

sharply at 31°. Calcd. for $C_6H_9O_2N$: C, 56.6; H, 7.1. Found: C, 56.55; H, 7.2.

THE IMPERIAL COLLEGE OF
SCIENCE AND TECHNOLOGY
LONDON, S. W. 7, ENGLAND

FREDERICK C. B. MARSHALL

RECEIVED MAY 4, 1931
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COMMUNICATIONS TO THE EDITOR

THE CRYSTAL STRUCTURES OF ELECTRODEPOSITED ALLOYS. SILVER-CADMIUM

Sir:

The crystal structures of silver-cadmium alloys, ranging in composition from 20% Cd to 96% Cd, have been obtained from x-ray diffraction data. The alloys were deposited at room temperature according to the method of Stout [Preprint No. 29, *Trans. Am. Electrochem. Soc.*, **59** (1931)], using a current density of one ampere.

In general, the structures of the alloys are quite different from those of thermal alloys of corresponding composition which have been brought to equilibrium before examination. The alloys prepared under equilibrium conditions [Astrand and Westgren, *Z. anorg. allgem. Chem.*, **175**, 90 (1928)] show the following phases.

Percentage Cd

0-44	α -solid solution of Cd in Ag
44-49	$\alpha + \beta$
49-51	β - C_2Cl type cubic lattice. β' -close-packed hexagonal lattice, similar to ϵ , obtained when β is heated above 400° and suitably quenched. It differs from ϵ in axial ratio
51-57	$\beta + \gamma$
57-66	γ -body-centered cubic lattice
66-69	$\gamma + \epsilon$
69-83	ϵ -close-packed hexagonal lattice
83-95	$\epsilon + \eta$
95-100	η -solid solution of Ag in Cd

Westgren notes that β should also be formed at high temperatures in the γ -range but his attempts to produce it by heating the γ -phase failed.

The electrodeposited alloys show the following structures: (1) 40% Cd—contains the α , β' and γ phases and may contain the β phase; (2) 46-75% Cd—only the ϵ phase is deposited. The crystals show a preferred orientation with respect to the base metal, and this orientation differs with the composition; (3) 89-96% Cd—the ϵ and η phases are deposited.

Our results do not agree with microscopic data recently published by Fink and Gerapostolou [*Metal Ind.* (N. Y.), **28**, 519, 562 (1930)].

It is evident that under the conditions of deposition used in these experi-

ments the ϵ -phase is produced throughout the greater part of the range, and is apparently a metastable phase at least through the approximate range 46–66% of Cd. This is consistent with the behavior of some pure metals, which are known to be electrodeposited in metastable forms.

It is important to know how the conditions of deposition affect the crystal structure of an alloy of any given composition, since hardness and other physical properties depend upon the structure.

We are at present investigating (1) the effect of current density and temperature on crystal structure, the composition of the deposit remaining constant; (2) the recrystallization temperatures of Cd-Ag alloys.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
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CHARLES W. STILLWELL

EXPLOSION DURING THE CATALYTIC REDUCTION OF NITROANISOLE IN THE LIQUID PHASE

Sir:

Brown, Etzel and Henke [*J. Phys. Chem.*, **32**, 631–635 (1928)] quantitatively reduced a number of nitro compounds in the liquid phase at about 215°, under a hydrogen pressure of about 500 lb. per sq. in., using a nickel catalyst. The reduction could be made either without a solvent or with benzene and ethyl alcohol. Their work was done on small quantities (about 5 g.) of material, in a shaking autoclave maintained at the desired temperature by immersion in an oil-bath.

