n})_x$ and presumably consists of polymeric hydrocarbons and carbon, possibly with some polymerized formaldehyde. This would explain the dark-coloured material deposited in the apparatus. The number of moles of gaseous products per mole CH_3NO_2 calculated from analysis at various stages of the reaction varied between 2·3 and 2·4, and the overall pressure increase, 130 %, corresponds to 2·3.

Kinetics.—The rate at zero time was obtained by drawing a tangent at $t = 0$ to the experimental pressure time curve. Since the analytical results showed that a pressure increase of about 130 % is to be expected for the initial reaction, the first order rate constant was obtained by

$$k = \frac{(dp/dt)_{t=0}}{1{\cdot}3\, p_0},$$

where p_0 is the initial pressure of nitromethane. It was found that the first one or two runs after the apparatus had been exposed to the air were erratic, but reproducible results to about ± 10 % were obtained afterwards. That the reaction was first order was shown by plotting k as obtained above against p_0 over the range $p_0 = 40$ to 400 mm. The results for 410·4° C are plotted in Fig. 2, which shows that the reaction is of the first order at pressures over 200 mm. At the lowest temperature studied, there was a slight upward drift in k with increasing pressure.

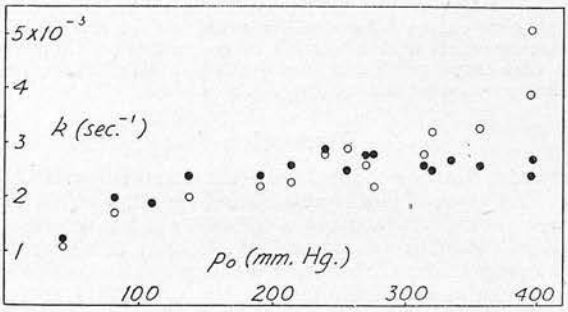

FIG. 2.—Plot of k against p_0 (mm.).

● Initial slope k. ○ Guggenheim k.

The reaction was carried out in a vessel to which broken Pyrex capillary tubing was added ; the rate was increased and the form of the pressure-time curve changed showing a smaller increase and a maximum. This phenomenon was also noticed by Taylor and Vesselovsky.[5] However, when the ends of the capillary tubing were fire polished, addition of Pyrex capillary to increase the surface volume ratio by a factor of 12 had no effect.

Addition of NO had little effect on the reaction. A very slight inhibition may have been due to a minor alteration of products.

A plot of $\log_{10} k$ against $1/T$, shown in Fig. 3, was fitted to a straight line by the method of least squares, giving

$$k = 10^{14{\cdot}6} \exp\,(-\,53{,}600/RT)\ \text{sec.}^{-1}.$$

The results of 85 runs were used, but in Fig. 3 the k's for runs at the same temperature have been averaged. The standard deviation of an individual determination of $\log_{10} k$ is 0·056, or about ± 14 %. Because of the large number of runs considered, the standard deviation of the activation energy is only ± 900 cal. This of course refers only to random error. Because of the many uncertainties introduced by the complexity of the reaction, the activation energy of the main reaction cannot be said to be known so accurately as this, nor is it possible to give a satisfactory estimate of the error. Values of k calculated from the quarter lives quoted by Taylor and Vesselovsky [5] are given for comparison. The results do not differ greatly, and the difference is because the pressures used by these workers were in general lower than those used by us. In their run at 390° C, however, a pressure of 307 mm. was used, and their result is in close agreement with ours.

The importance of using initial rates, as done here, to avoid complications has been stressed by Letort,[11] and the analytical results obtained for nitromethane showed that it is necessary. However, it was noticed that individual

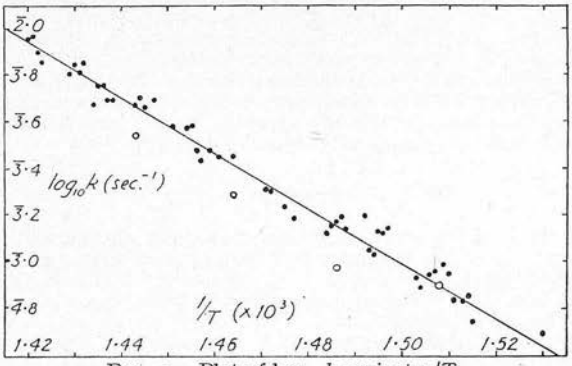

FIG. 3.—Plot of $\log_{10} k$ against $1/T$.
● This research. ○ Taylor and Vesselovsky.[5]

overall pressure-time curves follow the first-order law for much of their length. First-order rate constants were calculated by the method of Guggenheim [12] and it was found that they agreed fairly well with the initial slope rate constants but were rather pressure dependent (see Fig. 2).

Discussion

The first-order kinetics coupled with the complexity of the products and the fact that the reaction is uninhibited by nitric oxide suggest that the reaction is probably a non-chain radical reaction with a slow initial split into radicals which is rate controlling. Before detailing the mechanism which we propose for the reaction we may show that the initial step proposed by Taylor and Vesselovsky,[5]

$$CH_3NO_2 \rightarrow CH_3NO + O,$$

is unlikely on energetic grounds. The heat of formation, ΔH_f (g, 298·1° K) of nitromethane is − 12·2 kcal.,[13] and that of atomic oxygen in the lowest state is 59·1 kcal.[14] The heat of formation of CH_3NO is not known, but it is certainly greater than that of formaldoxime, to which it has been supposed to isomerize readily. ΔH_f(g, 298·1° K) for formaldoxime may be estimated as $\sim$ 2 kcal., on the assumption that the heat change in the isomerization of formamide to formaldoxime is the same as that of the isomerization of acetamide to acetaldoxime. The heats of formation of these substances are known,[15] and their latent heat of vaporization may be estimated from Trouton's rule. Thus $\Delta H°$ (298·1°) for the reaction postulated by Taylor and Vesselovsky is greater than, and probably much greater than 73 kcal., which effectively rules it out.

The initial step which seems most likely energetically is

$$CH_3NO_2 \rightarrow CH_3 + NO_2. \quad . \quad . \quad . \quad . \quad (1)$$

$\Delta H°$ (298·1°) for this reaction is 52·3 kcal., obtained by taking the heat of formation of CH_3 as 32·0 kcal., and that of NO_2 as 8·1 kcal.[14] Comparison of a heat of reaction at 25° C with an activation energy obtained

[11] Letort, *Bull. Soc. Chim.*, 1942, **9**, 1.
[12] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.
[13] Holcomb and Dorsey, *Ind. Eng. Chem.*, 1949, **41**, 2788.
[14] *Selected Values of Chemical Thermodynamic Properties* (National Bureau of Standards, 1948).
[15] Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Rheinhold, New York, 1936).

at 400° C involves the assumption that the heat of reaction does not change much with temperature. For a reaction of this type the uncertainty is unlikely to be more than 1-2 kcal. The observed activation energy of the reaction may be expected to be equal to this provided that: (i) the activation energy for recombination is zero, (ii) all subsequent reactions are fast compared with the initial step. The assumption of zero activation energy for radical recombination is commonly made, and generally leads to consistent results. In particular, since we are dealing with a reaction producing NO_2, it is of interest to note that the activation energy for the dissociation of N_2O_4 to $2NO_2$ is very nearly the same as the heat of reaction.[16] Before condition (ii) can be said to hold it is necessary to outline the probable subsequent reactions, and to estimate their velocity.

The complexity of the products is such that a complete kinetic analysis is not possible. Nevertheless the following reactions are probably important:

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \quad . \quad . \quad . \quad . \quad (1)$$

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 \quad . \quad . \quad . \quad (2)$$

$$CH_2NO_2 + NO_2 \rightarrow CH_2O + NO + NO_2 \quad . \quad . \quad (3)$$

$$CH_2O + NO_2 \rightarrow CO + NO + H_2O \text{ etc.} \quad . \quad . \quad (4)$$

and

$$CH_3 + CH_3 \rightarrow C_2H_6 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

must take place to some extent. We require to estimate the rates of these reactions. Reaction (2) is analogous to a number of methane-forming reactions, which have an activation energy of 8-10 kcal.[17] The reaction

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$$

has recently been studied by Trotman-Dickenson and Steacie[18] who obtained $E = 9{\cdot}7$ kcal., assuming $E_5 = 0$. They also found that the ratio of the steric factor of the methane-forming reaction to the square root of that of (5) is 10^{-3}. Recent work by Gomer[19] has shown k_5 to be 7×10^{10} (mole/l.)$^{-1}$ sec.$^{-1}$ at 175° C., and Lucas and Rice[20] using a different technique obtained 6×10^{10} at 200° C. These results show that the steric factor of this reaction does not differ greatly from unity, a conclusion which has recently been reached independently by Szwarc and Roberts.[21] Thus we may estimate

$$k_2 \simeq 10^{-3}Z \exp(-9{,}000/RT) \simeq 5 \times 10^5 \text{ (mole/l.)}^{-1} \text{ sec.}^{-1} \text{ at } 700° \text{ K.}$$

If reactions (1)-(4) are the only ones which occur, $[CH_3] = k_1/k_2 \simeq 10^{-8}$ mole/l. Thus, if $[CH_3NO_2] = 8 \times 10^{-3}$ mole/l., $d[CH_4]/dt \simeq 4 \times 10^{-5}$ (mole/l.) sec.$^{-1}$. In this it has been assumed that ethane production by (5) is small compared with (2). We can test this assumption by obtaining $d[C_2H_6]/dt$ by (5) when $[CH_3] = 10^{-8}$ mole/l. If $k_5 = 10^{11}$, $d[C_2H_6]/dt = 10^{-5}$ (mole/l.) sec.$^{-1}$, or a quarter of the rate of methane production, in reasonable agreement with hypothesis and with experiment. The amount of ethane found is, however, not necessarily an indication of the rate of ethane production, because ethane may be oxidized at this temperature, or may react with nitrogen dioxide to give nitroethane, which decomposes unimolecularly to give ethylene, nitric oxide and oxidation products.[22] There is no independent evidence for reaction (3), but it is likely to be very exothermic. It may also take place as

$$CH_2NO_2 \rightarrow CH_2O + NO_2 \quad . \quad . \quad . \quad (3a)$$

which involves rather more rearrangement of the CH_2NO_2 molecule than

[16] Richards and Reid, *J. Chem. Physics*, 1933, **1**, 114.
[17] Steacie, *Atomic and Free Radical Reactions* (Reinhold, New York, 1946).
[18] Trotman-Dickenson and Steacie, *J. Chem. Physics*, 1950, **18**, 1097.
[19] Gomer, *ibid.*, 1950, **18**, 998.
[20] Lucas and Rice, *ibid.*, 1950, **18**, 993.
[21] Szwarc and Roberts, *Trans. Faraday Soc.*, 1950, **46**, 625.
[22] Cottrell, Graham and Reid, *ibid.* (in press).

(3), provided (3) is assumed to take place via an activated complex of the form O—N . . . O . . . CH_2 . . . NO_2. On the other hand this reaction probably has rather a low steric factor. The precise form of (3) is not material to the argument. Reaction (4) has been studied by Pollard and Wyatt.[9] The reaction is complex and the mechanism appears to change with temperature. It becomes explosive in the region of 180° C, and extrapolation of their value for k at temperatures above 160° C might be expected to give a lower limit for k_4. Thus $k_4 > 10^3$ (mole/l.)$^{-1}$ sec.$^{-1}$ at 700° K. We have

$$[NO_2][CH_2O] = \frac{k_1}{k_4}[CH_3NO_2].$$

Assuming

$$[CH_2O] = [NO_2] \text{ and } [CH_3NO_2] = 8 \times 10^{-3} \text{ mole/l.}$$
$$[NO_2] < 2{\cdot}5 \times 10^{-2}\,[CH_3NO_2],$$

in reasonable agreement with experiment. Reaction (4) is faster than other possible reactions[9] involving NO_2. Reactions (2)-(4) are clearly much faster than (1).

The scheme suggested is clearly a considerable oversimplification. Even reaction (4) is not an accurate description of the formaldehyde reaction. In particular, the scheme requires that 0·5 mole CH_4 and 0·5 mole CO should be produced, whereas in fact only about 0·3 of each are found, and apart from small amounts of ethane and carbon dioxide, probably formed by (5) and a variation of (4), the carbon unaccounted for is in the form of polymeric material and carbon. The polymerization of ethylene is known to be sensitized by methyl and methylene radicals,[17] and ethylene might be produced from ethane as suggested above, or from methylene radicals, possibly produced by

$$CH_3 + CH_3 \rightarrow CH_4 + CH_2. \qquad (6)$$

This may be a surface reaction, and it is noteworthy that when the surface is increased with broken glass the increase in pressure is reduced and followed by a decrease, suggesting that polymerization is taking place. The radical-sensitized polymerization is inhibited [17] by NO, the concentration of which increases as the reaction proceeds, which explains the increasing proportion of carbon found in the permanent gas fraction as the reaction proceeds.

A further possibility is the reaction

$$CH_3 + NO \rightarrow ? \qquad (7)$$

which will probably take place to some extent as the NO concentration rises. It is not of importance at the beginning of the reaction, because NO appears to be produced quantitatively, but Fig. 1 shows that the proportion of NO drops as the reaction proceeds, perhaps by this step. The thermal decomposition of the alkyl nitrites [17] is another example of a radical reaction producing NO which does not appear to play a major part in the reaction.

The main result which emerges from this discussion is that the measured activation energy is likely to be that of (1). Thus the dissociation energy of the C—N bond in nitromethane is about 53 kcal.

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THE THERMAL DECOMPOSITION OF NITROETHANE AND 1-NITROPROPANE.

By T. L. Cottrell, T. E. Graham and T. J. Reid

Received 6th February, 1951

The thermal decomposition of nitroethane has been studied by a static method over the temperature range 355-405° C, and shown to be a largely homogeneous reaction of the first order in the pressure range 50-300 mm. Under the conditions used, the extent of heterogeneous reaction was estimated to be about 10 %, with the consequence that the estimated equation for the rate constant of the homogeneous reaction, $k = 10^{13\cdot0}\, e^{-47,000/RT}$ sec.$^{-1}$, is subject to an uncertainty which is not easy to estimate. The activation energy is, however, unlikely to be in error by more than 2 kcal. The main gaseous products are ethylene and nitric oxide, with some oxides of carbon. 1-Nitropropane, which was studied in less detail, has an activation energy of about 50 kcal., and the products include propylene. The mechanism is considered to be a unimolecular reaction to give the olefin and HNO_2, followed by oxidation of some of the olefin.

It has been shown [1] that the thermal decomposition of nitromethane probably takes place by C—N bond fission, followed by fast non-chain reactions. It was thought that studies of the thermal decomposition of higher nitroparaffins might be of interest in determining the C—N bond strength in these compounds, and nitroethane and 1-nitropropane were examined. At a fairly early stage in the work, however, evidence was obtained which suggested that this mechanism was not involved, and that these compounds decomposed unimolecularly, by way of an intramolecular rearrangement. The study was therefore not so detailed as the earlier one of nitromethane.

Experimental

Materials.—The compounds were purified by fractional distillation. Comparison of their spectra with the infra-red spectra of liquid nitroethane and 1-nitropropane given by Smith, Pan and Nielsen [2] was used as a check on purity.

Apparatus.—The apparatus, with Pyrex reaction vessel, was as described previously.

Results

Nitroethane.—The reaction was followed by pressure measurement, the overall increase being about 155 % of the initial pressure. First-order rate constants were obtained by the Guggenheim [3] method. The initial slope of the pressure-time curve divided by the initial pressure should give the rate constant multiplied by the ratio of the overall increase to initial pressure, if the reaction is the same throughout. This ratio, obtained in this way from initial slopes, averaged 1·53 over 44 runs, although there was a certain amount of variation from run to run. That the reaction was first order over the pressure range considered is shown by the table of rate constants (Table I), obtained by the Guggenheim method, against initial pressure.

A plot of $\log_{10} k$ against $1/T$ gave a good straight line, shown in Fig. 1. The points shown are averages of several runs at the same temperature, 44 runs in

[1] Cottrell, Graham and Reid, *Trans. Faraday Soc.* (in press).
[2] Smith, Pan and Nielsen, *J. Chem. Physics*, 1950, **18** 706.
[3] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

all being used. These results were fitted to the line by the method of least squares, giving the equation

$$\log_{10} k = -\frac{9{\cdot}995}{T \times 10^{-3}} + 12{\cdot}695.$$

The effect of surface was examined by carrying out the reaction in a vessel containing fire-polished capillary tubing to increase the surface/volume ratio to 12·2 times its previous value. The results were not very reproducible, the reaction being accelerated by a variable amount. The pressure increase was

TABLE I

403·3° C		380·0° C	
p_0 (mm.)	k (sec.$^{-1}$)	p_0 (mm.)	k (sec.$^{-1}$)
30	$8{\cdot}0 \times 10^{-3}$	129	$2{\cdot}3 \times 10^{-3}$
46	8·1	153	2·5
104	9·1	171	2·5
173	8·0	172	2·7
174	8·0	205	2·4
189	9·4	262	2·5
250	8·5	283	2·3
280	9·0	317	2·3
		331	2·4

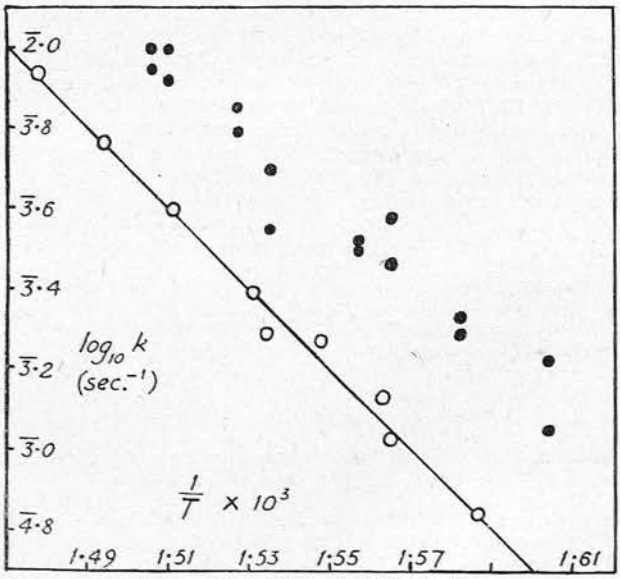


FIG. 1.—Plot of $\log_{10} k$ against $1/T$.
○ Unpacked vessel. ● Packed vessel.

reduced, and the reaction order appeared to be less than unity, although the lack of reproducibility made it difficult to be certain of this. This was not obvious from any individual run, most of which gave reasonably good Guggenheim plots, but the rate constants so obtained showed a slight tendency to decrease with increasing pressure. The results are plotted in Fig. 1. It will be noticed that the surface process appears to be more prominent at lower

temperatures; a rough estimate of an increase in rate by a factor of 2 at the higher temperatures, and a factor of 3 at the lower seems reasonable. Taking into account the factor of 12 for increase in surface, the equation describing the homogeneous reaction is estimated to be

$$k = 10^{13.0}\ e^{-47,000/RT}\ \text{sec.}^{-1}.$$

If the increase at the higher temperatures is by a factor of 2, and that at the lower is as great as by a factor of 4 (and inspection of the Fig. 1 shows that it is unlikely to be greater than this) the activation energy would be increased to 49 kcal./mole. Thus 47 ± 2 kcal./mole is a reasonable estimate of the activation energy. Addition of nitric oxide has no effect on the reaction rate.

The spectrum of the products from the reaction was examined from 3-15 μ in a double-beam recording infra-red spectrometer. The most intense bands were those due to ethylene, which was the main absorbing constituent in the mixture, and others were identified as being due to nitric oxide and carbon dioxide. Other constituents, such as methane, nitrous oxide, and carbon monoxide, were possibly present in small amount. One or two chemical analyses were carried out by methods described earlier.[1] Approximately 8 % CO_2, 45 % NO, and 36 % C_2H_4 (+ CO) were obtained from runs stopped after different pressure increases. The remainder was not analyzed.

