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A MASS-SPECTROMETRIC INVESTIGATION OF SULFUR VAPOR AS A FUNCTION OF TEMPERATURE

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M Charles Zietz

(Thesis)

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A MASS-SPECTROMETRIC INVESTIGATION OF SULFUR VAPOR AS A FUNCTION OF TEMPERATURE

M. Charles Zietz
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ABSTRACT

A mass-spectrometric investigation was performed on sulfur vapor, which was in equilibrium with the condensed phase, in the temperature range of 120 to 210°C. The principal finding was that, in this temperature range, equilibrium sulfur vapor contains appreciable quantities of S_8, S_7, S_6, and S_5 only.

The sulfur vapor emanated as a small well-collimated molecular beam from a specially constructed source into an ionization chamber which was designed to exclude from analysis any sulfur vapor that had impinged on the walls or the hot electron filament. The ions were analyzed with a 6-in.-radius 60-deg.-deflection single-direction focusing mass spectrometer. The sulfur used for this study was purified by prolonged boiling with MgO followed by vacuum distillation.

In addition to establishing the principal species in the vapor phase, the results of this work provided essentially identical ionization potentials for S_8, S_7, S_6, and S_5 of 9.8 ± 0.4 ev. Also, the heat of vaporization of S_7 was calculated to be approximately

2.5 kcal greater than that of S_8. It was not possible to determine the quantitative composition of sulfur vapor. However, upper limits for S_8 and S_7 at 120°C of 86% and 14% respectively were obtained.

It is proposed that S_8 is the vaporizing species and that S_7, S_6, and S_5 result from dissociation of S_8, and that all four molecules have a ring configuration.

INTRODUCTION

Sulfur has been known since ancient times, and there are records of its use for medicinal and fumigation purposes at least as early as 1000 B.C. It was commonly used in the practice of alchemy, and in early times was referred to as "brimstone".[1]

Despite this long history of man's awareness of sulfur, the multitude of forms the solid liquid and vapor can assume have made it a frequent subject of investigation, and even with the tremendous advances in experimental techniques and apparatus during this century, there still exist fundamental gaps in our knowledge of sulfur. (For an excellent review article, written in 1955, see Gee.[2])

Perhaps least completely known is the composition of the vapor in equilibrium with the condensed phase. At sufficiently low temperatures the vapor presumably consists totally of S_8 molecules, and at sufficiently high temperatures it consists entirely of atomic sulfur. However, conclusions about the composition of the vapor between these temperature extremes have been almost exclusively by inference from vapor-density measurements.

The first of these measurements, in the temperature range of 300 to 850°C, was published in 1909 by Pruener and Schupp.[3] Braune, Peter, and Neveling believed Pruener and Schupp to be in error and in 1951 published vapor-density measurements for the temperature range 350 to 1000°C.[4] The results of both investigations could be interpreted only by assuming that the vapor composition was complex. Pruener and Schupp were able to explain their data by assuming the existence of S_8, S_6, and S_2, while Braune, Peter, and Neveling found it necessary to assume the existence of S_4 as well as S_8, S_6, and S_2 in order to explain their experimental results satisfactorily.

Guthrie, Scott, and Waddington[5] have calculated thermodynamic functions and the heat of formation of S_8 gas. In order to make these calculations for the full temperature range in which sulfur exists as a liquid, they extrapolated the equilibrium constants of Braune et al to obtain the partial pressures of S_8 in the equilibrium vapor, and also used the excellent total vapor pressure measurements of West and Menzies[6] in addition to spectroscopic data.

There have also been two mass-spectrometric investigations of sulfur vapor, one by Bradt, Mohler, and Dibeler,[7] and the other by Goldfinger, Ackerman, and Jeunehomme.[8] The work of Bradt and co-workers was in connection with a program to establish reference samples of natural isotopic abundance, so that sulfur vapor was investigated at only one temperature, 95°C. They evaporated sulfur from a few milligrams of coarse powder contained in a capillary tube inside a 6-mm tube that extended about 2 cm to the entrance port of the ionization chamber. The vapor pressure in the ionization chamber was less than 10^{-4} mm of Hg, and its temperature was 186° C. The results of their relative ion intensity measurements, recalculated for $S_8^+ = 100$, are given in column II of Table I. Bradt and co-workers also found appearance potentials of S_8^+ as 8.9 ± .2 ev, of S_2^+ as 8.3 ± .2 ev, and S^+ as approximately 2 ev greater than either of these. Their method consisted of plotting the current-voltage curves on semi-log paper and normalizing the ion current to unity at 50 ev. Then the value of the electron energy that corresponded to an ion current of

