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The Dissociation of HCN, C_2H_2, C_2N_2 and C_2H_4 by Electron Impact

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The dissociation of HCN and C_2H_4 by electron impact has been investigated. An analysis of the results for these two molecules together with an analysis of previously published results on the dissociation processes occurring in C_2H_2 and C_2N_2 is presented. It is possible to assign reasonable processes of formation to all the observed ions from a knowledge of their appearance potentials, the known ionization potentials of certain atoms and atomic aggregates and the energies of dissociation of the parent molecule into various configurations. By a comparison of the results obtained for these four molecules, upper limits are assigned to the ionization potentials of various fragments obtained as dissociation products of hydrocarbons.

INTRODUCTION

THIS paper is the report of a series of experiments on the dissociation of organic molecules by electron impact. The dissociation of benzene and related molecules has recently been investigated in this laboratory. It is apparent from the results obtained that an understanding of the processes occurring in complex molecules is difficult to obtain without some further study of relatively simple organic compounds. Smith[1] has recently observed the dissociation processes occurring in methane and has made an analysis of them. The present work concerns an analysis of new data obtained on dissociation processes in hydrogen cyanide (HCN) and in ethylene (C_2H_4). An analysis of previous data by Tate, Smith and Vaughan[2] on cyanogen (C_2N_2) and on acetylene (C_2H_2) will also be presented.

A comparison of the results obtained on the dissociation processes of several related molecules will yield more information about the properties of the ions produced and about the nature of the processes than a consideration of results on any single molecule alone can yield. For example, an ion may conceivably be produced from a molecule by several different processes. If sufficient data are available to determine the energy of dissociation of these processes, and if the energy required to produce the ion from the parent molecule is known, alternative upper limits for the ionization potential may be computed for each of the processes. Comparison with alternative upper limits for the ionization potential computed for the same ion produced from another molecule, may permit the determination of a unique upper limit of the ionization potential, as well as a determination of the process responsible for its formation. Similar combinations of data may permit the determination of the energies of dissociation of the various processes which may occur.

The mass spectrograph is capable of providing considerable information about dissociation processes occurring in gaseous molecules. It is possible to determine the nature of the ions produced under various conditions by an approximate determination of the M/e of the observed ion. Such information gives valuable clues as to the arrangement of atoms within a molecule. The relative probability of formation of the ions may be observed for various pressures and electron energies. The variation of ion intensity with pressure will indicate whether an ion is produced from the parent molecule by a single electron collision or whether collisions with other ions or molecules are responsible for its formation. Smyth and Mueller[3] have observed, for example, that the peak due to H_3O^+, observed in the dissociation of water, varies in intensity approximately as the square of the pressure in the ionizing chamber, whereas the peak due to H_2O^+ varies in intensity approximately linearly with the pressure. This indicates that H_2O^+ is formed as a primary product, but H_3O^+ by some process of recombination.

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[1] Smith, Phys. Rev. **51**, 263 (1937).

[2] Tate, Smith and Vaughan, Phys. Rev. **48**, 523 (1935).

[3] Smyth and Mueller, Phys. Rev. **43**, 116 (1933).

The minimum energy required to produce the ion may also be determined. This energy, usually designated by the term appearance potential, is the sum of a dissociation energy, an ionization potential and the minimum excitational and kinetic energy, hereafter called the excess energy, with which the products can dissociate. If the appearance potential and two of the other quantities involved in this relationship are known, the remaining quantity may, of course, be determined. Even if either the ionization potential or the dissociation energy and the excess energy are unknown, upper limits may be set on the remaining quantity. The usual experience is that the excess energy is small, and that the upper limit set on an ionization potential or a dissociation energy in this way is quite close to its true value. Any large amount of kinetic energy imparted to an ion in the dissociation process would be manifested by a displacement of the peak from its ideal position. In the present series of experiments the kinetic energy was in all cases less than a half-volt. No statement can, in general, be made about the excitational energy with which the fragments dissociate. Since the excess energy is not known for any of the cases which will be discussed in this paper, a criterion of the goodness of the assignment of any process to an observed ion will be the requirement that the excess energy be small.

APPARATUS

The same mass spectrograph was used for the present series of observations as was used in the recent study of dissociation processes occurring in benzene. It is similar to that used by Tate, Smith and Vaughan[2] in their work on cyanogen and acetylene. The resolving power was sufficiently great to resolve all the peaks observed for ethylene and for hydrogen cyanide.

Ordinary anaesthetic ethylene, purified by distillation at liquid-air temperatures was used. The hydrogen cyanide was distilled from liquid anhydrous HCN prepared by Kahlbaum. Both of these gases were admitted to the mass spectrograph through capillary leaks patterned after one described by Smythe.[4]

Argon was used to calibrate the mass scale and to determine the corrections to be applied to the apparent accelerating potential on the electrons. This correction was at all times small and remained practically constant throughout the course of the investigation.

RESULTS AND ANALYSES

To simplify the presentation of the analyses the following nomenclature will be used:

$A(X^+)\equiv$ Appearance potential of the ion X^+.
$I(X)\equiv$ Ionization potential of X.
$D(X)\equiv$ Energy of dissociation of X to atoms in the gaseous state.
$Q(X)\equiv$ Energy evolved in the formation of X from its elements in the states in which they exist at room temperature and atmospheric pressure.
$W(X^+)\equiv$ Excess energy required to produce the ion X^+ from the parent molecule.
$L(C)\equiv$ Heat of sublimation of carbon.

1. Hydrogen cyanide

All the ions observed as dissociation products of HCN together with their relative intensities at an electron energy of 75 volts and their appearance potentials are listed in Table I. Observations were made on the variation of peak heights as a function of pressure. Since the relative peak heights remained essentially constant it is safe to say that the ions are the result of direct dissociation of HCN by a single electron impact.