The writer attempted to apply this method to the reduction of *o*-nitroanisole. As no danger was anticipated, the work was done on a *technical* scale, using 400 g. of the nitro compound. A shaking autoclave of steel was used, of about 3000 cc. total capacity, heated electrically. The first experiment was made using benzene as a solvent, with a nickel catalyst, and gave approximately a 50% yield of amine. In the next, the solvent was omitted and the catalyst was carefully prepared to give a very active product; 250 g. of nickel nitrate was ignited at 400°, and then heated for three hours in a muffle at 560°. The oxide was reduced in the autoclave under a stream of hydrogen at a temperature of 280–300°. Four hundred grams of the nitroanisole, freshly distilled, was then added and hydrogen was passed in to a pressure of 500 lb. At a temperature of 250°, with shaking, the hydrogen was rapidly taken up, and the pressure dropped in about fifteen minutes to 250 lb. It then began to rise rapidly, and reached a total of 500 lb. in about five minutes. In thirty seconds more the pressure jumped to 1000 lb. The writer then opened the needle valve on the autoclave in the hope of relieving the pressure. Gas and liquid shot out of the valve, and an instant later the autoclave exploded with great violence.

The autoclave, a steel shell three-sixteenths of an inch thick by about fifteen inches long and six inches in diameter, failed by splitting open on one side. Before use, it had been tested to 1500 lb. pressure. The detonation was of sufficient violence to blow out all the windows of the laboratory and shake a large concrete building.

The explosion could not have been caused by any mixture of hydrogen and oxygen in the autoclave, as the autoclave had been thoroughly swept out with hydrogen during the reduction of the catalyst. As was indicated by the initial pressure drop, reduction was taking place very satisfactorily. It seems probable that the explosion was caused by decomposition of the nitro compound itself, possibly by auto-oxidation, or possibly by rapid oxidation by the nitro body of an intermediate product of the reduction. This may have been induced by the catalyst, which was evidently quite vigorous, and it may have been aided by local high temperature attained by the rapid reduction. In the original work of Brown, Etzel and Henke, such dangers as these were eliminated by the small scale on which they worked and by the adequate cooling afforded by the oil-bath.

The purpose of this note is to call the attention of other investigators to the dangers of this type of reduction when carried out on other than a very small scale.

MONSANTO CHEMICAL WORKS
ST. LOUIS, MISSOURI
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T. S. CARSWELL

THE RAMAN SPECTRA OF FORMALDEHYDE, TRIOXYMETHYLENE, ETHYLENE GLYCOL, AND OF SOME VISCOUS LIQUIDS

Sir:

The Raman spectrum of a 37% solution of formaldehyde in water consists of at least nine lines corresponding to frequencies, expressed in wave numbers of 802, 909, 1055, 1285, 1479, 2840, 2915, 3015 and 3087. Trioxymethylene gives modified lines corresponding to 497, 579, 674, 908, 1050, 1232, 1285, 1376, 1477 and 1527 wave numbers. Ethylene glycol gives lines corresponding to 341, 491, 526, 869, 1040, 1274, 1460, 2725, 2874, 2948, 3048 and 3131 wave numbers. Except for a fairly consistent shift toward the higher frequencies, of about 25 wave numbers, the stronger Raman lines from the aldehyde solution correspond both in intensity and in distribution to those from ethylene glycol. No lines are found typical of the C=O linkage (1675-1725) for formaldehyde. On the other hand, the line at 1050 typical of C-O is fairly strong. These observations would seem to indicate the formation of methylene glycol by formaldehyde in aqueous solution. This is compatible with the observations of Auerbach and Barschall [*Chem. Zentr.*, II, 1081 (1905)] and Walker [*J. Phys. Chem.*,

35, 1104 (1931)], who came to the same conclusion from cryoscopic and vapor pressure measurements. The absence of frequencies less than 800 wave numbers indicates that the concentration of higher polymers in a solution of this concentration must be small. The absence of a modified line in the 1675-1725 region for the trioxymethylene and the presence of a line corresponding to the C-O linkage may be due to the formation of a trimer in the manner suggested by Venkateswaren and Bhagavantam [*Proc. Roy. Soc. (London)*, **128**, 260 (1930)] for paraldehyde. The presence of only three frequencies below 900 wave numbers may indicate that the polymer consists of not more than three aldehyde units. Lines corresponding to C-H linkage for the trioxymethylene are very weak and as yet have not been definitely identified.

