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## Hydrocarbon Ion Appearance Potentials

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(Received June 7, 1948)

Discussion of the effect of impact parameter, distribution of electron energy and transition efficiency upon the appearance potential for ions from hydrocarbons in the mass spectrometer leads to the conclusion that initial ion current onset is a correct measure of the appearance potential. In order to calibrate the appearance potential voltage scale, the spectroscopic ionization potentials for seven gases were correlated with their apparent appearance potentials to give a calibration curve. Heretofore only one gas had been used to give a simple additive constant.

Appearance potentials were determined for ions from six paraffins and four olefins. For methane, ethane and propane the agreement with previous determinations is excellent. For the other hydrocarbons the values reported here are higher than those reported by others. It is concluded that dissociation energies computed from these appearance potentials are greater than true bond energies because electron collision processes give rise to excited fragments. The excitation energy appears to be greater for larger molecules.

## INTRODUCTION

IT has been recognized for many years that the electron energy necessary to produce ions from gas molecules under electron bombardment is intimately connected with the energy states both of the ion and of the molecule from which it was formed. If in some way that energy could be used to determine the strengths of bonds in the molecule under study, one would be in an advantageous position for the prediction of its behavior in chemical reactions. The desire to determine molecule energy states and bond strengths has led to a considerable amount of work on hydrocarbon ion appearance potentials in the mass spectrometer.<sup>1-18</sup> No one can argue

that the results obtained are not important. However, their interpretation in terms of energy states and bond strengths is not yet on solid ground. The difficulties arise from two sources, the problem of deducing the appearance potential accurately from the experimental data and the problem of relating the appearance potentials to molecular energy states. This paper will first discuss the former problem, then give the results obtained by applying the conclusions derived, and finally will discuss the latter problem of applying the results.

## DETERMINING APPEARANCE POTENTIALS

As a first step in developing a proper interpretation of the experimental data, some thought should be given to the way in which the data are obtained. In Fig. 1 is shown schematically the ionization chamber of the mass spectrometer used in this work.\*\* Gas molecules present are ionized by the electron beam *E* to give rise to the ion beam *I*. The electrons come from filament *A* and are accelerated by potentials on electrodes *B* and *C*. The ions in ion beam *I* will thus have been produced by electrons with an energy in electron volts numerically equal to the potential drop between *A* and *C*. Since the ionization

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<sup>1</sup> S. H. Bauer and T. R. Hogness, *J. Chem. Phys.* **3**, 687-692 (1935).

<sup>2</sup> W. Bleakney, E. U. Condon and L. G. Smith, *J. Phys. Chem.* **41**, 197-208 (1937).

<sup>3</sup> C. S. Cummings and W. Bleakney, *Phys. Rev.* **58**, 787-792 (1940).

<sup>4</sup> J. M. Delfosse and W. Bleakney, *Phys. Rev.* **56**, 256-260 (1939).

<sup>5</sup> V. H. Dibeler, *J. Research Nat. Bur. Stand.* **38**, 329-336 (1947).

<sup>6</sup> J. A. Hipple and W. Bleakney, *Phys. Rev.* **47**, 802(A) (1935).

<sup>7</sup> J. A. Hipple, *Phys. Rev.* **53**, 530-533 (1938).

<sup>8</sup> J. A. Hipple and D. P. Stevenson, *Phys. Rev.* **63**, 121-126 (1943).

<sup>9</sup> R. E. Honig, *J. Chem. Phys.* **16**, 105-112 (1948).

<sup>10</sup> A. Hustrulid, P. Kusch and J. T. Tate, *Phys. Rev.* **54**, 1037-1044 (1938).

<sup>11</sup> M. B. Koffel and R. A. Lad, *J. Chem. Phys.* **16**, 420-422 (1948).

<sup>12</sup> P. Kusch, A. Hustrulid and J. T. Tate, *Phys. Rev.* **52**, 843-844 (1937).

<sup>13</sup> L. G. Smith, *Phys. Rev.* **51**, 263-275 (1937).

<sup>14</sup> D. P. Stevenson, *J. Am. Chem. Soc.* **65**, 209-212 (1943).

<sup>15</sup> D. P. Stevenson and J. A. Hipple, *J. Am. Chem. Soc.* **64**, 1588-1594 (1942).

<sup>16</sup> D. P. Stevenson and J. A. Hipple, *J. Am. Chem. Soc.* **64**, 2766-2768 (1942).

<sup>17</sup> D. P. Stevenson and J. A. Hipple, *J. Am. Chem. Soc.* **64**, 2769-2772 (1942).

<sup>18</sup> J. T. Tate, P. T. Smith and A. L. Vaughan, *Phys. Rev.* **48**, 525-531 (1935).

\*\* Consolidated Engineering Corporation Type 21-101.

chamber is part of a mass spectrometer, the ion beam can be resolved so that the current due only to ions of a given mass to charge ratio will be measured. If now the gas pressure and the current in the electron beam are kept constant, then changing the potential between *A* and *C* gives rise to a change in ion current such as is shown by the points in Fig. 2. The curve defined by these points is called the ionization efficiency curve, in this case, for  $C_3H_7^+$  ( $m/e=43$ ) from *n*-butane.

All of this is elementary and straightforward. However, as is generally the case with experimental data if a sufficiently open scale is used, these points lie about rather than on a smooth curve. Thus, if the scale is open enough to permit accurate location of the points, very small ion currents and instrument background are so difficult to separate that it becomes quite impossible to pick out the exact electron voltage at which ions of given  $m/e$  first appear.

#### TRANSFER OF ENERGY FROM ELECTRON TO MOLECULE

Various procedures can be and have been used to resolve this impasse. The most logical scheme would be one based on a hypothesis explaining the shape of the ionization efficiency curve. There are several factors which contribute to the curve shape. In what follows each will be treated as if it were the sole determining factor. The first factor to be considered is the transfer of energy from an electron to the molecule with which it collides. Oldenberg<sup>19</sup> has pointed out that the transfer of kinetic energy of the electron into internal energy in the molecule will start with zero probability of transfer for electrons with just the energy necessary for the formation of an ion and increase with increasing electron energy. This statement is based on a consideration of the collision process. If the electron has exactly the critical energy, it must make an exactly central impact in order to excite the molecule. As the energy of the electrons becomes larger, the allowable impact parameter increases from the zero value for central impact to values corresponding to glancing collisions. If now  $P$  is the energy of the electrons and  $V_0$  the critical

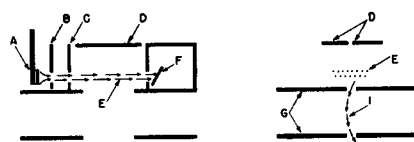


FIG. 1. Schematic cross sections (at right angles to each other) through a typical ionization chamber. *A*, filament supported on heavy legs; *B*, first electron accelerating plate; *C*, second electron accelerating plate; *D*, "pusher" plates to supply small ion ejecting field; *E*, electron beam; *F*, electron catcher; *G*, ion accelerating plates; and *I*, ion beam.

energy in electron volts and if one assumes that the molecules are hard spheres and that if it were not for this effect the ionization efficiency curve would be a straight line, one can write for the ion current  $I_p$  at electron energy  $P$  the following equations:

$$\begin{aligned} I_p &= 0 & P &\leq V_0, \\ I_p &= (1 - V_0/P)(a + bP) & P &> V_0. \end{aligned}$$

The curve drawn in Fig. 2 shows the result of fitting these equations by least squares to the experimental data shown by the points. It is clearly apparent that the critical energy  $V_0=7.46$  electron volts determined by this curve is not a good representation of the data.