CO was an important impurity in the mass spectrograph and occurred from an undetermined

TABLE I. *Ions observed in hydrogen cyanide. Column (1) observed ions; (2) relative intensity; (3) appearance potential (volts); (4) probable process. HCN→; (5) calculated minimum energy (volts); (6) excess energy or deduced ionization potential (volts).*

(1)	(2)	(3)	(4)	(5)	(6)
HCN^+	100	13.7 ± 0.1	HCN^+	$I(HCN)$	$I(HCN)=13.7$
CN^+	14.8	20.1 ± 0.2	CN^++H	$3.7+I(CN)$	$I(CN)\leqslant16.4$
NH^+	0.12	24.9 ± 0.5	NH^++C	$5.7+I(NH)$	$I(NH)\leqslant19.2$
N^+	1.1	25.6 ± 0.5	N^++H+C	24.4	$W(N^+)\geqq1.2$
CH^+	1.2	21.8 ± 0.5	CH^++N	$6.4+I(CH)$	$I(CH)\leqslant15.4$
C^+	3.0	23.8 ± 0.5	C^++N+H	21.1	$W(C^+)\geqq2.7$
HCN^{++}	1.2	40.0 ± 1.0	HCN^{++}	$I(HCN)+I(HCN^+)$	$I(HCN^+)=26.3$

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[4] Smythe, Rev. Sci. Inst. 7, 435 (1936).

source. About 20 percent of the peak observed for C^+ and indicated in Table I is due to the presence of this CO. Vaughan[5] has measured the appearance potential of C^+ produced from CO as 22.5 ± 0.2 volt. This value is so close to that observed in the present case, that it is not certain that the present value is due to C^+ produced from HCN. The intensity of the peak N^+ of $M/e=14$ is in error to a small extent due to the presence of CO^{++} of identical M/e. Because of the high appearance potential of CO^{++}, no error is introduced in the value $A(N^+)$. Considerable molecular hydrogen was observed, but since its appearance potential was the same as the ionization potential of H_2, it was concluded that the H_2 existed as an impurity and not as a product of dissociation of HCN. The very small amount of atomic hydrogen present could be satisfactorily accounted for as the result of dissociation of H_2.

Table II shows the energies of the possible states of combination in which a carbon, a hydrogen and a nitrogen atom may exist.

Bichowsky and Rossini[6] give $Q(\mathrm{HCN})=-30.7$ kcal·mole$^{-1}=-1.33$ volt. Sponer[7] gives $D(H_2)=4.46$ volt and $D(N_2)=7.35$ volt. Considerable doubt exists as to the value of the quantity $L(\mathrm{C})$. Goldfinger and Jeunehomme[8] conclude that the balance of evidence is in favor of the value $L(\mathrm{C})=5.36\pm0.02$ volt, and this value will be used throughout. Smith[1] has used this value in his work on the dissociation of methane and finds that it is compatible with his observed energies.

For the determination of $D(\mathrm{HCN})$ the following cycle may be written:

$$\begin{aligned}H_2+N_2+2C_{\mathrm{dia}}&=2\mathrm{HCN}+2Q(\mathrm{HCN}),\\ 2C_{\mathrm{dia}}+2L(\mathrm{C})&=2C_{\mathrm{gas}},\\ H_2+D(H_2)&=2\mathrm{H},\\ N_2+D(N_2)&=2\mathrm{N},\\ 2\mathrm{H}+2\mathrm{N}+2C_{\mathrm{gas}}&=2\mathrm{HCN}+2D(\mathrm{HCN}).\end{aligned}$$

This shows that

$$2D(\mathrm{HCN})=D(H_2)+D(N_2)+2L(\mathrm{C})+2Q(\mathrm{HCN}),$$

which yields

$$D(\mathrm{HCN})=9.93 \text{ volt}.$$

Table II. *Energies of possible states of combination in which a carbon, hydrogen and nitrogen atom may exist.*

State	Configuration	Energy (Volts)
a	H+C+N	9.9
b	CH+N	6.4
c	NH+C	5.7
d	CN+H	3.7
e	HCN	0

This value determines the energy of the state *a* in Table II.

Some doubt exists as to the value of $D(\mathrm{CH})$. Sponer[7] gives a value of 3.5 volt, estimated from spectroscopic data. This value differs from the value 4.323 volt given by Pauling and Sherman[9] for the energy of the C−H bond. Dietz[10] has calculated the energy of the C−H bond to be 3.97 volt. The energy of the C−H bond, as calculated from the known energies of formation of organic molecules, may, of course, be expected to be higher than the spectroscopically determined $D(\mathrm{CH})$. If we use the value given by Sponer, the energy of the state *b* is 3.5 volt below that of *a*.

The energy of the state *c* is 4.2 volt below that of *a*, calculated from Sponer's value, $D(\mathrm{NH})=4.2$ volt. Finally the state *d* is 6.2 volt below *a*, calculated from a value given by Herzberg,[11] $D(\mathrm{CN})=6.159$ volt.

All available evidence of a chemical and spectroscopic nature points to the conclusion that hydrogen cyanide exists in the configuration

$$\mathrm{H-C\equiv N}.$$

However, a small proportion of hydrogen cyanide, variously estimated at from 0.5 to 4 percent, exists in the isomeric configuration HNC. Williams[12] has come to this conclusion from a comparison of the infrared absorption of organic cyanides and their isomeric configurations with that of hydrogen cyanide. Reichel and Strasser[13] have come to the same conclusion from a similar comparison in the ultraviolet. Dadieu[14] has found lines in the Raman spectrum of hydrogen cyanide

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[5] Vaughan, Phys. Rev. **38**, 1687 (1931).

[6] Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold, 1936).

[7] Sponer, *Molekulspektren* (J. Springer, (1935)).

[8] Goldfinger and Jeunehomme, Proc. Faraday Soc. **32**, 1591 (1936).

[9] Pauling and Sherman, J. Chem. Phys. **1**, 606 (1933).

[10] Dietz, J. Chem. Phys. **3**, 58 (1935).

[11] Herzberg, Nature **137**, 620 (1936).

[12] Williams, J. Chem. Phys. **4**, 84 (1936).

[13] Reichel and Strasser, Ber. der Deutschen Chem. Gesellschaft **64B**, 1997 (1931).

[14] Dadieu, Ber. der Deutschen Chem. Ges. **64B**, 358 (1931).

whch could only be associated with the isomeric form HNC.

The state c in Table II has, therefore, a real significance, and since HCN and HNC probably have very nearly equal heats of dissociation, the energy assigned to state c is correct to within the limits of error of the energies involved in its computation.

HCN^+. The observed ionization potential of HCN is 13.7±0.1 volt. Sponer[7] quotes the value 14.8 volt from old sources. Price[15] has observed a series of absorption bands of HCN in the region 1450A to below 1000A. Some of these bands seem to form a Rydberg series converging to an ionization potential of about 14.8 volt.

CN^+. Since CN^+ can occur only by the transition $e\rightarrow d$, we can write at once:

$$A(CN^+)=D(HCN)-D(CN)+I(CN)+W(CN^+),$$

$$I(CN)=16.4\text{ volt}-W(CN^+),$$

or

$$I(CN)\leq 16.4\text{ volt},$$

depending on the excess energy required to produce CN^+.

