

the material up mechanically; for BeO, there was no such difficulty.

Other sources of deviations from the theory may be the following:

(1) The microcrystals not randomly oriented. This may occur when the sample is prepared by extrusion.

(2) The temperature of the sample not small compared to its Debye temperature. Then an appreciable amount of inelastic scattering would be expected. This would render the peaks less sharp and would introduce appreciable scattering below the first Bragg limit.

(3) The crystal contains two or more isotopic constituents which have appreciably different scattering properties. The incoherent scattering background would then be appreciable. However, it is necessary that there be a very strong dependence of the scattering amplitude on the isotopic identity of the nucleus for this to be a large effect.

(4) The nuclei of the sample have a spin different from zero and the scattering is strongly spin dependent. This would again lead to an incoherent background which would be large only if the spin dependence of the scattering were very strong.

(5) If the sample used is made up of a very fine powder, the surface area will be so large that there is a chance

that adsorbed surface films may contribute appreciably to the cross section. This may lead to an erroneous interpretation of the results, particularly if one is trying to distinguish between two possibilities corresponding to two different combinations of the signs of the scattering amplitudes. If a large amount of water, for example, is adsorbed on the crystals, there will be a smooth background cross section rising rapidly at low energies which could easily transform the lower curve in Fig. 2 into a curve that could hardly be distinguished from the upper curve.

If care is taken to avoid the difficulties mentioned above, it is believed that the transmission method offers a good procedure for determining the relative phases of the scattering of pairs of nuclei which can be compounded to form a microcrystalline material. This would then make it possible to determine the absolute sign of the scattering phases of a series of nuclei if the phase were determined for one particular nucleus.

The numerical work required for determining the theoretical curves in Figs. 1 and 2 was carried out by M. G. Goldberger.

## Peak Contour and Half-Life of Metastable Ions Appearing in Mass Spectra

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A method is described for determining the half-lives of metastable ions by varying the voltage which sweeps the ions from the ionization chamber of a mass spectrometer. The half-life of the state corresponding to the transition  $C_4H_{10}^+ \rightarrow C_3H_7^+ + [CH_3]$  has been found to be  $2.0 \times 10^{-6}$  second and the value found for the transition  $C_4H_{10}^+ \rightarrow C_3H_6^+ + [CH_4]$  was  $1.7 \times 10^{-6}$  second. In answer to the objection that the diffuse peaks should not be prominent in the  $180^\circ$  instrument if they are to be attributed to spontaneous dissociation during transit, it is shown that this result is to be expected for metastable transitions. The relative number of ions in the metastable states initially is estimated.

### INTRODUCTION

THE diffuse peaks appearing in the mass spectra of hydrocarbons have recently been attributed to the spontaneous dissociation of metastable ions during transit.<sup>1,2</sup> Several workers in the field have objected to this interpretation

on the basis that the appearance of diffuse peaks in the  $180^\circ$  instrument is unexplained—the peaks having roughly the same appearance as in the sector-field instrument such as that employing a deflection of  $90^\circ$ . In the latter instrument there is a considerable distance between the ion source and the deflecting magnetic field where the dissociation could occur without an appreciable deflection of the ions, and this situation does not obtain in the former case. This paper will attempt to show that a diffuse peak observed

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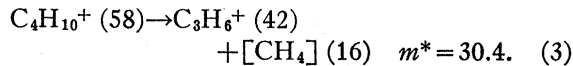
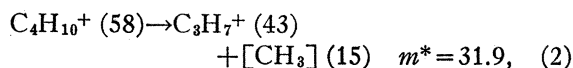
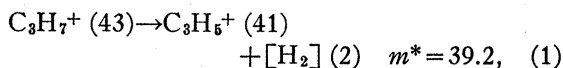
<sup>1</sup> J. A. Hipple and E. U. Condon, *Phys. Rev.* **68**, 54 (1945).

<sup>2</sup> J. A. Hipple, R. E. Fox, and E. U. Condon, *Phys. Rev.* **69**, 347 (1946).

with the 180° instrument will be quite similar in position and contour with the corresponding peak with the sectored-field instrument. In order to do this, it will be necessary to determine approximately the half-life of the metastable ion. The peak contour will then be constructed for simplified conditions to ascertain whether the actual contour can be explained reasonably by dissociation during transit.