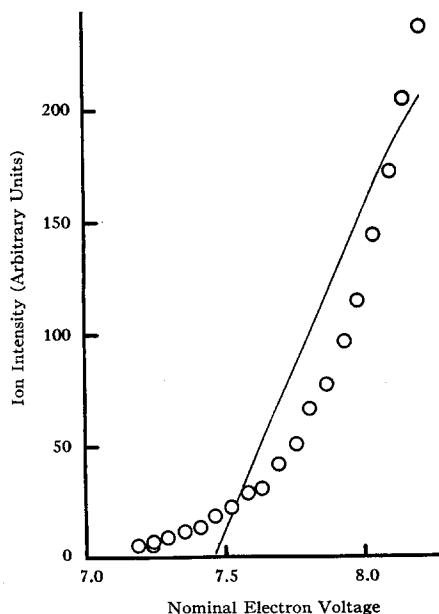


FIG. 2. Ionization efficiency curve showing experimental points for  $C_3H_7^+$  from *n*-butane. The smooth curve is that fitted to this data by least squares using an equation based on the electron impact parameter.

<sup>19</sup> O. Oldenberg, J. Chem. Phys. **13**, 196-198 (1945).

## ELECTRON ENERGY SPREAD

Up to this point it has been assumed tacitly that the electrons are mono-energetic. Inasmuch as the electrons are emitted from a hot filament this is not true. They possess a distribution of energies based on  $P$  and corresponding to the absolute temperature  $T$  of the filament. If one assumes that this distribution is Maxwellian<sup>20</sup> and that the number of ions produced is directly proportional to the excess of the electron energy  $P$  above a critical value  $V_0$ , one can write for the ion current  $I_p$  produced by electrons accelerated through a potential  $P$ :<sup>21</sup>

$$I_p = A \left( \frac{3}{2} \frac{T}{11,606} + P - V_0 \right) \quad \text{for } P \geq V_0,$$

$$I_p = \frac{2A}{(\pi)^{1/2}} \frac{T}{11,606} \left\{ \frac{3}{2} B^{1/2} \exp(-B) + \frac{(\pi)^{1/2}}{2} \left[ \frac{3}{2} - B \right] \right. \\ \left. \times [1 - H(B^{1/2})] \right\} \quad \text{for } P < V_0,$$

where

$$B = (11,606/T)(V_0 - P),$$

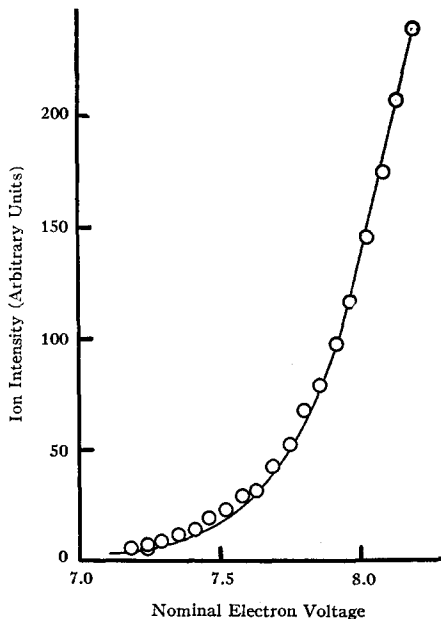


FIG. 3. The same data as in Fig. 2 fitted by a curve based on the energy spread of electrons from a hot filament. Apparent temperature 2349°K; apparent appearance potential, 8.06 volts.

<sup>20</sup> C. del Rosario, Phys. Rev. 28, 769-780 (1926).

<sup>21</sup> D. P. Stevenson and J. A. Hipple, Phys. Rev. 62, 237-240 (1942).

and

$$H(B^{1/2}) = \frac{2}{(\pi)^{1/2}} \int_0^{B^{1/2}} \exp(-x^2) dx.$$

Figure 3 shows how well one can fit these equations to the data by a few steps of successive approximation. The curve, which is defined by the parameters  $A = 534$ ,  $V_0 = 8.06$  electron volts, and  $T = 2349^\circ\text{K}$ , fits the data with a standard error of estimate of  $s = \pm 3.6$  divisions of ion intensity. Although the parameter  $T$  corresponds to a fairly reasonable temperature for a tungsten filament and the fit is also reasonable, the fact that there must be an additional electron energy spread as a result of voltage drop along the filament throws considerable doubt on the validity of identifying  $V_0 = 8.06$  volts with the appearance potential.

After the experimental work reported in this paper was completed, a paper by R. E. Honig<sup>9</sup> appeared in which is described a procedure for locating  $V_0$  also based on the view that the curvature of the foot of the ionization efficiency curve is due to the electron energy spread. The procedure uses a critical slope to locate the point at which the electron energy  $P$  corresponds to a critical voltage  $V_0$ . Although the critical slope is derived on the assumption of a Maxwellian electron energy distribution and of the ion current being proportional to the square of the excess of the electron energy over the critical voltage, the fact that the effective absolute temperature of the electrons was measured independently from the ionization efficiency curve eliminates the difficulty just raised about potential drop along the filament. Using this effective temperature, Honig was able to fit his ionization efficiency curves very accurately. More important is the fact that the values for  $V_0$  determined by the critical slope for the rare gases and nitrogen agree with the spectroscopic values within experimental error. On the other hand, it is also a fact that the simpler procedure of identifying initial current onset with  $V_0$  also gives results agreeing with spectroscopic values for the rare gases.

## TRANSITION EFFICIENCIES

Since it is the curved foot of the ionization efficiency curve which causes the difficulty in

estimating an appearance potential from the data, any argument which would validate the use of an extrapolation of the straight line portion would remove the difficulty. Vought<sup>22</sup> has advanced a plausible argument which asserts that the voltage determined by the extrapolation of the straight line portion is just that necessary for the most probable or Franck-Condon transition to the ionized state. This argument ascribes a good portion of the curvature to the transition probabilities between the lowest electron energy state of the molecule and that which leads to ionization. Thus the analysis which was just developed of the curvature in terms of electron energy spread can be only partially correct.

Table I shows how well experimentally determined appearance potentials correlate with spectroscopic ionization potentials for seven gases. It will be noted that the correlation is every bit as good for appearance potentials determined from the extrapolated straight line portions of the ionization efficiency curves as those determined from the estimated first appearance of ions.