NH^+. This ion can also occur in only one way, and as above we can find:

$$I(NH)\leq 19.2\text{ volt}.$$

This value might be compared to a similar value calculated from the dissociation of NH_3. Bartlett[16] has observed the appearance potentials of the ions NH_3^+, NH_2^+ and NH^+ to be 11.2, 12.0 and 11.2 volt, respectively. He believes the ions NH_2^+ and NH^+ to be the result of some secondary process. Even if no dissociation energy were required to produce NH^+ from ammonia, his low appearance potential cannot be reconciled with the high upper limit of its ionization potential found in the present case. It seems likely that his value is due to overlapping of neighboring peaks.

The fact that the peak NH^+ occurs at all lends strong support to other evidence that hydrogen cyanide exists in the isomeric configuration HNC. No valid estimate of the abundance of HNC in HCN can be made from the present work. From the low intensity of the NH^+ peak it can be seen that the concentration of HNC is small.

N^+. From the energies shown in Table II and from the ionization potential $I(N)=14.5$ volt, the minimum energy required for the formation of N^+ by the transition $e\rightarrow a$ is found to be 24.4 volt, and by the transition $e\rightarrow b$, 20.9 volt. The excess energy required for the formation of N^+ from HCN is the difference between the observed appearance potential, $A(N^+)=25.6$ volt, and the minimum required energy. The excess energy required in the transition $e\rightarrow a$ is 1.2 volt and in the transition $e\rightarrow b$ 4.7 volt. While the second of these transitions cannot be definitely excluded, it seems probable that N^+ is produced by the first, and that the process responsible for its formation is

$$HCN\rightarrow N^+ + H + C.$$

CH^+. No good value is available for the ionization potential of CH. Since CH^+ can arise only from the process,

$$HCN\rightarrow CH^+ + N,$$

the upper limit $I(CH)\leq 15.4$ volt may be calculated from the appearance potential and the energies in Table II. Smith[1] has calculated two alternative values of the ionization potential of CH, depending on the two possible alternatives for the formation of CH^+ from CH_4. If

$$CH_4\rightarrow CH^+ + 3H,\quad I(CH)\leq 11.7\text{ volt},$$

and if

$$CH_4\rightarrow CH^+ + H_2 + H,\quad I(CH)\leq 11.7+D(H_2)=16.2\text{ volt}.$$

If the first of these processes is correct the minimum excess energy required for the formation of CH^+ from HCN is 3.7 volt. If the second

TABLE III. *Ions observed in acetylene. Column (1) observed ions; (2) appearance potential (volts); (3) probable process. $C_2H_2\rightarrow$; (4) calculated minimum energy (volts); (5) excess energy or deduced ionization potential (volts).*

(1)	(2)	(3)	(4)	(5)
$C_2H_2^+$	11.2±0.1	$C_2H_2^+$	$I(C_2H_2)$	$I(C_2H_2)=11.2$
C_2H^+	17.8±0.2	$C_2H^+ + H$	$4.0+I(C_2H)$	$I(C_2H)\leq 14.3$
C_2^+	23.8±0.3	$C_2^+ + 2H$	$7.3+I(C_2)$	$I(C_2)\leq 16.5$
CH^+	22.2±0.5	$CH^+ + CH$	$5.8+I(CH)$	$W(CH^+)\geq 1.0$
C^+	24.5±1.0	$C^+ + C + 2H$	24.0	$W(C^+)=0.5$
H^+	21.7±1.0	$H^+ + H + C_2$	20.8	$W(H^+)=0.9$
	25.6±1.0	$H^+ + CH + C$	22.8	$W(H^+)=2.8$

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[15] Price, Phys. Rev. **46**, 529 (1934).

[16] Bartlett, Phys. Rev. **33**, 169 (1929).

is correct the minimum excess energy for the formation of CH^+ from CH_4 is 0.8 volt. The second of these two processes, therefore, seems the more probable one.

C^+. The minimum energy required for the formation of C^+ from HCN by the transition $e \rightarrow a$ is 21.1 volt and by the transition $e \rightarrow c$ is 16.9 volt, where $I(C) = 11.2$ volt. The observed appearance potential, $A(C^+) = 23.8$ volt, almost certainly excludes the second of these possibilities. $A(C^+)$ may be in error due to the presence of C^+ from CO, so that the calculated excess energy, $W(C^+) = 2.7$ volt may be in error. The process responsible for the formation of the C^+ is certainly

$$HCN \rightarrow C^+ + H + N.$$

HCN^{++}. The second ionization potential of HCN is found to be 26.3 volt.

A summary of the principal results obtained is included in Table I.

The assignment of processes to the ions observed in HCN is in accord with an observation which Smith[1] has made in the case of CH_4, that the possible processes which require the largest calculated minimum energies are those which actually occur.

2. Acetylene

The data to be used in the present analysis have been obtained by Tate, Smith and Vaughan[2] and are listed in Table III. Table IV shows the possible states of combination of two hydrogen and two carbon atoms and the energies associated with these states. The energies were computed in the same way and from the same sources of data as in the case of HCN. For the additional quantity $D(C_2)$, Sponer's value of 5.5 volt was used. Since all chemical and spectroscopic evidence points to the fact that C_2H_2 is a linear symmetrical molecule of the form

$$H-C\equiv C-H,$$

ions of the type CH_2^+ would not be expected to occur. The nonoccurrence of such ions lends further support to this picture. The state CH_2+C has not therefore been included in Table IV, nor has its energy been calculated.

TABLE IV. *Energies of possible states of combination in which two hydrogen and two carbon atoms may exist.*

STATE	CONFIGURATION	ENERGY (VOLTS
a	$2C+2H$	12.8
b	$CH+C+H$	9.3
c	$2C+H_2$	8.4
d	C_2+2H	7.3
e	$CH+CH$	5.8
f	C_2+H_2	2.8
g	C_2H+H	3.5
h	C_2H_2	0

$C_2H_2^+$. The observed ionization potential of C_2H_2 is 11.2 ± 0.1 volt. Price[17] has obtained the value 11.35 volt by determining the convergence limit of a Rydberg series of bands in the ultraviolet. Mulliken[18] estimates the vertical ionization potential of acetylene at 11.9 volt, which is probably several tenths of a volt higher than the adiabatic ionization potential measured in electron impact experiments and in spectroscopic determinations.