That strong continuous Raman spectra may be a property common to viscous liquids has received some substantiation from the Raman spectra of sodium silicate, orthophosphoric acid, potassium hydrogen phosphite and ethylene glycol solutions. The continuous spectra decrease on dilution and on temperature elevation. This behavior is similar to that observed with glycerin by Venkateswaren [*Indian Journal Phys.*, **3**, 105 (1928)]. This phenomenon may possibly owe its origin to intermolecular attraction, the continuous spectra arising from the probability of a large number of energy levels. The Raman spectrum of α -chloronaphthalene consists of 16 lines and shows some similarities to that of chlorobenzene and naphthalene.

A detailed account of these experiments will be communicated later.

THE GEOPHYSICAL LABORATORY
CARNEGIE INSTITUTION OF WASHINGTON
WASHINGTON, D. C.

JAMES H. HIBBEN

RECEIVED MAY 8, 1931
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THE IONIZATION CONSTANT OF ACETIC ACID

Sir:

We have obtained a precise value of the ionization constant of acetic acid at 25° from the results of new conductance measurements, made in this Laboratory, on acetic acid, hydrochloric acid, sodium chloride and sodium acetate at low concentrations (the lowest in each case being about 0.00003 *N*). The principles underlying the computations are essentially those which have been outlined by one of the undersigned [MacInnes, *THIS JOURNAL*, **48**, 2068 (1926)]. The calculations take account of the change of the mobilities of the ions as required by the Debye-Hückel-Onsager theory and of the ion activities as predicted by the Debye-Hückel theory. The computations, which involve a short series of approximations, consist in estimating the proportion of ions at each acetic acid concentration by comparing the measured equivalent conductance with that

of completely dissociated acetic acid, Λ_e , at the same ion concentration. Values of Λ_e are found by using Kohlrausch's law of independent ion migration, which is valid at the low ion concentrations involved. Applying the mass action law to the resulting degrees of dissociation we find a series of "constants," K' , which, to obtain the thermodynamic ionization K , must be multiplied by the product of the ionic activity coefficients, γ^2 .

It is noteworthy that to obtain a true constant the activity coefficients required are exactly those given by the Debye-Hückel theory in its limiting form

$$-\log \gamma^2 = 2 \times 0.5065 \sqrt{C_i}$$

in which C_i is the ion concentration. The results for the more dilute solutions are given in Table I.

TABLE I
RESULTS FOR THE MORE DILUTE SOLUTIONS

Concentration, equivalents per liter $\times 10^3$	Ion concn., C_i $\times 10^3$	K' $\times 10^3$	γ^2	K $\times 10^3$
0.028014	0.015092	1.7626	0.9910	1.747
.15321	.044005	1.7733	.9846	1.746
.21844	.054096	1.7766	.9830	1.746
1.0283	.12714	1.7937	.9741	1.747
1.3638	.14779	1.7961	.9721	1.746
2.4139	.19992	1.8053	.9776	1.747
3.4407	.24069	1.8104	.9645	1.746
5.9115	.31895	1.8189	.9592	1.745
9.8421	.41517	1.8285	.9536	1.744

Although extraordinarily constant in the range given, at higher concentrations there is a decrease in the value of K . This variation is due to several effects which may for the present be lumped together as "effect of the medium." The bearing of this value of K on the P_H scale will be discussed later and full accounts of these researches will shortly be submitted to THIS JOURNAL.

LABORATORIES OF
THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.
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D. A. MACINNES
THEODORE SHEDLOVSKY

THE DIRECT REACTION BETWEEN OXYGEN AND ETHYLENE

Sir:

The direct reaction between oxygen and ethylene is of general theoretical and technical interest. Study of the reaction in this Laboratory has shown that the slow non-explosive thermal reaction is complex. Two compounds have been found to be formed in the reaction whose presence has not been demonstrated before; these compounds are ethylene oxide and dioxy-

methyl peroxide,¹ $\text{CH}_2\text{OHOCH}_2\text{OH}$. Investigation of the reaction at temperatures from 300 to 525° under widely different conditions has shown that the two principal primary reactions are the formation of ethylene oxide and of formaldehyde. The other reaction products, dioxymethyl peroxide, acetaldehyde, formic acid, the oxides of carbon, hydrogen and water are formed in a step-wise sequence² of follow reactions. At temperatures above 500° the thermal polymerization of ethylene becomes an important reaction even in the presence of appreciable amounts of oxygen and inert gases.³