An equally plausible argument has been advanced<sup>23</sup> to show that, with the sensitivity of the modern mass spectrometer, the point of first onset of ion current is more closely related to the energy differences of molecular and ionic energy states than is the linear extrapolation. However, the real test of a hypothesis is not how plausible it may be but how well it stands up in a crucial experimental test. Stevenson and Hipple<sup>21</sup> showed that whereas the onset of ion current for  $A^+$  and  $A^{++}$  gave appearance potentials spaced according to the corresponding spectroscopic ionization potentials the linear extrapolations gave values which differed from the spectroscopic values by considerably more than experimental precision. Other workers<sup>24</sup> using the initial current onset showed that relative to  $A^+$  the mass spectrometer gave the correct ionization potentials for  $He^+$ ,  $Ne^+$ ,  $Ne^{++}$ ,  $A^{++}$ ,  $Kr^{++}$  and  $Xe^+$ . It can be argued, with some force, that these results refer only to monatomic molecules. However, as Hagstrum<sup>25</sup> points out, the use of

TABLE I. Calibration curves for two interpretations of ionization efficiency data.

Set of data	Calibration curve for extrapolated straight line	Fit of curve (standard error of estimate in volts)	Calibration curve for first appearance of ions	Fit of curve (standard error of estimate in volts)
1	$V_0 = 5.98 + 24.0P + 411P^2$	0.25	$V_0 = 7.78 - 0.704P + 618P^2$	0.25
2	$V_0 = 5.47 + 32.2P + 411P^2$	0.29	$V_0 = 6.12 + 38.0P + 407P^2$	0.25
3	$V_0 = 4.25 + 61.3P + 251P^2$	0.24	$V_0 = 4.76 + 76.2P + 171P^2$	0.24

the potential for initial current onset as the appearance potential for ions from  $H_2$ ,  $N_2$  and  $NO$  gives rise to dissociation energies for the corresponding molecules which agree very well with spectroscopic values.

Thus, although the data of Table I are inconclusive, it appears from independent evidence that the initial onset of ion current should be identified with the appearance potential. The decision to use initial current onset was clinched when it was found that appearance potentials based on straight line extrapolations for  $C_2H_5^+$  from ethane, *n*-butane and *n*-pentane when used to compute bond strengths in the manner of D. P. Stevenson<sup>26</sup> gave 122 and 144 kcal/mole as the energy to remove the first hydrogen from ethane and propane respectively, whereas the initial current onset interpretation of the same data gave 114 and 134 kcal/mole. While the fact that the bond strengths calculated using the straight line extrapolation interpretation were further from chemical experience and thus led to the decision to use the initial current onset interpretation, present ignorance with regard to the excitation of the fragments produced by electron collision prevents one from claiming on the basis of this evidence that one interpretation is more nearly correct than the other.

#### EXPERIMENTAL PROCEDURE

The ionization chamber shown in Fig. 1 was operated in the standard manner recommended by the manufacturer except for the potentials on electrodes *C* and *D*. Electrode *B* was maintained at +40 volts with respect to the filament *A*. Electrode *F* was kept at the same potential as *C*, and the electron current to it was kept constant at 9.0 microamperes. The ionization chamber is wholly immersed in an homogeneous magnetic

<sup>22</sup> R. H. Vought, Phys. Rev. **71**, 93-101 (1947).

<sup>23</sup> T. Mariner and W. Bleakney, Phys. Rev. **72**, 807-814 (1947).

<sup>24</sup> V. H. Dibeler, F. L. Mohler and R. M. Reese, J. Research Nat. Bur. Stand. **38**, 617-620 (1947).

<sup>25</sup> H. D. Hagstrum, Phys. Rev. **72**, 947-963 (1947).

<sup>26</sup> D. P. Stevenson, J. Chem. Phys. **10**, 291 (1942).

field parallel to the electron beam, the energizing current for which was kept constant at 0.54 ampere.

The various gases to be studied were allowed to leak into the ionization chamber from a 2-liter sample flask in which the initial pressure was in the neighborhood of  $40 \times 10^{-3}$  mm of Hg. The leak rate of the gas out of the sample flask into the chamber was about  $-0.3$  percent/min. for  $m/e = 58$  from  $n\text{-C}_4\text{H}_{10}$ . The ions to be studied were then brought into register on the current detector of the mass spectrometer by adjustment of the ion accelerating voltage. Under

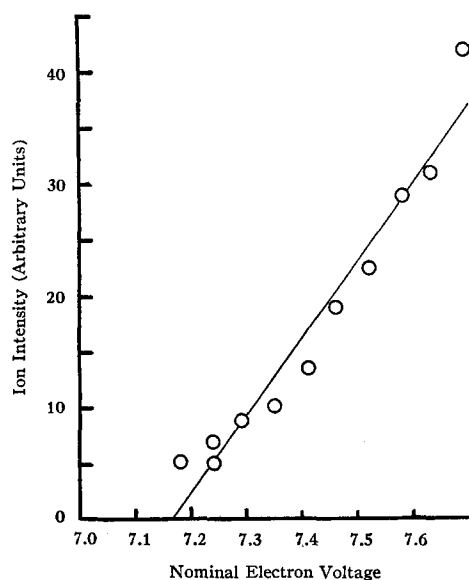


FIG. 4. Part of the data of Figs. 2 and 3 plotted on an enlarged scale. The straight line is that fitted by least squares. Its intersection with the zero axis is taken to be the  $\text{C}_4\text{H}_7^+$  appearance potential.

these conditions  $m/e = 58$  from  $n\text{-C}_4\text{H}_{10}$  gave 16 chart divisions per  $10^{-3}$  mm of Hg sample pressure at the beginning of the work and declined steadily to 3 divisions per  $10^{-3}$  mm of Hg five months later.

Even though the decision has been made to use the "first break" or initial onset of ion current as a measure of appearance potential, one must carefully define the location of this point. Inasmuch as the ionization efficiency curves approach the axis in an exponential manner, one must have some objective method of locating a break-off point. Stevenson and Hipple have proceeded by plotting each set of data on a scale adjusted

so as to make the curves similar. They then extrapolate by eye to the zero axis. This is an advance over simple extrapolation by eye. However, any extrapolation by eye becomes an exercise in personal judgment when the data are plotted on a scale large enough to permit accurate extrapolation.

Figure 4 shows an application of the scheme adopted in this work for locating the initial onset of ion current. After the ion accelerating voltage had been adjusted to bring the ion to be studied into focus (705 volts for  $m/e = 58$ ), the potential on electrode *C* (see Fig. 1), and hence the electron voltage, was raised in steps of 0.05 volt from a point well below the expected appearance potential. At each step the ion accelerating voltage was swept from a value slightly greater than the value for focus to one slightly below. The ion current was determined by the height of the peak produced on the chart. This was continued until the peak height reached about one chart division. The values found were then corrected to specific ion intensity by dividing by the pressure of the sample. On the basis of the observation that this short section of the ionization efficiency curve differed negligibly from a straight line, such a line was fitted to the specific ion intensity data. Its intersection with the zero axis was then taken to be a measure of the appearance potential.

#### ELECTRON ENERGY SCALE

Although this procedure identifies a point on the electron energy axis with the appearance potential, there is still the problem of defining the scale to be used on this axis in order to obtain true values. There are several factors which cause the actual electron energies to be different from those expected from the potentials impressed on the accelerating electrodes.

