Education, to which thanks are due. It is a great pleasure to thank Dr. Rufus Lumry of the University of Minnesota, for his theoretical advice.

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Cross-sections of Molecules for Ionization by Electrons

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It is shown that for a wide variety of substances including hydrocarbons and their substitution derivatives, the total relative ionization cross-sections as measured in ion gages or mass spectrometers (low pressures and low energy electrons), or by total ion production in gases (at or near atmospheric pressure) by C^{14} or Sr^{90}–Y^{90} β-particles, are a constitutive molecular property. It is further shown that, particularly for ionization by single electron impact and to a lesser degree for total ion production by β-particles, the atomic ionization cross-sections of the elements are given by the sum of the valence electrons weighted by the mean square radii of those electrons as calculated for hydrogen-like wave functions for the electrons. A table of calculated atomic ionization cross-sections is given for elements with $1 \leq Z \leq 56$, and $Z = 80$, 81 and 82. The utility of the rules for ionization cross-sections in various analytical applications is described and illustrated.

Total cross-sections[1] of molecules for ionization by electrons form the basic calibration data for a variety of analytical instruments such as ionization manometers,[2] ionization chambers[3] and mass spectrometers.[4] Furthermore these quantities have the same basic significance for the initiation of reactions by ionizing radiation as do absorption coefficients for photo-chemical reaction initiation. Although considerable attention has been paid to the manner in which the ionization cross-sections of individual substances vary with the energy of the ionizing radiation,[1] relatively little is to be found in the literature concerning the variation of these cross-sections from substance to substance for a specific ionizing agent. The most detailed discussion of this latter question is that given by Dushman[2] for the variation of the sensitivity of ionization manometers, particularly the VG-1 Gauge, with the substance whose pressure is to be measured. Dushman's discussion is purely empirical, and the conclusion reached is that the best representation of the variation of ionization cross-sections (as measured by relative sensitivity of the VG-1 Gauge) is obtained by taking the cross-section to be linearly related to the total number of atomic or molecular electrons. The nature of Dushman's discussion of his correlation suggests that a theoretical result due to Bethe,[5] was inadvertently overlooked. This result of Bethe is that the ionization cross-section, Q^{i}_{nl}, of an atomic electron with quantum numbers, (n,l) is approximately proportional to the mean square radius of the electron shell, (n,l).[6]

This paper has the dual purpose of presenting evidence that the relative total ionization cross-sections of atoms are given to a good approximation by the weighted sum of the outer, or valence, electrons of the atoms, where the weights are the mean square radii of the electrons, and that the relative total ionization cross-sections of molecules are constitutive molecular properties, *i.e.*, the sum of the atomic cross-sections. The additivity rule of ionization cross-sections is shown to be equally valid for ionization by single electron impact by slow (50 to 100 volt) electrons, such as are employed in mass spectrometry, and for ionization in gases at atmospheric pressure by such energetic β-particles as those emitted by carbon-14 and strontium-90–yttrium-90. This may be considered to be an extension and generalization of the "Bragg Rule,"[7] based on observations of ion production by α-particles from naturally occurring α-emitters.

The paper is divided into three sections: in the first portion there is briefly described the method of calculation of relative atomic ionization cross-sections, and there are tabulated the results of calculations for fifty-nine elements. Comparison of calculated and observed atomic ionization cross-sections is presented. The second section is concerned with evidence of the additivity of ionization cross-sections in molecules with particular reference to mass spectrometric and low pressure ionization chamber data, and the applicability of the calculated (Section I) atomic cross-sections to the computations of molecular cross-sections. In the third section the evidence for the applicability of the additivity rule to ion production in gases at atmospheric pressure by carbon-14 and strontium-90–yttrium-90 β-particles is presented.

I. Relative Atomic Ionization Cross-sections.—For hydrogen-like wave functions the mean square radius of an electron, (n,l), is given by[8]

$$\bar{r}^2_{nl} = a_0^2\, n'^4 (Z - S_{nl})^{-2} - 1 + \frac{3}{2}\left(1 - \left\{\frac{l(l+1) - 1/3}{n'^2}\right\}\right) \quad (1)$$

where the effective quantum number, n', and the screening constant, S_{nl}, of Slater are computed according to the rules summarized by Eyring, Walter and Kimball.[9] There are given in Table I the mean square radii of the various electrons of the

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[1] H. S. W. Massey and E. A. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, Oxford, 1952.