Table I

Ion intensities from Bradt, Mohler, and Dibeler and from Goldfinger, Ackerman, and Jeunehomme

Ion	Bradt et al.	Goldfinger et al.			
	Capillary Tube	Graphite Crucible	Two-Temperature Tube		
	T = 368°K	T = 330°K	T_1 = 345°K T_2 = 349°K	T_1 = 355°K T_2 = 360°K	T_1 = 380°K T_2 = 365°K
S_9^+		0.4			
S_8^+	100.0	100.0	100.0	100.0	100.0
S_7^+	6.1	0.5	56.1	11.0	12.4
S_6^+	59.2	15.0	151.0	89.8	64.8
S_5^+	96.2	24.0	48.8	39.0	≥ .6
S_4^+	150.0	47.0	112.0	42.3	60.7
S_3^+	87.0	20.0	65.9	39.8	33.1
S_2^+	1850.0	77.0	488.0	169.0	138.0
S_1^+	250.0	11.0	166.0	38.1	22.0

0.3% of the 50-volt value was chosen as the appearance potential. This value was corrected for contact potentials obtained from the difference between the appearance potential and the ionization potential of mercury vapor, which was introduced with the sulfur vapor. There were variations in the slopes of these appearance-potential curves which led the investigators to report additional uncertainties in the above values. Bradt and co-workers concluded that S_8 and S_2 were present in their ionization chamber. Whether or not neutral species corresponding to the other ions were present could not be decided.

The efforts of Goldfinger and co-workers were primarily directed toward studying the vaporization of compounds and alloys at high temperature and the dissociation of these vapors. They studied sulfur vapor to facilitate their interpretation of the evaporation behavior of sulfur compounds. Two types of evaporation systems were used. In one, the sulfur vapor originated from an open graphite crucible, and in the other, the vapor passed through a 0.15-mm-diameter orifice in a two-temperature tube furnace. The graphite crucible data are given in Table I, column III, and a portion of the two-temperature-tube data in columns IV, V, and VI. To permit ready comparison, all data not based on $S_8 = 100$ have been recalculated on that basis. Goldfinger et al. stated, "It seems fairly certain that a considerable part of the ionic intensities of S_8^+, S_7^+, S_6^+, and S_2^+ are due to ionization of parent molecules," and "probably most of the ionic species result from direct ionization of the parent molecules and not from electron fragmentation."

The results of these several studies of the vapor of sulfur have led the various investigators to the conclusion that some complex mixture of polyatomic molecules is present, but the exact nature of this mixture has remained quite uncertain.

The object of this investigation was, therefore, to attempt to determine directly the composition of saturated sulfur vapor as a function of temperature.

EXPERIMENTAL APPARATUS

Mass Spectrometer

A 6-inch-radius, 60-deg deflection, single-direction focusing mass spectrometer was the analytical instrument used for this investigation. The magnetic field of this mass spectrometer was provided by a continuously variable electromagnet capable of producing a maximum field of 9300 gauss across a 9/16-in. gap. The accelerating voltage was provided by a well-regulated 3-kv power supply, which also provided voltages for drawing ions from the ionization chamber and for focusing these ions. The ions could be positioned after the magnetic deflection by two electrostatic deflection plates. The ion detector was a sixteen-stage electron multiplier (developed at this Laboratory by Reynolds[9]) terminated by a 10^9-ohm resistor. The voltage across this resistor was measured by a vibrating-reed electrometer which drove a recording strip-chart potentiometer.