C_2H^+. No very satisfactory value can be obtained for the energy of the state *g*. However, the energy required to remove two hydrogen atoms from C_2H_2 is 7.3 volt. Since the energy required to remove the first of these hydrogen atoms can be expected to be less than that required to remove the second one, a reasonable assumption is that the state *g* is 3.5 volt above *h*. The energy required to remove the second hydrogen atom is then 3.8 volt, 0.3 volt more than that required to remove the first one.

In any case,

$$A(C_2H^+) = D(C_2H_2) - D(C_2H) + I(C_2H) + W(C_2H^+),$$

so that

$$I(C_2H) - D(C_2H) \leq 5.0 \text{ volt.}$$

This value will subsequently be used in the analysis of the data on ethylene. If the state *g* is 3.5 volt above *h*,

$$I(C_2H) \leq 14.3 \text{ volt.}$$

C_2^+. C_2^+ may be produced from acetylene either by the transition $h \rightarrow d$ or by the transition $h \rightarrow f$. For the transition $h \rightarrow d$:

$$A(C_2^+) = D(C_2H_2) - D(C_2) + I(C_2) + W(C_2^+)$$

or

$$I(C_2) \leq 16.5 \text{ volt,}$$

and for the transition $h \rightarrow f$:

$$I(C_2) \leq 16.5 + D(H_2) = 21.0 \text{ volt.}$$

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[17] Price, Phys. Rev. **47**, 444 (1935).

[18] Mulliken, J. Chem. Phys. **3**, 517 (1935).

There is no way of determining the correct $I(C_2)$ and the process responsible for the formation of C_2^+ from the data on acetylene alone. However in the work on cyanogen which will be discussed later it will be shown that

$$I(C_2) \leq 9.1 \text{ volt},$$

or $$I(C_2) \leq 9.1 + D(N_2) = 16.5 \text{ volt}.$$

The results for these two molecules can be brought into reasonable accord only if $I(C_2) \leq 16.5$ volt. The process responsible for the formation of C_2^+ from C_2H_2 is

$$C_2H_2 \rightarrow C_2^+ + 2H$$

Bleakney, Condon and Smith[19] have found $I(C_2) = 14.7$ volt by the same argument. Their calculations are based on a different value of $L(C)$, than that used here. Their conclusion as to the process which occurs is identical to that obtained here.

CH^+. Either the transition $h \rightarrow b$ or the transition $h \rightarrow e$ may give rise to CH^+. From the first

$$I(CH) \leq 12.9 \text{ volt},$$

and from the second,

$$I(CH) \leq 12.9 + D(CH) = 16.4 \text{ volt}.$$

In the discussion on HCN it has been shown that

$$I(CH) \leq 15.4 \text{ volt}.$$

If CH^+ is produced from C_2H_2 by the transition $h \rightarrow b$, the minimum excess energy required for the formation of CH^+ from HCN is 2.5 volt. If the transition $h \rightarrow e$ is the correct one, the minimum excess energy required for the formation of CH^+ from C_2H_2 is 1.0 volt. Since both of these values are quite reasonable no choice of process can be made. However, if the transition $h \rightarrow b$ is the correct one, then the transition for the production of CH^+ from CH_4 with which the value, $I(CH) \leq 11.7$ volt, is associated must be the correct one. This, as was shown, earlier, gives a rather high value for the excess energy required to produce CH^+ from HCN. It, therefore, seems safe to say that the process:

$$C_2H_2 \rightarrow CH^+ + CH$$

accounts for the formation of CH^+ from C_2H_2.

C^+. The minimum energies required for the formation of C^+ from C_2H_2 by the possible transitions are:

$$h \rightarrow a \quad 12.8 + 11.2 = 24.0 \text{ volt},$$
$$h \rightarrow b \quad 9.3 + 11.2 = 20.5 \text{ volt},$$
$$h \rightarrow c \quad 8.4 + 11.2 = 19.6 \text{ volt}.$$

The observed appearance potential of 24.5 volt correlates most nearly with the first of these. In this case $W(C^+) = 0.5$ volt. The other transitions cannot be excluded, but give rise to rather high excess energies.

H^+. The minimum energies required for the formation of H^+ by the following transitions are:

$$h \rightarrow a \quad 12.8 + 13.5 = 26.3 \text{ volt};$$
$$h \rightarrow b \quad 9.3 + 13.5 = 22.8 \text{ volt},$$
$$h \rightarrow d \quad 7.3 + 13.5 = 20.8 \text{ volt},$$
$$h \rightarrow g \quad 4.0 + 13.5 = 17.5 \text{ volt}.$$

The two observed appearance potentials are 21.7 ± 1.0 and 25.6 ± 1.0 volt. The higher of these two values agrees with the calculated minimum energy for the transition $h \rightarrow a$ within experimental error. Very little excess energy is available in that case. If the higher value applies to the transition $h \rightarrow b$, the excess energy is 2.8 volt. The second transition seems more probable. If the lower of the two appearance potentials applies to the transition $h \rightarrow d$ the excess energy is 0.9 volt. If it applies to the transition $h \rightarrow g$ the excess energy is 4.2 volt, which seems rather high. The most probable processes for the formation of H^+ from C_2H_2 are:

$$C_2H_2 \rightarrow H^+ + CH + C \cdot W(H^+) = 2.8 \text{ volt},$$
$$C_2H_2 \rightarrow H^+ + H + C_2 \cdot W(H^+) = 0.9 \text{ volt}.$$

A summary of the principal results obtained on acetylene is included in Table III.

3. Cyanogen

The data used in the present analysis are taken from a paper by Tate, Smith and Vaughan[2] and from a report by Dorsch and Kallman.[20] The data are tabulated in Table V. The authors have not given the probable error in the determination of the appearance potentials, nor have they given the relative abundances of the various ions. Tate, Smith and Vaughan observed C^+ and N^+ but the origin of these peaks was uncertain due to

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[19] Bleakney, Condon and Smith, J. Phys. Chem. **41**, 197 (1937).

[20] Dorsch and Kallman, Zeits. f. Physik **60**, 376 (1930).