Nitropropane.—The decomposition of nitropropane was not studied in detail. The reaction was followed by pressure measurement, the ratio of initial slope divided by initial pressure to rate constant being about 1·8 in reasonably good agreement with the pressure increase. As for nitroethane, the reaction was first order over the pressure range studied, as shown in the accompanying Table by the results of runs at 388·0° C.

$\text{Log}_{10}\ k$ plotted against $1/T$ gave a good straight line, which had the equation

$$\log_{10} k = \frac{-10{\cdot}84}{T \times 10^{-3}} + 12{\cdot}97,$$

fitted by least squares to the results of 32 runs, corresponding to an activation energy of 49·6 kcal.

The infra-red spectrum of the products was similar to that of the products from nitroethane, with the replacement of ethylene by propylene. No further work on this reaction was carried out.

p_0 (mm.)	k (sec.$^{-1}$)
82	$3{\cdot}8 \times 10^{-3}$
103	3·9
170	4·0
199	4·1
244	4·4
292	4·1

Discussion

From the experimental results it is seen that the thermal decomposition of nitroethane is a largely homogeneous reaction, first order over a fairly large pressure range, with a normal frequency factor. The rate is unaffected by nitric oxide. The main products are ethylene and nitric oxide. The thermal decomposition of 1-nitropropane appears to be similar.

Energetic considerations show that the initial step cannot involve splitting of the C—N bond unless there is a chain reaction. Using the C—H bond energies for C_2H_5·—H and C_3H_7—H obtained by Polanyi, quoted by Steacie,[4] and the heats of combustion of nitroparaffins given by Holcomb and Dorsey,[5] we obtain for the reactions:

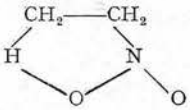
$$C_2H_5NO_2 \rightarrow C_2H_5 + NO_2,\ \Delta H^\circ_{25^\circ C} = 57{\cdot}6 \text{ kcal.} \quad . \quad . \quad (1)$$
$$n\text{-}C_3H_7NO_2 \rightarrow C_3H_7 + NO_2,\ \Delta H^\circ_{25^\circ C} = 55{\cdot}9 \text{ kcal.} \quad . \quad (2)$$

These are higher than the observed activation energies by an amount greater than can reasonably be ascribed to experimental error. The effect of nitric oxide, and of increased surface, make a chain reaction rather unlikely; these steps may therefore be ruled out. Further, it is not easy to account for the observed products on this mechanism. The

[4] Steacie, *Atomic and Free Radical Reactions* (Reinhold, New York, 1946).
[5] Holcomb and Dorsey, *Ind. Eng. Chem.*, 1949, **41**, 2788.

C—N bond is the weakest in the molecule, so any other direct split into radicals or atoms need not be considered.

The most likely initial reaction is therefore an intramolecular rearrangement, giving the olefin and nitrous acid. The latter might be expected to decompose rapidly into products which would oxidize some of the olefin. This seems reasonable by analogy with the production of olefin and hydrochloric acid in the unimolecular decomposition of chlorinated hydrocarbons.[6, 7] Examination of models shows that a five-membered ring transition state,



should involve little strain. This suggests that, other things being equal, the activation energy might be less than that for ethyl chloride, 59·5 kcal.[7] This is so, but the quite large variation in activation energy for the dehydrochlorination of different substituted hydrocarbons by the same method shows that other factors are more important. The reaction is possible from an energetic point of view. It is not possible directly to calculate ΔH for the reaction

$$C_2H_5NO_2(g) \rightarrow C_2H_4(g) + HNO_2(g) \quad . \quad . \quad . \quad (3)$$

because the heat of formation of gaseous HNO_2 is not known. If this quantity is estimated on the assumption that the same energy is involved in vaporizing nitrous acid from solution as in vaporizing nitric acid, we obtain for (3), $\Delta H^{\circ}_{25^{\circ}\,C} \sim 20$ kcal. A check on the estimate of the heat of formation of $HNO_2(g)$ and thus of ΔH for (3), may be obtained by deducing from it, ΔH for the reaction

$$2HNO_2(g) \rightarrow H_2O(g) + NO(g) + NO_2(g) \quad . \quad . \quad (4)$$

which comes out at nearly zero, a result which is not likely to be seriously in error. Such a reaction would lead to the following stoichiometric equations for the decompositions :

$$12C_2H_5NO_2 \rightarrow 11C_2H_4 + 8H_2O + 12NO + 2CO_2 \quad . \quad . \quad (5)$$
$$18C_3H_7NO_2 \rightarrow 17C_3H_6 + 12H_2O + 18NO + 3CO_2 \quad . \quad (6)$$

which give overall pressure increase of 175 % and 178 % respectively. This is in agreement with the experimental result for 1-nitropropane, but is slightly higher than that for nitroethane. For nitroethane, eqn. (5) requires that the product gases should contain 8 % CO_2, 44 % C_2H_4, and 48 % NO, which is in fairly good agreement with experiment. The small discrepancy may well be due to the heterogeneous reaction, which gives a smaller pressure increase and which occurs to the extent of about 10 %. The study of the reaction is not sufficiently detailed to warrant much discussion of the assumed decomposition of nitrous acid and oxidation of olefin.

Wayne and Yost[8] have studied the reverse of reaction (4) and combination of their rate constant with their equilibrium constant suggests that reaction (4) occurs very rapidly even at room temperature. The subsequent oxidation may be due to nitrogen dioxide, but other methods of breakdown of nitrous acid and oxidation may occur.

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Nobel Division, Research Department,
Stevenston, Ayrshire.

[6] Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725.
[7] Barton and Howlett, *J. Chem. Soc.*, 1949, **155**, 165.
[8] Wayne and Yost, *J. Chem. Physics*, 1950, **18**, 767.

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Preprinted from the Journal of the Chemical Society, February 1953, (112), pages 556—563.

112. *The Kinetics of the Oxidation of Ethylene by Nitrogen Dioxide.*

By T. L. Cottrell and T. E. Graham.

The reaction between nitrogen dioxide and ethylene has been studied by the static method, the total pressure and the nitrogen dioxide concentration being followed for initial pressures of between 3 and 12 cm. Hg of the reactants. The pressure at high temperatures rises rapidly, whereas at low temperatures there is a pressure drop followed by a rise. The NO_2 concentration decreases monotonically throughout the reaction. Rates of reaction were measured by drawing tangents to the curves of $[NO_2]$ against time.

The results were systematised by considering the initial slope of the $[NO_2]$–time curve :

$$-(d[NO_2]/dt)_{=0} = k_{III}[NO_2]^{1\cdot8}[C_2H_4]^{1\cdot2}$$

A plot of $\log_{10} k_{III}$ against $1/T$ gave two intersecting straight lines with equations :

$$k_{III} = 10^{8\cdot5} \exp(-12{,}500/RT)\ \text{l.}^2\ \text{mole}^{-2}/\text{sec.}^{-1}\ (160—220°),$$
$$k_{III} = 10^{10\cdot9} \exp(-18{,}000/RT)\ \text{l.}^2\ \text{mole}^{-2}/\text{sec.}^{-1}\ (220—280°).$$

The $[NO_2]$–t curve in the course of a run was approximately of first order, more nitrogen dioxide having disappeared at a given time than would be expected from the third-order law, presumably because it reacts further with a product of the initial reaction. The process governing the rate of pressure rise had an activation energy of 17,000 cal.

The gaseous products were almost entirely carbon dioxide, carbon monoxide, and nitric oxide. The other products included an oil and a small amount of carbon-like material. Addition of nitric oxide or of air had no effect on the kinetics of disappearance of nitrogen dioxide. Increasing the surface : volume ratio by a factor of 8 had no effect at high temperature, and only a slight effect at low temperatures.

These facts are consistent with the view that nitrogen dioxide adds on to ethylene in the molecular ratio of 2 : 1, and that this product decomposes to give fragments capable of reacting with further nitrogen dioxide with complete oxidation.

In the combustion of organic nitrates, nitrogen dioxide is considered to be split off and to oxidise the other fragments (Phillips, *Nature*, 1947, **160**, 753; 1950, **165**, 564). Thus oxidation of organic compounds by nitrogen dioxide may be important in the chemistry of the propagation of reaction in nitrates. The oxidation of formaldehyde (Pollard and Wyatt, *Trans. Faraday Soc.*, 1949, **45**, 760, 767) has therefore already been studied. Acetaldehyde (McDowell and Thomas, *ibid.*, 1950, **46**, 1030) and acetylene (Thomas, personal communication) have also been studied, although for other reasons. It was of interest to examine the oxidation of ethylene, as a representative olefin and because it has been suggested that ethylene formed by the unimolecular decomposition of nitroethane would be readily oxidised by nitrogen dioxide produced from the nitrous acid left after the initial stage of the decomposition (Cottrell, Graham, and Reid, *ibid.*, 1951, **47**, 1089).

Experimental

Materials.—Nitrogen dioxide, prepared by heating mixed lead nitrate and sand over which dry oxygen was flowing, was distilled several times over phosphoric oxide and stored at liquid-nitrogen temperature. Commercial ethylene was passed over phosphoric oxide and potassium hydroxide and distilled several times.

Apparatus.—The "Pyrex" reaction vessel of volume 500 cm.^{3} was heated in a vertical electrical furnace, controlled to $\pm 0{\cdot}1°$ by a "Sunvic" resistance thermometer controller. Temperature measurement was by calibrated chromel–alumel thermocouple. A glass spiral manometer (Yorke, *J. Sci. Instr.*, 1945, **22**, 196; 1948, **25**, 16), attached to the vessel by heated capillary tubing, was enclosed in a heated oil-bath. Pressures were read to $\pm 0{\cdot}02$ cm. of Hg, by use of a light source, mirror on the gauge, and scale. The furnace had windows through which a light beam was passed on to a photo-cell, whose output was balanced in a bridge circuit. The bridge reading was calibrated against the nitrogen dioxide concentration (McDowell and Thomas, *loc. cit.*).

The system was evacuated by a mercury diffusion pump. Nitrogen dioxide was admitted to the reaction vessel, the pressure and bridge reading being noted (thus checking the calibration of the photo-cell bridge circuit). Ethylene was then admitted during about 5 seconds and the reaction followed by noting the pressure and bridge reading. The products could be removed and admitted to a trap cooled in liquid nitrogen, which could warm to $-80°$, and the permanent gases could then be removed by a Töpler pump, either to a cell for infra-red spectroscopic examination or to a gas sampler for chemical analysis in a Bone and Wheeler apparatus.

Kinetic Results.—At 290° the kinetic results were not very reproducible, and at pressures of over 30 cm. explosions occurred. It was established in these runs that the pressure increase is proportional to the initial pressure of nitrogen dioxide, and is equal to $0{\cdot}45[NO_2]_{t=0}$, ethylene being present in excess. A few of the later runs at lower temperatures were continued sufficiently to check this. They agreed, except at the lowest temperatures where the pressure increase was less. Details of selected runs are given in Tables 1—3. In Table 1 are given the

TABLE 1. *Ethylene–nitrogen dioxide reaction. Details of selected runs.*

Run	Temp.	p-NO_2, cm.	p-C_2H_4, cm.	$\left(\frac{d[NO_2]}{dt}\right)_{t=0}$ cm./min.	k_{III}, cm.$^{-2}$ min.$^{-1}$	k_I, sec.$^{-1}$	Remarks
94	279·5°	5·87	5·68	8·0	$4{\cdot}1 \times 10^{-2}$	$5{\cdot}3 \times 10^{-3}$	
107	,,	5·98	2·12	3·4	4·5	4·8	
113	,,	5·86	10·56	14·2	3·9	5·4	
132	,,	1·96	5·88	0·95	4·2	—	
138	,,	7·96	5·99	16·0	4·2	5·5	
150	269·0	6·20	5·80	5·9	$2{\cdot}6_8 \times 10^{-2}$	$3{\cdot}2 \times 10^{-3}$	
151	,,	6·00	2·85	$2{\cdot}3_4$	$2{\cdot}6_6$	3·0	
153	,,	6·30	9·10	9·5	$2{\cdot}4_4$	$3{\cdot}1_5$	
172	,,	4·55	6·15	$3{\cdot}1_5$	$2{\cdot}3_4$	—	6·05 cm. of NO added
178	,,	3·31	11·89	4·0	$2{\cdot}3_9$	—	
179	,,	11·08	3·17	7·5	$2{\cdot}4_9$	—	
181	258·3	5·94	6·15	$4{\cdot}5_0$	$2{\cdot}0_6 \times 10^{-2}$	$2{\cdot}2_7 \times 10^{-3}$	
186	247·8	6·12	6·10	3·6	$1{\cdot}5_8 \times 10^{-2}$	$1{\cdot}96 \times 10^{-3}$	
189	,,	11·45	3·75	6·3	$1{\cdot}6_1$	$1{\cdot}7_7$	
193	,,	3·95	8·05	2·20	$1{\cdot}5_2$	$1{\cdot}8_8$	
197	233·9	6·25	6·22	$2{\cdot}2_5$	$9{\cdot}3 \times 10^{-3}$	—	
203	218·5	6·05	5·90	$1{\cdot}1_9$	$5{\cdot}5 \times 10^{-3}$	$6{\cdot}1 \times 10^{-4}$	
210	205·1	5·95	5·95	0·90	$4{\cdot}3 \times 10^{-3}$	$4{\cdot}3 \times 10^{-4}$	
212	,,	12·03	2·98	1·34	$4{\cdot}1_2$	2·8	
216	190·8	5·92	5·69	0·64	$3{\cdot}2 \times 10^{-3}$	—	
229	164·8	5·95	6·12	0·35	$1{\cdot}6_1 \times 10^{-3}$	—	
235	,,	20·05	9·90	$5{\cdot}3_8$	$1{\cdot}5_6$	—	
240	270·8	7·00	7·00	$8{\cdot}3_5$	$2{\cdot}4_3 \times 10^{-2}$	—	Packed reaction vessel
241	191·5	6·25	7·60	$1{\cdot}2_5$	$4{\cdot}0_5 \times 10^{-3}$	—	,, ,,
243	271·3	6·21	6·45	6·4	$2{\cdot}5_5 \times 10^{-2}$	—	Packed vessel, 6·20 cm. of air added

temperature, the initial pressures of reactants, the initial slope of the $[NO_2]$–time curve, a third-order constant, and a first-order constant. In Table 2 are given the pressure–time data, and in Table 3 the $[NO_2]$–time data. At 279·5° the $[NO_2]$–time curves are not very satisfactory, because the reaction is too fast to follow accurately. The runs are numbered in chronological order. The results show that, although at higher temperatures the pressure increases with time, yet at lower temperatures there is a decrease followed by a rise. The NO_2 concentration decreases monotonically throughout the reaction. Typical runs are shown in Fig. 1. The pressure change is not simply related to the amount of NO_2 reacting, and thus the pressure–time curves may not be susceptible of a straightforward kinetic interpretation.

Apparently two reactions, addition of nitrogen dioxide (with pressure decrease) and oxidation (with pressure increase) are proceeding, either in series or in parallel, with different

TABLE 2. *Ethylene–nitrogen dioxide reaction. Pressure–time data.*

Run	Δp (cm. Hg) at t (min.)													
t =	0	¼	½	¾	1	1½	2	3	4	6	8	10	20	
94	0·00	0·16	0·28	0·41	0·59	0·84	1·02	1·37	1·59	1·70	—	—	—	—
107	0·00	0·09	0·14	0·29	0·39	0·60	0·82	1·10	1·38	1·70	1·94	2·10	2·58	—
113	0·00	0·06	0·18	0·35	0·46	0·67	0·85	1·12	1·33	1·60	—	—	—	—
132	0·00	0·02	0·02	0·03	0·04	0·12	0·15	0·22	0·30	—	—	—	—	—
138	0·00	0·22	0·45	0·62	0·81	1·09	1·31	1·69	1·93	—	—	—	—	—
150	0·00	0·00	0·02	0·10	0·20	0·41	0·60	0·86	1·09	1·39	1·59	1·78	—	—
151	0·00	0·00	0·05	0·14	0·21	0·34	0·54	0·75	0·96	1·26	1·50	1·70	—	—
153	0·00	0·00	0·08	0·18	0·29	0·46	0·60	0·89	1·10	1·43	1·65	—	—	—
172	0·00	0·00	0·00	0·00	0·04	0·13	0·23	0·44	0·64	—	—	—	—	—
178	0·00	0·01	0·01	0·02	—	0·14	0·20	0·34	0·40	—	—	—	—	—
179	0·00	0·20	0·35	0·56	0·75	1·08	1·29	1·81	2·20	—	—	—	—	—
181	0·00	0·02	0·04	0·05	0·12	0·26	0·39	0·56	0·77	1·05	1·28	1·45	—	—
t =	0	½	1	1½	2	2½	3	4	5	6	8	10	20	60
186	0·00	0·00	0·05	0·11	0·22	0·31	0·40	0·59	0·71	0·86	1·06	1·26	—	—
189	0·00	−0·10	+0·01	0·19	0·39	0·55	0·70	0·99	1·25	1·51	1·92	2·29	—	—
193	0·00	−0·09	−0·09	−0·05	0·00	0·05	0·10	0·20	0·28	0·37	0·52	0·62	—	—
197	0·00	−0·21	−0·27	−0·30	−0·24	−0·21	−0·12	−0·02	0·09	0·23	0·42	0·58	1·22	2·15
t =	0	1	2	4	6	8	10	15	20	25	30	40	50	60
203	0·00	−0·38	−0·54	−0·53	−0·37	−0·23	−0·05	0·30	0·59	0·84	1·00	1·31	1·54	1·66
t =	0	1	2	4	7	10	15	20	30	40	60	80	100	120
210	0·00	−0·35	−0·59	−0·77	−0·80	−0·72	−0·48	−0·25	0·15	0·44	0·85	1·13	—	—
212	0·00	−0·49	−0·72	−0·91	−0·88	−0·69	−0·31	0·07	0·69	1·22	2·03	2·64	3·11	3·50
216	0·00	−0·31	−0·54	−0·88	−1·11	−1·21	−1·19	−1·11	−0·92	−0·50	−0·33	−0·07	0·15	—
229	0·00	−0·20	−0·39	−0·72	−1·10	−1·39	−1·67	−1·87	−2·05	−2·09	—	—	—	—
235	0·00	−2·45	−4·00	−5·45	−5·80	−5·31	−4·12	−3·06	−1·42	−0·46	+0·77	1·60	2·19	—
t =	0	¼	½	¾	1	1½	2	3	4	6	8	10	20	30
240	0·00	0·10	0·35	0·60	0·90	1·38	1·70	2·15	2·42	2·77	—	—	—	
241	0·00	—	−0·27	—	−0·42	−0·60	−0·70	−0·88	−0·93	−1·00	−1·00	—	−0·60	−0·26
243	0·00	0·05	0·22	0·41	0·60	0·88	1·12	1·36	—	—	—	—	—	—