The velocity of reaction is proportional to the cube of the ethylene concentration and is almost independent of oxygen, as has been shown by Thompson and Hinshelwood.⁴ Comparison of the rates of reaction in packed and unpacked vessels shows that the reaction is mainly homogeneous. The reaction has an induction period which decreases with increase in temperature. It appears that the reaction follows a chain mechanism though it is necessary to assume that the chains can be both continued and stopped by the surface of the vessel.

Evidence of the formation of hydrogen peroxide as a reaction product has been obtained.

A full account of this work will appear shortly.

EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND Co.
WILMINGTON, DELAWARE
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SAMUEL LENHER

INTERATOMIC FORCES IN BINARY LIQUID ALLOYS. QUANTITATIVE DETERMINATION FROM THERMODYNAMIC DATA

Sir:

It is generally agreed that the attractive force between non-polar molecules varies inversely as some high power (*e. g.*, the 9th) of the distance. Langmuir [This JOURNAL, **38**, 2246 (1916)] has emphasized that the forces holding together such molecules are acting almost wholly between molecules *in contact* and that, as a very good approximation, all forces acting at greater distances may be neglected. The quantitative treatment of the properties of liquids in terms of power laws of force involves great mathematical difficulties when one attempts to consider molecules of irregular shape. Langmuir has shown that the problem may be greatly simplified

¹ Legler, *Ann.*, **217**, 381 (1883); Nef, *ibid.*, **298**, 202 (1897); Baeyer and Villiger, *Ber.*, **33**, 2479 (1900); Fenton, *Proc. Roy. Soc. (London)*, **A90**, 492 (1914); Rieche, "Alkylperoxide und Ozonide," Theodor Steinkopff Verlag, Dresden und Leipzig, Germany, 1931, p. 48.

² Bone and Wheeler, *J. Chem. Soc.*, **85**, 1637 (1904); Blair and Wheeler, *J. Soc. Chem. Ind.*, **42**, 415T (1923).

³ Willstätter and Bommer, *Ann.*, **422**, 36 (1921).

⁴ Thompson and Hinshelwood, *Proc. Roy. Soc. (London)*, **A118**, 170 (1928).

by regarding these van der Waals forces as coming into play between molecules only at the areas of contact. By using the concepts of surface area of individual molecules, and of interfacial energy for the contact surfaces, and assuming random orientation, he has developed through the Boltzmann equation ["Colloid Symposium Monograph," **3**, 48 (1925)] an expression for the deviation of activities from Raoult's law in binary liquid mixtures. So far as I know this relation has never been tested in binary liquid alloys where the situation is much simpler than in the cases of the organic mixtures discussed by Smyth and Engel [THIS JOURNAL, **51**, 2646 (1929)]. The equation is $\ln a_1/N_1 = \beta^2 S_1 \lambda/kT$ or $\ln a_2/N_2 = \alpha^2 S_2 \lambda/kT$, where $a = p/p^\circ$, p being the partial vapor pressure, p° the vapor pressure of the pure liquid, N the mole fraction, S the surface area per molecule, λ the energy per sq. cm. of interface between the two kinds of molecules, k the Boltzmann constant, T the absolute temperature and α and β are the surface fractions of the two components in the solution defined by $\alpha = N_1 S_1 / (N_1 S_1 + N_2 S_2)$ and $\beta = N_2 S_2 / (N_1 S_1 + N_2 S_2)$. The activity a may also be evaluated from electromotive forces of concentration cells. The ordinary molecular volume V which equals molecular weight/density, must be multiplied by 0.76 to take account of cubic or hexagonal close packing in the liquid, and divided by the Avogadro number to get the effective volume of a single molecule, $v = 4/3\pi r^3$. From this $S = 4\pi r^2$.