The thermal energy of the electrons and the contact potentials of the electrode surfaces have an effect on the total electron energy. Even more important the "pushers" (see Fig. 1) are kept at a constant potential of +3.1 volts, a portion of which contributes to the electron beam acceleration. In all of the previously published work<sup>1-18</sup> on appearance potentials, this difference between applied electron accelerating voltage and actual electron energy has been adjusted for by means

TABLE II. Convenient gases of known spectroscopic ionization potential

Gas	Spectroscopic ionization potential (volts)	Experimental precision (volts)
Argon <sup>a</sup>	15.75	0.02*
Nitrogen <sup>b</sup>	15.572	0.002
Carbon Monoxide <sup>c</sup>	14.1	0.1
Carbon Dioxide <sup>d</sup>	13.78	0.02
Water <sup>e</sup>	12.61	0.02
Ethylene <sup>f</sup>	10.50	0.04
Acetone <sup>g</sup>	10.26	0.04*

<sup>a</sup> G. Herzberg, *Molecular Spectra*, I (Prentice-Hall, Inc., New York, 1939).

<sup>b</sup> R. E. Worley and F. A. Jenkins, *Phys. Rev.* **54**, 305 (1938).

<sup>c</sup> A. D. Walsh, *Trans. Faraday Soc.* **42**, 56 (1945).

<sup>d</sup> W. C. Price and D. M. Simpson, *Proc. Roy. Soc.* **169A**, 501-512 (1938).

<sup>e</sup> W. C. Price, *J. Chem. Phys.* **4**, 147-153 (1936).

<sup>f</sup> W. C. Price and W. T. Tuttle, *Proc. Roy. Soc.* **174A**, 207-220 (1940).

<sup>g</sup> A. B. F. Duncan, *J. Chem. Phys.* **3**, 131-132 (1935); **8**, 444-446 (1940).

\* These precisions are not those given by the reference but are merely estimates.

of an additive constant. The apparent appearance potential  $V$  of a monatomic gas, such as mercury or argon, has been compared to its accurately known spectroscopic ionization potential  $V_0$ . The difference between the two is then added algebraically to the apparent appearance potentials for other ions to obtain true values. This procedure of using one calibrating point and the assumption of a calibration curve which is a straight line of unit slope should not be expected to yield accurate results for appearance potentials very different from that of the calibrating gas. For that reason in the present work seven gases whose spectroscopic ionization potentials were known were used to construct a calibration curve. Table II shows the ionization potentials which were used. Of these values only that for CO is at all doubtful. The reference<sup>27</sup> given by Walsh<sup>28</sup> for 14.1 electron volts relates only to transition to the  $3\pi$  state of CO. A more recent paper of Long and Walsh<sup>29</sup> cites a value of 14.55 electron volts calculated from a Rydberg series by B. M. Anand.<sup>30</sup> However, this value does not fit in at all smoothly with the mass spectrometer results found in this work. What is more, a value of 14.006 electron volts corresponds to the limit of a Rydberg series assigned

<sup>27</sup> L. Gerö, G. Herzberg and R. Schmid, *Phys. Rev.* **52**, 467 (1937).

<sup>28</sup> See Table II, reference c.

<sup>29</sup> L. H. Long and A. D. Walsh, *Trans. Faraday Soc.* **43**, 342 (1947).

<sup>30</sup> B. M. Anand, *Science and Culture* **8**, 278-279 (1942).

TABLE III. Calibration curves.

Date	Curves	Standard error of estimate (electron volts)
5-31-46	$V_0 = 7.362 + 5.262V + 555.3V^2$	0.14
	$V_0 = 2.742 + 108.7V$	0.21
6-25-46	$V_0 = 7.230 + 4.835V + 569.6V^2$	0.14
	$V_0 = 2.516 + 110.7V$	0.21
7-12-46	$V_0 = 6.523 + 18.27V + 479.9V^2$	0.16
	$V_0 = 2.314 + 110.0V$	0.22
7-26-46	$V_0 = 6.086 + 31.50V + 415.7V^2$	0.12
	$V_0 = 2.56 + 109.7V$	0.15
8- 6-46 <sup>a</sup>	$V_0 = 9.78 - 55.15V + 939.8V^2$	0.26
	$V_0 = 3.94 + 98.6V$	0.45
8- 7-46	$V_0 = 4.79 + 62.69V + 272.0V^2$	0.23
	$V_0 = 2.62 + 112.3V$	0.22
9- 5-46	$V_0 = 8.06 - 23.85V + 679.0V^2$	0.17
	$V_0 = 1.48 + 112.3V$	0.28
9-12-46	$V_0 = 10.06 - 56.91V + 821.6V^2$	0.27
	$V_0 = 2.46 + 104.5V$	0.36
9-13-46 <sup>a</sup>	$V_0 = 7.57 - 7.10V + 600.9V^2$	0.24
	$V_0 = 2.13 + 109.6V$	0.30
9-17-46	$V_0 = 10.53 - 72.68V + 933.4V^2$	0.31
	$V_0 = 1.85 + 110.7V$	0.37
9-23-46	$V_0 = 7.61 - 11.56V + 589.7V^2$	0.19
	$V_0 = 1.87 + 107.1V$	0.25
10- 3-46	$V_0 = 7.13 - 2.561V + 55.0V^2$	0.16
	$V_0 = 1.60 + 110.2V$	0.22
2-13-47	$V_0 = 7.78 - 0.704V + 618.5V^2$	0.25
	$V_0 = 3.18 + 108.5V$	0.30
2-20-47	$V_0 = 6.12 + 37.98V + 406.9V^2$	0.25
	$V_0 = 3.04 + 110.4V$	0.24
3- 5-47	$V_0 = 4.76 + 76.25V + 170.8V^2$	0.24
	$V_0 = 3.43 + 106.8V$	0.21
3-30-47	$V_0 = 7.11 + 16.72V + 511.3V^2$	0.14
	$V_0 = 3.17 + 108.7V$	0.20
3-30-47 <sup>b</sup>	$V_0 = 8.48 + 39.00V + 653.3V^2$	0.22
	$V_0 = 6.78 + 110.1V$	0.28
3-30-47	$V_0 = 7.05 + 15.16V + 536.8V^2$	0.23
	$V_0 = 3.02 + 110.4V$	0.26

<sup>a</sup> Calibration made at high electron catcher bias.

<sup>b</sup> Calibration made at high pusher bias.

$V_0$  is the true appearance potential;  $V$  is the potentiometer reading.

by Takamine, Tanaka and Iwata<sup>31</sup> to the (0, 0) vibration series in CO. Inasmuch, as 14.1 electron volts agrees with this and with earlier electron collision results,<sup>32</sup> it has been used as a calibration point but with a reduced weight corresponding to the larger precision limit of  $\pm 0.1$  electron volt.

The apparent appearance potentials in the mass spectrometer of these seven gases were used to construct a calibration curve. In order to determine the applied electron voltage accurately a constant fraction from a voltage dividing network was measured with a semi-precision potentiometer (Leeds and Northrup Type 7655). The potentiometer readings were used directly with

<sup>31</sup> T. Takamine, Y. Tanaka and M. Iwata, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* **40**, 371-378 (1943).

