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Mass-Spectrometer Study of the Rare Gases

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A study of the appearance potentials and isotope abundance of the rare gases has been made with a Consolidated Engineering Corp. mass spectrometer as a check on the operation of the instrument. The results are comparable to previously published data. In addition, some new experimental values of ionization potentials have been obtained. Generally, good agreement of the isotope abundance measurements with previously published values obtained on other types of instruments and with chemically determined atomic weights, indicates a minimum of discrimination effects. The relative values of the ion currents for the rare gases were obtained and plotted against the atomic number. No simple relation between sensitivity and atomic number is evident.

I. Introduction

Mass spectrometer studies of all the rare gases have been published. Bleakney [1],[1] and more recently Stevenson and Hipple [2], have measured the appearance potentials of singly and multiply charged ions in helium, neon, and argon. Nier [3], Aldrich and Nier [4], and Vaughan, Williams, and Tate [5] have published accurate values of the isotope ratios of the rare gases. A survey of all the rare gases with a Consolidated Engineering Corporation mass spectrometer was primarily undertaken by the authors as a check on the performance of the instrument. As the results supplement published work in several respects, and as a precision has been obtained that is comparable with the best published work, it seemed worth while to publish the results. The relative values of ion currents obtained under similar conditions in a series of gases having similar electronic structure but differing in atomic weight are of interest. Some new values of ionization potentials have also been obtained. The observed values of the isotope ratios serve further to corroborate accepted values of isotope ratios and computed atomic weights. Some recent papers by Coggeshall [6] and Washburn and Berry [7] concerning discrimination in the ion source indicate that this may appreciably influence observed isotope ratios. In this connection, a comparison of the results obtained by different types of instruments is useful.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. Experimental Procedure

The Consolidated mass spectrometer used in the present work has been described elsewhere [8]. Briefly, it consists of a tungsten-filament source of electrons, the energies of which can be controlled between 0 and 100 v by a wire-wound potentiometer and measured to ± 0.5 percent by a calibrated voltmeter. The positive ions formed in the electron beam are drawn out by a fixed potential of about 3 v for appearance potential measurements, whereas a variable potential (approximately 1 percent of the ion accelerating voltage) is used in the isotope abundance measurements. The positive ions are then accelerated by a variable electric field and deflected into 180-degree arcs by a suitable magnetic field. They are separately amplified by an electrometer tube and recorded by galvanometers. The recorder contains four galvanometers in parallel with sensitivities in the ratios of 1 : 3 : 10 : 30. Thus the 8-in. photographic record has an effective width of 240 in.

The appearance potential measurements were made in the usual manner and evaluated according to the method of "initial breaks" described by Stevenson and Hipple [9].

Whenever possible, the isotope abundance measurements were made at several different pres-

sures and values of electron energy and current. Lack of discrimination in the apparatus was shown by indepedence of the abundance ratios of these values [3].

The rare gases used in this investigation were portions of samples submitted to this laboratory for mass spectrometric analysis by the Bureau of Mines helium plants and the Air Reduction Sales Co. All were of greater purity than 99.5 percent by volume, the helium containing less than 0.1 percent by volume of total impurity.

III. Discussion of Results

1. Ionization Potentials

Figure 1 shows the initial portions of the ionization efficiency curves for the singly charged ions of helium and neon and the singly and doubly charged ions of argon. Their critical potentials are summarized in table 1 and compared with some previously reported data obtained both by electron impact and by optical methods. The doubly charged helium ion was not measured because of interference by H_2^+ ion. The hydrogen was possibly released from the interior surfaces of the mass spectrometer when helium was admitted as background runs showed no trace of H^+ ion or H_2^+ ion. To simplify the figure, the doubly charged neon curve is not shown. It has a very low intensity with an attendant increase in error of the determination of the appearance potential. The slope of the ionization efficiency curve for doubly charged argon continues to increase for approximately 9 v after the initial break, whereas that portion of the curve for singly charged argon is about 2.5 v. This agrees with observations reported by Stevenson and Hipple [2]. The observed critical potentials are in good agreement with computed values in spite of the shape of the curves.