#### DETERMINATION OF HALF-LIFE

Table I is a reproduction of a portion of Table II from an earlier paper.<sup>2</sup> The more rapid increase with ion-draw-out voltage ( $\beta = V_1 - V_0$ ) of the peaks at the apparent mass numbers  $m^* = 39.2$ , 31.9, and 30.4 relative to the rest of the spectrum of *n*-butane was a potent argument for their origin being the spontaneous dissociations:



As before, brackets are placed around the neutral fragment since the mass spectrometer cannot determine the nature of the neutral fragment or fragments. The metastable ions will decay exponentially with time, and the higher values of  $\beta$  will cause them to reach the region where they may be detected as diffuse peaks earlier in their lifetime leading to a higher peak. A study of Table I in conjunction with the geometry of the instrument should make possible an estimate of the decay constant,  $\lambda$ .

Referring to Fig. 1, let it first be assumed that all ions that dissociate later than  $t_2$  will contribute to the height of the diffuse peak. This

TABLE I. Relative peak heights at various voltages ( $V_1 - V_0 = \beta$ ) (from Table II of Hipple, Fox, and Condon, Phys. Rev. 69, 347, 1946).

$\beta$	$\alpha'(\beta)$ 58	$\alpha'(\beta)$ 40	$n'(\beta)$ 39.2	$n'(\beta)$ 31.9	$n'(\beta)$ 30.4
1.0	1.00	1.00	1.00	1.00	1.00
2.0	1.73	1.57	2.22	2.21	3.82
3.0	1.78	1.67	2.62	2.72	5.26
4.0	1.75	1.69	3.11	2.97	5.52
5.0	1.75	1.69	3.33	3.29	6.07

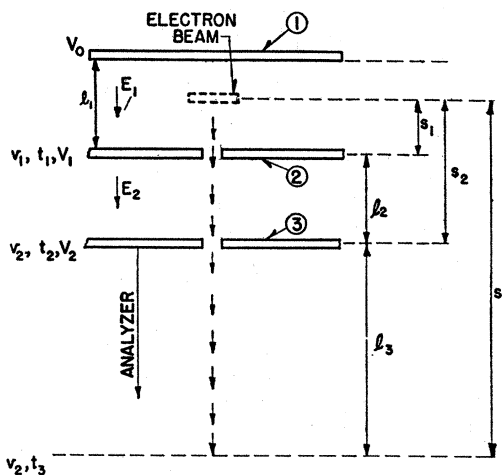


FIG. 1. Schematic diagram of ion source to relate the time of dissociation in terms of the geometry and the accelerating fields.

should hold fairly accurately for the sectored-field instrument if the half-life is quite short compared with the transit time through the analyzer. In this discussion only the field  $E_1$  will be changed so  $t_2(\beta)$  is defined as the value of  $t_2$  when  $V_1 - V_0 = \beta$ , and  $n^0(\beta)$  is the number of ions in a particular metastable state passing through the slit in electrode 3 when  $V_1 - V_0 = \beta$ . Considering the peak at  $m^* = 31.9$ , the collected ion current of mass 43 having 43/58 of the original energy will then be given by

$$n^0(\beta) = n_0 \exp - [\lambda t_2(\beta)], \quad (4)$$

$n^0(\beta)$  may be interpreted either as the number of ions of mass 58 left in a metastable state after passing through the slit in electrode 3, or the number of ions of mass 43 having 43/58ths of the original energy received at the ion collector (assuming all dissociate before reaching the collector and all these are collected).  $n_0$  is the number of ions of mass 58 originally in the beam in the metastable state responsible for the diffuse peak at  $m^* = 31.9$ . As the normal stable ions increase in intensity with  $\beta$ , the metastable ions will also have this normal increase  $\alpha(\beta)$  and hence