[2] S. Dushman, "Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949.

[3] J. W. Otvos, *Phys. Rev.*, **73**, 537 (1948); D. J. Pompeo and J. W. Otvos, U. S. 2,641,710 (June 9, 1953).

[4] E. P. Barnard, "Modern Mass Spectrometry," The Institute of Physics, London, 1953.

[5] H. Bethe, *Ann. Physik*, **5**, 352 (1930).

[6] M. S. Mott and H. S. W. Massey, "The Theory of Atomic Collisions," Oxford University Press, Oxford, Second Edition, 1949, p. 243.

[7] W. H. Bragg, *Phil. Mag.*, **10**, 318 (1905).

[8] L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," McGraw-Hill Book Co., New York, N. Y., 1935, p. 144.

[9] H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 162.

rare gas atoms, in units of the square of the radius of the Bohr orbit, a_0^2, as calculated from equation 1.

TABLE I

MEAN SQUARE RADII OF THE ATOMIC ELECTRONS OF THE RARE GASES

(units, a_0^2)

	He	Ne	A	Kr	Xe
1s	1.04	0.032	0.0096	0.0024	0.0010
2s		1.23	0.218	0.041	0.017
2p		0.878	0.156	0.030	0.012
3s			4.53	0.338	0.113
3p			3.94	0.294	0.099
3d				0.572	0.117
4s				6.98	0.688
4p				6.37	0.628
4d					1.60
5s					9.47
5p					8.87

The stepped line through the table separates the electrons into two classes, those with ionization potentials greater than (to the right) and those with ionization potentials less than (to the left) 35 e.v. It is seen that the combined effects of the n'^4, in the numerator, and the large screening constant of outer electrons in the denominator, results in disproportionately large mean square radii of the outer or valence electrons.

The ionization cross-sections of the outer electrons are proportional to their $\bar{r}_{nl}^2$ while those of the inner electrons are proportional to their $\bar{r}_{nl}^2$ less a term in Z_{eff}.[6] These facts combined with the empirical observation that the energy lost by ionizing electrons is on the average 30 to 40 e.v. per ion pair, suggests that to calculate the ionization cross-section for an atom one should simply sum over the electrons with ionization potentials less than 35 e.v., weighted by their $\bar{r}_{nl}^2$. The relative atomic ionization cross-sections for the elements hydrogen through barium, and mercury, thallium and lead, computed in the indicated manner are given in Table II. The electrons included as outer or valence electrons for each element are also given in the table. For a number of the elements, particularly those of groups II, III and IV, the sums have been made over the electrons for the valence state of the atom, *i.e.*, s^1p^1 for group II, s^1p^2 for group III and s^1p^3 for group IV.

TABLE II

RELATIVE IONIZATION CROSS-SECTIONS OF THE ELEMENTS

(Q^i(hydrogen atom) = 1)