<sup>32</sup> H. D. Hagstrum and J. T. Tate, *Phys. Rev.* **59**, 354 (1941).

the corresponding spectroscopic appearance potentials to give points to which a second degree curve was fitted by least squares. Table III shows both these curves and the corresponding least squares straight lines. It is interesting to note that the slopes of these latter are not the same and hence any assumption of a simple additive constant for a Consolidated mass spectrometer cannot be correct.\*\*\* The standard errors of estimate,  $S_2 = \pm(\sum d_i^2/(n-3))^{1/2}$ , for the second degree curves are in general smaller than those,  $S_1 = \pm(\sum d_i^2/(n-2))^{1/2}$ , for the straight lines so all of the true appearance potentials have been calculated from the second degree curve determined just prior to the experimental determinations.

Since this work was completed, Honig<sup>9</sup> has made some experimental observations which throw doubt on this scheme of calibrating. First, he demonstrated that, when using his interpretation of the ionization efficiency curve, it was necessary to use a mixture of the calibrating gas and the gas giving the ions to be measured.

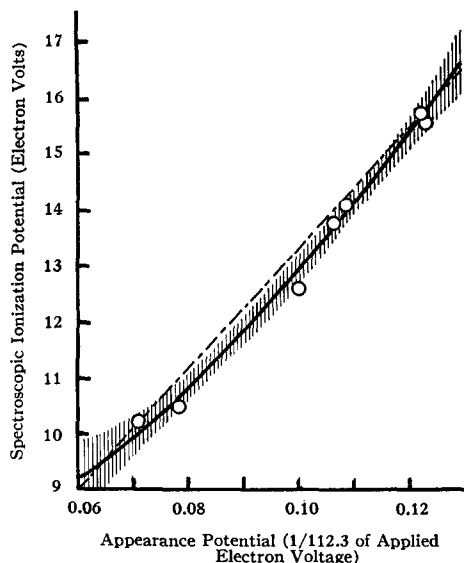


FIG. 5. The solid curve is the calibration curve produced by fitting a second degree curve by least squares to the seven points given by acetone, ethylene, water, carbon dioxide, carbon monoxide, argon, and nitrogen (reading from left to right). The shaded area is the 95 percent confidence band. The dashed straight line is the calibration curve one would get using only argon and a simple additive correction voltage.

\*\*\* A slope of 112.3 corresponds to unit slope if both variables are expressed in volts since  $112.3 \pm 0.1$  is the voltage divider factor.

Otherwise the effective electron temperature would be different for different gases and the critical slope would be shifted. Since the shape of the lower part of the ionization efficiency curve must be due in part to electron energy spread, shifts in effective electron temperature could conceivably interfere with calibration. Second and more serious, the fact that there is agreement between mass spectrometer and spectroscopic results for rare gases and nitrogen but not for ethylene or benzene in Honig's work raises the issue of whether polyatomic molecules such as acetone and ethylene should be used as reference points. The view taken in the work reported here is that electron impact and photon absorption should give the same ionization potentials on the ground that a Rydberg series of electronic states is observed only when the electronic state potential curves are located directly above each other so that only the 0-0 band appears for each state.<sup>33</sup> Thus the idea of a simple additive calibration constant which gives a discrepancy between appearance potential and spectroscopic ionization potential for some molecules has been abandoned in favor of a calibration based on the identity of the two values for all molecules where a Rydberg series is available. This issue will be discussed further in connection with a comparison of the results obtained by the two methods.

It should be pointed out that since the spectroscopic values, the ordinates of the calibration curve, are more accurately known than the experimental apparent appearance potentials, which are the corresponding abscissas, the usual least squares method theoretically should not have been used. The usual method assumes complete accuracy in the abscissas and ascribes all the error to the ordinates. However, application of the exact method<sup>34</sup> gave results which did not differ significantly from the usual method so that the latter was used because of its simplicity. Figure 5 shows some of the additional information that the exact method yielded with regard to one of the cases (9-13-46 calibration) for which it was applied. The dashed straight line is

<sup>33</sup> G. Herzberg, *Molecular Spectra and Molecular Structure. I. Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939), page 231.

<sup>34</sup> W. E. Deming, *Statistical Adjustment of Data* (J. Wiley and Sons, Inc., New York, 1938).



TABLE IV. Stability of calibration scheme with regard to ionization chamber voltages.

Compound and ion	Electrode voltage Pusher bias*	Apparent appearance potential (potentiometer reading)	True appearance potential (electron volts)
<i>n</i> -Butane, $m/e=58$	+ 3.1	0.0740	11.15
	+10.9	0.0386	10.96
	+ 3.1	0.0739	11.10
Electron catcher bias*			
Ethylene, $m/e=27$	0	0.1114	13.92
	+47.5	0.1089	13.93
<i>n</i> -Pentane, $m/e=57$	0	0.1109	13.95
	0	0.0861	11.25
	+47.5	0.0840	11.22
	0	0.0862	11.20

\* These electrodes are biased with respect to the final electron accelerating electrode which is at the same potential as the plate containing the first ion beam defining slit.

the calibration curve one would obtain by using argon alone as a calibrating gas. It can be seen that it lies partly outside the shaded area representing the 95-percent confidence band. This band, which can be calculated from information derived from the exact least squares method, defines the range of ordinate within which the chance is 95 out of 100 that, for a particular value of  $V$ , the true appearance potential is located. Thus there is a region in which the straight line can be considered to be in error.

#### EXPERIMENTAL VERIFICATION OF THE CALIBRATION METHOD

In order to be certain that the above calibration scheme was one which would compensate for changes in ionization chamber conditions, the voltages impressed on the pushers and the electron catcher were deliberately varied by large amounts. Table IV shows that the calibration procedure is stable against changes which are far more severe than would ever be met in practice.

#### EXPERIMENTAL RESULTS

The hydrocarbon ion appearance potentials shown together with their standard deviations in Tables V, VI and VII were measured with Phillips Research Grade hydrocarbons. These hydrocarbons are 99-mole percent pure or better. The appearance potentials are given in terms of

TABLE V. Ionization potentials of hydrocarbons.

Hydrocarbon	No. of measurements	$V_0$ (kcal/mole)	Literature value (kcal/mole)	Reference
Methane	2	$300.8 \pm 0.5$	$304.5 \pm 9.2$	13
			$299.9 \pm 4.6$	11
			$300.8 \pm 0.5$	9
Ethane	6	$271.7 \pm 0.5$	$269.0 \pm 2.3$	15
			$265.3 \pm 4.6$	11
			$271.3 \pm 0.5$	9
Propane	4	$260.7 \pm 1.2$	$260.2 \pm 2.3$	17
			$258.4 \pm 6.9$	11
			$258.6 \pm 0.2$	9
<i>n</i> -Butane	8	$256.3 \pm 0.9$	$240.1 \pm 2.3$	15
			$237.6 \pm 6.9$	11
			$249.1 \pm 0.2$	9
Isobutane	1	255.1	$240.1 \pm 2.3$	15
			$237.6 \pm 4.6$	11
<i>n</i> -Pentane	2	$250.8 \pm 0.2$	$242.2 \pm 6.9$	11
			$243.4 \pm 0.2$	9
Propylene	1	231.8	$226.8 \pm 2.3$	17
			227.0	9
Butylene-1	1	230.7	$222.6 \pm 2.3$	13
			225.1	9
Isobutylene	5	$222.6 \pm 1.6$	$206.0 \pm 2.3$	17

kilocalories per mole so that they may be compared directly with thermochemical data.<sup>†</sup>

Figures 6 and 7 have been plotted to show the trends established for the appearance potentials of ions from succeeding members of the normal paraffin series.