TABLE 3. *Ethylene–nitrogen dioxide reaction.* $[NO_2]$–*t data.*

Run	$[NO_2]$, cm., at t (min.)													
t=	0	¼	½	¾	1	1¼	1½	1¾	2	2½	3	3½	4	5
94	$5{\cdot}8_5$	$4{\cdot}3_0$	$3{\cdot}0_2$	$2{\cdot}2_3$	$1{\cdot}6_0$	—	$1{\cdot}2_0$	—	$0{\cdot}9_0$	—	—	—	—	—
107	$6{\cdot}0_0$	$5{\cdot}4_0$	$4{\cdot}6_0$	4·1	3·8	3·3	3·0	2·8	2·6	—	—	—	—	—
113	5·8	3·2	1·8	1·2	0·8	0·7	—	—	—	—	—	—	—	—
132	$1{\cdot}9_5$	$1{\cdot}7_2$	$1{\cdot}4_9$	$1{\cdot}3_0$	$1{\cdot}1_0$	$0{\cdot}9_5$	$0{\cdot}8_5$	$0{\cdot}7_0$	$0{\cdot}5_5$	—	—	—	—	—
138	8·0	4·9	$3{\cdot}1_5$	$2{\cdot}3_0$	1·8	1·5	—	—	—	—	—	—	—	—
150	6·2	5·0	3·9	3·1	2·4	2·1	1·7	1·4	1·3	—	—	—	—	—
151	6·0	5·5	5·1	$4{\cdot}6_5$	$4{\cdot}1_5$	3·7	3·4	3·1	2·8	—	—	—	—	—
153	6·3	4·5	2·9	$2{\cdot}1_5$	$1{\cdot}5_5$	1·1	—	—	—	—	—	—	—	—
172	4·6	3·9	3·2	2·8	$2{\cdot}2_5$	1·9	$1{\cdot}6_5$	$1{\cdot}4_5$	1·3	—	—	—	—	—
178	3·3	2·4	$1{\cdot}7_5$	1·3	1·0	0·8	$0{\cdot}6_5$	$0{\cdot}5_5$	$0{\cdot}4_5$	—	—	—	—	—
179	11·1	$10{\cdot}0_5$	8·3	7·2	6·3	5·6	5·1	4·6	$4{\cdot}3_5$	$3{\cdot}8_5$	3·5	—	—	—
181	6·0	$5{\cdot}6_5$	$4{\cdot}1_5$	3·4	2·8	2·4	2·0	$1{\cdot}6_5$	$1{\cdot}4_5$	$1{\cdot}1_5$	1·0	—	—	—
186	6·1	5·3	4·6	3·9	$3{\cdot}3_5$	$2{\cdot}8_5$	$2{\cdot}4_5$	$2{\cdot}1_5$	$1{\cdot}8_5$	$1{\cdot}4_5$	1·2	—	—	—
189	11·5	10·3	9·1	8·0	$7{\cdot}1_5$	6·5	$5{\cdot}8_5$	$5{\cdot}4_5$	$5{\cdot}0_5$	4·4	4·0	—	—	—
193	$3{\cdot}9_5$	3·4	2·9	$2{\cdot}5_5$	2·2	$1{\cdot}9_5$	1·6	1·4	$1{\cdot}2_5$	$0{\cdot}9_5$	—	—	—	—
197	6·3	$6{\cdot}0_5$	5·6	5·1	4·6	$4{\cdot}1_5$	3·9	$3{\cdot}4_5$	$3{\cdot}1_5$	2·7	2·3	$2{\cdot}0_5$	$1{\cdot}7_5$	—
203	6·1	5·9	5·6	$5{\cdot}3_5$	5·1	$4{\cdot}8_5$	4·6	$4{\cdot}3_5$	4·1	3·7	3·3	$3{\cdot}0_5$	2·8	2·3
t =	0	½	1	1½	2	2½	3	3½	4	4½	5	6	8	10
210	6·0	5·6	5·3	4·9	4·6	4·2	3·9	3·7	3·4	3·2	3·0	2·7	2·2	—
212	12·0	11·5	10·9	$10{\cdot}3_5$	$9{\cdot}9_5$	9·5	9·1	8·8	$8{\cdot}4_5$	$8{\cdot}0_5$	$7{\cdot}8_5$	$7{\cdot}3_5$	$6{\cdot}6_5$	6·1
216	5·9	5·6	5·3	5·0	4·8	4·5	$4{\cdot}3_5$	4·2	4·0	3·8	3·6	3·4	$2{\cdot}9_5$	$2{\cdot}5_5$
229	$5{\cdot}9_5$	5·8	5·6	$5{\cdot}4_5$	5·3	5·2	5·1	5·0	4·9	$4{\cdot}7_5$	4·6	$4{\cdot}3_5$	4·0	$3{\cdot}6_5$
235	20·0	17·7	15·9	14·6	13·5	12·4	11·6	11·1	10·5	9·9	9·5	8·8	7·7	6·9
t =	0	¼	½	¾	1	1¼	1½	1¾	2	2½	3	3½	4	
240	7·0	5·3	3·9	2·8	2·3	1·8	1·6	1·3	1·1	—	—	—	—	—
241	6·3	—	5·7	—	5·2	—	4·9	—	4·5	4·2	3·9	3·7	3·5	—
243	6·2	4·8	3·7	2·9	2·5	2·0	1·7	1·5	1·4	—	—	—	—	—

activation energies. Attempts at kinetic analysis were largely confined to the $[NO_2]$–time curves. Runs at 269° were first considered. The initial slope of the $[NO_2]$–time curve was obtained by plotting the readings, drawing tangents at various pressures of NO_2, and extrapolating back to the known original pressure. The initial slope depended on $[NO_2]^{1\cdot8}$ and $[C_2H_4]^{1\cdot2}$. The results at 279·5°, however, seemed to be better expressed by the simple powers 2 and 1. The non-integral powers may be due to a side reaction which is less important at high temperature.

In Table 1 are given the constants obtained at all temperatures, it being assumed that $(-d[NO_2]/dt)_{t=0} = k_{III}[NO_2]^{1\cdot8}[C_2H_4]^{1\cdot2}$, except for 279·5°, where the powers 2 and 1 are used. The constancy of k_{III} for changes by a factor of 3 or 4 in the pressures of the reactants is good; clearly, the initial step is kinetically the same throughout the temperature range. This implies that the addition and oxidation reactions must take place in series.

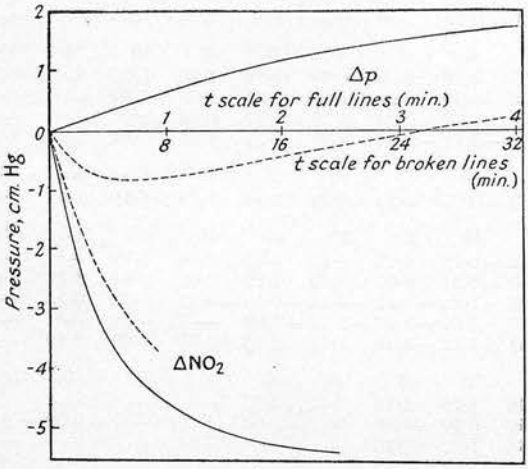

FIG. 1. *p–t and* $[NO_2]$*–t plots for run* 106 ———, *and run* 210 – – – –.

A plot of $\log_{10} k_{III}$ against $1/T$ for all runs falls into two straight-line segments, which have the equations given on p. .

The slope of the $[NO_2]$–t curve was approximately proportional to the pressure of NO_2 during a run up to about 50% reaction, *i.e.*, $-d[NO_2]/dt = k'[NO_2]_t$, although of course k' depended on the initial pressures of NO_2 and ethylene. This apparent first-order rate of disappearance of NO_2 was checked by calculating first-order constants by using the integrated form of the first-order law. The " constants " decreased slightly as the reaction proceeded, except at the lowest temperatures, when the decrease was rapid. The approximation was less good for high and for low initial concentration of NO_2.

The vessel was packed with Pyrex capillary tubing to give an increase in the surface : volume ratio by a factor of 8. At high temperatures k_{III} was unchanged; at low temperatures it was increased by about 30%, showing that the surface effect is slight. Addition of NO (runs 170—172) and air (run 243) had little effect on k_{III}.

Although a simple molecular interpretation of the pressure–time curves was not expected, the part involving pressure increase was roughly of first order, as determined by Guggenheim's method (*Phil. Mag.*, 1926, **2**, 538). At high temperatures the maximum slope of the pressure–time curve was roughly proportional to the initial pressure of NO_2 only. In all these runs, the ethylene was present in excess, so that the amount of an intermediate formed might be expected to be proportional to the initial pressure of NO_2. The first-order constants obtained from the pressure increase are given in Table 1 as k_I. The temperature dependence of k_I is given by $k_I = 10^{4\cdot35}e^{-17,000/\boldsymbol{R}T}$ sec.$^{-1}$. For those runs in which the NO_2/C_2H_4 ratio is large, k_I is smaller than usual. These results were not included in the activation-energy plot.

Whereas the addition of NO had no effect on the $[NO_2]$–t curves, yet it had a marked effect on the pressure–time curve, causing an apparent induction period before the pressure started to increase.

Stoicheiometry and Analyses.—Where there was no initial pressure drop the total pressure increase of 45% of the initial pressure of NO_2 may be compared with a 50% pressure increase calculated for $6NO_2 + C_2H_4 \longrightarrow 2CO_2 + 2H_2O + 6NO$. As mentioned above, the pressure increase is not simply related to the change in NO_2 pressure. In the runs at low temperature,

where there is an initial pressure decrease, the ratio of the initial slope of the $[NO_2]$–t curve to the initial slope of the pressure–time curve was noted (Table 4). At temperatures immediately

TABLE 4. *Ratio of* $(d[NO_2]/dt)_{t=0}$ *to* $(dp/dt)_{t=0}$ *for various runs.*

Run	Temp.	Ratio	Mean	Run	Temp.	Ratio	Mean
203	218·5°	2·4		210	205·1°	2·0	
204	,,	2·6		211	,,	2·0	
207	,,	2·6	2·60	212	,,	2·0	2·03
208	,,	2·5		213	,,	2·1	
209	,,	2·9		214	,,	2·1	
229	164·75	1·8		215	,,	2·0	
230	,,	1·8	1·72	216	190·75	2·1	
233	,,	1·7		218	,,	1·9	1·93
235	,,	1·6		221	,,	1·8	

above those for which results are given in the Table, the pressure decrease was too rapid to be measured accurately, and at even higher temperatures it was not observed. The ratio is greater the higher the temperature. There are only a few possible addition compounds, so the number of simple equations which can be written to explain the pressure drop is small. Three which give products for which there is evidence at lower temperatures (cf. Levy, Scaife, and Smith, *J.*, 1946, 1096) are

$$2NO_2 + C_2H_4 \longrightarrow C_2H_3{\cdot}NO_2 + \tfrac{1}{2}(H_2O + NO + NO_2) \qquad \Delta[NO_2]/\Delta p = 3$$
$$2NO_2 + C_2H_4 \longrightarrow C_2H_3{\cdot}NO_2 + HNO_2 \qquad \Delta[NO_2]/\Delta p = 2$$
$$2NO_2 + C_2H_4 \longrightarrow C_2H_4(NO_2)_2 \qquad \Delta[NO_2]/\Delta p = 1$$

Presumably formation of nitroethylene is favoured at higher temperatures, whereas formation of dinitroethane (the structure being unspecified for the present) is favoured at lower temperatures.

Direct interpretation of these p–t results in terms of such equations is not quantitatively possible because of side reactions. Polymerisation of nitroethylene might well take place, causing a smaller value of $\Delta[NO_2]/\Delta p$, and in addition the results of gas analyses show that some complete oxidation has taken place even at very short times, which would cause a larger value of $\Delta[NO_2]/\Delta p$ than expected.

Qualitative analysis by infra-red spectroscopy of the gaseous products showed carbon dioxide, carbon monoxide, nitric oxide, and unchanged ethylene. Particularly at the lower temperatures, the products when removed for analysis contained a high-boiling oil, which was not analysed, but was thought to be a mixture of nitroethylene, dinitroethane, and possibly nitroethyl nitrite. A deposit of dark material was gradually formed in the tubes leading to the reaction vessel. The gaseous products were analysed in the Bone and Wheeler apparatus for carbon dioxide, nitric oxide, ethylene, and carbon monoxide, potassium hydroxide, ferrous sulphate, silver sulphate and concentrated sulphuric acid, and ammoniacal cuprous chloride being used as absorbents. The residue was generally 2—3% and never more than 5%. There is some interaction between these reagents, and at the times of greatest interest, near the beginning of the reaction, the samples were small, so that the results were not very reproducible. Accordingly, only a few analyses were carried out, all for runs at 190·6°, with 10 cm. of NO_2 and 5 cm. of C_2H_4. After short times (1—2 minutes) the permanent gas contained carbon dioxide and carbon monoxide in the ratio of about 5 : 1, nitric oxide roughly equivalent to the oxides of carbon, and unchanged ethylene. The NO analyses were particularly variable because of the possibility of carrying a small amount of NO_2 over into the Töpler pump, where it would react to give NO. Typical results for the composition of the permanent gas are given in Table 5 :

TABLE 5. *Typical compositions of permanent-gas products from reaction of* 10 *cm. of* NO_2 *and* 5 *cm. of* C_2H_4 *at* 190·6°.

Time stopped	CO_2, %	NO, %	C_2H_4, %	CO, %
1½ min.	4·5	14·1	75·0	1·0
1½ min.	4·0	19·5	73·4	0·9
2 min.	5·4	14·5	74·0	1·1

the residue was not analysed, and probably consisted of nitrogen with possibly a little nitrous oxide. No attempt was made to refine the method of analysis because products are likely to be too complex.

Discussion

The results suggest that 2 mols. of nitrogen dioxide are added to one of ethylene, a process which can take place in two different ways with activation energies of approximately 18 and 12·5 kcal. to give an addition product which decomposes, possibly with nitroethylene as an intermediate, to fragments which are completely oxidised by more nitrogen dioxide. The process controlling the oxidation has an activation energy of about 17 kcal.

In discussing the initial rate of reaction of NO_2, it will be assumed that the main process is of the second order in NO_2 and the first order in ethylene, although the exact figures are 1·8 and 1·2. Two mechanisms for an apparent third-order reaction suggest themselves, as follows :

$$\text{Scheme I}\quad NO_2 + C_2H_4 \longrightarrow NO_2{\cdot}C_2H_4 \quad (1)$$
$$NO_2{\cdot}C_2H_4 \longrightarrow NO_2 + C_2H_4 \quad (2)$$
$$NO_2 + NO_2{\cdot}C{\cdot}H_4 \longrightarrow C_2H_4(NO_2)_2 \quad (3)$$
$$\text{Scheme II}\quad NO_2 + NO_2 \longrightarrow N_2O_4 \quad (4)$$
$$N_2O_4 \longrightarrow NO_2 + NO_2 \quad (5)$$
$$N_2O_4 + C_2H_4 \longrightarrow C_2H_4(NO_2)_2 \quad (6)$$

Applying the usual stationary state assumption to $NO_2{\cdot}C_2H_4$, we find that Scheme I gives

$$-\,d[NO_2]/dt = 2k_1k_3[NO_2]^2[C_2H_4]/(k_2 + k_3[NO_2])$$

and applying it to N_2O_4, we find that Scheme II gives

$$-\,d[NO_2]/dt = 2k_4k_6[NO_2]^2[C_2H_4]/(k_5 + k_6[C_2H_4])$$

Hence, in each scheme if the second term in the denominator is small compared to the first, third-order kinetics are obtained. If the second term has an effect in Scheme I, the dependence on NO_2 might be slightly less than on the second power, whereas in Scheme II the ethylene dependence might be slightly less than the first power. Thus Scheme I is to be preferred on these grounds.

The experimental activation energy is 12·5 kcal. at low temperatures and 18·0 kcal. at higher temperatures. Scheme I gives the activation energy as $E_1 + E_3 - E_2$; E_2 and E_3 might be expected to be small, so that the overall activation energy is expected to be $\sim E_1$. The reaction (1) involves the formation of a C–N bond and the conversion of a C=C bond into a C–C bond. The bond energies given by Coates and Sutton (*J.*, 1948, 1187) being used, this reaction should be exothermic to the extent of about 10 kcal., so there is no energetic reason why E_1 should not be 12—18 kcal. Scheme II gives the activation energy as $E_4 + E_6 - E_5$; $E_4 - E_5$ is known to be about -13 kcal. (Richards and Reid, *J. Chem. Physics*, 1933, **1**, 114), so the overall activation energy, $E = E_6 - 13$ kcal. Thus E_6 must be 25—31 kcal. if Scheme II is correct. Reaction (6) is certainly exothermic, though this seems perhaps rather a high value for E_6.

The experimental frequency factors are $10^{8\cdot5}$ and $10^{10\cdot9}$ l.^{2} mole^{-2}/sec.$^{-1}$. Scheme I makes the overall factor the product of two bimolecular factors divided by the unimolecular factor for reaction (2). If the factor for reactions (1) and (3) is equal to the collision frequency, then the numerator is 10^{20}—10^{24}, and the denominator 10^{12}—10^{14}. This allows the overall frequency factor to be between 10^6 and 10^{12}. The experimental values lie within this range, but surprisingly high in it; in many reactions involving NO_2 the bimolecular frequency factor is appreciably less than the collision number. This could be accounted for if the frequency factor for unimolecular radical decompositions were less than that usually found for molecules, and there is some evidence of this (cf. Howlett, *Trans. Faraday Soc.*, 1952, **48**, 25). Scheme II gives a similar result, but here the frequency factor of (5) is known to be at the high end of the range for unimolecular frequency factors (Richards and Reid, *loc. cit.*), and thus the overall factor is likely to be lower than that for Scheme I if it is assumed that all the bimolecular reactions have the same frequency factors. Since the experimental frequency factor is if anything rather high, this examination favours Scheme I.

A further support for Scheme I lies in the possibility of explaining the two activation energies of the reaction. The O–N–O molecule can form either a C–N bond or a C–O bond when adding to a carbon atom, and it is not to be expected that these two processes will have the same activation energies or frequency factors. That both modes of addition are possible has been shown by the Billingham workers who have obtained nitroethyl nitrate and dinitroethane from the reaction between nitrogen dioxide and ethylene (Levy, Scaife, and Smith, *loc. cit.*). It is also significant that in the reaction between nitrogen dioxide and formaldehyde, in which addition is also postulated, there are also two activation energies which might be explained similarly. On the other hand, if N_2O_4 is a symmetrical plane molecule of the formula $\begin{matrix}O\\O\end{matrix}\!>\!N\!-\!N\!<\!\begin{matrix}O\\O\end{matrix}$ as is suggested by spectroscopic (cf. Herzberg, "Infra Red and Raman Spectra," New York, 1945) and *X*-ray (Broadley and Robertson, *Nature*, 1949, **164**, 915) evidence, then it is much less easy to see how addition could take place in two different ways. Also, it is not possible to see how N_2O_4 would add on to ethylene even in one way, except by breaking and forming several bonds in the one putatively elementary step.

The relation between the initial rates of disappearance of NO_2 and of pressure decrease shown in Table 4 points to the formation of nitroethylene, probably by decomposition of nitroethyl nitrite. The nitroethylene formation appears to be temperature-dependent and to become the main reaction by about 220°, the temperature at which there appears to be a break in the activation energy curve. To take this into account, reaction Scheme I would have to consist of reactions (1), (2), and (3) as before, with the addition of

$$NO_2 + NO_2{\cdot}C_2H_4 \longrightarrow C_2H_4(O{\cdot}NO)(NO_2) \quad \ldots \quad (3a)$$

$$C_2H_4(O{\cdot}NO)(NO_2) \longrightarrow C_2H_3{\cdot}NO_2 + \tfrac{1}{2}(H_2O + NO + NO_2) \quad \ldots \quad (7)$$

The compounds in parentheses are assumed to result from the decomposition of HNO_2.

This gives, with the obvious stationary-state assumptions,

$$\frac{-\,d[NO_2]}{dt} = \frac{k_1(2k_3 + k_{3a})[NO_2]^2[C_2H_4]}{k_2 + (k_3 + k_{3a})[NO_2]}$$

a relation of precisely the same form as before, and one which should lead to an activation energy plot with different slopes in the regions corresponding to the predominance of reaction (3) and of reaction (3*a*). With these activation energies not very different, a sharply segmented plot would not be expected, and the true activation energies and frequency factors would differ slightly from those deduced simply by drawing two straight lines through the experimental points. This consideration, which applies equally to the work of Pollard and Wyatt on formaldehyde (*loc. cit.*), makes only a slight difference to the numerical values and does not affect the argument.