Element	Electrons	Q^i	Element	Electrons	Q^i
H	$1s^1$	1.00	Ga	$4s^1\ 4p^2$	17.9
He	$1s^2$	0.694	Ge	$4s^1\ 4p^3$	18.4
			As	$4s^2\ 4p^3$	18.7
Li	$2s^1$	8.29	Se	$4s^2\ 4p^4$	18.5
Be	$2s^1\ 2p^1$	6.31	Br	$4s^2\ 4p^5$	18.0
B	$2s^1\ 2p^2$	5.02	Kr	$4s^2\ 4p^6$	17.4
C	$2s^1\ 2p^3$	4.16			
N	$2s^2\ 2p^3$	3.84	Rb	$4s^2\ 4p^6\ 5s^1$	58.4
O	$2s^2\ 2p^4$	3.29	Sr	$4s^2\ 4p^6\ 5s^2$	64.3
F	$2p^5$	1.85	Y	$4d^1\ 5s^1\ 5p^1$	59.5
Ne	$2p^6$	1.75	Zr	$4d^2\ 5s^1\ 5p^1$	59.8
			Nb	$4d^4\ 5s^1$	57.6
Na	$3s^1$	14.3	Mo	$4d^5\ 5s^1$	52.5
Mg	$3s^1\ 3p^1$	15.9	Tc	$4d^6\ 5s^1$	48.0
Al	$3s^1\ 3p^2$	15.4	Ru	$4d^7\ 5s^1$	44.1
Si	$3s^1\ 3p^3$	14.4	Rh	$4d^8\ 5s^1$	40.6
P	$3s^2\ 3p^3$	13.8	Pd	$4d^{10}$	25.1
S	$3s^2\ 3p^4$	12.8	Ag	$4d^{10}\ 5s^1$	34.8
Cl	$3s^2\ 3p^5$	11.8	Cd	$5s^1\ 5p^1$	22.1
A	$3s^2\ 3p^6$	10.9	In	$5s^1\ 5p^2$	24.8
			Sn	$5s^1\ 5p^3$	25.8
K	$3p^6\ 4s^1$	38.8	Sb	$5s^2\ 5p^3$	26.1
Ca	$3p^6\ 4s^1\ 4p^1$	42.1	Te	$5s^2\ 5p^4$	25.6
Sc	$3d^1\ 4s^1\ 4p^1$	38.3	I	$5s^2\ 5p^5$	25.0
Ti	$3d^2\ 4s^1\ 4p^1$	36.8	Xe	$5s^2\ 5p^6$	24.1
V	$3d^3\ 4s^1\ 4p^1$	34.6			
Cr	$3d^5\ 4s^1$	28.1	Cs	$5s^2\ 5p^6\ 6s^1$	73.5
Mn	$3d^5\ 4s^1\ 4p^1$	30.1	Ba	$5s^2\ 5p^6\ 6s^2$	78.1
Fe	$3d^6\ 4s^1\ 4p^1$	28.0			
Co	$3d^7\ 4s^1\ 4p^1$	26.1			
Ni	$3d^8\ 4s^1\ 4p^1$	24.4	Hg	$6s^1\ 6p^1$	27.4
Cu	$3d^{10}\ 4s^1$	18.4	Tl	$6s^1\ 6p^2$	30.1
Zn	$4s^1\ 4p^1$	16.0	Pb	$6s^1\ 6p^3$	31.2

There are shown in Fig. 1 the calculated atomic cross-sections as a function of the atomic number for the elements. There is also shown in this Fig. 1, as the dashed curve, the quantity, $10.9Z/18$, the relative atomic cross-section if an unweighted sum over all atomic electrons were the measure. The numerical factor of the atomic number, Z, adjusts the scales of cross-sections to coincidence at argon. The points of Fig. 1 are experimental values of atomic cross-sections relative to that of argon equal to 10.9. The values for helium, neon, hydrogen, carbon, nitrogen, oxygen and mercury (low value) are from the measurements of Tate and Smith as summarized by Massey and Burhop,[1] and correspond to ionization by *ca.* 75 volt electrons. The atomic cross-sections of H, N and O, are taken as half the values of the cross-sections of the diatomic molecules, and that of C is the cross-section of carbon monoxide less the cross-section of O. The cross-sections of krypton, xenon, cadmium,

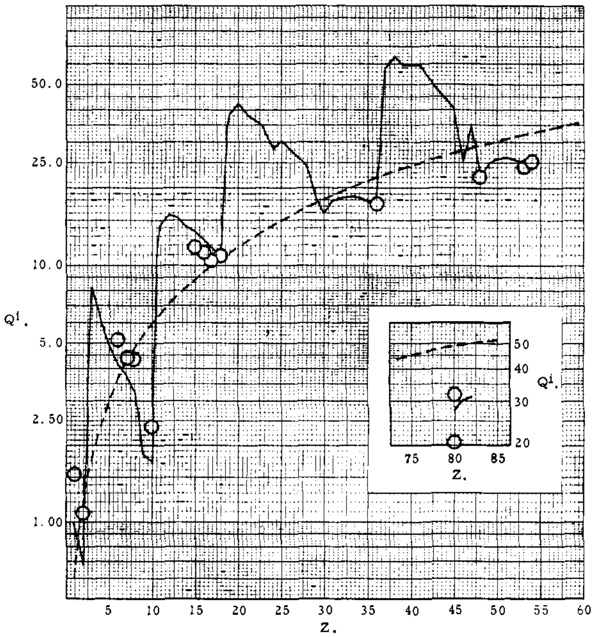

Fig. 1.—Atomic ionization cross-sections for the elements.