The thermodynamic data presented herewith are based upon electromotive force measurements of N. W. Taylor [THIS JOURNAL, **45**, 2884 (1923)] and of Hildebrand and Sharma [*ibid.*, **51**, 467 (1929)]; density values from Hogness [*ibid.*, **43**, 1621 (1921)] have been used.

INTERFACIAL ENERGIES BETWEEN METAL ATOMS IN LIQUID ALLOYS

System	Temp., t	Component 1	Component 2	Log a/N $N = 0$	$S \times 10^{16}$, sq. cm.	λ Ergs/sq. cm.
Zn-Cd	540°	Zn		0.490	25.8	48.8
Zn-Cd	540°		Cd	.615	32.8	48.2
Cd-Pb	544°	Cd		.480	32.8	37.7
Cd-Pb	544°		Pb	.582	40.6	37.0
Cd-Sn	544°	Cd		.246	32.8	19.4
Cd-Sn	544°		Sn	.270	37.3	18.7
Tl-Sn	352°	Tl		.444	37.6	23.4
Tl-Sn	352°		Sn	.44	36.7	23.9
Zn-Sn	539°	Zn		.240	25.8	23.9
Zn-Sn	539°		Sn	.60	37.3	41.3

The test of the Langmuir equation lies in a comparison of the two λ values calculated for each system from $\log a/N$ and S of each component independently. For all systems except zinc-tin the agreement is good to 3%. Since the $\log a_2/N_2$ values for the second component of each system were evaluated by the Duhem relation they are themselves uncertain to 1 or 2%. They are somewhat smaller than the values given in my original

paper which were based upon an incorrect extrapolation. The system zinc-tin is certainly abnormal as I pointed out in my original paper in 1923. In this case influences are present which inhibit random orientation of the molecules.

The Hildebrand equation for "Regular Solutions" $RT \ln a_1/N_1 = bN_2^2$ or $RT \ln a_2/N_2 = bN_1^2$ can be strictly true only when the two components have the same surface area per molecule. S_{T1} exceeds S_{Sn} by only 2%, and this is the reason for the result found by Hildebrand and Sharma that "so far as the variation with N is concerned, this system corresponds perfectly to the definition of a regular system given by the senior author" (THIS JOURNAL, 51, 66 (1929)).

The evidence presented thus lends support to Langmuir's equation and to the assumptions upon which it is based.

More extensive data and a fuller treatment of this problem will be presented in a later publication.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA
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NELSON W. TAYLOR

RADIOCHEMICAL EQUILIBRIUM IN AMMONIA SYNTHESIS

Sir:

The attempt to calculate chemical equilibrium or a steady state attained by alpha radiation from the known yield per ion pair of the two opposing non-thermal reactions was first made for the synthesis and decomposition of water [Lind, *Trans. Am. Electrochem. Soc.*, 34, 214 (1918)]. The case for ammonia is much more suitable since the system remains entirely homogeneous. The decomposition of ammonia has been measured by Wourtzell [*Le Radium*, 11, 342 (1919)]. The yield in synthesis was determined in a flow system by Lind and Bardwell [THIS JOURNAL, 50, 745 (1928)] to lie in the range $+M_{NH_3}/N_{(N_2 + H_2)} = 0.2-0.3$. Choosing 0.2 as the most probable value of $+M/N$ and the round number 1.0 (from Wourtzell) for the decomposition ($-M/N$), Lind and Bardwell calculated that the equilibrium (at 25°) would be $(1.0/1 + 0.2) = 83.3\%$ decomposition, corresponding to 9.09% NH_3 by volume.

Later Ponsaert [*Bull. soc. chim. Belg.*, 38, 110 (1929)] redetermined the yield for synthesis as 0.32 and taking 1.08 from Wourtzell for decomposition calculated equilibrium at 13.5% NH_3 by volume. The actual equilibrium has now been experimentally determined by D'Olieslager and Jungers [*Bull. soc. chim. Belg.*, 40, 75 (1931)] as only 4.7% NH_3 by volume.