Although the experimental results could probably be fitted to a smooth curve in the region of intersection of the straight lines actually drawn, in neither set is the precision sufficiently great to justify this procedure. Exactly similar kinetic results would follow if the mechanism of formation of nitroethylene involved hydrogen abstraction, as in (3*b*):

$$C_2H_4{\cdot}NO_2 + NO_2 \longrightarrow C_2H_3{\cdot}NO_2 + HNO_2 \quad \ldots \quad (3b)$$

The subsequent apparent first-order decrease of NO_2 with time in any given run can be explained on the view that it is reacting further with fragments from the decomposition of the addition compounds. It is not possible to put forward a detailed scheme for this, as the number of possible intermediates is large, but that such a scheme could in principle explain the results was shown by the numerical solution * of the differential equations describing the reactions

$$2A + B \longrightarrow C \ (8); \quad A + C \longrightarrow D \ (9)$$

Here A and B are nitrogen dioxide and ethylene, and C may be a series of intermediates the last member of which reacts with nitrogen dioxide. In Fig. 2 are plotted the

* The authors are indebted to Mr. N. Ream for the numerical solution, which was obtained by using the differential analyser at the Butterwick Research Laboratories.

experimental results for the disappearance of NO_2 in run 203 (for example) and the theoretical curves corresponding to

$$-\,da/dt = ka^2b \text{ (3rd order)}$$

and

$$-\,da/dt = ka_0b_0a \text{ (1st order with same initial slope)}$$

Here concentrations are indicated by lower case letters, the subscript 0 referring to zero time. Also shown is the curve corresponding to the system of equations (8) and (9) with $\kappa = 6\ k_9/k_8b_0 = 80$.

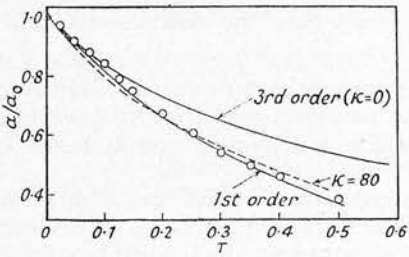

FIG. 2. *Showing apparent first-order decrease of* NO_2: o *experimental points for run* 203.

(The time scale is dimensionless, $\tau = k_8a_0b_0t$.) This curve fits the results fairly well. The rate constant for the second-order reaction (k_9) may be obtained from κ since k_8 (the third-order rate constant) is known from the initial slope; this gives a value for k_9 of approximately 10 l. mole^{-1} sec.$^{-1}$ which, if combined with an activation energy of 17,000 cal., gives a frequency factor of $10^{8\cdot5}$ l. mole^{-1} sec.$^{-1}$, a reasonable value for a second-order reaction frequency factor.

The " first-order rate constant " characterising the pressure rise cannot be interpreted on a molecular basis. The low frequency factor ($10^{4\cdot35}$ compared with 10^{13} for a unimolecular reaction) shows that the process is not a simple first-order reaction, as also does the fact that the " constant " decreases when $[NO_2]/[C_2H_4]$ is large. The process has an activation energy of 17 kcal., which is not very different from that found for the oxidation of aldehydes by nitrogen dioxide.

The mechanism put forward above is very similar to that suggested by Pollard and Wyatt (*loc. cit.*) for the oxidation of formaldehyde. Although the latter is kinetically of the second order, this could be so if, in Scheme I, $k_2 < k'_3[NO_2]$ for the analogous reactions with formaldehyde. The " dinitro " derivative of formaldehyde would probably not exist as such. On the other hand, McDowell and Thomas (*loc. cit.*) favour hydrogen abstraction as the initial reaction of nitrogen dioxide with aldehydes. Hydrogen abstraction is unlikely as a mechanism for the ethylene reaction, both because of the experimental evidence on the pressure and because the C–H bond in ethylene is much stronger than C–H bond in formaldehyde. Addition has also been shown to be the probable first step.

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The Kinetics of the Oxidation of Propylene by Nitrogen Dioxide.

By T. L. Cottrell and T. E. Graham.

[Reprint Order No. 5508.]

The kinetics of the reaction between nitrogen dioxide and ethylene have been investigated in some detail (Cottrell and Graham, *J.*, 1953, 556). The present note records a similar but less detailed study of the reaction with propylene in the temperature range 160—260° c.

The experimental technique was much the same as before, except for the determination of the nitrogen dioxide concentration as a function of time. The output from the photocell was connected to a rapidly recording potentiometer; the change in photocell output corresponding to the introduction of 12 cm. Hg of nitrogen dioxide caused approximately two thirds full-scale deflection. By this means quite rapid reactions could be followed because the instrument had a response time of about 2 sec., and the chart could be run at about 2 in./min. The recording system was calibrated at the beginning of each run by admitting the nitrogen dioxide stepwise in known amounts until the required pressure was obtained.

The nitrogen dioxide concentration and total pressure were both followed. The nitrogen dioxide concentration falls throughout the reaction, and kinetic analysis was confined to the initial slopes of the curves of nitrogen dioxide against time. The initial rate of disappearance of nitrogen dioxide was nearly proportional to the second power of its concentration and the first power of the propylene concentration, the more accurate exponents being 1·8 and 1·2. An Arrhenius plot of the third-order rate constant (k_3) against temperature gave $k_3 = 10^{9\cdot7} \exp(-13{,}600/\boldsymbol{R}T)$ l.^{2} mole^{-2} sec.$^{-1}$ (160—260°). Below 160° there was an apparent decrease in the activation energy. Surface effects were found to be negligible in the range 190—260°.

At high temperatures there was a pressure rise, while at lower temperatures there was an initial pressure drop followed by a rise, much as in the reaction with ethylene. At the higher temperatures, when there was no apparent initial pressure decrease, the ratio of the pressure increase to the initial pressure of nitrogen dioxide was 0·48. This is to be compared with 0·55 for the reaction :

$$C_3H_6 + 9NO_2 \longrightarrow 3CO_2 + 3H_2O + 9NO$$

The reaction is very similar to that with ethylene, but about 3—4 times faster. This result is in line with the correlation proposed by Walsh (*Fuel*, 1954, **33**, 243) between the ionisation potential of a substrate and the activation energy of its reaction with nitrogen dioxide.

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(19)

Importance of Gas Spaces in the Propagation of Detonation of Granular Explosives

It has been suggested that in low- and medium-velocity detonation in condensed explosives, propagation may be due to heating in the shock front of gas entrapped in the explosive[1]. The temperature in these gas pockets has been shown to be very high[2], and the hypothesis is confirmed by the known effect of increase in gas pressure in stopping detonation in certain granular explosives[1]. The temperature attained in the gas depends on the compression ratio and the ratio of the specific heats of the gas, γ. If the hypothesis is correct, increase of γ should cause an increased temperature, and hence an increased rate of reaction, which should be manifested as an increase in the velocity of detonation of the explosive fired at cartridge diameters below that required for maximum velocity. We have now demonstrated this effect experimentally.

We have examined the effect of replacing air ($\gamma = 1{\cdot}40$) by argon ($\gamma = 1{\cdot}67$) as the surrounding medium on the velocity of detonation of two granular explosives. These were granular T.N.T. (Grade 1, 22–30 B.S.S.) of density 1·00 gm./cm.^{3} and cartridge diameter $1\frac{1}{4}$ in., and an 82/18 mixture of ammonium nitrate (specific surface 1,200 cm.^{2}/gm.) and aluminium (specific surface 1,600 cm.^{2}/gm.) of density 0·75 gm./cm.^{3} and cartridge diameter $\frac{7}{8}$ in. The velocity of detonation was measured photographically.

For the T.N.T. the velocity of detonation in air was 1,380 $\pm$ 20 m./s., and in argon 1,580 $\pm$ 15 m./s. For the ammonium nitrate composition, the velocities were 2,850 $\pm$ 30 m./s., and 3,100 $\pm$ 30 m./s., respectively, the limits quoted being standard deviations. There is clearly a significant increase in velocity, which further confirms the view that the mechanism of propagation of detonation involves heating of the gas spaces by the shock front.

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TRANSITION PROBABILITY IN MOLECULAR ENCOUNTERS
PART 1. THE EVALUATION OF PERTURBATION INTEGRALS

TRANSITION PROBABILITY IN MOLECULAR ENCOUNTERS

PART 1. THE EVALUATION OF PERTURBATION INTEGRALS

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The object of this work was to evaluate the perturbation integral for transitions between internal states produced by encounters between two molecules, with particular reference to the effect of choosing alternative functions to represent intermolecular force. The numerical work was restricted to an investigation of the excitation of the 1306 cm^{-1} vibration in methane, the intermolecular potential being represented by the (12 : 6) and (9 :6) Lennard-Jones functions or by a Morse function, but the methods are of general application. It may be concluded from the work that for molecules with a spherically symmetrical potential, a comparison of the perturbation integrals resulting from different force functions can be based on direct encounters alone, that the second virial coefficient gives almost no information about the intermolecular force at distances small enough to affect the perturbation integral, and that the relevant distances are sufficiently short to make questionable the assumption that the centre of force is at the centre of mass. The validation of first-order perturbation theory, which depends on the perturbation being small, may require examination of the behaviour of the perturbation integral throughout the encounter.

1. INTRODUCTION

Excitation of vibrational energy in molecular encounters in gases is known to be in certain circumstances a very inefficient process. This is well established experimentally, and has been treated theoretically by several authors.[1-5]

All theoretical treatments involve considerable approximations, and the precise conditions under which these approximations are reasonable can perhaps best be discussed by examining their consequences in some detail. For this reason we are at present engaged in a quantitative examination of some aspects of the theoretical treatments.

The problem of the calculation of transition probabilities may be tackled in two ways : one is to treat molecular encounters quantum-mechanically throughout ; the other is to use classical dynamics to discuss the encounter and the results of the quantum-mechanical time-dependent perturbation theory to discuss the transition probability. The latter method, though it has various drawbacks, has the advantage that it is equally straightforward in its application to indirect as to direct collisions. An important aspect of the time-dependent perturbation method is the calculation of the perturbation integral itself, and this paper gives an account of the treatment of the problem.

The fundamental approximation made in the treatment of the dynamics of the encounter classically is that the effect of the change in internal state upon the dynamics of the encounter can be neglected, that is, the effect of a transition on the kinetic energy of the motion is ignored. This, the Born approximation, is valid if fast encounters are chiefly responsible for energy transfer ; it has been discussed in more detail by Zener [6] who has shown for a simple case that if the Born approximation holds the fully quantum-mechanical results reduce to those of time-dependent perturbation theory.

We now derive the formula for the perturbation integral in the form which we intend to use. Zener [1] has shown that the probability P_{01} of causing the

transition $0 \rightarrow 1$ in the internal state of an atom or molecule in an encounter, is given according to time-dependent perturbation theory by

$$P_{01} = (4\pi^2/\hbar^2)\left|\int_{-\infty}^{+\infty} V_{01}\{r(t)\} \exp 2\pi i\nu t \, dt\right|^2,$$

where $\hbar\nu$ is the amount by which the internal energy is changed and V_{01} is the matrix element of the potential for the transition; r is the intermolecular distance. The conditions under which this integral may be converted into one involving the force have been discussed by Williams.[7] Applying his treatment to the problem of excitation of vibration, we write, for one-dimensional collisions,

$$V = V_0 + x\partial V/\partial x,$$

where x is the displacement of the oscillator along the line of centres. Hence

$$V_{01} = (\phi_0|V_0 + xF|\phi_1^*),$$

where the ϕ's are the wave functions of the oscillator and F is a force independent of the internal co-ordinates. Writing $(\phi_0 \mid x \mid \phi_1^*) = X_{01}$, we obtain

$$P_{01} = (16\pi^2/\hbar^2)X_{01}^2 I^2,$$

where

$$I = \int_0^{\infty} F(t) \cos 2\pi\nu t \, dt. \tag{1.1}$$

t is measured from the instant of closest approach. For three-dimensional collisions the result still holds good provided the orientation of a molecule relative to the centre of force remains constant during the encounter; this assumption is unlikely to be seriously in error for nearly direct collisions, and the subsequent analysis indicates that the overall transition probability is mainly determined by these.

The force $F(t)$ may be taken to be the intermolecular force if at distances of approach effective in causing vibrational transitions the force between two molecules is effectively that between the nearest atoms. A more detailed investigation of the connection between intermolecular force and the internal co-ordinates of the molecules is required before the transition probability can be calculated, and it is proposed to discuss this in a subsequent paper. For the present study it is necessary that the internally effective force should be proportional to the external, or intermolecular force, which seems a reasonable assumption for the purpose of comparing different force functions.

This assumption was made implicitly in a classical treatment of the problem by Landau and Teller,[2] who conclude that the transition probability should be proportional to I^2, as given in (1.1). They deduce the temperature dependence of transition probability, and Massey and Burhop [8] have pointed out that for CO_2 and N_2O the calculated dependence can be brought into agreement with the observed using very reasonable values of the parameter characterizing the intermolecular repulsive force. Also Kittel [9] has shown that a calculation using (1.1) but making several very inexact assumptions in the analysis gives order of magnitude agreement with the actual value of the transition probability.

There are, however, indications that this agreement may give an unduly favourable impression of the theory. Use of Kittel's treatment to give the temperature dependence of transition probability leads to the result that either the temperature dependence or the absolute value can be fitted by suitable choice of parameters, but not both simultaneously. Further, Fogg, Hanks and Lambert [10] have shown that the relaxation time in a series of related molecules appears to show an independence of molecular weight which does not accord with the result predicted both by Landau and Teller's theory and also by a quantum-mechanical approach.[8]

These circumstances suggest the desirability of a more detailed treatment, which we are at present carrying out. In the present paper attention is focused on the behaviour of I, the perturbation integral defined in (1.1).

The calculation of I is divided into two parts: the determination of the time-distance relationship from a knowledge of $F(r)$ and the evaluation of (1.1) using this relationship. In a few cases both these steps admit of an analytical solution, but, in general, numerical methods must be used.

In the present paper the numerical work is restricted to an investigation of the exciting of the 1306 cm^{-1} vibration of methane, the force being represented by a Lennard-Jones or a Morse function, but the methods and some of the results have wider applications. Methane was chosen as the subject of the numerical work for the following reasons: (i) its relaxation time as a function of temperature is known, (ii) the constants in a spherically symmetrical intermolecular force function for methane have been derived from second virial coefficient and other data.

In the course of the work it was found that a special method of integration of (1.1) was required, because of the slow rate of change of $F(t)$ compared with that of $2\pi\nu t$. The method can be applied generally to evaluation of integrals of the form (1.1) whenever $F(t)$ is generated by motion in a field of force.

2. EQUATIONS OF MOTION

This section gives for completeness a standard treatment of the classical dynamics of an encounter between two particles interacting in a spherically symmetrical potential field. For a similar treatment, see Hirschfelder, Bird and Spotz.[11]

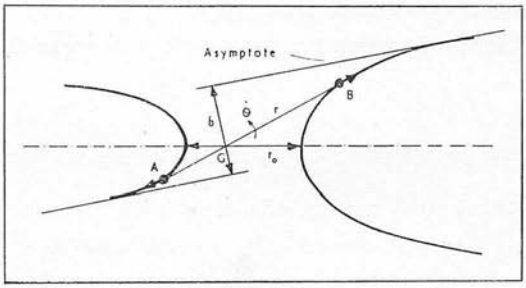

FIG. 1.—Geometry of an encounter.

The geometry of the encounter is shown in fig. 1. A, B are the particles representing the molecules and G is their centre of mass. Since the probability of three-body collisions is assumed to be negligible, the motion of G is uniform and may be ignored. The equations of motion in polar co-ordinates are

$$m(\ddot{r} - r\dot{\theta}^2) = F(r), \tag{2.1}$$

$$r^2\dot{\theta} = r_0^2\dot{\theta}_0, \tag{2.2}$$

where m is the reduced mass of the system and r_0, $\dot{\theta}_0$ are the values of r, $\dot{\theta}$ at the point of closest approach. Taking $t = 0$ at this point, and using the potential energy function,

$$V(r) = \int_r^\infty F(r)\mathrm{d}r, \tag{2.3}$$

gives the time-distance relationship

$$t = \int_{r_0}^r \left[v^2\left(1 - \frac{r_0^2}{r^2}\right) + \frac{2}{m}\left\{V(r_0)\frac{r_0^2}{r^2} - V(r)\right\}\right]^{-\frac{1}{2}} \mathrm{d}r, \tag{2.4}$$

where

$$v^2 = \dot{r}_\infty^2 = \frac{2}{m}V(r_0) + r_0^2\dot{\theta}_0^2. \tag{2.5}$$

v is the relative velocity of the particles at the beginning and end of the encounter.

An encounter between a given pair of molecules is thus specified by the parameters v and r_0, and (2.4) is a convenient form for computation. An alternative parameter to r_0 is the " impact parameter " b, defined as the distance separating the asymptotes to the paths of the molecules. The advantage of using b is that it is statistically independent of v for an assembly of molecules in a gas. From (2.2) and (2.5) we have

$$bv = r_0^2\dot{\theta}_0,$$

or

$$b^2 = r_0^2\{1 - 2V(r_0)/mv^2\}. \tag{2.6}$$

3. CALCULATION OF THE TIME-DISTANCE RELATIONSHIP

In this section are described, first the general method of evaluating (2.4) by numerical integration, next a particular application to Lennard-Jones force functions, and finally an analytical solution for direct encounters when a Morse function can be used for the intermolecular force.

(i) GENERAL NUMERICAL METHOD

The main contribution to (1.1) comes from small values of t, so the only difficulty in integrating (2.4) is the infinite integrand at $r = r_0$. This is removed by the substitution $x^2 = (r/r_0) - 1$. For present purposes it was found sufficient to integrate numerically with respect to x, up to $x = 1$ in steps of 0·1.

(ii) FORMULAE FOR LENNARD-JONES FUNCTION

The general Lennard-Jones function for intermolecular potential may be written

$$V(r) = \frac{V_0}{p-q}\left\{q\left(\frac{a}{r}\right)^p - p\left(\frac{a}{r}\right)^q\right\}, \tag{3.1}$$

where p, q, a and V_0 are positive constants, with $p > q$. Usually $q = 6$ and $p = 9$ or 12.

It is convenient to work in terms of dimensionless variables ρ, σ, τ given by

$$\rho = r/a,\ \sigma = mv^2/2V_0,\ \tau = t(2V_0/ma^2)^{\frac{1}{2}}, \tag{3.2}$$

then (2.4) gives $\tau(\rho)$ with ρ_0 and σ as parameters.

(iii) PARTICULAR ANALYTICAL SOLUTION

(2.4) can be integrated analytically for *direct encounters* ($b = 0$) when the potential is given by the Morse function

$$V(r) = \lambda \exp(-2\alpha r) - \mu \exp(-\alpha r). \tag{3.3}$$

For direct encounters (2.4) becomes

$$t = \int_{r_0}^{r} [v^2 - (2/m)V(r)]^{-\frac{1}{2}}\, dr,$$

and using (3.3) we have

$$t = \frac{1}{\alpha v}\cosh^{-1}\left[\frac{mv^2 \exp(\alpha r) + \mu}{(2mv^2\lambda + \mu^2)^{\frac{1}{2}}}\right],$$

whence

$$F(t) = \alpha m v^2 \frac{1 - \cosh \alpha v t \sin\phi}{(\cosh \alpha v t - \sin\phi)^2} \tag{3.4}$$

where

$$\tan^2\phi = \mu^2/2mv^2\lambda.$$

We may continue the analysis directly to obtain I from (1.1). The value of the integral is found by contour integration to be

$$I = \frac{2\pi^2 m\nu}{\alpha}\cosh\frac{\pi\nu(\pi + 2\phi)}{\alpha v}\operatorname{cosech}\frac{2\pi^2\nu}{\alpha v}. \tag{3.5}$$

When $(\pi^2\nu/\alpha v) > 3$ a sufficiently accurate form of (3.5) is

$$I = \frac{2\pi^2 m\nu}{\alpha} \exp\left\{-\frac{\pi\nu(\pi - 2\phi)}{\alpha v}\right\}. \tag{3.6}$$

4. THE NEED FOR A SPECIAL METHOD OF INTEGRATION OF (1.1)

It is convenient at this stage to obtain an idea of the order of magnitude of the integrand and the integral (1.1). In this section an approximate treatment is examined and it is shown that a special method is required for the numerical integration.