TABLE V. *Ions observed in cyanogen. Column (1) observed ions; (2) appearance potential (volts), (a) Tate, Smith and Vaughan, (b) Dorsch and Kallman; (3) probable process. $C_2N_2\rightarrow$; (4) calculated minimum energy (volts); (5) excess energy or deduced ionization potential (volts).*

	(2)				
(1)	(*a*)	(*b*)	(3)	(4)	(5)
$C_2N_2^+$	14.1	13.5	$C_2N_2^+$	$I(C_2N_2)$	$I(C_2N_2)=14.1$
C_2N^+	19.8		C_2N^++N	$6.2+I(C_2N)$	$I(C_2N)\leq 13.6$
CN^+	21.3	18	CN^++CN	$2.7+I(CN)$	$W(CN^+)\geq 2.2$
C_2^+	18.6	17	$C_2^++N_2$	$2.1+I(C_2)$	$I(C_2)\leq 16.5$
C^+		22.5	C^++CN+N	20.0	$W(C^+)=2.5$

TABLE VI. *Energies of possible states of combination in which two nitrogen and two carbon atoms may exist.*

STATE	CONFIGURATION	ENERGY (VOLTS)
a	$2C+2N$	15.0
b	C_2+2N	9.5
c	$CN+C+N$	8.8
d	$2C+N_2$	7.6
e	C_2N+N	6.2
f	$CN+CN$	2.7
g	C_2+N_2	2.1
h	C_2N_2	0

the fact that their sample of cyanogen contained CO and N_2.

Table VI shows the possible states of combination of two nitrogen and two carbon atoms and the energies associated with these states. The energies were calculated as before. No data from which to calculate the energy of the state *e* are available. In this case it is assumed that the binding energy of N to C_2N is equal to the dissociation energy of CN. This estimate cannot be in error to any large degree, for if we assume that the total energy of dissociation is equal to the sum of the energy of the C–C bond as given by Dietz[10] and two of the assumed energies of the CN bond, we obtain $D(C_2N_2)=15.5$ volt. This value lies close to the value calculated from thermochemical data.

Since the ion CN_2 has not been observed, the energy of the state CN_2+C has not been calculated.

$C_2N_2^+$. The ionization potential of C_2N_2 is 14.1 volt. No other values with which to compare this result seem to be available.

C_2N^+. This ion must arise from the transition $h\rightarrow e$. We may then write

$$A(C_2N^+)=D(C_2N_2)-D(C_2N)+I(C_2N)+W(C_2N^+).$$

This reduces to

$$I(C_2N)\leq 13.6 \text{ volt.}$$

CN^+. The ion CN^+ may arise from the transition $h\rightarrow c$ or from the transition $h\rightarrow f$. The upper limit for $I(CN)$ in the first case is 12.5 volt, and in the second case, 18.6 volt. Now from the work on HCN an upper limit for $I(CN)$ has been shown to be 16.4 volt. If the transition $h\rightarrow c$ is the correct one, the minimum excess energy required for the formation of CN^+ from HCN is 3.9 volt. If the transition $h\rightarrow f$ is the correct one, the minimum excess energy required for the formation of CN^+ from C_2N_2 is 2.2 volt. Because of the smaller excess energy the transition $h\rightarrow f$ seems more probable. In the molecule C_2N_2, the binding energy between the carbon atoms is much smaller than that between a carbon and a nitrogen atom. Now the transition $h\rightarrow f$ requires only that the C–C bond be broken, while the transition $h\rightarrow c$ requires that a C≡N bond be broken as well. This argument lends weight to the above conclusion that the transition $h\rightarrow f$ offers a better explanation of the occurrence of CN^+ as a dissociation product of C_2N_2, than does the transition $h\rightarrow c$. The most probable process for the formation of CN^+ from C_2N_2 is then

$$C_2N_2\rightarrow CN^++CN. \quad W(CN^+)\geq 2.2 \text{ volt.}$$

C_2^+. C_2^+ may arise by either of the transitions $h\rightarrow b$ or $h\rightarrow g$. An upper limit for $I(C_2)$ is 9.1 volt if the transition $h\rightarrow b$ occurs, and 16.5 volt if the transition $h\rightarrow g$ occurs. By comparison with the work on acetylene it is seen that the upper limit for $I(C_2)$ is 16.5 volt. The process responsible for the formation of C_2 from C_2N_2 is then

$$C_2N_2\rightarrow C_2^++N_2.$$

C^+. The minimum energies required to produce C^+ by all the possible transitions are as follows:

$$h\rightarrow a,\ 26.2 \text{ volt},$$
$$h\rightarrow c,\ 20.0 \text{ volt},$$
$$h\rightarrow d,\ 18.8 \text{ volt}.$$

The observed appearance potential, $A(C^+)=22.5$ volt, does not permit the transition $h\rightarrow a$ to occur. The excess energies for the transitions $h\rightarrow c$ and $h\rightarrow d$ are 2.5 and 3.7 volt, respectively. No data are available to permit a choice to be made between these two cases. Because of the smaller excess energy, and because of the known structure of the molecule, the transition *h*→*c* seems a little more likely than the transition *h*→*d*.

Table V includes a summary of the principal results obtained for cyanogen.

4. Ethylene

All the ions observed as dissociation products of ethylene together with their relative intensities at an electron energy of 75 volts and their appearance potentials are listed in Table VII. A mass spectrum of those ions containing two carbons is shown in Fig. 1 and of those containing one carbon in Fig. 2. The peaks in Fig. 2 show considerable tailing to high mass numbers which indicates that a continuous distribution of kinetic energy is imparted to the ions during formation. The peak CH_2^+ has a satellite separated from the main peak by about 2.2 volt. The satellite may be fairly well resolved from the main peak at low values of the magnetic field. That this satellite originates from dissociation processes rather than from the geometry of the apparatus is attested by the fact that other peaks in the immediate vicinity possess no such satellites, and that the appearance potential of the satellite is much higher than that of the main peak. In this case the appearance potential of the satellite was found to be about 40 volt. The H^+ peak possesses a similar satellite, separated from the main peak by about 2.8 volt. Similar peaks have been observed in our recent work on benzene.

A satellite peak is believed to be due to ion of the same kind as the main peak, but produced by another process in which considerable kinetic energy is imparted to the ion.

The relative positions of all the peaks with M/e values between 28 and 12 were carefully compared. None of the peaks show any displacement from their ideal relative positions, within experimental error. The kinetic energy associated with any of these peaks is certainly less than 0.3 volt. This partially justifies a later assumption that the excess energy is small.

A search was made for negative ions, but none were observed.