#### DISCUSSION OF RESULTS

There are several remarks which should be made about the data in Tables V, VI and VII before discussing their interpretation. First, the experimental precision is as good as any previously published results. These precisions are standard errors,  $S_0 = \pm(\sum d_i^2/n(n-1))^{1/2}$ , for the averages of independent determinations. They do not take into account explicitly the accuracy of calibration. This latter has been computed as standard error of estimate,  $S = \pm(\sum d_i^2/(n-3))^{1/2}$ , which expresses only the "vertical" fit of the calibration curve to the points from which it was constructed. Thus, it would not be easy to state the absolute accuracy of the appearance poten-

<sup>†</sup> The conversion factor used was 1 international electron volt per molecule equals  $23.0682 \pm 0.0024$  kilocalories per mole.

TABLE VI. Paraffin ion appearance potentials.

Ion ( $m/e$ )	No. of measurements	$V_0$ (kcal/mole)	Literature value (kcal/mole)	Reference
Methane				
15	2	$336.3 \pm 1.2$	$334.5 \pm 9.2$ $332.2 \pm 6.9$	13 11
Ethane				
15	6	$361.5 \pm 3.2$	$329.9 \pm 6.9$ $334.5 \pm 6.9$ $280.5 \pm 2.3$ $279.1 \pm 4.6$	7 11 15 11
28	4	$263.9 \pm 1.2$	$297.8 \pm 2.3$ $295.3 \pm 4.6$	15 11
29	6	$293.0 \pm 0.9$		15
Propane				
15	1	584.1	$392.2 \pm 4.6$	17
28	1	268.3	$274.0 \pm 2.3$ $272.2 \pm 6.9$ $283.3 \pm 2.3$ $283.3 \pm 6.9$	17 11 17 11
29	2	$277.2 \pm 2.1$	$286.0 \pm 6.9$ $281.4 \pm 6.9$	4 11
42	1	281.4	$270.8 \pm 2.3$ $265.3 \pm 6.9$	17 11
43	2	$271.3 \pm 2.3$		11
<i>n</i> -Butane				
15	1	473.1	> 460	15
27	1	331.7	$327.6 \pm 6.9$ $362.2 \pm 6.9$ $266.7 \pm 2.3$ $263.0 \pm 4.6$ $279.4 \pm 2.3$ $290.6 \pm 6.9$ $303.6 \pm 2.3$ $306.8 \pm 6.9$	15 11 15 11 15 11 11 11
28	3	$279.1 \pm 0.7$	$254.0 \pm 2.3$ $246.8 \pm 6.9$ $258.6 \pm 2.3$ $251.4 \pm 6.9$	15 11 15 11
29	9	$290.0 \pm 3.0$	$279.1 \pm 6.9$ $272.2 \pm 6.9$	15 11
41	2	$315.6 \pm 7.2$		15
42	2	$258.1 \pm 0.7$		11
43	4	$259.7 \pm 1.4$		15
56	2	$287.2 \pm 3.7$		15
57	4	$293.6 \pm 1.8$		11
Isobutane				
27	4	$327.8 \pm 2.8$	$339.1 \pm 6.9$ $366.8 \pm 6.9$ $279.1 \pm 4.6$ $313.7 \pm 6.9$ $295.3 \pm 4.6$ $392.2 \pm 11.5$ $249.4 \pm 2.3$ $246.8 \pm 4.6$ $254.0 \pm 2.3$ $253.8 \pm 6.9$ $267.6 \pm 6.9$ $267.6 \pm 6.9$	15 11 15 11 15 11 15 11 11 15 15 11
28	4	$323.4 \pm 4.4$		15
29	6	$353.2 \pm 8.5$		11
42	2	$255.8 \pm 1.8$		15
43	2	$259.7 \pm 0.9$		11
57	4	$284.4 \pm 2.3$		15
<i>n</i> -Pentane				
27	1	335.0	$426.8 \pm 4.6$	11
28	2	$299.6 \pm 2.8$	$449.5 \pm 11.5$	11
29	8	$310.0 \pm 1.2$	$343.7 \pm 6.9$	11
41	1	299.4	$332.2 \pm 4.6$	11
42	5	$246.8 \pm 8.3$	$258.4 \pm 4.6$	11
43	5	$256.0 \pm 0.7$	$272.2 \pm 4.6$	11
56	1	267.1	$260.7 \pm 6.9$	11
57	5	$260.4 \pm 0.9$	$267.6 \pm 6.9$	11
70	1	295.0		11
71	5	$307.0 \pm 6.9$	$279.1 \pm 6.9$	11

tials presented. However, since the various determinations of any appearance potential were

TABLE VII. Olefin ion appearance potentials.

Ion ( $m/e$ )	No. of measurements	$V_0$ (kcal/mole)	Literature value (kcal/mole)	Reference
Ethylene				
27	4	$321.1 \pm 0.2$	$327.6 \pm 2.3$	12
Propylene				
15	3	$532.2 \pm 30.4$		
27	3	$314.4 \pm 1.6$	$336.8 \pm 6.9$	4
28	2	$296.4 \pm 1.8$		
41	2	$276.8 \pm 1.8$	$277.5 \pm 2.3$	17
Butylene-1				
27	2	$383.6 \pm 10.2$		
28	1	284.9		
29	4	$316.3 \pm 1.6$	$276.1 \pm 2.3$	14
40	1	283.7	$269.9 \pm 4.6$	14
41	2	$268.7 \pm 2.3$	$268.7 \pm 2.3$	14
55	2	$276.1 \pm 2.5$	$255.4 \pm 2.3$	14
Isobutylene				
28	2	$281.0 \pm 0.9$	$281.4 \pm 11.5$	17
40	3	$276.8 \pm 0.9$	$269.7 \pm 2.3$	17
41	5	$272.2 \pm 2.8$	$267.1 \pm 2.3$	17
55	5	$278.9 \pm 1.6$	$262.7 \pm 2.3$	17

carried out using different calibrations, the excellent precision shown must include implicitly the effect of calibration accuracy. Second, the agreement for the normal paraffins through propane between these data and those previously published is excellent. The agreement between the results of Koffel and Lad<sup>11</sup> and other workers is remarkable in view of the fact that the former used the straight line extrapolation interpretation and the latter used the ion current onset or critical slope interpretation. The literature results prior to 1941 in Tables V, VI and VII have been corrected for the change in the value of  $e$  and the consequent change in calibration point. Third, as evidenced in Table V, for the paraffins beyond propane and for olefins the ionization potentials obtained in this work are systematically higher than others reported. It is interesting to note, that, if one recalculates literature values for the olefin molecule ions so as to shift from one point calibration to seven points, the discrepancies are reduced as is shown in Table VIII. The shift in calibration was effected by substituting in the calibration curve,