(i) LANDAU AND TELLER'S METHOD

The method used by Landau and Teller [2] is useful in determining orders of magnitude. They consider a direct encounter when the intermolecular force is an exponential repulsion, the form (3.3) with $\mu = 0$. (3.5) then becomes

$$I = \frac{\pi^2 m\nu}{\alpha} \operatorname{cosech} \frac{\pi^2\nu}{\alpha v}$$

$$\sim \frac{2\pi^2 m\nu}{\alpha} \exp\left\{-\frac{\pi^2\nu}{\alpha v}\right\}. \tag{4.1}$$

At a given temperature T the statistical weight $Q(v)\,dv$ to be given to velocities in the range v, $v + dv$ contains a factor $\exp(-mv^2/2kT)$, where k is Boltzmann's constant. If the values are such that the behaviour of $I(v)$ and $Q(v)$ is determined principally by the exponentials, the maximum of I^2Q occurs near the minimum of

$$(2\pi^2\nu/\alpha v) + (mv^2/2kT), \tag{4.2}$$

giving

$$v = (2\pi^2 kT\nu/\alpha m)^{\frac{1}{3}}. \tag{4.3}$$

This is approximately the velocity at which a transition is most likely to occur in the gas at temperature T. The value of (4.2) is then

$$(27\pi^4 m\nu^2/2\alpha^2 kT)^{\frac{1}{3}}.$$

It is worth noting here that this exponent is the same as that obtained by Schwartz *et al.*[4] from a wholly quantum-mechanical treatment. The discrepant factor $(2\pi)^{\frac{2}{3}}$ mentioned by these authors as arising between their result and that of Landau and Teller is due to the fact that the former authors used ν in cyclic frequency, as we do here, whereas the latter used ν for frequency in radian measure. The agreement between the two treatments was pointed out much earlier by Zener.[6]

Consider, for example, the probability of exciting the 1306 cm^{-1} vibration in methane at 300° K. Taking $\alpha = 2 \times 10^8\ \text{cm}^{-1}$, we have $v = 2{\cdot}3 \times 10^5\ \text{cm sec}^{-1}$, or about five times the velocity of sound in methane at this temperature. From (4.1) we deduce

$$I = (5{\cdot}2 \times 10^{-17}) \exp(-8{\cdot}5) = 1{\cdot}1 \times 10^{-20}\ \text{g cm sec}^{-1}.$$

At 600° K we have

$$v = 2{\cdot}9 \times 10^5\ \text{cm sec}^{-1},$$

$$I = (5{\cdot}2 \times 10^{-17}) \exp(-6{\cdot}8) = 5{\cdot}9 \times 10^{-20}\ \text{g cm sec}^{-1}.$$

(ii) APPLICATION TO THE INTEGRATION

Using the numerical values obtained above, we may now examine the calculation of the integral. From (3.4) with $\mu = 0$ we have

$$F(t) = \alpha m v^2 \operatorname{sech}^2 \alpha v t, \tag{4.4}$$

and for sufficiently large values of t,

$$F(t) \sim 4F(0) \exp(-2\alpha v t),$$

so that the duration of the encounter, defined as the time taken for the force to fall to 1 % of its maximum, is roughly

$$t = (\alpha v)^{-1} \ln 20 = 3(\alpha v)^{-1}.$$

With this value of t, (4.1) and (4.4) give

$$\frac{I}{tF(0)} = \frac{2\pi^2\nu}{3\alpha v} \exp\left(-\frac{\pi^2\nu}{\alpha v}\right).$$

Numerical values from § 4(i) give

$$I/\{tF(0)\} = 1{\cdot}2 \times 10^{-3} \text{ for } 300^\circ \text{ K, and } 5{\cdot}0 \times 10^{-2} \text{ for } 600^\circ \text{ K.}$$

These values show that the value of the integral is small compared to the maximum of the integrand, particularly at the velocities dominant at lower temperatures: this is because the cosine factor in (1.1) produces nearly equal positive and negative contributions to the integral. The number of cycles of oscillation between $t = 0$ and the 1 % level of $F(t)$ is $3\nu/\alpha v = 2{\cdot}6$ or $2{\cdot}1$, and the small value of I means that the contributions from values of t beyond the 1 % level cannot be ignored. These considerations preclude direct numerical integration.

5. NUMERICAL EVALUATION OF PERTURBATION INTEGRAL

This section describes a method of integration developed for this purpose and its application to the Lennard-Jones force function.

(i) DESCRIPTION OF METHOD

The behaviour of the integrand described above suggests using a method which replaces $F(t)$ by a function varying more rapidly near $t = 0$. The shape of the typical force function is such that successive derivatives of $F(t)$ vary more rapidly with t, which suggests integrating (1.1) by parts before applying numerical integration. We note that a physically reasonable force function tends to zero with all its derivatives as $t \to \infty$; also since $t = 0$ occurs at the instant of closest approach, $F(t) = F(-t)$ and all odd derivatives are zero at $t = 0$. Integrating by parts $2n$ times yields

$$I = \left\{\frac{-1}{(2\pi\nu)^2}\right\}^n \int_0^\infty F^{(2n)}(t) \cos 2\pi\nu t \, \mathrm{d}t. \tag{5.1}$$

It may be seen that the larger ν is, the more effective is this process in reducing the maximum value of the integrand. There is, however, an optimum value of n beyond which the maximum increases again: for a typical force function $(-1)^n F^{(2n)}(t)$ is positive at $t = 0$ and has $(n + 1)$ zeros in the range of integration; this expression decreases more rapidly from its initial value as n is increased and its smallest zero occurs at smaller values of t. For a certain value of n, depending on ν and the dynamics of the encounter, this zero is as near as possible to the point $\nu t = 1/4$ at which $\cos 2\pi\nu t$ is zero. This is the best value of n from the point of view of numerical accuracy, since the contributions to the integral from the first and second quadrants of $2\pi\nu t$ have the same sign; it follows that this gives a value of $\{-(2\pi\nu)^2\}^{-n} F^{(2n)}(0)$ near the minimum.

The obvious drawback to this method is that the successive derivatives become steadily more laborious to calculate; it is not necessary, however, to resort to numerical differentiation. Use is made of the fact that $F(t)$ results from the solution of the equations of motion. If dots denote differentiation with respect to t and dashes differentiation with respect to r, we have

$$\dot{F} = \dot{r}F',$$
$$\ddot{F} = \dot{r}^2 F'' + \tfrac{1}{2}(\mathrm{d}\dot{r}^2/\mathrm{d}r)F'.$$

Similarly,

$$F^{(2n)}(t) = \dot{r}^2 \frac{\mathrm{d}^2}{\mathrm{d}r^2}\{F^{(2n-2)}(t)\} + \tfrac{1}{2}\frac{\mathrm{d}\dot{r}^2}{\mathrm{d}r}\frac{\mathrm{d}}{\mathrm{d}r}\{F^{(2n-2)}(t)\}. \tag{5.2}$$

Since $\dot{r}^2$ is known as a function of r from the equations of motion, (5.2) gives $F^{(2n)}(t)$ as a function of r provided $F^{(2n-2)}(t)$ is known as a function of r. Thus starting from $F(r)$, successive applications of (5.2) yield the higher derivatives.

(ii) FORMULAE FOR LENNARD-JONES FUNCTION

In the notation of section 3(ii) the following equations define new quantities ω, $f(\rho)$ and J in terms of which the perturbation integral and the force function have simple forms.

$$\omega = 2\pi\nu t/\tau = 2\pi\nu(ma^2/2V_0)^{\frac{1}{2}}, \tag{5.3}$$

$$f(\rho) = \rho^{-p-1} - \rho^{-q-1}, \tag{5.4}$$

$$J = (q^{-1} - p^{-1})(\tfrac{1}{2}mV_0)^{-\frac{1}{2}}I = \int_0^\infty f(\tau)\cos\omega\tau\ d\tau. \tag{5.5}$$

The general formulae for higher derivatives are complicated, and in practice the insertion of numerical values of p and q is desirable. For direct encounters the term in $(\rho_0/\rho)^2$ does not appear and this shortens the calculations considerably. Formulae obtained using typical values of p and q are given in appendix 1.

6. NUMERICAL RESULTS FOR METHANE

This section applies the method described in § 5 to the calculation of the perturbation integrals for the 1306 cm^{-1} vibration in methane. The results are compared with those obtained by analytical integration and are used to draw conclusions about the calculation of transition probability in general.

(i) (12 : 6) LENNARD-JONES FUNCTION

Corner [12] gives the following values for the constants in the (12 : 6) Lennard-Jones function for methane :

$$V_0 = 148k = 2{\cdot}04 \times 10^{-14}\ \text{erg};\quad a = 4{\cdot}25 \times 10^{-8}\ \text{cm}. \tag{6.1}$$

With $\nu = 1306\ cm^{-1}$, and $m = 13{\cdot}38 \times 10^{-24}$ g, (5.3) and (5.5) give

$$\omega = 189,\quad \log_{10}(I/J) = -17{\cdot}353. \tag{6.2}$$

A rough idea of the most important velocity at a given temperature is given by (4.3) with $\alpha = 2 \times 10^8\ cm^{-1}$. This gives the following values of σ and ρ_0^{-6} for direct encounters :

T(°K)	v(cm sec^{-1})	σ	ρ_0^{-6}
300	$2{\cdot}3 \times 10^5$	17	5·2
600	2·9	27	6·3
900	3·3	36	7·1
1200	3·6	43	7·6
1500	3·9	50	8·1

Values of J were therefore calculated for direct encounters with $\rho_0^{-6} = 4(1)10(2)14$ the higher values being added since computation becomes simpler as v is increased. A smaller number of values were calculated for indirect encounters. The results are given in table 1, which contains the following information : (i) values of σ and $\log_{10} J$ for direct encounters, using the above values of ρ_0^{-6}, (ii) for some of these values of σ, values of $\log_{10} J$ for indirect encounters with ρ_0^{-6} decreased by one or two units, (iii) for each of the above, the value of the impact parameter $(b/a)^2$, the value of n used in the numerical integration, and the values of r_0 and v.

(ii) INTERPRETATION OF THE RESULTS

In order to explain the significance of these results and justify subsequent comparisons, we now give a short account of the effect of statistical weighting on the collision parameters : a detailed analysis will be given elsewhere.

In a diffuse gas, directions of motion are random. Then in an encounter between two molecules with given relative velocity v, all directions of the relative velocity vector are equally probable. Therefore the number of such encounters with impact parameters in the range b, $b + \mathrm{d}b$ is proportional to $b\mathrm{d}b = \frac{1}{2}\mathrm{d}b^2$ and so the transition probability summed over all encounters with velocity v is obtained by integrating the square of the perturbation integral with respect to b^2.

TABLE 1.—RESULTS FOR (12 : 6) LENNARD-JONES FUNCTION

σ	v (cm sec^{-1})	ρ_0^{-6}	r_0 (cm)	$(b/a)^2$	n	$\log_{10} J$	$\log_{10} I$
direct encounters							
8	$1{\cdot}56 \times 10^5$	4	$3{\cdot}37 \times 10^{-8}$	0	3	− 3·350	− 20·703
15	2·14	5	3·25	0	3	− 2·301	− 19·654
24	2·71	6	3·16	0	3	− 1·650	− 19·003
35	3·27	7	3·07	0	3	− 1·206	− 18·559
48	3·83	8	3·01	0	3	− 0·883	− 18·236
63	4·38	9	2·95	0	2	− 0·637	− 17·990
80	4·94	10	2·90	0	2	− 0·447	− 17·800
120	6·05	12	2·81	0	1	− 0·184	− 17·537
168	7·16	14	2·74	0	0	0·002	− 17·351
indirect encounters							
15	$2{\cdot}14 \times 10^5$	4	$3{\cdot}37 \times 10^{-8}$	0·29	2	− 3·205	− 20·558
24	2·71	5	3·25	0·22	2	− 2·222	− 19·575
35	3·27	5	3·25	0·33	2	− 2·144	− 19·497
		6	3·16	0·17	2	− 1·600	− 18·953
48	3·83	7	3·07	0·14	2	− 1·191	− 18·544
63	4·38	8	3·01	0·12	2	− 0·879	− 18·232

Now table 1 shows that the value of J depends mainly on the distance of closest approach r_0 and is only slightly affected by changes in v for a given r_0. When $\rho_0^{-6} = 5$ we have

σ	= 15	24	35
$\log_{10} J$	= − 2·301	− 2·222	− 2·144

so the variation of $\log J$ with σ can be regarded as linear. The rapid decrease in J with increasing b is illustrated by the figures for $\sigma = 35$:

ρ_0^{-6}	7	6	5
$(b/a)^2$	0	0·17	0·33
$\log_{10} J$	− 1·206	− 1·600	− 2·144

Combined with the previous figures, this shows that for integration with respect to b^2 the required values of $\log J$ for higher values of b may be obtained by linear extrapolation of $\log J$ with respect to σ for given r_0. By doing this the number of values of J to be calculated is much reduced.

Thus the procedure in summing the transition probability over all encounters is to convert the obtained table of values of $J(\sigma, r_0)$ into a table of $J(\sigma, b^2)$, extrapolating where necessary, then integrate with respect to b^2 for a set of given σ, and finally integrate over the velocity distribution.

A further simplification can be introduced without much loss of accuracy by ignoring the variation of J for a given r_0. This results in making J a function of r_0 only, and the total transition probability can be expressed as a single integral incorporating the Maxwell velocity weighting factor. Finally, by an argument similar to the one used in § 4(i), the probability can be related to the behaviour of the perturbation integral near the most effective velocity. In so far as it concerns the present investigation this means that the effect of altering the force function can be deduced from the values of the perturbation integral for direct encounters alone. The remaining results accordingly relate to direct collisions.

(iii) (9 : 6) LENNARD-JONES FUNCTION

The following values for the (9 : 6) constants fit the second virial coefficient derived from the (12 : 6) function for $T > 300°$ K.

$$V_0 = 111{\cdot}1k = 1{\cdot}533 \times 10^{-14}\ \text{erg};\quad a = 4{\cdot}52 \times 10^{-8}\ \text{cm}, \tag{6.3}$$

giving

$$\omega = 232,\quad \log_{10}(I/J) = -17{\cdot}239. \tag{6.4}$$

The approximate expression (4.3) with $\alpha = 2 \times 10^8$ as before gives the following values for the most effective velocity, and the corresponding values of σ and ρ_0^{-3}

T(°K)	v (cm sec^{-1})	σ	ρ_0^{-3}
300	$2{\cdot}3 \times 10^5$	23	2·9
600	2·9	37	3·2
900	3·3	48	3·4
1200	3·6	57	3·6
1500	3·9	66	3·8

Values of J were calculated for direct encounters with $\rho_0^{-3} = 3, 4, 5$ (table 2).

TABLE 2.—RESULTS FOR (9 : 6) LENNARD-JONES FUNCTION (DIRECT ENCOUNTERS)

σ	v(cm sec^{-1})	ρ_0^{-3}	r_0 (cm)	n	$\log_{10} J$	$\log_{10} I$
27	$2{\cdot}49 \times 10^5$	3	$3{\cdot}14 \times 10^{-8}$	3	− 2·451	− 19·690
80	4·28	4	2·85	2	− 0·950	− 18·189
175	6·34	5	2·64	1	− 0·274	− 17·513

(iv) MORSE FUNCTION

The attractive term is retained so that the constants may be related to the second virial coefficient. The Morse function resembles the Lennard-Jones function in that the goodness of fit to the virial coefficient is not sensitive to the choice of α provided the other constants are given suitable values. The two representative functions were fitted to the virial coefficient derived from the (12 : 6) Lennard-Jones function, and the virial coefficients diverge by less than 2 cm^3 mole^{-1} down to $T = 350°$ K. The first function gives a weak repulsion at short range, the second a strong one: the constants in (3.3) are

$$\text{I.}\quad \alpha = 1{\cdot}27 \times 10^8\ \text{cm}^{-1},\ \lambda = 1{\cdot}54 \times 10^{-9}\ \text{erg},\ \mu = 1{\cdot}20 \times 10^{-11}\ \text{erg}, \tag{6.5}$$

$$\text{II.}\quad \alpha = 2{\cdot}83 \times 10^8\ \text{cm}^{-1},\ \lambda = 3{\cdot}38 \times 10^{-5}\ \text{erg},\ \mu = 2{\cdot}79 \times 10^{-9}\ \text{erg}. \tag{6.6}$$

Table 3 gives values of the perturbation integral calculated from (3.5). Values are also given with $\phi = 0$, to show the effect of ignoring the attractive term. For

TABLE 3.—RESULTS FOR MORSE FUNCTION (DIRECT ENCOUNTERS)

v(cm sec^{-1})	ϕ^0	$\log_{10} I$	r_0 (cm)	$\log_{10} I(\phi = 0)$	$r_0(\phi = 0)$ (cm)
I. Constants from (6.5)					
0	90	− 30·32	$3{\cdot}82 \times 10^{-8}$	− ∞	—
1×10^5	30·6	− 24·81	3·51	− 29·30	$3{\cdot}95 \times 10^{-8}$
2	16·4	− 21·48	3·18	− 22·69	3·41
4	8·4	− 19·082	2·74	− 19·391	2·86
6	5·6	− 18·153	2·47	− 18·290	2·54
8	4·2	− 17·662	2·26	− 17·740	2·32
10	3·4	− 17·360	2·09	− 17·410	2·14
II. Constants from (6.6)					
0	90	− 20·51	$3{\cdot}33 \times 10^{-8}$	− ∞	—
1×10^5	42·9	− 19·55	3·25	− 22·37	$3{\cdot}54 \times 10^{-8}$
2	24·9	− 18·581	3·14	− 19·402	3·30
4	13·1	− 17·704	2·97	− 17·919	3·05
6	8·8	− 17·325	2·86	− 17·420	2·91
8	6·6	− 17·109	2·77	− 17·163	2·81
10	5·3	− 16·969	2·70	− 17·005	2·73

most of the values of v used in the table, (3.6) gives a sufficiently good approximation: for $v \leqslant 10^6$ in case I, $v \leqslant 4{\cdot}5 \times 10^5$ in case II.

(v) COMPARISON BETWEEN FORCE FUNCTIONS

Fig. 2 gives curves of $\log_{10} I$ against v for direct encounters for the various force functions described above, and fig. 3 gives the corresponding curves of r_0 against v. For the larger values of v the curves in fig. 2 are in the reverse order

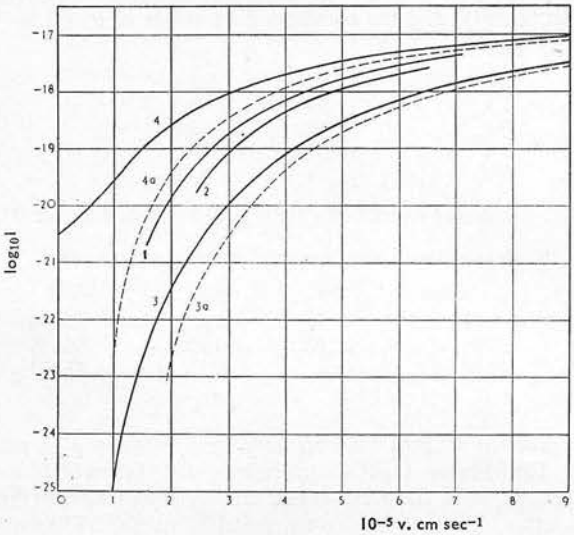

FIG. 2.—Curves of $\log_{10} I$ against v for direct encounters.

1. (12 : 6) Lennard-Jones function.
2. (9 : 6) Lennard-Jones function.
3. Morse function with $\alpha = 1{\cdot}27 \times 10^{-8}$ cm^{-1}.

3*a*. no attractive term.

4. Morse function with $\alpha = 2{\cdot}83 \times 10^{8}$ cm^{-1}.

4*a*. no attractive term.

