

pears to be within the combined experimental errors in all cases.

The agreement in frequency for the H_2O line at low and high pressures is surprisingly good. It means that at least for this case, the strong collision approximation of Van Vleck and Weisskopf⁵ must be rather good, and there can be very little frequency shift due to pressure as would otherwise be expected.⁶

Further effort will be made to obtain more accurate values for intensities and half-widths of these lines.

¹ S. H. Autler, G. E. Becker, and J. M. B. Kellogg, *Phys. Rev.* **69**, 694 (1946); G. E. Becker and S. H. Autler, *Phys. Rev.* **70**, 300 (1946).

² R. L. Kyhl, R. H. Dicke, and R. Beringer, *Phys. Rev.* **69**, 694 (1946).

³ C. H. Townes, *Phys. Rev.*, to be published.

⁴ R. M. Hainer, G. W. King and P. C. Cross, *Phys. Rev.* **70**, 108 (1946).

⁵ J. H. Van Vleck and V. F. Weisskopf, *Rev. Mod. Phys.* **17**, 227 (1945).

⁶ H. M. Foley, *Phys. Rev.* **69**, 616 (1946).

Effects of High Initial Energies on Mass Spectra

HAROLD W. WASHBURN AND CLIFFORD E. BERRY
Consolidated Engineering Corporation, Pasadena, California
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IT has been pointed out that discrimination at the second slit of a mass spectrometer occurs as a result of initial thermal or dissociation energies.¹ We find that similar effects can also occur at the exit slit. The total effect of such discrimination is to reduce the number of ions of a given mass which are able to traverse the slit system. The efficiency of collection is found to be a function of V/V_T for any given geometry, where V is the accelerating voltage and V_T is the voltage equivalent corresponding to the apparent absolute temperature (including any dissociation energy) of the ion in question.

The fact that discrimination occurs provides a way of experimentally measuring rather small energies of dissociation. Figure 1 shows curves of relative abundance *vs.* ion

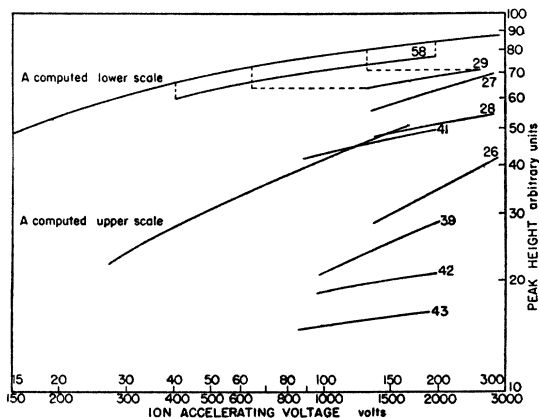


FIG. 1. Relative abundance of a number of ions from *n*-butane as a function of ion accelerating voltage.

TABLE I. Initial energies of several ions from *n*-butane.

Mass	Initial energy* ev	Abundance ratios		
		Magnetic scanning $V = 1400$ v	Electric scanning $B = 2200$ gauss	True abundance by extrapolation
26	2.4 ± 0.7	36	42	134
27	0.36 ± 0.6	235	267	367
28	0.12 ± 0.3	199	225	238
29	0.08 ± 0.01	270	303	302
39	0.83 ± 0.06	102	98	243
41	0.11 ± 0.01	192	200	378
42	0.085 ± 0.04	83	88	90
43	0.045 ± 0.005	660	699	665
58	0.041	100	100	100
58 sensitivity		81	73	100

* Includes thermal energy of 0.041 v corresponding to operating temperature of 475°K. Ionizing voltage = 50 v.

accelerating voltage for a number of ions obtained from *n*-butane. Curve *A* is a computed curve (derived in a manner similar to that of Coggeshall) which has been fitted to the experimental curve for the mass 58 ion, which we believe has only thermal energy. The computed curve is assumed to be a good extrapolation of the experimental curve both to low and to high voltages. To find the value of the initial energy of any ion, it is merely necessary to find the point on the voltage scale at which its curve fits the computed curve. The factor by which the voltage scale must be multiplied to accomplish this fit is the factor by which the temperature of the gas must be multiplied to give the apparent temperature of the ion. It should be noted that values obtained by this method do not take into account the true distribution of initial velocity, but rather assumes it to be Maxwellian. The amount of error from this source has not at this time been determined.

Table I shows the initial energies of several ions from *n*-butane. The spread of initial energy values indicated in Table I shows the range of values obtained in a single set of experiments. The spread could be reduced by using a greater range of voltages and by obtaining many experimental points on the curves. The absolute accuracy of the method was established for one case by obtaining the mass 58 curve at two temperatures. The two temperatures were 473°K and 550°K as measured by a thermocouple. The ratio of the temperatures as measured by the method described in this note was within ± 2 percent of the ratio determined by the thermocouple readings.

In a properly designed ion source the effects of motion of the electron beam due to changing either the electric field or the magnetic field are found to be negligible compared with the effects of initial energies. As a result of initial energies, neither electric field scanning nor magnetic field scanning can produce true abundance ratios. This is clear from a study of the curves of Fig. 1, and from reference to the last three columns of Table I, which show the ratios obtained by each type of scanning, and the estimated true abundance ratios obtained by extrapolating the curves of Fig. 1 to very high voltages. From this standpoint, the choice of type of scanning seems to be one of convenience.

¹ N. D. Coggeshall, *J. Chem. Phys.* **12**, 19-27 (1944).