Eisenhut and Conrad[21] have observed the ions produced in an arc at fairly high pressures. They have observed the same ions as have been observed in the present case. In addition they have

TABLE VII. *Ions observed in ethylene. Column (1) observed ions; (2) relative intensity (volts); (3) appearance potential (volts); (4) probable process.* $C_2H_4\rightarrow$*; (5) calculated minimum energy (volts); (6) excess energy or deduced ionization potential (volts).*

(1)	(2)	(3)	(4)	(5)	(6)
$C_2H_4^+$	100	10.80±0.05	$C_2H_4^+$	$I(C_2H_4)$	$I(C_2H_4)=10.80$
$C_2H_3^+$	57.2	14.1 ±0.1	$C_2H_3^++H$	$3.1+I(C_2H_3)$	$I(C_2H_3)\leq 11.0$
$C_2H_2^+$	51.3	13.4 ±0.2	$C_2H_2^++H_2$	13.1	$W(C_2H_2^+)=0.3$
C_2H^+	8.8	19.2 ±1.0	$C_2H^++H+H_2$	$5.4+I(C_2H)$	$I(C_2H)\leq 13.8$
C_2^+	2.7	26.4 ±1.0	$C_2^++2H+H_2$	$9.2+I(C_2)$	$W(C_2^+)\geq 0.7$
CH_4^+	0.06				
CH_3^+	0.6				
CH_2^+	5.2	19.2 ±0.3	CH_2^++CH+H	$8.7+I(CH_2)$	$I(CH_2)\leq 10.5$
			$CH_2^++C+H_2$	$7.7+I(CH_2)$	$I(CH_2)\leq 11.5$
			$CH_2^++CH_2$	$5.2+I(CH_2)$	$W(CH_2^+)\geq 2.0$
CH^+	2.5	22.9 ±0.5	CH^++CH+H_2	$7.7+I(CH)$	$I(CH)\leq 15.2$
			CH^++CH_2+H	$8.7+I(CH)$	$I(CH)\leq 14.2$
C^+	1.7	24.6 ±0.5	C^++C+2H_2	21.4	$W(C^+)=3.2$
			$C^++CH+H+H_2$	22.4	$W(C^+)=2.2$
			C^++CH_2+2H	23.4	$W(C^+)=1.2$
H_2^+	0.13	22.4 ±1.5	H_2^++2CH	23.1	$W(H_2^+)\sim 0$
			$H_2^++C+CH_2$	23.1	$W(H_2^+)\sim 0$
			$H_2^++H_2+C_2$	20.1	$W(H_2^+)=2.3$
			$H_2^++H+C_2H$	20.8	$W(H_2^+)=1.6$
H^+	0.51	26.2 ±1.5			
		28.2 ±1.5			
CH_2^++K.E.		~40	$CH_2^++CH_2^+$	33.6	K.E. = 2.2
H^++K.E.		~40			K.E. = 2.8
$C_2H_4^{++}$	0.3				
$C_2H_3^{++}$	0.3	36.0 ±1.0			
C_2H^{++}	0.006				

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[21] Eisenhut and Conrad, Zeits. f. Elektrochem. **36**, 654 (1930).

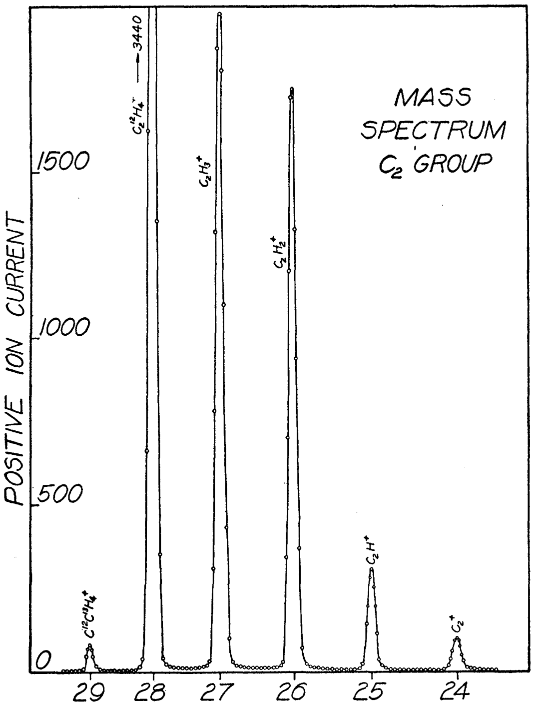

FIG. 1. Mass spectrum of ions containing two carbons.

found larger ions, presumably built up by some secondary process.

It is not certain whether the observed peaks, CH_3^+ and CH_4^+ are genuine products of dissociation of ethylene or whether they are due to small amounts of hydrocarbon impurities in the ethylene.

A small peak was observed due to $C_2{}^{13}H_4{}^{++}$. From the height of this peak and from the known abundance ratio of the carbon isotopes, C_{12} and C_{13}, it was possible to determine what part of the peak at $M/e=14$ was due to $C_2H_4{}^{++}$ and what part was due to $CH_2{}^+$. A small part of the peak designated as CH^+ may be due to $C_2H_2{}^{++}$, and a part of the peak designated as C^+ may be due to $C_2{}^{++}$. Corrections were made, whenever possible, for the presence of the C_{13} isotope of carbon.

Table VIII shows the energies of the possible states of combination in which two carbon and four hydrogen atoms may exist. The states are arranged in such a way that the lighter fragments occur in the upper part of the table. The energy of the state *a* is determined in the usual manner from the thermochemical and spectroscopic data. The energies of the states *b*, *c*, *d*, *e*, *f*, *g*, *o*, *p*, and *q* can be determined from that of state *a* by use of the quantities $D(C_2)$, $D(CH)$ and $D(H_2)$. To determine the energies of the states *h*, *i*, *j*, *k*, *l*, *m* and *n* the same values $D(CH_2)=7.0$ volts, $D(CH_3)=10.6$ volts, and $D(CH_4)=15.1$ volts were used as were used by Smith in his work on methane. The states *t* and *u* were determined by use of the previously given

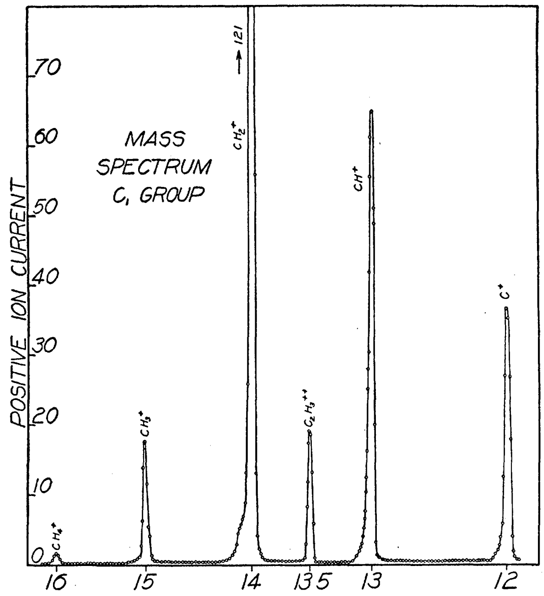

FIG. 2. Mass spectrum of ions containing one carbon.