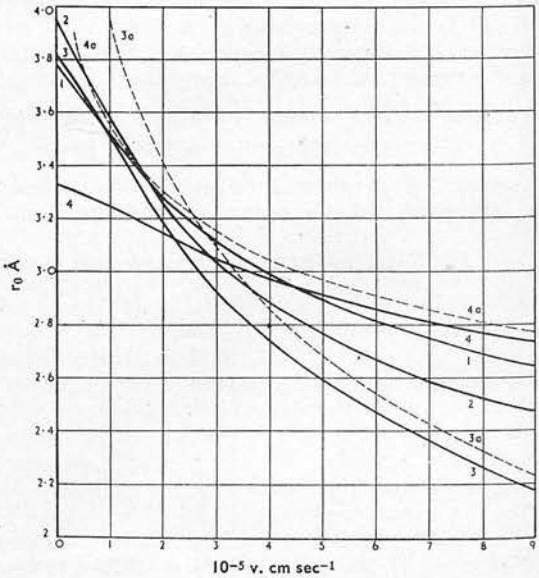

FIG. 3.—Curves of r_0 against v for direct encounters; key as for fig. 2.

to those in fig. 3, showing that the transition probability increases with the steepness of the repulsion potential as might be expected from formula (4.1) for the single exponential function. At lower velocities, although the order of the curves in fig. 3 is not maintained, the order of those in fig. 2 is the same as the order of the slopes of the curves in fig. 3.

Approximate values of the "most effective" velocity at a given temperature are found from (4.3) with the values of α given in section 6 (iv):

	$10^{-8}\alpha = 1{\cdot}27$	2·83
$T = 300°$ K,	$10^{-5}v = 2{\cdot}7$	2·0
600	3·4	2·6
900	3·8	2·9
1200	4·2	3·2
1500	4·6	3·5

If curves 3 and 4 in fig. 2 are compared at equal temperatures instead of equal velocities, the differences are slightly reduced. At $I = 300°$ K the difference between the two values of $\log_{10} I$ is 2·3 and at $T = 1500°$ K it is 1·1.

7. PERTURBATION INTEGRAL BETWEEN FINITE LIMITS

The transition probability is proportional to the square of (1.1) only if a transition can be regarded as a small perturbation of the dynamical system concerned. This must hold at any time during the encounter. To establish validity it is necessary to calculate

$$K(t) = \left| \int_{-\infty}^{t} F(s) \exp 2\pi i\nu s \, \mathrm{d}s \right|^2 \tag{7.1}$$

as a function of t. The ratio $K(t)/K(\infty) = K(t)/4I^2$ then gives the ratio between the probability at time t and the overall probability. No analytical method is available, so the method of § 5 must be used.

Write

$$C(t) = \int_0^t F(s) \cos 2\pi\nu s \, \mathrm{d}s, \quad S(t) = \int_t^\infty F(s) \sin 2\pi\nu s \, \mathrm{d}s. \tag{7.2}$$

Then, using (1.1) and (7.1),

$$K(t) = \{I + C(t)\}^2 + \{S(t)\}^2, \quad t > 0 \tag{7.3}$$

$$= \{I - C(-t)\}^2 + \{S(-t)\}^2, \quad t < 0. \tag{7.4}$$

The integration-by-parts formulae corresponding to (5.1) are as follows:

$$\begin{aligned} C(t) = \{-(2\pi\nu)^2\}^{-n} \int_0^t & F^{(2n)}(s) \cos 2\pi\nu s \, \mathrm{d}s \\ & + \{(2\pi\nu)^{-1} \sin 2\pi\nu t \,.\, F(t) + (2\pi\nu)^{-2} \cos 2\pi\nu t \,.\, F'(t)\} - \ldots \\ & + (-)^{n-1}\{(2\pi\nu)^{-2n+1} \sin 2\pi\nu t \,.\, F^{(2n-2)}(t) + (2\pi\nu)^{-2n} \cos 2\pi\nu t \,.\, F^{(2n-1)}(t)\} \end{aligned} \tag{7.5}$$

$$\begin{aligned} S(t) = \{-(2\pi\nu)^2\}^{-n} \int_t^\infty & F^{(2n)}(s) \sin 2\pi\nu s \, \mathrm{d}s \\ & + \{(2\pi\nu)^{-1} \cos 2\pi\nu t \,.\, F(t) - (2\pi\nu)^{-2} \sin 2\pi\nu t \,.\, F'(t)\} - \ldots \\ & + (-)^{n-1}\{(2\pi\nu)^{-2n+1} \cos 2\pi\nu t \,.\, F^{(2n-2)}(t) - (2\pi\nu)^{-2n} \sin 2\pi\nu t \,.\, F^{(2n-1)}(t)\}. \end{aligned} \tag{7.6}$$

Values of $K(t)$ have been calculated by this method for the (12 : 6) Lennard-Jones function, $\sigma = 24$, direct encounter. The resulting curve of $K(t)/K(\infty)$ against t is shown in fig. 4. It shows that shortly after the instant of closest approach the contribution of the first vibrational eigenfunction to the true eigenfunction of the oscillator is some 25 times its value at the end of the encounter. This must be taken account of when the validity of the small-perturbation hypothesis is examined.

8. DISCUSSION

In this section some conclusions are drawn from the results of the previous sections. They are therefore based mainly on the numerical results for methane;

but it seems likely that they will hold for encounters between other molecules whose intermolecular potentials may be represented in a similar way.

The chance of a transition in an encounter with a given velocity falls off rapidly with increase in the impact parameter. The variation of transition probability with velocity can therefore be estimated with sufficient accuracy from the values for direct encounters, so that valid comparisons between the effects of different spherically symmetrical force functions may be made on the basis of direct encounters. Estimation of the numerical value for the overall probability requires consideration of the integration over all types of encounters. This problem will be treated elsewhere.

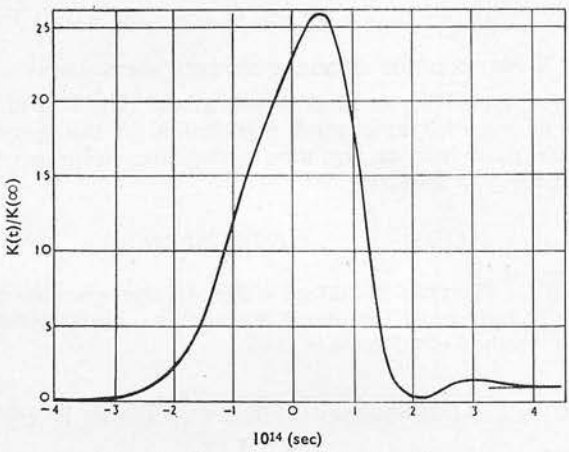

FIG. 4.—Curve of $K(t)/K(\infty)$ against t.

There is no qualitative difference between Lennard-Jones and Morse functions in their effect on the perturbation integral. It is necessary to retain the attractive term in the latter so as to fit the second virial coefficient; however, this coefficient is not sensitive to changes in exponent or index of the repulsive term which can change the transition probability by a factor of 100 (possibly 10^4 at low velocities). Thus the second virial coefficient gives almost no information about the nature of the intermolecular force at distances small enough to be important to the perturbation integral. Consequently there is no objection to representing the force by a simple exponential repulsion until a more sensitive measure is available.

The indifference of the virial coefficient to the force function at this range raises the question of the validity of using such simple expressions for the force law. For example, $v = 2{\cdot}5 \times 10^5$ cm sec^{-1} is a typical "most effective velocity" for transition at ordinary temperatures. At this velocity the closest distance r_0 of approach calculated from the (12 : 6) Lennard-Jones function is 3·19 Å, for a direct encounter. Assuming approach along the line of the bonds and taking 1·09 Å as the C—H distance in methane, the distance between hydrogen atoms at r_0 is 1·01 Å. Now the repulsive potential at this distance between two hydrogen atoms in the $^3\Sigma$ state of the hydrogen molecule is about 5×10^{-12} erg, whereas the relative kinetic energy of the methane molecules at this velocity is about 4×10^{-13} erg, less by a factor of 10. This means that the true repulsive potential at this range is probably much steeper than that calculated regarding the centre of mass as the centre of force; a consideration which suggests the investigation of encounters between molecules based on a repulsive potential of the form $\exp\{-\alpha(r - r_1)\}$.

As the steepness of the repulsive potential is increased the value of the perturbation integral increases but its proportional rate of change with velocity

decreases. This, combined with the considerations of the previous paragraph, may explain the overestimation of the temperature dependence of the effect.

The validity of the perturbation theory depends on the size of the perturbation integral throughout the encounter. It is apparently not sufficient to show that the chance of excitation is small after the encounter: the evidence suggests that the integral may, near the point of closest approach, attain a value many times its value at the end of the encounter.

In conclusion we may enumerate the other aspects of the calculation of transition probability which have not been treated in this paper: (*a*) the statistics of encounters, (*b*) the connection between the quantum-mechanical treatment of collision problems and time-dependent perturbation theory, (*c*) the connection between close range interatomic forces and intermolecular force, (*d*) the coupling between translational and internal energy.

APPENDIX 1

EVEN TIME-DERIVATIVES OF LENNARD-JONES FORCE FUNCTION

The following formulae are needed for numerical evaluation of the perturbation integral[1]. For notation, see 5 (ii).

(12 : 6) FUNCTION

$$f = \rho^{-13} - \rho^{-7},$$

$$f^{\mathrm{II}}(\tau) = \rho^{-9}\{-56\sigma + (182\sigma - 154)\rho^{-6} + 540\rho^{-12} - 260\rho^{-18}\} + \rho^{-11}\rho_0^2(\sigma + 2\rho_0^{-6} - \rho_0^{-12})(63 - 195\rho^{-6}).$$

$$\begin{aligned} f^{\mathrm{IV}}(\tau) = {} & 12\rho^{-11}\{-420\sigma^2 + (3{,}640\sigma^2 - 4{,}172\sigma)\rho^{-6} + (30{,}107\sigma - 7{,}315)\rho^{-12} \\ & - (21{,}385\sigma - 51{,}485)\rho^{-18} - 62{,}730\rho^{-24} + 19{,}890\rho^{-30}\} \\ & + 12\rho^{-13}\rho_0^2(\sigma + 2\rho_0^{-6} - \rho_0^{-12})\{1{,}155\sigma - (8{,}840\sigma - 5{,}005)\rho^{-6} \\ & - 34{,}377\rho^{-12} + 23{,}595\rho^{-18}\} + \rho^{-15}\rho_0^4(\sigma + 2\rho_0^{-6} - \rho_0^{-12})^2(-9{,}009 + 62{,}985\rho^{-6}). \end{aligned}$$

For direct encounters, $\sigma + 2\rho_0^{-6} - \rho_0^{-12} = 0$ and

$$\begin{aligned} f^{\mathrm{VI}}(\tau) = {} & 216\rho^{-13}\{3{,}080\sigma^3 + (61{,}880\sigma^3 - 78{,}624\sigma^2)\rho^{-6} + (1{,}072{,}288\sigma^2 \\ & - 389{,}816\sigma)\rho^{-12} - (1{,}116{,}115\sigma^2 - 4{,}660{,}390\sigma + 504{,}735)\rho^{-18} \\ & - (7{,}819{,}140\sigma - 5{,}754{,}980)\rho^{-24} + (3{,}143{,}140\sigma - 12{,}500{,}180)\rho^{-30} \\ & + 9{,}200{,}400\rho^{-36} - 2{,}174{,}640\rho^{-42}\}. \end{aligned}$$

(9 : 6) FUNCTION

Direct encounters only ($\sigma + 3\rho_0^{-6} - 2\rho_0^{-9} = 0$).

$$f = \rho^{-10} - \rho^{-7}.$$

$$f^{\mathrm{II}}(\tau) = \rho^{-9}(-56\sigma + 110\sigma\rho^{-3} - 231\rho^{-6} + 595\rho^{-9} - 310\rho^{-12}).$$

$$\begin{aligned} f^{\mathrm{IV}}(\tau) = {} & 3\rho^{-11}\{-1{,}680\sigma^2 + 5{,}720\sigma^2\rho^{-3} - 25{,}032\sigma\rho^{-6} + 93{,}822\sigma\rho^{-9} \\ & - (63{,}140\sigma + 65{,}835)\rho^{-12} + 282{,}975\rho^{-15} - 330{,}540\rho^{-18} + 115{,}010\rho^{-21}\}. \\ & + 115{,}010\rho^{-21}\}. \end{aligned}$$

$$\begin{aligned} f^{\mathrm{VI}}(\tau) = {} & 9\rho^{-13}\{73{,}920\sigma^3 + 400{,}400\sigma^3\rho^{-3} - 2{,}830{,}464\sigma^2\rho^{-6} + 14{,}779{,}800\sigma^2\rho^{-9} \\ & - (12{,}658{,}800\sigma^2 + 21{,}050{,}064\sigma)\rho^{-12} + 117{,}633{,}870\sigma\rho^{-15} \\ & - (166{,}966{,}020\sigma + 40{,}883{,}535)\rho^{-18} + (68{,}075{,}700\sigma + 249{,}490{,}395)\rho^{-21} \\ & - 470{,}831{,}130\rho^{-24} + 352{,}961{,}700\rho^{-27} - 92{,}008{,}000\rho^{-30}\}. \end{aligned}$$

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TRANSITION PROBABILITY IN MOLECULAR ENCOUNTERS
PART 2.—VIBRATIONAL RELAXATION TIME IN METHANE

TRANSITION PROBABILITY IN MOLECULAR ENCOUNTERS

PART 2.—VIBRATIONAL RELAXATION TIME IN METHANE

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The object of this work was to calculate the vibrational relaxation time in methane from fundamental theory. This involves calculating the probability of vibrational de-excitation for typical encounters between pairs of molecules and averaging over all encounters. The statistics of encounters and the most suitable approximate methods of averaging are discussed. The force acting between methane molecules at close range is investigated, and formulae are obtained for the intermolecular force in terms of the interatomic forces involved. The coupling between intermolecular force and the excitation of vibration is studied, and the concept of the effective vibrational mass of a polyatomic molecule is used as a measure of this coupling. Numerical values of relaxation time are obtained, and compared with experimental results. The order of magnitude of the calculated values is correct but the calculated temperature dependence is much too steep. Possible reasons for this discrepancy are examined, and it is noted that it is also characteristic of simpler solutions of the relaxation time problem.

1. Introduction and general theory

(i) Statement of problem and resumé of previous work

The exchange of energy between translation and vibration of molecules in a gas is often a slow process, and a disequilibrium between these two forms of energy may decay slowly enough to be observed experimentally. The main object of the work reported here was to obtain a quantitative estimate of this effect from fundamental theory.

The gas chosen for investigation was methane, whose lowest vibration frequency, 1306 cm^{-1}, is large enough to ensure that the proportion of vibrationally excited molecules is small at moderate temperatures, and whose molecules have approximate spherical symmetry. The basic problem is to calculate for a given gas temperature the average time spent by a methane molecule in the first excited state, and this involves calculating the probability of vibrational de-excitation for typical encounters between pairs of molecules and averaging over all encounters.

It was decided to begin the investigation by examining the effect on transition probability of the type of function used to represent intermolecular force. This was done using the method of impact parameters; the results have already been reported as part 1 of this series.[1] In was concluded that transition probability depends mainly on the classical distance of closest approach, most transitions occurring in nearly direct encounters; and that it depends on features of the force function that cannot be ascertained from other properties of the gas such as the second virial coefficient. Several results from part 1 are used in the present treatment.

(ii) Fundamental theory and a particular solution

The general quantum-mechanical theory of the transitions produced in an encounter has been treated by Mott and Massey.[2] The wave equation for the

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system of two interacting molecules is separated into the equation of relative motion of the two mass-centres and the equations of motion of the individual atoms of each molecule relative to the mass-centre. The appropriate method of solution is the method of distorted waves, which takes into account the change in translational energy produced by an internal transition: a formal solution to the problem is obtained in chap. VIII, § 5 of ref. (2). We have now to obtain numerical results from it without excessive labour.

A particular solution of the general equations has been given by Jackson and Mott,[3] who used it to calculate the accommodation coefficient for gas atoms normally incident on a plane solid surface. In their solution one body is the incident atom, mass m, the other is a bound atom vibrating in the internal field of the solid. Motion is restricted to one dimension with the two atoms moving collinearly, and the mutual atomic potential is a negative exponential in the inter-atomic distance. Thus the internal wave function ψ is that for a linear oscillator (harmonic for sufficiently small displacements) and the interaction potential is

$$V(r, r_a) = C \exp\,[-\,\alpha(r - r_a)] = V(r_a) \exp\,(\alpha r_a) \sim (1 + \alpha r_a) V(r),$$

where αr_a is small. Here r is the relative motion co-ordinate, and r_a the co-ordinate for motion of the bound atom. The general theory requires the evaluation of the matrix element

$$V_{nm}(r) = \int V(r, r_a, r_b)\psi_n\psi_m^* \mathrm{d}\tau_a \mathrm{d}\tau_b, \tag{1.1}$$

where again r is the relative motion co-ordinate, r_a and r_b are the internal motion co-ordinates for the two particles, and the ψ are internal wave functions. In the particular solution under discussion $V_{nm}(r)$ is found using the standard integrals for the harmonic oscillator, if 0 is the ground state of the oscillator

$$\begin{aligned} V_{00} &= V_{nn} = V(r), \\ V_{0n} &= 0, \text{ if } n \neq 1, \\ V_{01} &= V_{10} = \alpha(\boldsymbol{h}/8\pi^2 M\nu)^{\frac{1}{2}} V(r), \end{aligned} \tag{1.2}$$

where M is the effective mass and ν the frequency of the oscillator. If v_i is the initial relative velocity, the transition probability for the $1 \to 0$ transition is found to be

$$p_{10} = \frac{256\pi^6 m^2 \nu^2}{\alpha^2 \boldsymbol{h}^2} \frac{\boldsymbol{h}}{8\pi^2 M\nu} \frac{\sinh q_i \sinh q_j}{(\cosh q_i - \cosh q_j)^2}, \tag{1.3}$$

where $$q_i = 4\pi^2 m v_i / \alpha \boldsymbol{h}.$$

The subscripts i and j refer to the initial and final velocity.

(iii) Application of particular solution

Zener [4] has shown that the method of impact parameters using time-dependent perturbation theory,[5] when applied to the problem just described, yields the result (1.3) when $q_i \sim q_j$; this corresponds to large initial velocity when the motion of the incident atom is not sensibly affected by exchange of energy. He has also shown that the agreement between the two solutions is improved if the velocity $\frac{1}{2}(v_i + v_j)$ is used in the perturbation integral. These results may be confirmed by comparing (1.3) with eqn. (4.1) of part 1; they may also be extended to indirect encounters [6] and to the Morse function for the interaction potential.[7] We therefore assume that the conclusions mentioned in § 1 (i) would still hold if exact solutions by the distorted-wave method were available for indirect encounters and more complicated force functions, hence that these need not be further considered provided that a satisfactory interpretation of molecular interaction can be found to replace the physical model used in § 1 (ii) without seriously affecting the solution. The statistical weighting of indirect collisions deduced from the considerations of part 1 is discussed in § 2.

We therefore consider a direct encounter between two methane molecules subject to an exponential law of force between mass-centres. Since the vibrational wave-functions are unknown it is impossible to calculate V_{nm} from (1.1) exactly, and so it is necessary to find some approximation which yields V_{nm} and preserves the form (1.2). When conditions are such that the only interaction effective in causing a transition is that between the nearest atoms of the two molecules, and the effect of rotation can be neglected, each atom can be regarded as a bound atom in the sense of § 1 (ii); if also the chance of excitation is small, the only important excited states of the complete system will be those in which only one of the molecules is excited, and then the chance of a transition will be the same as if each molecule were being subjected separately to an appropriate interaction potential. To apply the solution (1.3) it is therefore only necessary to calculate an effective mass M for the oscillator; this may be done by observing that the transition matrix V_{nm} for a linear oscillator in a given force field is proportional to the classical displacement corresponding to an energy quantum, which may be taken to be the vibrational displacement of the atom concerned, in the direction of the applied force.