$$n^0(\beta)\alpha(\beta) = n(\beta). \quad (5)$$

Equation (4) now becomes

$$n(\beta) = \alpha(\beta)n_0 \exp - [\lambda t_2(\beta)]. \quad (6)$$

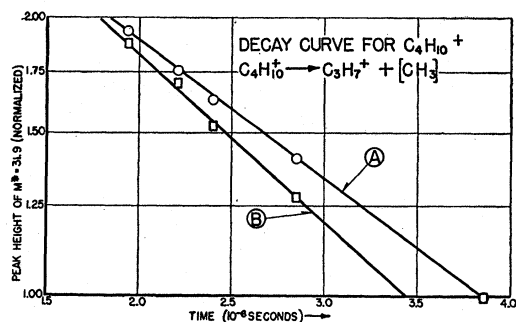


FIG. 2. Decay curve for the metastable state responsible for the diffuse peak at  $m^* = 31.9$  in  $n$ -butane. This is a plot of the data of Table I and Table II. For  $A$  mass 40 was used in normalizing and for  $B$  mass 58.

Equation (6) was derived with the assumption that all metastable ions passing through the slit in electrode 3 would contribute to the height of the diffuse peak regardless of the point at which they dissociate. Now suppose that, because of the geometry of the instrument, those ions which have travelled a distance greater than  $L$  in the analyzer will not contribute to the peak. Since the ion accelerating field  $E_2$  is held constant, and most of the energy is acquired between electrodes (2) and (3), the velocity of the metastable ions remains essentially constant. Therefore, it can be assumed that all the ions contributing to the ion current being measured will dissociate between  $t_2(\beta)$  and  $t_2(\beta) + \tau$  where  $\tau$  is a constant. From Eq. (6) this number is given by

$$\Delta n(\beta) = -\alpha(\beta)n_0 \exp[-\lambda[t_2(\beta) + \tau]] + \alpha(\beta)n_0 \exp[-\lambda t_2(\beta)]. \quad (7)$$

Normalizing to  $\beta = \beta_0$

$$\frac{\Delta n(\beta)}{\Delta n(\beta_0)} = \frac{\alpha(\beta)n_0 \exp[-\lambda t_2(\beta)][1 - \exp[-\lambda\tau]]}{\alpha(\beta_0)n_0 \exp[-\lambda t_2(\beta_0)][1 - \exp[-\lambda\tau]]}$$

$$\frac{\Delta n(\beta)}{\Delta n(\beta_0)} = \frac{\alpha(\beta)}{\alpha(\beta_0)} \exp[\lambda(t_2(\beta_0) - t_2(\beta))]. \quad (8)$$

From Eq. (8) it is evident that the half-life may be determined without regard to those ions which dissociate at a time later than  $t_2(\beta) + \tau$ , i.e., considering only ions dissociating between  $t_2(\beta)$  and  $t_2(\beta) + \tau$ . This, in turn, means that the half-life may be determined by varying  $\beta$  even though the half-life is not short compared with

the transit time. The values of

$$n'(\beta) = \Delta n(\beta) / \Delta n(\beta_0)$$

and  $\alpha'(\beta) = \alpha(\beta) / \alpha(\beta_0)$  for  $\beta_0 = 1$  volt are given in Table I. It remains to determine  $t_2(\beta)$ .

Referring to Fig. 1, it can be shown that  $v_1$ ,  $v_2$ ,  $t_1$ ,  $t_2$  and  $t_3$  are given by the following relations:

$$v_1 = (2\alpha_1 s_1)^{\frac{1}{2}}, \quad (9)$$

$$v_2 = (2\alpha_2 l_2 + 2\alpha_1 s_1)^{\frac{1}{2}}, \quad (10)$$

$$t_1 = (2s_1 / \alpha_1)^{\frac{1}{2}}, \quad (11)$$

$$t_2 = (v_2 - v_1) / \alpha_2 + t_1, \quad (12)$$

and

$$t_3 = l_3 / v_2 + t_2, \quad (13)$$

where  $\alpha_1 = E_1 e / 300m$  and  $\alpha_2 = E_2 e / 300m$ , and  $E_1$  and  $E_2$  are expressed in volts per centimeter,  $e$  is the charge of the ion in e.s.u., and  $m$  is the mass of the ion in grams. In the apparatus used for obtaining the data of Table I,  $l_1 = 0.39$  cm,  $l_2 = 1.0$  cm, and  $s_1$  is estimated to be 0.25 cm. The ion accelerating voltage was 600 volts and, therefore,