TABLE VIII. *Energies of possible states of combination in which two carbon and four hydrogen atoms may exist.*

State	Configuration	Energy (Volts)
a	$2C+4H$	19.2
b	$2C+2H+H_2$	14.7
c	$2C+2H_2$	10.2
d	$CH+C+3H$	15.7
e	$CH+CH+2H$	12.2
f	$CH+C+H+H_2$	11.2
g	$CH+CH+H_2$	7.7
h	CH_2+C+2H	12.2
i	CH_2+CH+H	8.7
j	CH_2+C+H_2	7.7
k	CH_2+CH_2	5.2
l	CH_3+C+H	8.6
m	CH_3+CH	5.1
n	CH_4+C	4.1
o	C_2+4H	13.7
p	C_2+2H+H_2	9.2
q	C_2+2H_2	4.7
r	C_2H+3H	9.9
s	C_2H+H+H_2	5.4
t	C_2H_2+2H	6.4
u	$C_2H_2+H_2$	1.9
v	C_2H_3+H	3.1
w	C_2H_4	0

value for $D(C_2H_2)$. No information seems to be available on the values $D(C_2H)$ and $D(C_2H_3)$. However, the energy required to remove two hydrogen atoms from C_2H_4 is 6.4 volts, and that required to remove four hydrogen atoms is 13.7 volts. Evidently the energy required for the removal of the first hydrogen atoms is not as great as that required for the removal of subsequent atoms. If the energy required to remove the successive hydrogen atoms is estimated at 3.1, 3.3, 3.5 and 3.8 volts the energies required to remove two and four hydrogen atoms have the correct values and a reasonable value is obtained for the energies required to remove one and three hydrogens. These values are then adopted in calculating the energies of the states r, s and v.

$C_2H_4^+$. The ionization potential of C_2H_4 has been measured as 10.80 ± 0.05 volt. Price[17] has calculated the ionization potential from the convergence of a Rydberg series of electronic bands in the ultraviolet at 10.41 volt. Mulliken[18] has estimated the vertical ionization potential, which may be from 0.3 to 0.6 volt above the observed adiabatic ionization potential, at 11.0 volt.

$C_2H_3^+$. This ion can arise only by the transition $w\rightarrow v$. An upper limit for its ionization potential can be obtained from the relationship

$$A(C_2H_3^+)=D(C_2H_4)-D(C_2H_3)+I(C_2H_3)+W(C_2H_3^+),$$

which yields

$$I(C_2H_3)\leq 11.0 \text{ volt},$$

depending on the excess energy. This value is subject to error due to uncertainty in the energy of the dissociation process

$$C_2H_4\rightarrow C_2H_3+H.$$

$C_2H_2^+$. This ion can arise either by the transition $w\rightarrow t$ or by the transition $w\rightarrow u$. By use of Vaughan's[2] value $I(C_2H_2)=11.2$ volt, the minimum energy required to produce $C_2H_2^+$ by the first of these processes is calculated to be 17.6 volt, and by the second 13.1 volt. In view of the observed appearance potential $A(C_2H_2^+)=13.4$ volt the second process,

$$C_2H_4\rightarrow C_2H_2^+ + H_2,$$

accounts for the appearance of the $C_2H_2^+$ ion, since the first requires more energy than is available. The excess energy is 0.3 volt. The process

$$C_2H_4\rightarrow C_2H_2^+ + 2H$$

may possibly occur, but in the region above 17.6 volt the curve relating ion intensity to electron energy, from which the appearance potential is determined, rises so rapidly that the onset of a new process would be undetectable.

C_2H^+. This ion can arise either from the transition $w\rightarrow r$ or from the transition $w\rightarrow s$. In the first case

$$A(C_2H^+)=D(C_2H_4)-D(C_2H)+I(C_2H)+W(C_2H^+),$$

which yields

$$I(C_2H)-D(C_2H)\leq 0.$$

In the second case

$$A(C_2H^+)=D(C_2H_4)-D(C_2H)-D(H_2)+I(C_2H)+W(C_2H^+),$$

which yields

$$I(C_2H)-D(C_2H)\leq 4.5 \text{ volt}.$$

In the work on acetylene it was found that

$$I(C_2H)-D(C_2H)\leq 5.0 \text{ volt}.$$

The process responsible for the formation of C_2H^+ from C_2H_4 is then

$$C_2H_4\rightarrow C_2H^+ + H + H_2.$$

An upper limit for the ionization potential is

$$I(C_2H)\leq 13.8 \text{ volt}.$$

C_2^+. Any one of the transitions $w\rightarrow o$, $w\rightarrow p$ or $w\rightarrow q$ may account for the presence of C_2^+. In the previous discussion it has been shown that

$$I(C_2)\leq 16.5 \text{ volt}.$$

If it is assumed, for the moment that the ionization potential is equal to the above value, the minimum energies required for the formation of C_2^+ from C_2H_4 are, for the various possible transitions:

$w\rightarrow o$,	30.2 volt,
$w\rightarrow p$,	25.7 volt,
$w\rightarrow q$,	21.2 volt.

Since the observed appearance potential of C_2^+ is

26.4±1.0 volt, the transition $w \rightarrow o$ is not energetically possible unless the true ionization potential of molecular carbon is at least 3.8 volt below the upper limit. This is improbable. Similarly the production of C_2^+ by the transition $w \rightarrow q$ requires a minimum excess energy of 5.2 volt. It seems probable that the transition $w \rightarrow p$ is responsible for the formation of C_2^+. The excess energy is then at least 0.7 volt, and the process

$$C_2H_4 \rightarrow C_2^+ + 2H + H_2.$$

CH_2^+. Smith[1] has observed two appearance potentials for CH_2^+ produced in CH_4. Since CH_2^+ can be produced from CH_4 in only two ways, the lower appearance potential can be assigned to the process requiring the least dissociation energy. From this process,

$$CH_4 \rightarrow CH_2^+ + H_2,$$

he concludes that $I(CH_2) \leq 12.0$ volt. For the other process,

$$CH_4 \rightarrow CH_2^+ + 2H,$$

he then concludes that $W(CH_2^+) \geq 2.8$ volt. CH_2^+ may be produced from C_2H_4 by any of the transitions $w \rightarrow h, i, j$ or k. If we assume for the moment that $I(CH_2) = 12.0$ volt, the minimum energies of formation of this ion by these transitions are 24.2, 20.7, 19.7 and 17.2 volt, respectively. These values are of course high by the discrepancy between the assumed and true ionization potential. This discrepancy is probably small. The transition $w \rightarrow h$ can definitely be excluded for the formation of CH_2^+, since this transition would require unreasonably large excess energies in Smith's cases. For the transition $w \rightarrow i$ the minimum excess energies for the formation of CH_2^+ from CH_4 by the two processes would be 1.5 and 4.3 volt. For the transition $w \rightarrow j$ they are 0.5 and 3.3 volt. For the transition $w \rightarrow k$ the minimum excess energy required for the formation of CH_2^+ from C_2H_4 is 2.0 volt. Since none of these processes seem more likely than any of the others, no choice can be made among them.