For methane, unfortunately, the first of these conditions does not apply. It is shown in § 4 that the simple assumption of interaction between single atoms is unsatisfactory. The concept of an equivalent transition matrix is therefore extended to an oscillator composed of several atoms. This is a transition matrix the elements of which are chosen to be equal to those of a harmonic oscillator of a certain "effective" mass. This mass is so chosen that the potential change $\mathrm{d}V$ representing the work done by the applied force in displacing the actual molecule vibrationally by an amount corresponding to a quantum of vibrational energy, is equal to that for a simple harmonic oscillator of the same frequency, situated at the mass centre of the molecule, and having its effective mass. Since transition probability is proportional to the square of the relevant matrix element, an average value of the transition matrix may be taken by summing the squares of $\mathrm{d}V$ over all equally probable orientations of the molecule and over all components of vibration when these are degenerate. A more detailed justification of this procedure is given in § 4.

(iv) Vibrational relaxation time

Assuming that a formula can be obtained giving the average number of transitions per molecule per second in the gas, it remains to relate this quantity to the observed variation of sound velocity with frequency. The theory of this effect has been dealt with by numerous authors.[8] It is assumed here, as usual, that the experimental effect can be represented by a relaxation time τ sec, equal to the reciprocal of the number of $(1 \rightarrow 0)$ transitions per molecule per second, P. Values of τ calculated from the theory are given in § 5.

2. The statistics of encounters

In part 1, § 6 (ii), a brief discussion was given of the relative importance of different types of encounter in the calculation of transition probability. This section provides a fuller treatment leading to an approximate formula for overall transition probability in terms of direct-encounter values.

(i) Probability distribution of v and b

The number of encounters per molecule per unit time in which the relative velocity lies between v, $v + \mathrm{d}v$, and the impact parameter between b, $b + \mathrm{d}b$ is[9]

$$4N(2\pi kT/m)^{\frac{1}{2}} by\, \mathrm{e}^{-y}\, \mathrm{d}b\, \mathrm{d}y, \tag{2.1}$$

where N is the molecule density, m is the reduced mass for an encounter, and y is a velocity parameter given by

$$y = mv^2/2kT. \tag{2.2}$$

If $p(y, b)$ is the transition probability per molecule in the encounter, the expected number of transitions per molecule per unit time is, from (2.1)

$$P = 4N(2\pi kT/m)^{\frac{1}{2}} \int_0^\infty \int_0^\infty p(y, b) by \, e^{-y} db dy. \tag{2.3}$$

To allow for exchange between translational and internal energy in a transition, the values of y and b in $p(y, b)$ need to be modified if the probability is calculated as a perturbation integral. It is sufficiently accurate to replace $p(y, b)$ in (2.3) by $p(\bar{y}, \bar{b})$ where the barred values correspond to the mean velocity and impact parameter

$$\bar{v} = \tfrac{1}{2}(v_i + v_j), \; \bar{b} = \tfrac{1}{2}(b_i + b_j), \tag{2.4}$$

where suffices i, j refer to values before and after the encounter and the values are related by the laws of conservation of energy and angular momentum.

(ii) Relationship between transition probability for direct and indirect encounters

In part 1 it was shown, by the perturbation integral method, that most transitions at a given velocity occur when b is small, and that it is a good approximation to write

$$p(y, b) = p(r_0), \tag{2.5}$$

where r_0 is the distance of closest approach in a classical encounter with parameters y, b. The next step is to express P as a function of r_0 by changing the variable of integration in (2.3). From the equations of motion, eqn. (2.6) of part 1, using the substitution (2.2) we have

$$by \, db = r_0 dr_0 \{y - (2V + r_0 V')/2kT\}. \tag{2.6}$$

Since r_0 and y are independent variables, (2.3) can now be integrated with respect to y. The smallest value of y corresponding to a given r_0 is (V/kT) when $V(r_0) > 0$ and 0 otherwise, so the double integral in (2.3) becomes, from (2.5) and (2.6),

$$\int_0^{r_1} r_0 p(r_0)(1 - r_0 V'/2kT) \exp(-V/kT) dr_0 + \int_{r_1}^\infty r_0 p(r_0)\{1 - (2V + r_0 V')/2kT\} dr_0, \tag{2.7}$$

where r_1 is the zero-potential value, $V(r_1) = 0$.

Since (2.7) does not contain v explicitly, all the encounters can now be taken to be direct encounters, and the probability P can be calculated from these alone. However, the expression can be further simplified by taking into account the orders of magnitude of the various terms. If the approximations made in deriving (2.7) are valid, the second integral must be negligible, because no direct encounter has $r_0 > r_1$ and so $p(r_0)$ is negligible in this term. (2.5) does not hold exactly in this region, but usually the decrease of p with increasing r_0 is sufficiently rapid for this to be unimportant. Secondly, the order of magnitude of $(r_0 V'/2kT)$ can be estimated from the values for an exponential potential at the "most effective velocity" for the 1306 cm^{-1} vibrational transition in methane. Typical potentials for methane are given in eqn. (6.5) and (6.6) of part 1, and using these it can be shown that $(-r_0 V'/2kT)$ is large compared to 1. Eqn. (2.3) now becomes

$$P = -4N(\pi/2mkT)^{\frac{1}{2}} \int_0^{r_1} r_0^2 V' p(r_0) \exp(-V/kT) dr_0 \tag{2.8}$$

$$= 4N(\pi/2mkT)^{\frac{1}{2}} \int_0^\infty r_0^2 p(V) \exp(-V/kT) dV, \tag{2.9}$$

taking $V(0) = \infty$. Energy exchange is allowed for by replacing $p(V)$ in (2.9) by $p(\overline{V})$, where

$$\overline{V} = \tfrac{1}{2}m\bar{v}^2. \tag{2.10}$$

(iii) AN APPROXIMATE FORMULA FOR P USING THE QUANTUM-MECHANICAL SOLUTION FOR p

Landau and Teller [10] have observed that in an integral such as (2.9) the main contribution comes from a small region surrounding the maximum of the integrand. It will be shown later that the intermolecular force constant is not known well enough to give more than order of magnitude accuracy in P, and the simplest approximations therefore suffice.

The numerical values in methane are such that in (1.3)

$$\sinh q_i \sinh q_j/(\cosh q_i - \cosh q_j)^2 \sim \exp\,(q_i - q_j) \tag{2.11}$$

for $(1 \to 0)$ transitions in which $q_i < q_j$. Since $v_j^2 - v_i^2 = 2h\nu/m$, we have

$$q_j - q_i = 4\pi^2\nu/\alpha.\bar{v} \tag{2.12}$$

This is Zener's relation between the perturbation integral and the "exact" quantum mechanical solution. From (1.3), (2.11) and (2.12) we have

$$p = B \exp\,(-\,4\pi^2\nu/\alpha\bar{v}), \tag{2.13}$$

where

$$B = (32\pi^4 m^2\nu/h\alpha^2 M). \tag{2.14}$$

In (2.9) the variation of P with temperature and its general order of magnitude are mainly determined by the exponential factor. If we ignore the difference between $\bar{v}$ and v_i we obtain Landau and Teller's result that the maximum of the integrand occurs near

$$v = v^* = (4\pi^2 kT\nu/\alpha m)^{\frac{1}{2}}. \tag{2.15}$$

At this point the exponent equals $(-\,3y^*)$ where y is defined by (2.2), and its series expansion about this point is

$$-\left(\frac{4\pi^2\nu}{\alpha v} + \frac{mv^2}{2kT}\right) = -\,3y^*\left\{1 + \left(\frac{v - v^*}{v^*}\right)^2 + \ldots\right\}. \tag{2.16}$$

The integral in (2.9) therefore has the approximate value

$$B \exp\,(-\,3y^*)\int_0^\infty mr_0^2 v \exp\,\{-\,3m(v - v^*)^2/2kT\}\mathrm{d}v. \tag{2.17}$$

The variation of r_0^2 in this integral may be ignored, and v^* may be assumed to be sufficiently large to make the exponential factor very small at the lower limit of integration. Then (2.17) becomes

$$(2\pi mkT/3)^{\frac{1}{2}} Br_0^2 v^* \exp\,(-\,3y^*). \tag{2.18}$$

From (2.9) and (2.18) we have

$$P = (4\pi/\sqrt{3})NBr_0^2 v^* \exp\,(-\,3y^*), \tag{2.19}$$

which is Landau and Teller's expression derived in such a way as to give a definite pre-exponential factor. From (2.2) and (2.15) we have

$$y^* = (2\pi^4 m\nu^2/\alpha^2 kT)^{\frac{1}{2}}. \tag{2.20}$$

3. INTERATOMIC AND INTERMOLECULAR FORCE

In this section we deal with the specification of the force which produces vibrational transitions in encounters between two methane molecules, assuming that the relevant information is contained in the value of the exponential coefficient α in the repulsive term, or some equivalent quantity. Such a treatment is necessarily incomplete because of the complexity of the molecules, but seems worth testing.

(i) General argument

When two molecules are several diameters apart they may be regarded as particles moving under a force acting between their centres of mass. Transition-producing encounters, however, involve a much closer approach, and it is then necessary to consider the effects of molecular structure, concerning (*a*) the dynamics of the encounter, (*b*) the interaction between relative motion and internal vibration, (*c*) the relationship between transition probability and other molecular properties.

The dynamical effect is easily dealt with. A basic assumption of the general theory used is that the dynamics of an encounter are determined by a spherically symmetrical force field acting between mass centres. The effect of molecular structure must therefore be symmetrized, e.g. by assuming all rotational positions of the molecules are equally likely and replacing the actual structure by a spherical shell with the same mass centre. The resultant force can then be referred to the mass centre and used in the original equations of motion.

The effect on the vibrational coupling is considered further in § 4; here we note that the potential concerned is the potential of atoms of one molecule in the field of the other, which, to satisfy the conditions leading to the particular solution used, must be proportional to the intermolecular or dynamically effective potential as a function of distance.

The relationship with other properties is dealt with in § 3 (ii) and 3 (iii). It was shown in part 1 that the second virial coefficient is of little use in determining the intermolecular force for the calculation of transition probability, because transitions occur in the rare high-velocity encounters which have little effect on the bulk properties of the gas. The present approach is to use independent calculations of interatomic force obtained quantum-mechanically, as described below.

(ii) Force between two equal spherical shells

One analytical device for obtaining spherically symmetrical intermolecular force functions is to replace each molecule by a uniform spherical shell and assume each element of one shell interacts with each element of the other according to a known potential function V_a. Expressions for V_b, the potential field due to one molecule, at a distance r from its centre, and for V_m, the intermolecular potential, at a distance r between centres, can be obtained in closed form if we use a power law for V_a rather than an exponential. If

$$V_a = W(c/r)^n, \tag{3.1}$$

where c is the radius of the shell, we have

$$V_b = \{W/2(n-2)\}(c/r)[\{(r/c)-1\}^{2-n} - \{(r/c)+1\}^{2-n}]. \tag{3.2}$$

and

$$V_m = \{W/4(n-2)(n-3)\}(c/r) \times [\{(r/c)-2\}^{3-n} - 2(r/c)^{3-n} + \{(r/c)+2\}^{3-n}]. \tag{3.3}$$

This formula is not valid when $n = 2$ or $n = 3$.

If V_a is a sum of inverse powers, V_b and V_m are the sum of the separate terms. The equation corresponding to (3.2) for the Lennard-Jones function was given by Lennard-Jones and Devonshire [11] and subsequently used by Hamann, McManamey and Pearse [12] to investigate the force between polyatomic molecules. The form (3.3) which should be a better representation of intermolecular force, has not been used hitherto.

(iii) Numerical values for methane

Eqn. (3.3) gives (V_m/W) as a function of (r/c) and n for the simple repulsion potential (3.1), used for analytical convenience. To obtain V_m, we use quantum-mechanically calculated values of the repulsive interaction potential between atoms to get approximate values of W and n valid over a restricted range of r. The repulsive interaction between two hydrogen atoms, in the $^3\Sigma$ state of H_2

may be expected to resemble the interaction between the hydrogen atoms in methane. Accurate numerical values are available.[13, 14] Another interaction which might be expected to resemble the relevant one is that between helium atoms, for which Slater [15] has given approximate theoretical results. We consider both possibilities.

We derive values of W and n by fitting these results for V_a to the potential (3.1), noting that n varies with r, and making a partial allowance for the variation of $n(r)$ by choosing the value of n at $r = r_m - 2c$, where r_m is the distance between the centres of the molecules. We put c equal to the C—H bond length in methane, 1·093 Å. The procedure may be followed by reference to fig. 1.

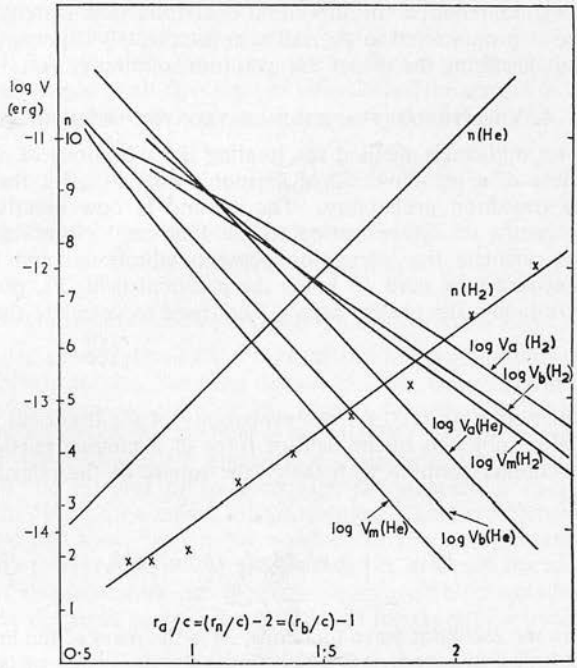

FIG. 1.—Interatomic and intermolecular potential functions.

The value of r_a corresponding to a given n is found from fig. 1; then with $r_m = r_a + 2c$, equivalent to the assumption that the power law between all atoms is the same as the "exact" law between nearest atoms, the value of $V_m(r_m)/V_a(r_a)$ is calculated from the formulae. To allow for the fact that a methane molecule has four peripheral atoms, the value of V_m given by (3.3) is multiplied by 16. Values of $V_b(r_b)/V_a(r_a)$, including a multiplying factor of 4, are calculated from (3.2) in the same way.

Curves of log V_m against (r_m/c) and log V_b against (r_b/c) are shown in fig. 1. From these curves are obtained the values of β, the coefficient in the expression $V \propto \exp(-\beta r/c)$, quoted in the next section.

(iv) INTERPRETATION

In part 1, § 6(v), the "most effective velocity" for transitions was calculated for gas temperatures of 300-1500° K. The two exponential functions used had $\beta = 2{\cdot}8$ and 6·2, and the velocities were in the range $v = 2{\cdot}7$-$4{\cdot}6$ and $2{\cdot}0$-$3{\cdot}5 \times 10^5$ cm sec^{-1} respectively. The corresponding values of V_m at closest approach are 0·5-1·4 and 0·3-0·8 $\times 10^{-12}$ erg respectively. Thus with the hydrogen-type

interaction the smallest distance we are concerned with is roughly $r_m/c = 3{\cdot}3$ and for the helium-type interaction the value is 3·0. For a range of two decades of V_m, the ranges of (r_m/c) of interest are 3·3-4·8 for hydrogen-type, and 3·0-3·9 for helium.

Over this range the curves of log V_a and log V_m in fig. 1 are nearly straight and parallel, showing that the elementary assumption that the interatomic and intermolecular potentials differ only by a constant factor is not unjustified. The exponential coefficients β_m range from 3·4-3·8 for hydrogen results to, say, 5·1-5·7 for helium; it is encouraging that these values lie within the range considered in part 1 which was arbitrarily fixed from an examination of the second virial coefficient.

Values of V_b are required for the vibrational transition matrix. These too can be regarded as proportional to V_m and as approximately exponential functions of distance, thus justifying the use of the quantum solution (1.3).

4. Vibrational transition matrix for methane

In § 1 (iii) we outlined a method for treating the vibrations of a polyatomic molecule as those of a one-dimensional harmonic oscillator, for the purpose of calculating the transition probability. The method is now described in more detail and the results of its application to the 1306 cm^{-1} vibration of methane are given. To calculate the interaction between vibrational and translational energy in an encounter we need to know the potential field, V_b, produced by a molecule; accordingly, the results from § 3 are used to calculate the vibrational coupling.

(i) General theory

The particular solution (1.3) for the probability of a vibrational transition of a linear oscillator subjected to the field of force of a moving particle in a one-dimensional encounter contains as a factor the square of the relevant transition matrix element

$$Y_{10} = \int_{-\infty}^{\infty} \psi_1 x \psi_0^* \mathrm{d}x = (\boldsymbol{h}/8\pi^2 M\nu)^{\frac{1}{2}}, \tag{4.1}$$

where ψ_0, ψ_1 are the oscillator wave functions, M is the mass of the bound particle and ν is the vibration frequency. We now forget the derivation of the right-hand expression and consider how it may reasonably be interpreted in less simple cases.

The interaction between vibrational and translational energy enters into (1.3) by virtue of the fact that a displacement of the bound particle, mass M, produces the same change in the interaction potential as an equal displacement of the free particle, mass m. We now make the assumption that we can carry this over to the interaction between two polyatomic molecules; the mass M must therefore be such that the change in potential due to the actual vibrational displacement, interpreted classically, equals the change in potential of a one-dimensional harmonic oscillator of frequency ν due to a vibrational displacement when M is the mass of the bound particle. M is now the "effective" mass of the oscillator. We thus need to calculate the change in potential $\mathrm{d}V$ due to the vibrational displacement of the atoms of one polyatomic molecule (A) in the field of the other (B). This field is as usual assumed to be spherically symmetrical about the mass centre of molecule B, so that if r_i are the distances of the atoms of A from this centre, the $\mathrm{d}r_i$ their displacements along these radii, we have

$$\mathrm{d}V = \Sigma_i V'_b(r_i)\mathrm{d}r_i. \tag{4.2}$$

In general, $\mathrm{d}V$ is a function of distance between centres, of the orientation of molecule A and of the particular vibration excited. In order to apply the solution

(1.3) the variation with distance must be approximately exponential with the same value of α as in the intermolecular force law. Changes with orientation must be averaged in some way; similarly, vibrational degeneracy may be dealt with by averaging over all possible components at a given frequency. Since p_{10} is proportional to Y_{10}^2, which depends on the square of the effective displacement, the averaging process operates on $(\mathrm{d}V)^2$.

In particular we consider the 1306 cm^{-1} vibration of methane. Results from § 3 suggest that the intermolecular force is mainly due to repulsion between the peripheral hydrogen atoms, and in any case the effect of the central atom on the force field is not known, so the potential change due to the displacement of the central atom is neglected. In this vibration, which is triply degenerate, there are three degrees of freedom which may be represented by the components λ, μ, ν of the vibration of the central atom relative to axes fixed in the molecule. Then if weight $\omega(\boldsymbol{\theta})$ is given to the vector orientation $\boldsymbol{\theta}$ of molecule A relative to the axis AB, and equal weight to all directions of vibration of the central atom, the average potential at a given distance is given by an equation of the form

$$(\overline{\mathrm{d}V})^2 = \int \ldots \int (\mathrm{d}V)^2 \omega(\boldsymbol{\theta})\, \mathrm{d}\boldsymbol{\theta}\, \mathrm{d}\lambda\, \mathrm{d}\mu\, \mathrm{d}\nu, \tag{4.3}$$

where integration with respect to λ, μ, ν is over the sphere

$$\lambda^2 + \mu^2 + \nu^2 = \text{constant} = a^2.$$

(ii) Displacement potentials for symmetrical orientations

The detailed specification of the form of the 1306 cm^{-1} vibration in methane, required to obtain the $\mathrm{d}r_i$, has been carried out, but the analysis is too laborious to be given here and we continue the present argument by giving the results. Although the object of the analysis is to calculate $\mathrm{d}V$ as defined by (4.3), the formulae are too complicated, and $\omega(\boldsymbol{\theta})$ too uncertain, to allow the analytical evaluation of the integral or to encourage the calculation of $\mathrm{d}V$ at enough orientations to obtain an accurate integral; instead, only symmetrical orientations are considered and these are equally weighted to give an approximate $\mathrm{d}V$. The averaging with respect to λ, μ, ν on the other hand, is carried out exactly.