$$V_0 = A + BV + CV^2,$$

the value for  $V$  from the relation

$$V' = a + 112.3V,$$

based on an additive constant giving  $V' = 15.75$

volts for the argon apparent appearance potential  $V$ .  $V=0.0662$  for propylene which, since it was referred to the calibration curve for 6-25-46 in Table III, corresponded to  $V_0=10.05$  ev  $V=0.1189$  for argon was used in calculating the 6-25-46 calibration so  $a=2.40$  and

$$V_0 = 7.39 - 0.174 V' + 0.045 V'^2.$$

Thus, the literature value for propylene,  $V'=9.83$  ev, corresponds to  $V_0=10.02$  ev. As illustrated in Fig. 5 for another pair of calibrations, the two schemes give the same electron voltage at two points. For the data just described these are 15.32 ev and 10.68 ev. Between these two values  $V_0 < V'$  and beyond them  $V_0 > V'$ . Thus the difference between results is evidently a difference in calibration method.

If, on the other hand, one were to assume that the apparent value for ethylene corresponds to 10.60 ev as stated by Honig<sup>9</sup> and that for acetone 10.46 ev should be used instead of the spectroscopic value, recalculation of the 6-25-46 calibration curve gives

$$V_0 = 8.25 - 13.12 V + 648.3 V^2$$

with a standard error of estimate of 0.15 ev. Thus a curve can be fitted to these data just as well as to the original ones. However, this calibration gives a propylene ionization potential of 10.22 ev or 235.8 kcal/mole.

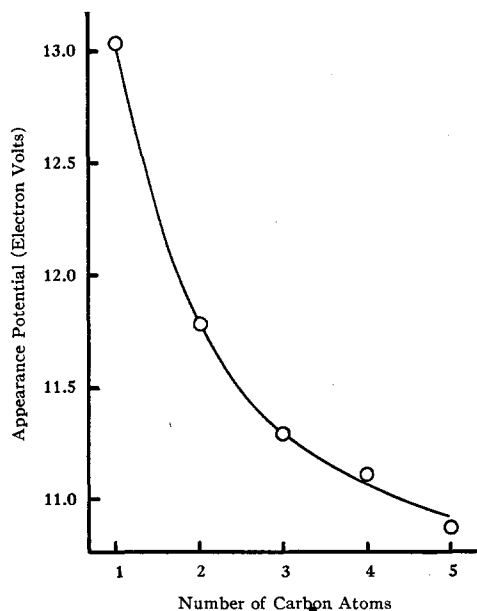


FIG. 6. The appearance potentials of the molecule ions from normal paraffins.

TABLE VIII. Result of changing basis of calibration.

Compound	Literature	Literature recalculated	Values from Table VII
Propylene	9.83 <sup>a</sup>	10.02	10.05
Butylene-1	9.65 <sup>b</sup>	9.88	10.00
Isobutylene	8.93	9.35	9.65

<sup>a</sup> See reference 17.

<sup>b</sup> See reference 14.

Since this procedure increases the discrepancy, it is evident that, at least in this case, the assumption that electron impact gives higher values than found in spectroscopic work for large molecules does not reconcile the two calibration schemes. If the difference in results is wholly due to different calibration procedure, then the two sets plotted against each other as in Fig. 8 can be used to convert from one voltage scale to the other. Until some independent means of calibration for the 10-volt region is available, there is no way to decide which is the correct scale.

Finally, as is apparent in Figs. 6 and 7, while the molecule ion appearance potentials for the normal paraffins form a decreasing sequence with the differences becoming smaller, the  $m/e=29$  ion appearance potentials for the same molecules show a reverse trend.

#### DISSOCIATION ENERGIES

Further discussion of the results tabulated in Tables V, VI and VII can best be carried on in

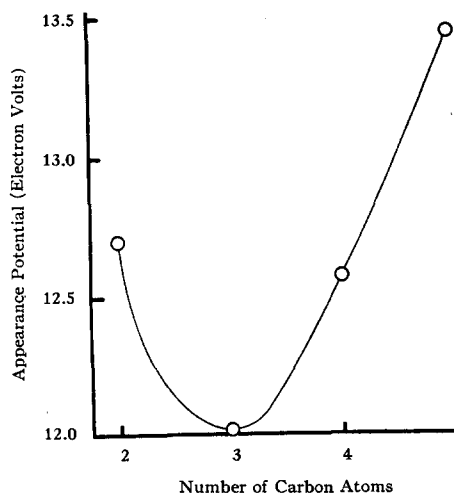


FIG. 7. Appearance potentials of the ion  $C_2H_5^+$  from the normal paraffins.

relation to a statement of the energies which define the appearance potential. In equation form, the statement reads:

$$V_0(R_1^+) = D(R_1-R_2) + I(R_1) \\ + E(R_1^+) + E(R_2) - E(R_1R_2) \\ + K.E.(R_1^+) + K.E.(R_2) - K.E.(R_1R_2).$$

In this equation  $V_0(R_1^+)$  represents the appearance potential, or the minimum energy necessary for the production of the ion  $R_1^+$  from the molecule  $R_1R_2$ .  $D(R_1-R_2)$  is the energy of the bond between  $R_1$  and  $R_2$  in the original molecule. It is defined as the energy necessary to produce the two fragments in their lowest energy states from the molecule in its lowest energy state.  $I(R_1)$  is the energy necessary to remove an electron from the fragment  $R_1$ . The various  $E$ 's represent internal energy which the corresponding fragments or molecule have in excess of that of their lowest energy state. The K.E.'s represent the kinetic energies of the molecules. Both  $E(R_1R_2)$  and  $K.E.(R_1R_2)$  can be neglected since the original gas will be at 250–300°C. Most molecules at that temperature are still in their lowest vibration state, and the corresponding kinetic energy is 0.05 electron volt. While the latter is of the order of experimental error, it is not large enough to account for the discrepancies to be described later. The kinetic energy of the neutral fragment can be deduced by conservation of momentum from that of the ion. Washburn and Berry<sup>35</sup> have

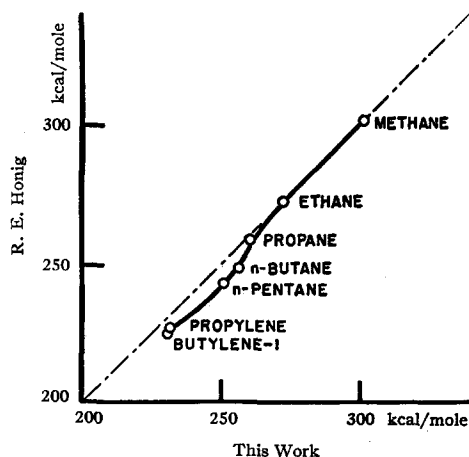


FIG. 8. Hydrocarbon ionization potentials.