CH^+. This ion may occur by any of the transitions $w \rightarrow d$, e, f, g, i or m. From the value $A(CH^+) = 22.9 \pm 0.5$ volt, the values $I(CH) \leq 7.2$, 10.7, 11.7, 15.2, 14.2 and 17.8 volt may be calculated for these transitions. From the work on HCN it was shown that $I(CH) \leq 15.4$ volt. The first three values calculated from the appearance of CH^+ as a dissociation product of C_2H_4 may be excluded since they would require large minimum excess energies for the formation of CH^+ from HCN. The transition $w \rightarrow m$ may probably be excluded on the basis that the known structure of the ethylene molecule would not permit dissociation in such a way. No choice is possible between the transitions $w \rightarrow g$ and $w \rightarrow i$.

C^+, H_2^+, H^+. As is evident from Table VIII, these three ions may be produced in a large number of ways. Of the nine possible transitions by which C^+ could be produced, all but three may be excluded, either because the minimum energy required to produce C^+ by these processes is greater than the observed appearance potential or else because the excess energy is 4.8 volt or greater. The three remaining processes are shown in Table VII. Similarly H_2^+ may occur as the result of nine different processes, all but four of which may be excluded on energy considerations. These four processes are shown in Table VII. H^+ may occur by fourteen different processes but after eliminating those that are unlikely or energetically impossible, six possible processes may be reasonably associated with each of the two observed appearance potentials. No conclusion is possible except that when H^+ does result from an electron impact, it occurs only when the C_2H_4 molecule is broken into a large number of fragments.

The possibility that a large number of processes actually occur in these cases cannot, of course, be overlooked. If the total observed peak is the result of several processes, the present experimental method would be unable to detect any but the process of least energy and any subsequent process requiring considerably more energy.

$CH_2^+ + K.E.$ A satellite was observed for the CH_2^+ peak which possessed a kinetic energy of about 2.2 volt and whose appearance potential was in the neighborhood of 40 volt. The process

$$C_2H_4 \rightarrow CH_2^+ + CH_2^+$$

requires a minimum energy of

$$D(C_2H_4) - 2D(CH_2) + 2I(CH_2).$$

If $I(CH_2) = 12.0$ volt, the minimum energy is

29.2 volt. To this must be added twice the kinetic energy of one of the fragments. This gives 33.6 volt as the minimum energy required to produce two CH_2^+ ions with kinetic energy from C_2H_4. The estimated value of the appearance potential is close enough to this value to make the above process a reasonable one for the formation of the observed satellite.

$H^+ + K.E.$ The satellite observed for the H^+ peak must also arise from some process involving the production of two charged particles, because of its high appearance potential. No exact explanation of its origin is possible.

A summary of the principal results obtained for the ions produced in ethylene is included in Table VII.

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Normal Energy Distribution of Photoelectrons from Thin Potassium Films as a Function of Temperature*

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With a retarding potential between plane parallel electrodes the normal energy distribution of photoelectrons from thin films of potassium on silver and platinum was studied as a function of temperature. The films were both greater and less than monatomic in thickness and were produced by the molecular ray method. Contact potential was determined by the Kelvin method to within less than 0.02 volt. The resulting current-voltage curves are found under optimum geometrical conditions to be parabolic in shape up to the point of zero field within experimental error. This is shown by plotting (current)$^{\frac{1}{2}}$ *vs.* voltage and testing with a straight line, and also by agreement with the theoretical Fowler curve. These results are compared with various theories. Mitchell's prediction for normal energy distribution has a large deficiency in slow electrons. Hill's calculations in which he uses an image barrier instead of the square barrier of Mitchell show that there should be very little deviation of the energy distribution from DuBridge's simple theory. The agreement of the results with DuBridge's distribution suggests that the image barrier is a much more reasonable approximation although the method is insensitive to small changes in the form of the barrier. The effects of temperature are: (1) temperature dependence of the rates of diffusion of potassium through and sublimation from the base metal, (2) irreversible changes with temperature in the state of the potassium surfaces as shown by changes in contact potential and saturation current, (3) *reversible* changes with temperature in the shape of the Fowler plots, (4) a change of photoelectric current with temperature only 10 to 30 percent of that predicted by DuBridge's theory. (4) is obtained from (3) by determining empirically the optimum temperature at which data should be plotted to give best fits and shifts for the Fowler curve. They range from 90°K to 175°K instead of the actual temperatures of 83°K to 296°K. The temperature effect seems less with thinner films. No theory for thin films predicts this last effect.

Introduction

In recent years many studies have been made of the variation of the photoelectric yield as a function of frequency and temperature from very carefully prepared solid surfaces in the attempt to verify Fowler's[1] theory but only a few studies have been made of the energy distribution. DuBridge[2] has developed a theory for the energy distribution, both total and normal,[3] as a function of temperature. Of this there have been two confirmations in the high energy range where the theory is most reliable. Roehr[4] investigated the total energy distribution and DuBridge and Hergenrother[5] the normal. Studies at a single temperature of the total energy distribution for distilled Na[6] indicate that the predicted curves

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* Part of a dissertation presented to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

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[1] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

[2] L. A. DuBridge, Phys. Rev. **43**, 727 (1933).

[3] By "normal" energy distribution will be understood the distribution associated with the velocity components normal to the emitting surface.

[4] W. W. Roehr, Phys. Rev. **44**, 866 (1933).

[5] L. A. DuBridge and R. C. Hergenrother, Phys. Rev. **44**, 861 (1933).

[6] A. G. Hill and L. A. DuBridge, Phys. Rev. **49**, 877 (1936).