In calculating the equilibrium from the yields at the beginning of the opposing reactions where back-reaction is negligible, it has been assumed that the mechanisms of the two reactions at equilibrium are independent of

each other in their intermediate steps. If this were true, it would require a value of $+M/N$ in synthesis of only 0.11 in order to give a steady state at 4.7% NH_3 . That the value for synthesis cannot be so low has been shown above. It therefore appears that the intermediate steps are not independent and that there must be an exchange of activation energy in the direction to produce additional decomposition.

The principal object of this communication is to point out that the shift of equilibrium from that predicted is in the right direction to be accounted for by an exchange of ionization from the elemental ions H_2^+ (16 volts) or N_2^+ (17 volts) to give NH_3^+ (11 volts). Such transfer of ionization would favor decomposition at the expense of synthesis, assuming always that H_2^+ and N_2^+ in some way cause synthesis and that NH_3^+ causes decomposition.

This same type and direction of shift may be general in other similar reactions in gaseous phase, since the larger molecules will usually have a lower ionization potential than either of its components.

An effort is being made to test this hypothesis quantitatively for ammonia by means of a complete kinetic equation which should fit the kinetics of either reaction and the equilibrium.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA
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S. C. LIND

THE IONIC NATURE OF THE HYDROGEN BOND

Sir:

In a recent paper, Linus Pauling [THIS JOURNAL, **53**, 1367 (1931)] has pointed out that the hydrogen bond postulated by Huggins, Latimer and Rodebush is to be expected only of molecules having ionic characteristics and that the bond itself is ionic. The evidence that is offered by Pauling is for the most part chemical, and it might be profitable to examine the question in the light of physical data not considered by him.

Work on the Raman effect [in particular Krishnamurti, *Nature*, **125**, 892 (1930)] has indicated that Raman lines are to be expected with atomic bonds (*i. e.*, shared electron pairs) rather than with ionic linkages. The reason for this is obscure; but at least in solutions it may be due in many cases to the magnitude of the energy states involved in the various types of molecules or "resistant groups." Raman data on the association of liquids (such as H_2O , NH_3 and SO_2) are inconclusive so far as offering information about the character of this bond. It might be possible to decide this question from the sharpness of the lines. However, in all of the work that has been done on the Raman effect of hydrates and solutions no lines have been reported that may be interpreted as showing an "atomic vibration" of the water "molecule" with respect to the metal ion. A literal applica-

tion of the older conception of this bond demands that there be such lines. The observed state of affairs is to be expected on the basis of Pauling's suggestion. Furthermore, if the hydrogen ion is connected to the water molecule by means of a shared electron pair in the oxonium ion, we would expect a Raman spectrum characteristic of the latter ion. This would mean that all solutions of acids would have lines in common. An examination of the data for nitric, hydrochloric and sulfuric acids shows that this is not the case.

Another interesting example is the ammonium ion. In solution this ion has no observable Raman lines. This indicates not only that the hydrogen ion connects itself to the ammonia molecule through an ionic linkage, but that in doing so it causes the other bonds to become ionic. It is entirely possible that the case of the oxonium ion is parallel, and that each hydrogen is connected to the oxygen through an ionic linkage.

As investigations in solutions are inherently under adverse conditions, the bond may actually be intermediate in character. At least the evidence indicates quite strongly that it is not of the extreme electron pair type formerly assumed.

U. S. BUREAU OF STANDARDS
WASHINGTON, D. C.

CHARLES KASPER

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THE CARBON-HALOGEN BOND AS RELATED TO RAMAN SPECTRA

Sir:

The purpose of the work described here was to determine the variation of the characteristics of the bond between carbon and another atom as the length and structure of the hydrocarbon chain is varied. The frequency which corresponds to the carbon-bromine bond in methyl bromide is 1.808×10^{13} per second, but in longer normal chains this is reduced to a constant value of 1.688×10^{13} . In an iso compound or in the presence of a double bond, this is reduced to about 1.61×10^{13} . These frequencies are of considerable interest, since in the simple theory they are supposed to be equal to the frequencies of the carbon-bromine bond in these compounds.