<sup>35</sup> H. W. Washburn and C. E. Berry, Phys. Rev. **70**, 559 (1946).

determined the kinetic energies of ions from *n*-butane bombarded by 50 electron volt electrons. These varied from 0.04 to 2.4 electron volts. For two ions of interest to this discussion,  $m/e=29$  and  $m/e=43$ , they found respectively  $0.08 \pm 0.01$  and  $0.045 \pm 0.005$  electron volt. In view of the fact that bombarding electron energies of about 15 electron volts are used in appearance potential work, the kinetic energies can be expected to be smaller, and one can neglect them in the same manner as one has the other terms just discussed.

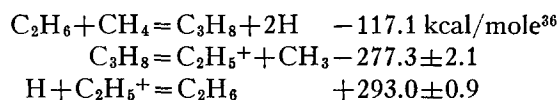
D. P. Stevenson<sup>26</sup> has gone a step farther and assumed that the excitation energies of the fragments are also negligible. On this basis, he was then able to set up closed energy cycles such

TABLE IX. Values of  $D(R'-R'')$  for the reaction  $R'R'' = R' + R'' - D(R'-R'')$  as calculated according to D. P. Stevenson.

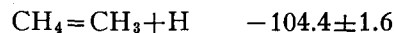
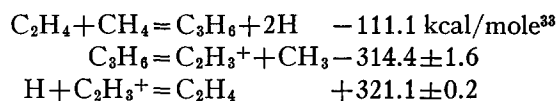
	H	CH <sub>3</sub>	(kcal/mole) CH=CH <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>3</sub> H <sub>7</sub>
R'					
H	103.8 <sup>a</sup>				
CH <sub>3</sub>	103.5 ± 1.5	87.8 ± 2.5			
CH=CH <sub>2</sub>	135.1 ± 2.0	125.4 ± 3.1	164.6 ± 2.8		
C <sub>2</sub> H <sub>5</sub>	111.5 ± 3.9	94.8 ± 4.6	133.8 ± 4.4	117.5 ± 5.5	
C <sub>3</sub> H <sub>7</sub>	130.8 ± 1.7	115.6 ± 3.0	154.9 ± 2.6	126.1 ± 4.2	148.2 ± 2.4

<sup>a</sup> See reference 11.

as the following:



or



In other words, from heats of formation and ion appearance potentials, one can calculate an energy related to a given bond in a molecule. In Table IX is a compilation similar to Stevenson's<sup>14</sup> of energies calculated from data from Tables V, VI and VII for the bonds indicated.

While the two energy cycles for  $D(CH_3-H)$  check each other and values obtained from ther-

<sup>36</sup> American Petroleum Institute Research Project 44 at the National Bureau of Standards, "Selected Values of Properties of Hydrocarbons," April 30, 1945.

mochemical data, such as  $D(\text{CH}_3-\text{H}) = 102 \pm 1$  kcal/mole,<sup>37</sup> Table IX shows that whatever confidence this engenders in the assumption of negligible excitation energies is destroyed by the upward trends in calculated energies with molecular weight. The differences between this table and the similar one presented by Stevenson<sup>14</sup> are the result of the differences in the corresponding appearance potentials.

In the light of thermochemical evidence with regard to chemical bonds, these upward trends must be taken to be the result of differences between dissociation energy as measured by electron impact and the corresponding bond energy. Long and Norrish<sup>38</sup> have pointed out that it would be surprising if inelastic collision produced unexcited fragments from large molecules. At least there will be an energy corresponding to the change in atomic arrangement between the fragment as it is in the molecule and the fragment after release from the molecule. For this reason they define a dissociation energy which may be represented as:

$$D'(R_1-R_2) = D(R_1-R_2) + E(R_1^+) + E(R_2).$$

Their position is that although the energy  $D'$  will be necessary to cause the breaking of the  $R_1-R_2$  bond, thermochemical data, being obtained under equilibrium conditions, will give values for the bond energy  $D$  because any excitation energies  $E$  imparted to the fragments in the process under study are returned to the reacting system. Electron impact, on the other hand, is a non-equilibrium process so that the excitation energies must be taken into account, and one obtains values for  $D'$  and not for  $D$ . An excellent example of electron collision producing an excited ion is found in the production of  $\text{CH}^+$  from HCN. Spectroscopic evidence<sup>39</sup> has shown that the mass spectrometer ionization potential for this ion<sup>12</sup> includes 85 kcal/mole "excess" energy. Thus, an accurate knowledge of the energy states of the fragments produced is necessary before ionization potentials can be used to calculate bond energies.

<sup>37</sup> H. C. Anderson and G. B. Kistiakowsky, *J. Chem. Phys.* **11**, 6-10 (1943); G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.* **12**, 469-478 (1944).

<sup>38</sup> L. H. Long and R. G. W. Norrish, *Proc. Roy. Soc.* **187A**, 337-357 (1946).

<sup>39</sup> A. E. Douglas and G. Herzberg, *Can. J. Rés.* **20A**, 71-82 (1942).

It is interesting to note that if one makes the crude assumption that the energy needed to produce the ion  $R_1^+$  from the molecule  $R_1R_2$  is in excess of  $D(R_1-R_2)$  and  $I(R_1^+)$  by an amount which is a linear function of the number of methylene groups in  $R_1R_2$  less one, one can obtain an approximately consistent correction for the excess energy for the production of  $\text{C}_2\text{H}_5^+$ . Since thermochemical data<sup>40</sup> give  $D(\text{C}_2\text{H}_5-\text{H}) = 98 \pm 2$  kcal/mole, one can compute that  $13.5 \pm 4.4$  kcal/mole, according to the assumption, is the excess energy for the production of  $\text{C}_2\text{H}_5^+$  from *n*-butane, and that therefore  $27 \pm 6$  kcal/mole is that for  $\text{C}_2\text{H}_5^+$  from *n*-pentane. The value  $D(\text{C}_3\text{H}_7-\text{H}) = 104 \pm 6$  kcal/mole, calculated from the corrected appearance potential of  $\text{C}_2\text{H}_5^+$  from *n*-pentane, is larger than that for  $D(\text{C}_2\text{H}_5-\text{H})$ , which is contrary to chemical experience,<sup>38</sup> but the experimental uncertainty is so large that one could say that the correction is roughly satisfactory.

## CONCLUSIONS

Although the appearance potentials discussed in this paper are as precise experimentally as any previously published, the difference between them and those published previously raises doubt as to the absolute accuracy of both sets of data. The difference arises from the method used for calibrating the voltage scale.

It seems entirely reasonable that for larger molecules the energy necessary to produce a given ion will be partially due to simultaneous internal excitation of the fragments produced and that the amount of excitation energy will increase with molecule size. Thus mass spectrometer appearance potentials cannot be used in calculating bond energies unless some knowledge about the states of the fragments produced is available.

## ACKNOWLEDGMENTS

We wish to thank the Misses C. I. Benson, C. McKinley, and R. H. Perkins for carrying out many of the measurements and calculations. We also wish to thank L. C. Roess for many helpful discussions.

<sup>40</sup> H. C. Anderson and E. R. Van Artsdalen, *J. Chem. Phys.* **12**, 479-483 (1944).