iodine and mercury (high value) are the relative sensitivities of response of VG-1 ionization manometers to these gases or vapors as measured and reported by Dushman.[2] As above, the atomic cross-section of I is half that of I_2. The cross-sections for phosphorus, sulfur and chlorine atoms are from measurements of mass spectrometric sensitivities of phosphine, hydrogen sulfide and hydrogen chloride, respectively, The atomic cross-sections in these latter three cases were calculated from the molecular cross-sections under the assumption that the cross-section of the hydrogens in these molecules is unity (per hydrogen atom). Justification for the means used to obtain atomic cross-sections from the molecular cross-sections is provided in the sections of this paper that follow, which deal with the additivity of ionization cross-sections.

On the whole the agreement between the calculated (Table II) and observed cross-sections is quite satisfactory. The theory accounts for the low (relative to atomic number) cross-sections of helium, neon and the heavier elements. It would be of great interest to have experimental values for the alkali metal vapors that the theory predicts to have very high relative ionization cross-sections.

II. Additivity of Molecular Ionization Cross-sections.—We have measured relative cross-sections for the ionization of molecules by single electron impact (*ca.* 75 volt electrons) by two methods. The first method employs the measurement of the total positive ion current generated in the ionization chamber of a mass spectrometer under definite conditions of gas flow and electron current. The ion sources of two quite different mass spectrometer tubes were used: (1) that of a Westinghouse Type LV and, (2) that of a Consolidated Engineering Corporation Diatron-20. In both of these the ion repellor electrode was connected to ground through the input resistance of a micro-microammeter and a positive bias with respect to ground (*ca.* 20 to 30 volts) was applied to the ion chamber box. The results obtained with the two instruments were not only mutually concordant, but the relative ionization cross-sections measured in this manner for the rare gases, helium, neon and argon are in excellent agreement with the absolute measurements of Tate and Smith.[10] This is very satisfying in view of the different geometries that obtain for the two mass spectrometer ion sources and the quite different pressures that obtain for a given rate of flow of gas.

The second method for the determination of relative ionization cross-sections of molecules was from the sum of the specific intensities of the ions of the resolved mass spectra of the substances, the mass spectra being obtained with the Westinghouse Type LV mass spectrometer. Across the range of mass to charge ratio, 12 to 100 A.W.U./unit-charge, the mass-dependent discrimination[11] of this $\pi/2$-sector analyzer mass spectrometer varies sufficiently slowly with the mass of the ions that the effects on the relative molecular ionization cross-sections calculated from these data are minor. The efficiency of collection of ions of $m/q = 90$ is but 15% greater than that for ions of $m/q = 20$, when 1000 volt ions are used for the mass analysis with magnetic field scanning.

In Table III there are intercompared the results of our three measurements of the relative ionization cross-sections of the rare gases and the measurements of Tate and Smith.[10] For this intercomparison the different intensity scales have been aligned by taking for each the total ionization cross-section of argon equal to unity. Since no correc-

TABLE III

IONIZATION CROSS-SECTIONS OF THE RARE GASES

Rare gas	Tate and Smith[a]	Type LV[b]	Diatron-20[b]	Mass spectra[c]
Helium	0.0898	0.0854	0.112	(0.074)[d]
Neon	0.156	0.165		0.153
Argon	1.00	1.00	1.00	1.00
Krypton		1.49	1.48	1.64

[a] Ref. 10 of text. [b] Total current in ion source. [c] Sum of mass spectral sensitivities, 1000 volt analyzing potential. [d] 2000 volt analyzing potential.