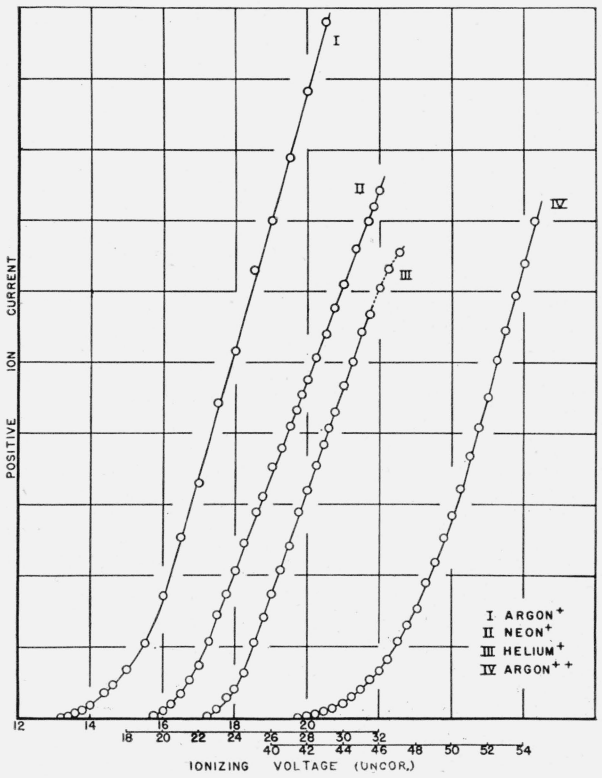

FIGURE 1.—*Initial portions of the ionization efficiency curves for the ions* He^+, Ne^+, A^+, *and* A^{++}.

The ordinate is arbitrary and different for some ions. The middle scale of the abcissa applies to curves II and III. The lower scale applies to curve IV.

TABLE 1.—*Appearance potentials of singly and mulitply charged ions of the rare gases relative to* A^+

[Appearance potential, volts]

Ion	This paper[a]	Optical sources[b]	Others
He^+	$24.4_6 \pm 0.2$	24.586	
Ne^+	$21.5_1 \pm 0.1$	21.58	21.5±0.1 [1].
Ne^{++}	61.7 ±2.0	62.7	63.0±0.5 [1].
			$(Ne^+)-(A^+)=5.6_5\pm0.15$ [3].
A^+	[c] 15.76	15.76	15.7±0.1 [1].
			$(A^{++})-(A^+)=28.0\pm0.5$ [3].
A^{++}	$43.6_1 \pm 0.2$	43.62	44.0±0.5 [1].
Kr^+	$13.9_6 \pm 0.1$	14.009	
Kr^{++}	38.6 ±0.2	38.6 [12]	
Xe^+	$12.1_6 \pm 0.1$	12.138	
Xe^{++}	34.1 ±0.2	33.3 [13]	

[a] Corrected scale, assuming $I(A^+)=15.76$ ev.

[b] Bacher and Goudsmit, Atomic energy states (McGraw-Hill Book Co., New York, N. Y., 1932). Conversion factor 8,066 cm^{-1} used to convert from wave numbers to electron volts.

[c] Observed value is $13.4_0 \pm 0.1$ v.

Figure 2 shows the initial portions of the ionization efficiency curves for singly and doubly charged ions of krypton and xenon. The plots for Kr^{++} ion and Xe^{++} ion are, like A^{++} ion, curved over a range of 8 to 10 v beyond the appearance potential.

2. Isotope Abundance Ratios

The measurement of the ratio of He^3 to He^4 is beyond the range of the Consolidated mass spectrometer, but has been measured by Aldrich and Nier [4] as 1.7×10^{-6}. They used a mass spectrometer

of sufficient resolving power to show that the mass 3 peak was not HD.

Table 2 lists the neon isotopes and the percentage abundance as determined in this laboratory and by Vaughan, Williams, and Tate [5]. The maximum deviation in the tables in this paper is intended only as an indication of the reproducibility of the measurements. The accuracy is believed to be of the order of 1 percent of the abundance for isotopic abundances greater than 10 percent. With the neon isotopic masses listed by Pollard [10] and converting from the atomic to the chemical scale, a chemical weight of 20.18_2 is obtained. The accepted value is 20.183 (International Atomic Weights, 1947).

TABLE 2.—*Abundance of isotopes of neon*

	m/e		
	20	21	22
	Percent	*Percent*	*Percent*
This paper	90.51	0.28	9.21
Maximum deviation	±0.15	±.02	±0.18
Vaughan, Williams, and Tate [8]	90.0	.27	9.73

Table 3 lists the argon isotopes and their respective percentage abundance. The comparative data are again those of Vaughan, Williams, and Tate [5], and the weight calculated from their values is 39.95_0. The accepted value is 39.944. The chemical weight computed from the abundance and the isotopic weights given by Pollard [10] is 39.94_9.

TABLE 3.—*Abundance of isotopes of argon*

	m/e		
	36	38	40
	Percent	*Percent*	*Percent*
This paper	0.35	0.08	99.57
Maximum deviation	±.01	±.01	±0.03
Vaughan, Williams, and Tate [8]	.307	.061	99.632

Table 4 lists the krypton isotopes and their respective abundance. Nier's values [3] converted from relative to percentage abundance are also included. The calculation of the chemical weight was made by using Aston's isotopic masses of krypton [11] and gives the value 83.80. Nier's