Values of displacements for particular symmetrical orientations at various intermolecular distances r_m have been obtained for the symmetrical orientations:

(*a*) The end-on position, with H atom 1 next to the centre of force, $r_1 = r_m - c$.

(*b*) The face-on position, with atom 1 opposite the centre of force, $r_1 = r_m + c$.

(*c*) The symmetrical edge-on position.

To get values of $\mathrm{d}V$ from these displacements it is sufficiently accurate to regard V_b as an exponential function of (r/c) with coefficients $\beta_b = 3$ for the hydrogen-like interaction and 5 for the helium-like. Then from (4.2) we have

$$\mathrm{d}V = -(\beta_b/c) V_b(r_m) \Sigma_i \mathrm{d}r_i \exp\{\beta_b(r_m - r_i)/c\}. \tag{4.4}$$

Numerical evaluation shows that the contributions of the furthest atoms to (4.4) may be neglected, and values obtained in this way have been used in the calculations.

(iii) Approximate averaging of the displacement potential

As an approximate value for the square of the displacement potential averaged over all orientaions we choose for simplicity

$$\overline{\mathrm{d}V^2} = \tfrac{1}{3}(\mathrm{d}V^2_{(a)} + \mathrm{d}V^2_{(b)} + \mathrm{d}V^2_{(c)}), \tag{4.5}$$

where $\mathrm{d}V_{(a)}$ is the displacement potential corresponding to orientation (*a*) averaged over the sphere $\lambda^2 + \mu^2 + \nu^2 = a^2$, and $\mathrm{d}V_{(b)}$ and $\mathrm{d}V_{(c)}$ are similarly defined.

The definition of the effective mass M has been given in § 4(i), and the relationship between M and $\mathrm{d}V$ is found as follows. The effective vibrational co-ordinate R is defined by the equation

$$V(r_m, R) = V(r_m - R),$$

which expresses the condition, required by the solution (1.3), that the interaction energy depend only on the difference between the external and internal co-ordinates. Assuming $V(r_m)$ is an exponential function, we have

$$\mathrm{d}V(R) = -\,\mathrm{d}V(r_m) = (\beta_m/c)V_m(r_m)\mathrm{d}R,$$

the mean value of R being zero by hypothesis. In the equivalent one-dimensional harmonic oscillator, $\mathrm{d}R$ is the classical vibrational displacement corresponding to potential $\boldsymbol{h}\nu$:

$$\mathrm{d}R = (\boldsymbol{h}/2\pi^2 M\nu)^{\frac{1}{2}};$$

thus

$$\mathrm{d}V = (\beta_m/c)(\boldsymbol{h}/2\pi^2 M\nu)^{\frac{1}{2}}V_m(r_m). \tag{4.6}$$

When $\mathrm{d}V$ is equated to $\overline{\mathrm{d}V}$ given by (4.5), the effective mass M is expressed in terms of the vibrational displacements of the complex molecule.

(iv) Effective mass for 1306 cm^{-1} vibration in methane

The magnitudes of the vibrational displacements of methane have been obtained in another investigation, the results only being used here. This information is used to obtain values of M from eqn. (4.5) and (4.6). In table 1 we list values of M/m, where m is the reduced mass for the encounter.

These results suggest a variation of M with r_m. However, the averaging procedure used here is approximate, and the effect of rotation, which we have neglected, is unknown, so that for present purposes we take $M/m = 0{\cdot}05$ and $0{\cdot}001$ for the hydrogen- and helium-type interactions respectively.

Table 1.—Values of M/m

(i) H_2-type interaction

r_m/c	3·5	4·0	4·5
$\boldsymbol{h}/2\pi^2 M\nu a^2$	41	71	74
M/m	0·07	0·04	0·04

(ii) He-type interaction

r_m/c	3·0	3·5	4·0
$\boldsymbol{h}/2\pi^2 M\nu a^2$	1200	2200	3100
M/m	0·002	0·001	0·001

The fact that M does not occur in the exponent in the final expression for relaxation makes us more prepared to accept a result at this level of approximation.

It will be noted that M is considerably less, not only than the mass of the methane molecule itself, but than the mass of the hydrogen atom which does most of the moving in the vibration. This means that transition takes place more readily in the encounter between polyatomic molecules than in the corresponding linear encounter between an atom and a bound atom of the same mass, in the model used to deduce eqn. (1.3).

The explanation of this at first sight surprising result is that in the original model the distance between the bound atom and the moving atom is equal to the distance between mass centres in the present problem, while the distance between some of the vibrating atoms in the polyatomic molecule is less than the distance between mass centres. Being closer, they are more powerfully acted on, which is equivalent to being lighter at a further distance.

5. Numerical values of relaxation time in methane

The exponential dependence of P on the parameter α, whose value is not known precisely, prevents the vibrational relaxation time being calculated from the theory to greater than order-of-magnitude accuracy. It is therefore sufficient to use the approximate expression (2.19), provided that the values of q_i and q_j can be shown to justify the approximation (2.12). With $\alpha = 4 \times 10^8\ \mathrm{cm}^{-1}$ the most effective velocity at 300° K is $2{\cdot}3 \times 10^5\ \mathrm{cm\ sec}^{-1}$, as shown in part 1. With $m = 8 \times 1{\cdot}67 \times 10^{-24}$ g, and $\nu = 3{\cdot}92 \times 10^{13}\ \mathrm{sec}^{-1}$, and the above values of α and v, $q_i = 20$, $q_j = 14$, which can be taken to justify (2.12).

Further numerical values are:

$$N = 7{\cdot}35 \times 10^{21}\, T^{-1} \text{ at atm pressure,}$$
$$B = 2{\cdot}47 \times 10^{20}\, (m/\alpha^2 M) \text{ from (2.14),}$$
$$r_0 = r_m = 3 \times 10^{-8} \text{ approximately,}$$
$$v^* = 2{\cdot}52 \times 10^7\, (T/\alpha)^{\frac{1}{2}} \text{ from (2.15),}$$
$$3y^* = 9{\cdot}2 \times 10^7\, (\alpha^2 T)^{-\frac{1}{3}} \text{ from (2.20).}$$

Hence from (2.19)

$$P = 3{\cdot}0 \times 10^{35}\, (m/M)(T^2\alpha^7)^{-\frac{1}{3}} \exp\{-9{\cdot}2 \times 10^7\, (\alpha^2 T)^{-\frac{1}{3}}\}. \tag{5.1}$$

Values of the "doubtful" quantities α, M are found from § 3 and 4. Taking $V_m = 0{\cdot}5 \times 10^{-12}$ as a reference value gives

$$\alpha = \beta m/c = \text{(i) } 3{\cdot}2 \times 10^8 \text{ for } H_2\text{-type interaction,}$$
$$\text{(ii) } 4{\cdot}9 \times 10^8 \text{ for He-type interaction.}$$

Using the values of M/m suggested in § 4, we now obtain

$$P = \text{(i) } 8{\cdot}6 \times 10^{16}\, T^{-\frac{2}{3}} \exp(-196\, T^{-\frac{1}{3}}),$$
$$\text{(ii) } 1{\cdot}6 \times 10^{18}\, T^{-\frac{2}{3}} \exp(-148\, T^{-\frac{1}{3}}).$$

Values of relaxation time $\tau = P^{-1}$ calculated from these formulae are given in table 2.

Table 2.—Theoretical values of relaxation time

(i) hydrogen-type interaction; (ii) helium-type interaction

T°K	300	600	900
τ sec	(i) 3×10^{-3}	1×10^{-5}	7×10^{-7}
	(ii) 1×10^{-7}	2×10^{-9}	2×10^{-10}
	expt. 1×10^{-6}(*a*)	5×10^{-7}	

(*a*) extrapolated.

The experimental values are derived from the ultrasonic results of Eucken and Aybar.[16]

6. Discussion of results

It is seen from table 2 that the theoretical results based on the two different methods of estimating the repulsive force constant bracket the experimental results. This is only a partial success for the theory, however, because it gives a very much steeper dependence of relaxation time on temperature than is observed. Since the temperature dependence is chiefly due to the exponential factor, which is the same in the present treatment as in that of Landau and Teller,[10] the present discussion is in this sense no advance on the earlier.

If the experimental results are accepted, possible explanations of this failure to obtain the observed dependence of relaxation time on temperature are (*a*) that the observed relaxation time is produced by a different process from that postulated here; or (*b*) that a transition theory of the kind envisaged in § 1 would give the observed results if it were not necessary to make numerous simplifying approximations.

The first explanation is at first sight unlikely to be correct since no other transition mechanism has been found to explain the general pattern of experimental results. It is possible, however, that the vibrational state of the de-exciting molecule, which is neglected in our treatment, may be important. The probability of a $1 \rightarrow 0$ transition may be greatly increased when *both* molecules in an encounter are initially excited, since excitation might be expected to impose a periodic term on the force function which can resonate with the natural frequency of the second molecule. If the probability is increased to nearly unity in a collision of the (1 : 1) type the relaxation time will be approximately exp $(h\nu/kT)$ times the reciprocal of the collision frequency per molecule.

Damköhler [17] has calculated the "activation energy" for energy transfer from the experimental results for several gases, and notes that, very roughly, the "activation energies" lie close to the lowest vibrational quantum of the molecule concerned. His explanation is that an excited molecule can lose its vibrational quantum by collision with another molecule when the colliding molecules possess a minimum energy of a vibrational energy quantum. He raises, but does not answer the question, of whether this energy is translational or whether the colliding molecule itself must be vibrationally excited. If the usual theory of energy exchange is even approximately true, the former possibility is ruled out, and we are left with the suggested powerful effect of excited molecules. On this view, the exponential dependence of τ on m, the reduced mass for the encounter, disappears, and the results of Fogg, Hanks and Lambert [18] become easier to understand. On the other hand, it runs counter to several other observations and is difficult to justify theoretically.

To discuss the second explanation we note that the only uncertain quantity in the exponent is α. We have taken values of α near 4×10^8 cm^{-1}, whereas in order to fit the observed temperature dependence (not the absolute values, because they depend on M as well), a value of about 3×10^9 cm^{-1} is required. Similarly high values of α are required for the interpretation of other ultrasonic results. Massey and Burhop,[19] for example, have deduced values of 4·5 and $2{\cdot}8 \times 10^8$ cm^{-1} for carbon dioxide and nitrous oxide respectively, but these values are in error by a factor of 2π (the exponent in their eqn. (135) is in error by a factor of $(2\pi)^{\frac{3}{2}}$) and should be 2·8 and $1{\cdot}8 \times 10^9$ cm^{-1} respectively. Thus, to make the theory fit the temperature dependence, higher values of α are required than would be expected on other grounds. It remains to determine the effect which this would have on the absolute value of the relaxation time. Apart from the fact that α enters into the pre-exponential factor itself, the value chosen for the repulsive force constant has a sharp effect on the estimate of the effective mass of the oscillator, increase in α decreasing the effective mass. Thus, increase in α would increase the pre-exponential factor in the expression for the probability, and decrease the calculated relaxation time. The effect of increasing α in the exponent would also be to decrease the calculated relaxation time. A change in α by a factor of 8 would decrease the calculated relaxation time by several powers of ten, and thus bring it well below the observed results. The reduction in τ, thanks to the exponential factor alone, would appear to be very large, so that the difficulty remains even if our method of deducing M is in error.

The main defect of the simplest approximate theory of transition probability in molecular encounters apparently persists when a more detailed treatment is given. The parameters in the theory can be chosen so that the calculated result either has the correct order of magnitude in the experimentally accessible region or has the correct logarithmic temperature dependence but not both, and values of the parameters which are not reasonable on other grounds are required to obtain the latter agreement.

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TRANSITION PROBABILITY IN MOLECULAR ENCOUNTERS

PART 3.—EXPERIMENTAL VALUES FOR RELAXATION TIME IN METHANE

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The vibrational relaxation time in methane has been determined by the ultrasonic velocity method to be $1{\cdot}7 \times 10^{-6}$ sec at 30° and 60° C. The temperature dependence is so slight as not to be observable in this range.

The only published values of the vibrational relaxation time of methane are those of Eucken and Aybar,[1] which show a smaller temperature dependence than that suggested by the theoretical treatment given in part 2 of this series.[2] Moreover, fragmentary results by Telfair [3] suggest that the relaxation time may be increasing with temperature in the region of 100° C. Both these sets of measurements were made at temperatures above 100° C, in order to obtain a large dispersion which could be easily measured. We have now measured the relaxation time at 30° and 60° C by the ultrasonic method. At these temperatures the total velocity dispersion is only 1·2 % and 1·8 % respectively of the velocity itself, but other experimental difficulties, particularly temperature control, are less.

EXPERIMENTAL

APPARATUS

The sound velocity was measured using a conventional ultrasonic interferometer of the basic Pierce [4] design, similar to that of Telfair and Pielemeier.[5] The reflector, which was of glass, was driven by a micrometer screw of nominal pitch 1/40 in., arranged to inject a signal once per revolution into the anode current of the oscillator. The apparatus was surrounded by a lagged water jacket through which thermostatted water was circulated. Exploration of the inside of the interferometer vessel by means of thermocouples showed it to be uniform in temperature to within 0·1° C.

X-cut quartz crystals were used in the anode-grid circuit of a modified Colpitts oscillator (fig. 1). The optimum setting was not exactly at resonance: the oscillator could operate stably on the "fast" side of the resonance dip, where the anode current is extremely sensitive to any small change in the circuit. The anode current was noted on a milliammeter and recorded by feeding the change in potential across a small resistance in series with the anode load to a fast Brown recording potentiometer. For the thicker, low frequency, crystals, it was helpful to have a small condenser, about 20 pF, across the crystal to make tuning easier. Since the crystals were in the anode-grid circuit, both terminals were at a higher potential than earth, and a glass reflector was necessary to eliminate a drift in anode current with reflector movement due to a condenser effect. The maxima in anode current caused by the reflector movement could be as large as 10 mA, but were generally kept to 1 mA. The crystals used had frequencies from 90 to 500 kc/sec. The actual frequency was measured by a wave meter which had been checked against a standard oscillator, and was known to better than 1 in 10,000.

The record obtained was a series of maxima in a trace of the anode current, interspersed with a series of marks signifying each complete turn of the micrometer screw, from which was deduced the number of wavelengths per turn of the screw, averaged over its travel. This quantity could be measured with a precision, judged by reproducibility from run to run, of better than 1 in 1000. The average pitch of the screw was determined by measuring the velocity of sound in argon, taking it to be the value calculated for the ideal gas.

MATERIALS

The argon was supplied by The British Oxygen Co. Ltd., with a stated purity of > 99·5 %. It was dried by passing over caustic potash and phosphoric oxide.

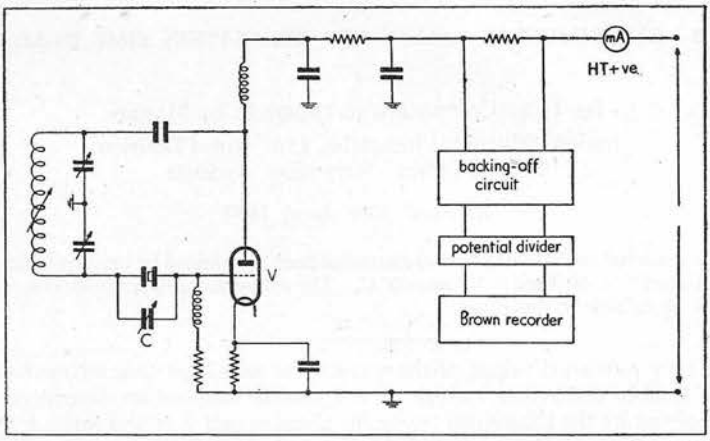

FIG. 1.—Diagrammatic circuit of interferometer. $C = 20$ pF; V is a C65.

The methane was natural gas, purified by bubbling through alkaline pyrogallol, sulphuric acid, passing over caustic potash and phosphoric oxide, and several fractional distillations. It has a vapour pressure at − 196° C of 11 mm Hg. Chemical analysis showed no CO_2, O_2, CO or N_2 within the limits obtained in the Bone and Wheeler apparatus —probably 0·5-1·0 %.

RESULTS

The precision of the apparatus is shown by the following values of the number of reflection maxima for one turn of the micrometer screw in argon at 30·0° C and a frequency of 91·04 kc/sec: 0·3532; 0·3532; 0·3531; 0·3530.

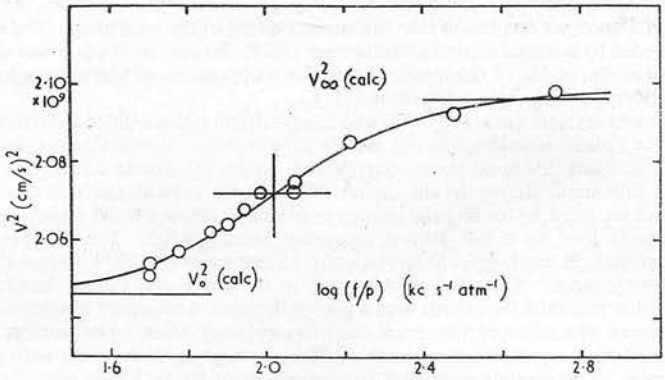

FIG. 2.—Plot of V^2 against log (f/p) for methane at 30° C.

Measurements were made in methane at 30° and 60° C, and a dispersion region centred on about 100 kc/sec at 1 atm was observed. With the lowest frequencies and highest pressures available it was not possible to define the low end of the dispersion curve, but the high frequency end gave mean values of 458·0 and 479·9 m/sec for V_∞, the velocity of sound at high frequency at 30° and 60°. The calculated values, assuming $C_{v\infty} = 3R$, are 457·8 and 479·9 m/sec. The agreement is good. The velocity was determined as a function of frequency/pressure over the range 50 kc sec^{-1} atm^{-1} to 800 kc sec^{-1} atm^{-1}, a typical

plot of V^2 against $\log(f/p)$ being shown in fig. 2. The observed values of the velocity were corrected for gas imperfection where this was significant by the formula quoted by Lambert and Rowlinson,[6] but the correction never exceeded 0·3 m/sec.

The relaxation time β was determined from the position of the inflexion point of the curve of V^2 against $\log(f/p)$ using the expression:[7]

$$\beta = \frac{1}{2(f/p)'} \frac{C_{v_0}}{C_{v_\infty}},$$

where $(f/p)'$ is the value of (f/p) at the inflexion point. It was located by the intersection of the line $(V_\infty^2 + V_0^2)/2$ with the curve. As V_0 was not directly observed, it was deduced by subtracting the theoretical width of the dispersion curve from V_∞, on the assumption that the relaxation involves the whole vibrational specific heat. The following results were obtained:

30° C, $\beta = 1{\cdot}7_9, 1{\cdot}6_3, 1{\cdot}6_1 \times 10^{-6}$ sec: mean $\beta = 1{\cdot}6_8 \times 10^{-6}$ sec;
60° C, $\beta = 1{\cdot}6_5, 1{\cdot}8_0$,, ,, mean $\beta = 1{\cdot}7_2$,,

The precision in β appears to be better than 10 % and within this limit the relaxation times at 30° and 60° C do not differ. The accuracy may be reduced by small quantities of impurity which would cause the results to be low, although this was guarded against to some extent by doing determinations on different samples. An uncertainty in the absolute measurement of the velocity should not affect the estimated position of the inflexion point, although a small uncertainty appears to exist, in that our measured velocity of sound in dry CO_2-free air was 0·15 % lower than that calculated from the thermodynamic properties of air.[8]

DISCUSSION

The relaxation time found here is about 70 % greater than that extrapolated from the results of Eucken and Aybar.[1] Considering the possible effect of small quantities of impurity on long relaxation times, this is quite good agreement. Extrapolation of their results suggests that the change in β in going from 30° to 60° C would be less than 10 %, which does not conflict with our results. Both investigations agree that the temperature dependence is very much less than that calculated in part 2 of the series[2] by the refined Landau-Teller expression, where a change by a factor of 2 from 30° to 60° C is predicted. A better theoretical account of the temperature dependence of relaxation time is therefore called for.

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