$$E_2 = 600 / 1.0 = 600 \text{ volts/cm.}$$

The values of  $t_2(\beta)$  for various values of  $\beta$  are shown in Table II together with the corresponding values of  $n'(\beta) / \alpha'(\beta)$ . In column 3 the values of  $\alpha'(\beta)$  for mass 40 are used and in column 4 the values for mass 58. The values of  $n'(\beta) / \alpha'(\beta)$  are plotted in Fig. 2. It would seem more reasonable to use the  $\alpha'(\beta)$  for mass 58 if the variation in height of a normal peak with changes in  $\beta$  is to be attributed to discriminating effects occurring before the ion enters the analyzer. The experimental results indicate that the change in the height of mass 58 due to the variation in the transit time of those ions of mass 58 in a metastable state is small. From

TABLE II. Normalized peak height ( $n'(\beta) / \alpha'(\beta)$ ) of  $m^* = 31.9$  for various values of  $\beta$  (ion-draw-out voltage).

$\beta$	$t_2(\beta) \times 10^6$ sec.	$\frac{n'(\beta)}{\alpha'(\beta)}$	$\frac{n'(\beta)}{\alpha'(\beta)}$
		31.9 40	31.9 58
1.0	3.86	1.00	1.00
2.0	2.86	1.41	1.28
3.0	2.40	1.63	1.53
4.0	2.21	1.76	1.70
5.0	1.94	1.94	1.88

Fig. 2, it is seen that the half-life is approximately  $1.6 \times 10^{-6}$  second when correcting with mass 58 and  $2 \times 10^{-6}$  second with mass 40.

#### REMEASUREMENT OF THE DECAY CURVE

The results obtained with the data previously published suggested the desirability of repeating the experiment for a more extended range of  $\beta$ . This has been done with another mass-spectrometer tube of the same type. The main ion accelerating voltage was raised to 1000 volts and  $\beta$  varied from 0.18 to 10.0 volts. The electron accelerating voltage was 75 volts. The data is summarized in Table III and points on Fig. 3 are plotted from this data in the same manner as curve B of Fig. 2 with the exception that it is assumed that the measured voltage scale must be corrected by adding 0.2 volt to the measured values. This is the same type of correction employed in the measurement of appearance potentials with the mass spectrometer and could be attributed to contact potentials, polarization effects, or incomplete shielding of the ionization region from the strong fields between neighboring electrodes. In the present example this added voltage is only 0.02 percent of the main accelerating voltage and it is reasonable to expect the field  $E_2$  to be shielded incompletely because of the slit in electrode 2. This correction is only important for small values of the ion-draw-out voltage. The experimental points are quite close to a straight line on the semi-log plot over a range from 1.5 to  $6 \times 10^{-6}$  second. The half-life from this curve is  $2.0 \times 10^{-6}$  second. Probably the greatest source of error is caused by the difficulty in determining  $s_1$  accurately.

TABLE III. Data similar to Table II but obtained with a different mass-spectrometer tube using 1000-volt ions and an extended range of  $\beta$ .

$\beta$ (volts)	$t_2(\beta) \times 10^6$ (sec- onds)	Peak height (arbitrary units)					$n'(\beta)/\alpha'(\beta)$	
		58	57	29	31.9	30.4	58	58
0.38	5.89	185.6	41.0	522.0	0.4		1.00	
0.45	5.44	393.5	81.7	1068.	1.2	0.6	1.41	1.00
0.70	4.43	530.0	111.0	1410.	2.1	1.0	1.84	1.24
0.95	3.84	551.0	115.6	1436.	2.7	1.6	2.27	1.91
1.20	3.46	547.0	114.6	1410.	3.1	1.7	2.63	2.04
3.20	2.25	556.0	116.6	1442.	4.9	3.0	4.09	3.54
5.20	1.84	560.0	—	1386.	5.3	3.3	4.39	3.87
10.20	1.41	444.0	91.0	1006.	5.1	3.1	5.33	4.58

The values below were obtained several days later and although  $\alpha'(\beta)$  and  $n'(\beta)$  are different, their ratio should fall closely on the curve if the method of correcting for the "normal" increase with ion-draw-out voltage is effective.