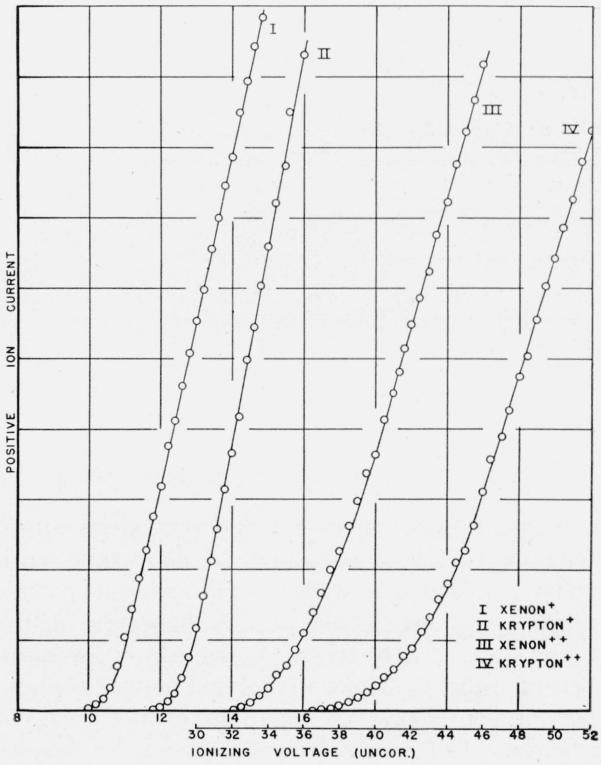

FIGURE 2.—*Initial portions of the ionization efficiency curves for the ions* Kr^+, Kr^{++}, *and* Xe^{++}.

The ordinate is arbitrary and different from some ions. The lower scale of the abcissa applies to curves III and IV.

values give a weight of 83.81. The accepted value is 83.7.

TABLE 4.—*Abundance of isotopes of krypton*

	m/e					
	78	80	82	83	84	86
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
This paper	0.36	2.25	11.57	11.44	57.14	17.24
Maximum deviation	±.01	±0.02	±0.04	±0.03	±0.03	±0.05
Nier [3]	.35	2.01	11.53	11.53	57.11	17.47

Table 5 lists the xenon isotopes and their respective percentage abundance. Again Nier's values [3] are included for comparison. The rather serious disagreement of the abundance of mass 130 may be due to the lower degree of resolution obtainable in the mass spectrometer used in this work compared to Nier's apparatus. Assuming a packing fraction of −5.3 [11] and

converting to the chemical scale, a weight of 131.3_2 is obtained. Nier's values give 131.29, and the accepted value is 131.3.

TABLE 5.—*Abundance of isotopes of xenon*

	m/e								
	124	126	128	129	130	131	132	134	136
	Per-cent	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*
This paper	0.102	0.098	1.93	26.51	3.68	21.04	27.12	10.54	8.98
Maximum deviation	±.009	±.003	±0.01	±0.02	±0.04	±0.09	±0.07	±0.05	±0.03
Nier [3]	.094	.088	1.90	26.23	4.07	21.17	26.96	10.54	8.95

3. Relative Ion Currents in Rare Gases

These measurements on the rare gases afford an opportunity to compare the ionization sensitivity for elements with a wide range of atomic number but similar electron configuration in the outer shell. "Sensitivity" is defined as the number of scale divisions of galvanometer defection per unit pressure (in microns) in the gas-inlet system. The sum of the deflections for all isotopes has been used, as in this case we are not concerned with the partial pressures of the separate isotopes. The pressure in the ionization chamber is probably very nearly proportional to the pressures in the inlet system. The ionizing electrons had an energy of about 70 v. Figure 3 and table 6 give data on sensitivity versus atomic number. The results indicate that there is not a simple relation between atomic number and sensitivity. Instrumental discrimination may slightly distort the relative values for light atoms as compared with heavy ones, but the effect would scarcely exceed a few percent.

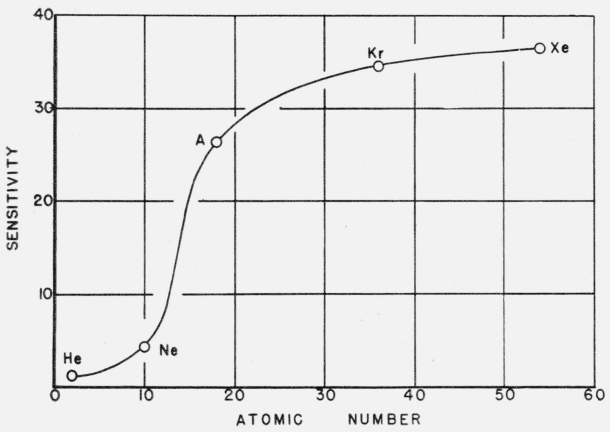

FIGURE 3.—*Number of recorder scale divisions per micron of sample pressure versus the atomic number for the singly charged ions of* He, Ne, A, Kr, *and* Xe.

Ordinates are the sum of deflections for all isotopes.

TABLE 6.—*Ion sensitivity of the rare gases as a function of the atomic number*

Ion	Atomic number	Sensitivity	
		Divisions/micron	Relative to helium
He^+	2	1.4	1.0
Ne^+	10	4.2	3.0
A^+	18	26.5	18.9
Kr^+	36	35.0	25.0
Xe^+	54	37.5	26.8

IV. References

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