TABLE IV

Substance	LV-Source	LV-Spectra	D-20-Source
H_2	2.56		2.84
He	0.935		0.865
Ne	1.80	1.67	
A	10.9	10.9	10.9
Kr	16.3	17.8	16.1
N_2	9.2	7.15	
O_2	8.2	5.96	
Air			6.35
CO	9.7	6.80	
CO_2	12.1	9.31	
N_2O	11.2	7.40	
CH_4	7.70	7.90	10.8
C_2H_4	11.9	13.9	12.8
C_2H_6	14.3	15.2	16.0
C_3H_6	17.4	21.0	19.3
C_3H_8	19.2	22.2	22.3
C_4H_8			25.9
C_4H_{10}	27.0	27.2	28.6
C_5H_{10}			31.2
C_5H_{12}		33.8	35.2
C_6H_6		33.4	
Cyclo-C_6H_8		33.7	
Cyclo-C_6H_{10}		36.0	
1,5-C_6H_{10}		29.8	
Cyclo-C_6H_{12}		35.8	
1-C_6H_{12}		33.0	
C_6H_{14}		39.5	
C_7H_{16}		48.6	
CH_3Cl	16.3		
CH_3Br	19.3		
CH_3I	22.2		
C_2H_4O	13.1		
CH_3CHO	13.7		
C_3H_6O	20.2		
$(CH_3)_2CO$	20.8		
$(CH_3)_2O$		16.6	
PH_3		14.7	
H_2S		13.1	
HCl		11.4	
HCN		8.80	
$(CN)_2$	18.6	14.0	
CS_2		26.8	

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(10) J. Tate and P. T. Smith, *Phys. Rev.*, **36**, 1293 (1930); **39**, 270 (1932).

(11) N. D. Coggeshall, *J. Chem. Phys.*, **12**, 19 (1944).

tion has been applied to the resolved mass spectral sensitivity data for mass dependent discrimination, the neon and krypton cross-sections relative to that of argon from the mass spectral data are expected to be low and high, respectively, as is found. It is of interest to note that the discrimination characteristics of the Westinghouse Type LV mass spectrometer are such that using 2000 volts analyzing potential for light ions, as is done in these laboratories, results in about the same efficiency for the collection of $m/q = 4$ as obtains for $m/q = 20$ when 1000 volts is used for the latter. There are summarized in Table IV the results of our measurements of relative molecular ionization cross-sections. The designations of the columns indicate the method, of those described above, that was employed in the measurement. In order to facilitate comparison of the observed relative cross-sections with those calculated from the atomic cross-sections of Table II the cross-section of argon has been set equal to its calculated value, 10.9 (relative to that of the hydrogen atom as unity), and all other data were adjusted accordingly.

The observed relative ionization cross-sections are compared with the cross-sections calculated from the atomic ones of Table II in Figs. 2 and 3. Where measurements on a particular substance were made by more than one of the methods described above the unweighted average has been plotted as the observed value. In order to maintain legibility, the data of Table IV have been separated in Figs. 2 and 3 into hydrocarbon and non-hydrocarbon, respectively. The straight lines of unit slope that should fit the data perfectly if the relative atomic cross-sections of Table II are applicable and the calculated cross-sections are additive as postulated is seen to represent the observations very well.

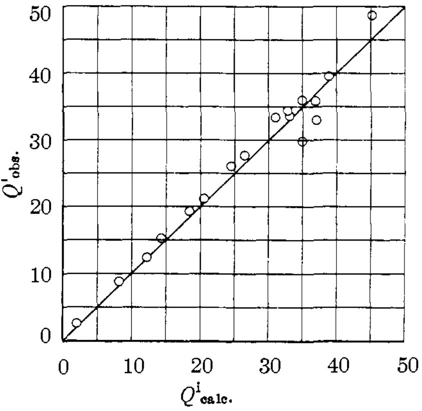

Fig. 2.—Calculated *vs.* observed cross-sections for hydrocarbons (single electron impact).

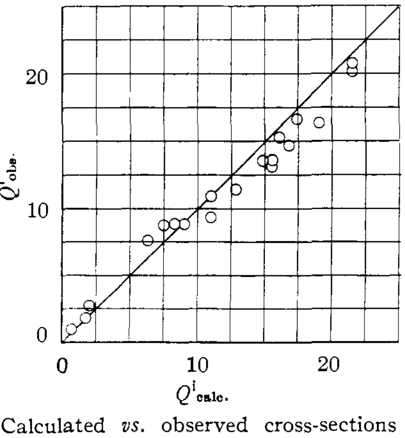

Fig. 3.—Calculated *vs.* observed cross-sections for non-hydrocarbons (single electron impact).