1.70	2.96	476.0	97.0	1154.	3.0	1.7	2.92	2.34
2.45	2.53	482.0	98.8	1200.	3.9	2.3	3.75	3.13

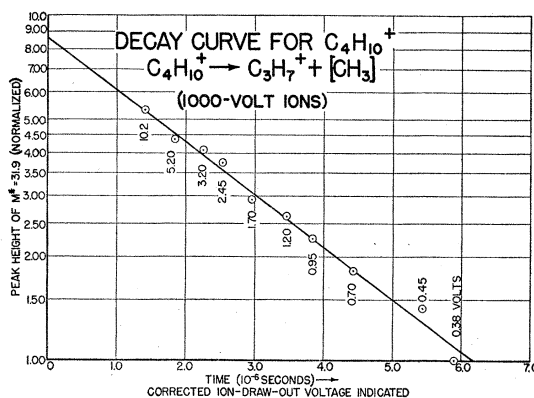


FIG. 3. Semi-log plot as in Fig. 2 but with new data over a more extended range.

#### PEAK CONTOUR IN 180° INSTRUMENT

Having determined the half-life, the next step is to relate the time at which the dissociation occurs with the apparent mass registered by the instrument. The simplifying assumptions will first be made that all the ions enter the analyzer normal to a line drawn between the entrance and exit slits, and the width of the entrance slit will be neglected. The metastable ion of mass  $m_0$  then enters the analyzer and first travels in a circular path of radius  $r_0$ ; after an angular deflection  $\theta$  or a time  $T$  after entering the analyzer, it dissociates and the ionic component of mass  $m$  then travels a circular path of radius  $r_0^* = (m/m_0)r_0$  (Fig. 4). When dissociation occurs at the moment of entry into the analyzer then  $r^* = r_0^*$ . The time  $T$  is given by

$$T = \frac{r_0}{v_2} \cos^{-1} \left[ \frac{2m_0^{\frac{1}{2}}(m_0^{*\frac{1}{2}} - m_0^{\frac{1}{2}}) - 4m^{*\frac{1}{2}}(m^{*\frac{1}{2}} - m_0^{\frac{1}{2}})}{2(2m^{*\frac{1}{2}} - m_0^{\frac{1}{2}})(m_0^{\frac{1}{2}} - m_0^{*\frac{1}{2}})} \right]. \quad (14)$$

In this equation  $m_0^*$ ,  $m_0$ ,  $v_2$ , and  $r_0$  are known from the experimental conditions and therefore  $T$  is known as a function of the apparent mass.

Since the half-life has been determined, the intensity as a function of  $T$  and through (14) as a function of the apparent mass  $m^*$  is known. In determining the peak contour of the diffuse peak at 31.9 in *n*-butane,  $m_0 = 58$  and  $m_0^* = (43)^2/58$ . Thus, the number of ions between  $m^*$  and  $m^* + \Delta m^*$  will be

$$n(m^*) - n(m^* + \Delta m^*) = \alpha n_0 \exp - [\lambda t_2] [\exp - [\lambda T(m^*)] - \exp - [\lambda T(m^* + \Delta m^*)]]. \quad (15)$$

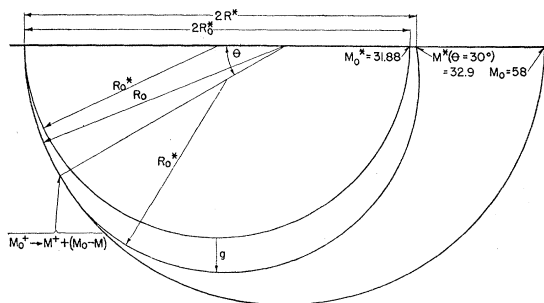


FIG. 4. Dissociation during transit through 180° analyzer. The dissociation may occur after appreciable travel in the analyzer without a large shift of the apparent mass from  $m_0^*$ .