What is sometimes called the "strength of a bond" may be represented by the force constant, which for the carbon-carbon single bond is about 5×10^5 dynes per cm. The values for the carbon-halogen bond do not seem to have been calculated for monohalogenes. They are given in Table I.

The force constant (*a*) is calculated in the ordinary way, and it is considered that the methyl group vibrates as a unit with respect to the halogen atom. In (*b*) a slight, somewhat arbitrary allowance has been made for the fact that this is not strictly true.

TABLE I

Compound	VALUES FOR THE CARBON-HALOGEN BOND					
	Wave number, cm. ⁻¹	Frequency per second × 10 ⁻¹³	Force constant × 10 ⁻⁶ dynes		Amplitude × 10 ¹⁰ cm.	
			<i>a</i>	<i>b</i>	<i>n</i> = 0	<i>n</i> = 1
CH ₃ Cl ¹	712	2.135	3.14	3.02	6.7	11.6
CH ₃ Br ²	603	1.808	2.70	2.60	6.65	11.5
CH ₃ I ²	534	1.601	2.25	2.17	6.9	11.9

The force constants decrease from the chloride to the iodide, in somewhat the same way as the corresponding energies of dissociation. Those given in Column (*a*) are much smaller than the values of the single bonds listed by Dadiou and Kohlrausch,¹ which are (in 10⁶ dynes per cm.) equal to 4.31 for C-C in ethane, 4.96 for C-O in methyl alcohol, and 4.89 for C-N in methylamine.

That the frequencies chosen in Table I are those characteristic of the carbon-halogen bond is shown by work on various bromides. These are listed in Table II.

TABLE II

CHARACTERISTIC WAVE NUMBERS FOR THE CARBON-BROMINE BOND IN ORGANIC BROMIDES

CH ₃ Br	603 (2)	(CH ₃) ₂ CH(CH ₃) ₂ Br	564
C ₂ H ₅ Br	566 (2)	(CH ₃) ₂ CHBr	540
<i>n</i> -C ₃ H ₇ Br	563	C ₂ H ₅ CHBrCH ₃	537
<i>n</i> -C ₄ H ₉ Br	563	(CH ₃) ₃ CBr	538
<i>n</i> -C ₅ H ₁₁ Br	564	CH ₂ :CHCH ₂ Br	535
		(CH ₂) ₂ CHCH ₂ Br	572

The remarkable fact revealed by these data is that the frequency of the carbon-bromine bond is constant in normal compounds with the exception of methyl bromide, and that it is the same for an iso compound provided the side chain is sufficiently distant from the bromine. However, an adjacent side chain, attachment to a secondary or a tertiary carbon atom, or the double bond of an adjacent unsaturated group as in allyl bromide, in all the given cases lowers the wave number from 563.5 to about 537 cm.⁻¹. Thus the carbon-bromine bond seems considerably weaker in this latter class of compounds (with the exception of isobutyl bromide).

It is apparent from the constant value of the wave number for the normal compounds that *the organic radical cannot vibrate as a whole with respect to the bromine atom*, for such an assumption leads to an absurd value for the force constant.

On the basis of the assumption that the effective mass of the methyl group with respect to the vibration toward bromine is 14.4 atomic weight units, the force constant for methyl bromide is 2.60 × 10⁶ dyne/cm.

¹ Wave number determined by Dadiou and Kohlrausch, *J. Opt. Soc. Am.*, **5**, 297 (1931).

² Wave number determined by Cleeton and Dufford, *Phys. Rev.*, **37**, 365 (1931).

(or 2.70 if CH_3 vibrates as a single unit of mass 15). If now the amyl group vibrates as a unit the force constant for amyl bromide would be 7.0×10^5 dyne/cm., or more than two and a half times larger than for methyl bromide. This is much too large.

If the force constant in all of the normal bromides is assumed to be constant and equal to 2.60×10^5 dyne/cm., the effective mass of the portion of the hydrocarbon chain which vibrates (with respect to the bromine) is 17. This indicates that the CH_2 group adjacent to the bromine possesses most of the mass which is effective. That is, the CH_2 group vibrates, but its effective mass is increased by the constraint due to its union with the rest of the hydrocarbon chain, and is influenced by the vibration of this part of the molecule.