Particularly worthy of note is the fact that the additivity of relative ionization cross-sections of the hydrocarbons applies without corrections for either the presence of rings or unsaturation in the molecule. Similarly, to the accuracy of the data, there are no other molecular structure effects. The point for hexane on the figure represents all five hexane isomers, and the heptane point represents all nine heptane isomers.

III. Ionization by β-Particles.—Measurements of ion production by β-particles in gases at approximately atmospheric pressure were made in two ways. In one method a small amount of either $C^{14}O$ or $C^{14}O_2$ was put into an ionization chamber together with 200–700 mm. pressure of the gas being studied. The ionization current produced by the C^{14} β-particles was measured at an ion collecting field strength of about 100 volts/cm. The relative ionization cross-section of the gas, X, with respect to CO or CO_2 was then obtained from the ratios of the partial pressure of CO or CO_2 that would have been necessary to give the same ionization current to the partial pressure of X actually used.

Such a method was required by the non-linear relationship that obtains between ionization current and pressure. This is illustrated in Fig. 4. The current produced by a fixed partial pressure of radioactive atoms rises less steeply as the total pressure increases because more and more β-particles are losing all their energy in the gas before they strike a wall. A limiting value is reached when essentially all the β-particle energy is dissipated in the gas. The shape and position of the curve in Fig. 4 is therefore necessarily dependent on the geometry of the ionization chamber and on the energy of the β-particles. The relative cross-section of all gases reported here were determined at at least two pressures, both low enough that the ionization current was still sensitive to pressure (relative current, as indicated in Fig. 4, between 0.3 and 0.7).

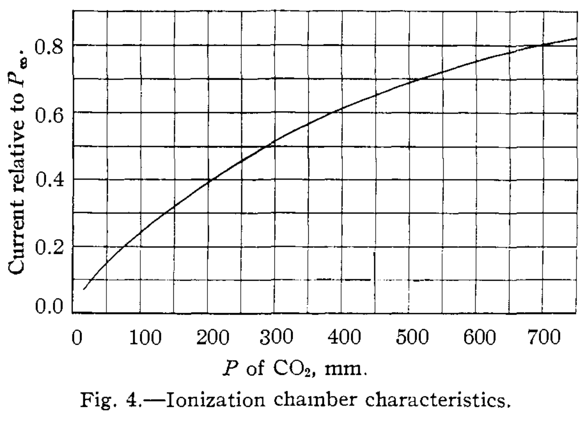

Fig. 4.—Ionization chamber characteristics.

In the other method for measurement of ion production by β-particles a Sr^{90}–Y^{90} source was used external to an ionization chamber. The chamber was filled with various gases, always at 760 mm. Since the average energy of the Sr^{90}–Y^{90} betas is about 20 times that of the C^{14} betas and since the chamber used for these measurements was smaller than the one to which Fig. 4 applies, the measurements were being made on the initial, or nearly linear, portion of the relative ion current curve. Hence the measured currents themselves represent the relative ionization cross-sections of the gases.

The results of the two sets of measurements are listed in Table V, and in Figs. 5 and 6 the relative ionization cross-sections, measured as described above, are plotted as ordinate against the calculated ionization cross-sections (from Table II) as abscissa. In each figure the solid line is the 45° line that would obtain for perfect agreement between observed and calculated cross-sections. In each figure the hydrocarbon data (including H_2 as the alkane of zero carbon number) fall on a straight (broken) line other than the ideal one. The slope of the best line for C^{14} data is greater than for the Sr^{90}–Y^{90} data. This is probably an absorption effect that arises from the geometries of the two experimental methods. The Sr^{90}–Y^{90} source, being external, is somewhat shielded from the remoter parts of the chamber by the sample gas. The gases with higher cross-sections will therefore give lower values in this apparatus than when they are mixed with $C^{14}O$ (or $C^{14}O_2$) throughout the chamber. Similarly the general tendency of the cross-sections for ionization by C^{14}-β-particles to be lower than calculated may be an absorption effect. At high pressures where the average electron produces more than one ion pair, absorption must act to cause underestimation of higher ionization cross-sections.