In order to plot the peak contour the term  $\alpha m_0 \exp -[\lambda t_2]$  may be taken as unity. If the half-life is  $2 \times 10^{-6}$  second then  $\lambda = 0.346 \times 10^{+6}$  sec $^{-1}$ . Taking intervals of  $\Delta m^*$  the corresponding values of the time  $T$  are obtained from (14). If we assume that the tube is designed for a radius of curvature in the analyzer of 12.5 cm ( $r_0^* = 12.5$  cm) then  $r_0 = 16.9$  cm. For ions of mass 58 and kinetic energy of 600 ev,  $v_2 = 4.46 \times 10^6$  cm/sec. The values of  $n(m^*) - n(m^* + \Delta m^*)$  for successive values of  $m^*$  are given in Table IV and from this data the histogram of Fig. 5 was plotted. This shows the general shape of the peak contour for the diffuse peak at mass 32 in *n*-butane which would be expected when this molecule is studied with the 180° instrument and the beam does not hit any part of the analyzer during transit. It is clear that the maximum appears at essentially the same position for the 180° instrument as for the sectored-field instrument. For a smaller value of the half-life, the ion current would have been even more concentrated about  $m^* = 32$ .

Now in the 180° instrument it is conventional to place fairly wide slits at various points in the analyzer to prevent the formation of "ghosts" by reflections from the walls. These slits will cut out all those ions in Fig. 5 except those having an apparent mass close to 31.9. For instance, suppose the excursion from the median ray ( $r_0^*$ ) is limited to a distance  $g$  in Fig. 4 by a slit at an angular deflection of 90° for this ray. Then for metastable ions dissociating after a small angular deflection  $\theta$  in the analyzer,  $g$  will be given by

$$g = (r_0 - r_0^*)(\theta). \quad (16)$$

If  $g = 0.6$  cm, then  $\theta = 8^\circ$ . In terms of  $m^*$  this

means that ions of  $m^* > 31.95$  (Fig. 5) will be eliminated.

It is apparently true that ions should be recorded only very close to  $m^* = 31.9$  in both the 180° instrument and the sectored-field instrument. The intensity should be somewhat greater in the sectored-field instrument. The difference, however, is not as great as one might expect. In the example just given, approximately 17 percent of the ions dissociating after entering the 180° analyzer would be collected. With the sectored-field instrument the ions are rapidly defocused when the dissociation occurs in the magnetic field. If a 90° instrument with a radius of curvature of 12.5 cm is considered (such as that used for obtaining the data used in this paper), the distance of travel between the ion source and the magnetic field region is about 12.5 cm when the fringing field is neglected. However, since the air gap is  $\sim 2.5$  cm, the fringing field is large for a considerable distance from the magnet and it would be unreasonable to assume that all ions resulting from dissociation in the first 12.5 cm of path in the analyzer will be properly focussed at  $m^* = 31.9$ . If this distance is assumed to be as great as 8 cm, then  $T = 1.8 \times 10^{-6}$  sec. and 46 percent of the ions will be collected, which is only about 3 times the value for the 180° instrument. The diffuseness of the peaks in each case could be attributed to a mutual kinetic energy imparted to the fragments at dissociation, or the defocusing of the paraxial rays as a result of dissociations occurring in the magnetic field.

However, some of the ions will strike the tube

TABLE IV. Number of ions as a function of  $m^*$ .

$m^*$	$\theta$ (radians)	$T$ (microseconds)	$n(m^*)$	$n(m^*) - n(m^* + \Delta m^*)$
31.88	0	0	1.00	
31.9	0.075	0.284	.906	0.094
31.95	.139	.527	.833	.073
32.0	.182	.690	.788	.045
32.05	.217	.822	.752	.036
32.1	.246	.932	.724	.028
32.15	.272	1.031	.700	.024
32.2	.297	1.125	.678	.022
32.3	.340	1.288	.640	.038
32.4	.377	1.429	.610	.030
32.5	.412	1.561	.583	.027
32.6	.443	1.679	.559	.024
32.7	.473	1.792	.538	.021
32.8	.500	1.895	.519	.019
32.9	.527	1.997	.502	.017
33.0	.551	2.088	.486	.016