The writers have determined the frequencies of the Raman lines of nine organic bromides. These give a large number of characteristic frequency differences as, for example, 1639 cm.^{-1} for the double bond of allyl bromide, but only the values characteristic of the carbon-bromine and other carbon-halogen bonds can be discussed here. The variation in the wave number corresponding to this bond is usually not more than one unit of wave number for any one compound, and the maximum variation for any compound is two units.

The equation for the force constant (k) is

$$\nu_0 = \omega_0 (n' - n'') = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} (n' - n'')$$

in which n represents a quantum number, μ the mutual mass, ν_0 the fundamental frequency of the radiation, and ω_0 the fundamental mechanical frequency. A further discussion will be presented in the final paper.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

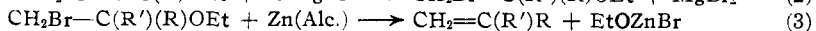
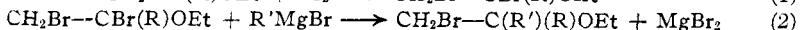
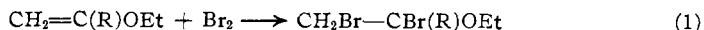
WILLIAM D. HARKINS
HAROLD E. BOWERS

RECEIVED MAY 22, 1931
PUBLISHED JUNE 8, 1931

PREPARATION OF UNSYMMETRICAL DIALKYL ETHYLENE DERIVATIVES

Sir:

The recent description of the preparation of α,β -unsaturated ethers by Lauer and Spielman [THIS JOURNAL, **53**, 1533 (1931)] makes possible an extension of our nuclear synthesis of olefins [*ibid.*, **52**, 3396 (1930); **53**, 1505 (1931)] to include the unsymmetrical dialkyl derivatives of ethylene. The essential steps in the process are clearly represented by the scheme.



Three hexenes have been prepared by this method, with the physical constants indicated.

Olefin	B. p. (760 mm.)	D_D^{20}	n_D^{20}	MR (Fd.)	MR (Calcd.)
2-Methyl-1-pentene	61.5-62.0	0.6831	1.3921	29.34	29.44
2-Ethyl-1-butene	66.2-66.7	.6938	1.3990	29.31	29.44
2,3-Dimethyl-1-butene	56.0-56.5	.6827	1.3905	29.55	29.44

The method is being extended to the preparation of other olefins and diolefins.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

CLAUDE G. SCHMITT
CÆCIL E. BOORD

RECEIVED MAY 26, 1931
PUBLISHED JUNE 8, 1931

THE DECOMPOSITION OF SODIUM AZIDE BY CONTROLLED ELECTRON BOMBARDMENT

Sir:

The decomposition of solid sodium azide has been achieved by subjecting a thin film to bombardment by electrons of known velocity. The reaction was carried out in a high vacuum using an oxide filament as the source of electrons and suitable electrodes for controlling the velocity. Impacts in the gas phase were shown to be absent. The nitrogen resulting from the decomposition was detected and measured by an ionization manometer. The gas evolved was shown to be nitrogen by critical impact measurements. Rate curves taken at various electron velocities gave a sharp intercept on the voltage axis, setting the minimum potential at 12 ± 1 volts. The rate curves showed discontinuities in the region of the critical potentials of nitrogen, thus affording additional proof of the nature of the gas. At no time was any thermal decomposition observed, nor any effect at or below 11.5 volts.

These measurements are being continued with slightly improved technique. The photochemical decomposition is being studied as well and will be the subject of a later communication.

DEPARTMENT OF CHEMISTRY
WASHINGTON SQUARE COLLEGE
NEW YORK UNIVERSITY
NEW YORK CITY

RALPH H. MÜLLER
G. CALVIN BROUS

RECEIVED MAY 29, 1931
PUBLISHED JUNE 8, 1931