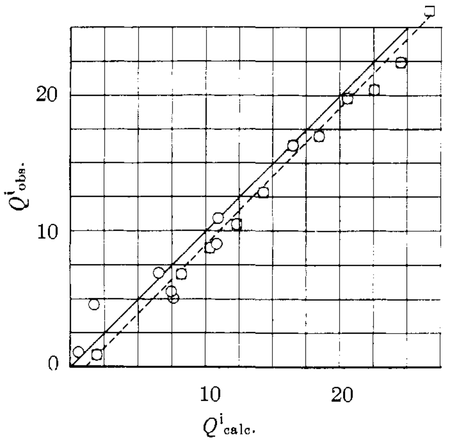

Fig. 5.—Calculated *vs.* observed cross-sections (C^{14} β-particles): □, hydrocarbons; ○, other.

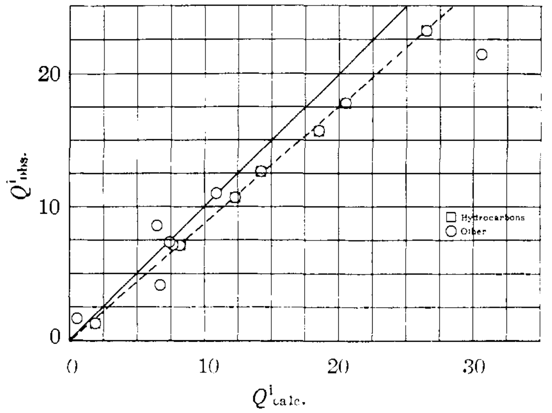

Fig. 6.—Calculated *vs.* observed cross-sections (Sr^{90}–Y^{90} β-particles).

Table V

Relative Ion Production by High Energy β-Particles

Substance	C^{14} betas	Sr^{90}–Y^{90} beta
H_2	0.87	1.23
He	1.13	1.64
Ne	4.64	....
A	(10.9)	(10.9)
CO	5.54	7.20
N_2	5.20	7.04
O_2	6.90	8.55
CO_2	9.10	10.8
N_2O	8.97	...
NH_3	....	4.14
CH_4	6.77	7.04
C_2H_2	8.8	....
C_2H_4	10.5	10.7
C_2H_6	12.8	12.7
C_3H_4	16.3[a]	....
C_3H_6	17.0	15.7
C_3H_8	19.8	17.8
C_4H_6	20.4[b]	....
C_4H_8	22.4	....
C_4H_{10}	26.3	23.1
CF_2Cl_2	....	21.4

[a] Methylacetylene. [b] 1,2-Butadiene.

It should be noted that there are systematic differences between the relative ionization cross-sections of the non-hydrocarbons as measured by the β-particle method. Whereas for ionization by single electron impact the cross-section of hydrogen greatly exceeds that of helium and is greater than that of neon, the ion production in helium exceeds that in hydrogen by 31% for C^{14} betas and 33% for Sr^{90}–Y^{90} betas, while ion production in neon by C^{14} betas is greater than that in hydrogen by a factor of 5.4. These effects are similar to those reported by Jesse and Sadauskis[12] on the strong enhancement (40%) by small amounts of argon, krypton and carbon dioxide of the ion currents produced in helium and in neon by α-particle bombardment. Jesse and Sadauskis account for the increased ion current by collisions of the second kind between foreign gas molecules and rare gas atoms (He, Ne) in metastable states that lie above the ionization energy of the added gas. The present observation with respect to neon also suggests that the inner electrons that were neglected in the calculation of cross-sections play a more important role when the ionizing electrons have very high energy. The cross-section of nitrogen for ionization by single electron impact is greater than that of oxygen while the converse is true for ion production in these gases

(12) W. P. Jesse and John Sadauskis, *Phys. Rev.*, **88**, 417 (1952).

by C^{14} and Sr^{90}–Y^{90} betas. Additivity of cross-sections still obtains, however. Thus the ion production in CO_2 equals that in CO plus half that in O_2, and ion production in N_2O equals that in N_2 plus half that in O_2.