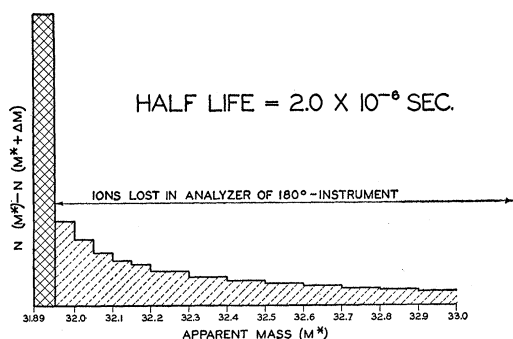


FIG. 5. Histogram illustrating that a large number of the ions dissociating after entering the analyzer of the  $180^\circ$  instrument will have an apparent mass close to  $m_0^*$  ( $=31.89$ ). Ions having  $m^*$  very much different from  $m_0^*$  will be lost in the analyzer.

walls in passing through the  $90^\circ$  analyzer so the percentage getting through would be less than 46 percent. The value obtained would depend somewhat on the position of the main magnet relative to the mass-spectrometer tube.

In discussing the peak contour the width of the entrance slit was neglected and the distribution in intensity was obtained along the focal plane of a normal ion beam (not metastable). Actually the data was taken with an exit slit at a fixed position and the spectrum was scanned by varying the magnetic field. This makes no essential difference in regard to the general conclusions. Clearly, of course, the exit slit must be sufficiently wide to allow the passage of ions in the range between  $m^*=31.89$  and  $m^*=31.95$  (see Fig. 5) in order that the peak height will be a measure of the number of metastable ions that have passed through the analyzer without being lost. This requirement is fulfilled in the analytical instruments of the  $180^\circ$  type in general use today. The entrance slit to the analyzer is generally much smaller than the exit slit and for this reason will not materially affect our conclusions.

#### RELATIVE NUMBER OF IONS IN THE METASTABLE STATE INITIALLY

Since the half-life has been determined, it should now be possible to estimate the relative number of ions of mass 58 originally in the metastable state responsible for the diffuse peak at

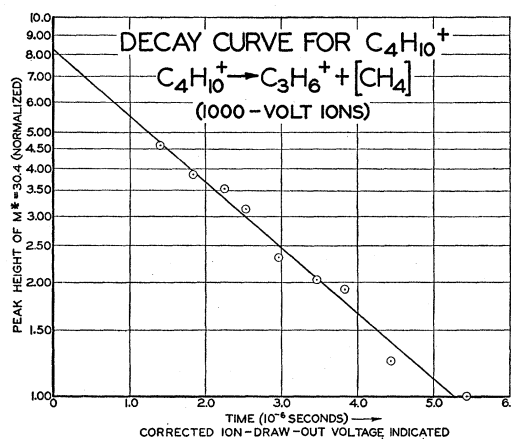


FIG. 6. Decay curve for metastable state responsible for the diffuse peak at  $m^*=30.4$  in *n*-butane.

$m^*=31.9$ . For  $\beta=3.2$  volts, the peak height of  $m^*=31.9$  is 4.9 divisions from Table III. If it is assumed on the basis of the previous discussion that only 40 percent of the ions that dissociate in the analyzer contribute to this peak height, then the peak height must be multiplied by 2.5 to obtain the value of  $n^0(\beta)$ , i.e.,  $n^0(\beta)=12.2$ . All the quantities in (4) are now known except  $n_0$  and this may be calculated:

$$n_0 = 12.2 \exp[(0.346 \times 10^6)(2.25 \times 10^{-6})] = 26.7.$$

This is only about 5 percent of the number of ions of mass 58 which reach the ion collector without dissociating.

The decay with time of the ions in the metastable state responsible for the diffuse peak at  $m^*=30.4$  is shown in Fig. 6. The transition involved here is



The data were obtained from the same charts used for the points in Fig. 3. This peak was smaller than that at  $m^*=31.9$ , and the current for  $\beta=0.38$  volts was too small to include in the measurements. From this curve the half-life is  $1.7 \times 10^{-6}$  second and the corresponding value for  $n_0$  is 18.8 divisions estimated in the same way as described for the other metastable transition. This is between 3 and 4 percent of the number of ions of mass 58 which reach the ion collector without dissociating.