Although the atomic ionization cross-sections of Table II have failings as far as ion production by relatively high energy β-particles is concerned, as recounted in the preceding paragraph, they provide a much superior first approximation to the usually used total number of electrons. In Fig. 7 the data of Figs. 5 and 6 replotted against the total (unweighted) number of electrons of the atom or molecule. The scatter of points is seen to be quite severe—the only type of correlation that is found is that each class of hydrocarbon, alkane and alkene, for example, has its ion production represented by a line and the lines for the different types of hydrocarbons are parallel.

It should be noted that the points for two substances in Fig. 6 fall very far below the best line representing the data for all other substances. These two are ammonia and Freon-12. It may be suggested that the deviations in these two cases result from the excessive formation of negative ions in these gases and thus an excessive recombination causing the apparent ion production to be low.

IV. Conclusions.—The various comparisons of observed and calculated molecular ionization cross-sections provide substantiation for the hypothesis of additive character of these cross-sections, and at least for many elements of the periodic system substantiation of the rule that the atomic cross-sections are given to good approximation by the sum of the valence electrons weighted by the $\bar{r}_{nl}^2$ of the valence electrons. In many respects the tests that may be made of the last named hypothesis leave much to be desired. The most marked deviation between the usually used rule for atomic cross-sections, namely, the unweighted sum of the number of electrons, and the modified rule, occur at the beginning of each period, where there are no experimental observations. Measurements on the alkali or alkaline earth metal vapors would provide the necessary data for a stringent test of the reliability of the new hypothesis, based on Bethe's theory.

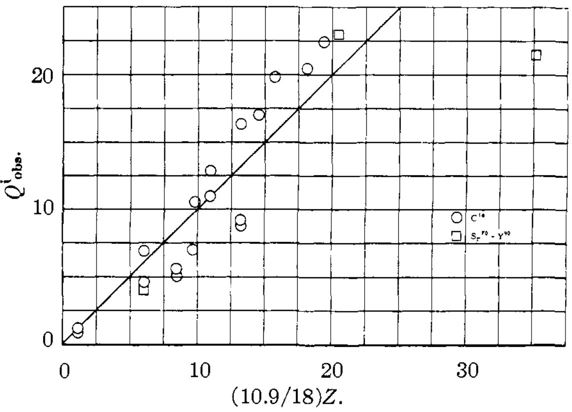

Fig. 7.—Observed cross-sections *vs.* total atomic number.

For analytical chemical purposes it is apparent that the rules advanced in this paper serve a potentially useful purpose. For many substances it is possible to measure the relative intensity of ions in their mass spectra, but not the specific intensities. This situation may arise in common substances such as formaldehyde or ketene, which polymerize with such extraordinary rapidity that volumetric measurement of the quantity admitted to a mass spectrometer inlet system is meaningless, or with very labile substances such as the free radicals that permit no direct volumetric measurement. The data presented in section II indicate that the total mass spectral sensitivities of such substances, relative to related ones that are measurable, are readily calculated with reliability.

The additive character of total ion production in hydrocarbon vapors produced by C^{14} betas has been a very useful fact. In C^{14} tracer studies of catalytic reactions of hydrocarbons, such as Fischer–Tropsch synthesis, it has eliminated the necessity for either conversion of the partially separated gases to a standard gas such as carbon dioxide or very detailed separation and extensive calibration of the ion chamber. If the gas mixtures can be analyzed by some means, as with a mass spectrometer, then the concentration of C^{14} can be calculated directly from ion current.

A somewhat more subtle application of the results lies in the coincidence that the relative atomic cross-sections of carbon and hydrogen and the relative atomic volumes of these elements in liquid hydrocarbons are in the same ratio, 4/1. The result of this coincidence is that the total mass spectral current of liquid hydrocarbons or their mixtures is very nearly a constant for all hydrocarbons when referred to unit liquid volume. Thus, if the intensities of ions in the mass spectra of hydrocarbons are expressed as fractions of the total mass spectral intensity for both pure substances and mixtures, analytical equations of the usual form obtain with concentration expressed in liquid volume fraction units, and there is no necessity to measure the quantity of hydrocarbon or mixtures introduced to the mass spectrometer for either calibration or analysis. These facts have been particularly useful in formulating methods for the "type analysis" of complex mixtures such as gasolines, kerosenes, and the like.[13]

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EMERYVILLE, CAL.

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