Vacuum System

The vacuum system is shown schematically in Fig. 1. The purpose of the water-cooled baffle directly over the jets of the diffusion pump was to reflux a large portion of the mercury, so that the pump did not become inoperative, owing to Hg on the CO_2 trap, until after a reasonable period of about 10 days. The position of the ion gauge was dictated by convenience, and it is believed that at worst the gauge indicated the pressure in the mass spectrometer to within an order of magnitude. The indium valve (developed by Reynolds[10]) was not usable, as the indium

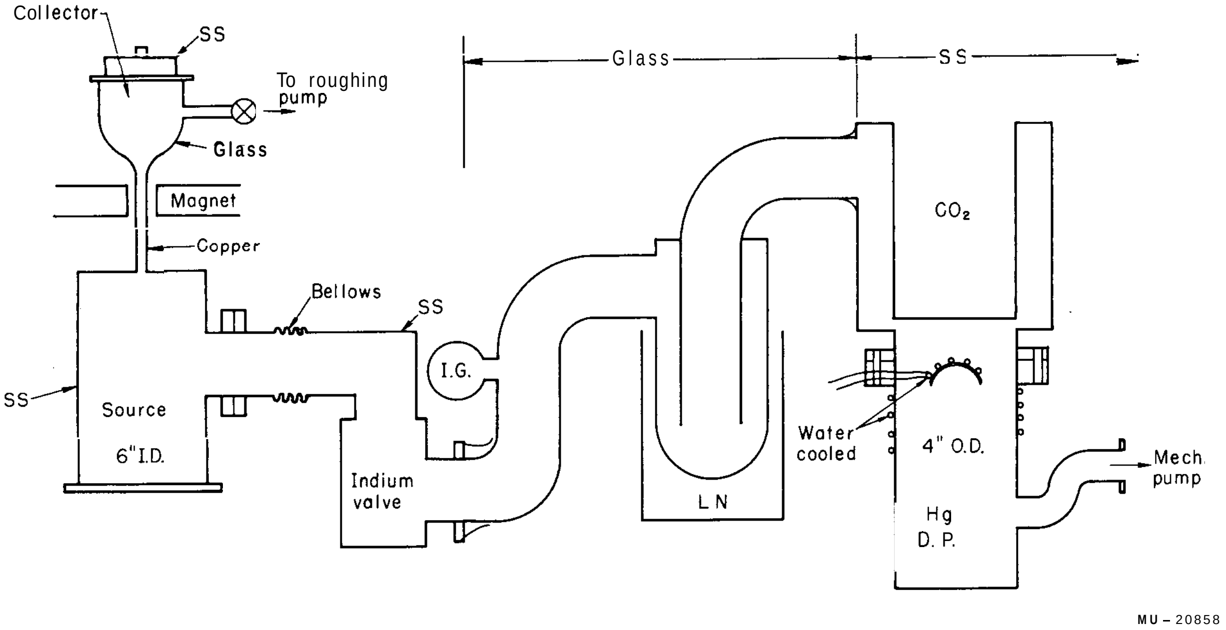

Fig. 1 Vacuum **system.**

sulfide that formed made it impossible to achieve a leak-tight seal.

The source envelope was a 6-in.-diameter cylinder, 13-in. long, with three 2-1/2-in.-diameter sidearms. One served as the exhaust port, the second had eleven Kovar electrical lead-throughs soft-soldered into a copper plate, and the third had a pyrex window. Flanges were heliarc-welded to both ends of the cylinder, one of which was bolted to a flanged plate hard-soldered to the 1-in. copper tube that was flattened to pass between the poles of the magnet.

The pyrex envelope surrounding the electron multiplier was attached to the copper tube by a graded seal. The envelope had tungsten lead-throughs for connection to the deflection plates, a 3/4-in. pumpout tube for use in conjunction with the indium valve, and was terminated in a 4-in. industrial glass pipe flange. Attached to this was a "hat" to which the multiplier was rigidly affixed. This hat had 16 Kovar lead-throughs around its circumference, a large teflon lead through in its top for the output current, and was covered with a brass cylinder for electrical shielding.

All demountable metal-to-metal seals were made with knife-edge-sealed copper gaskets 1/4 x 1/4 in. in cross section, and all demountable glass-to-metal seals were made with indium O rings. Both the copper and indium gaskets were reusable. The source envelope was wrapped with heating tape for outgassing purposes.

Ionization Chamber

The ionization chamber, shown in Fig. 2, was designed to minimize contributions to the ion current that could originate from

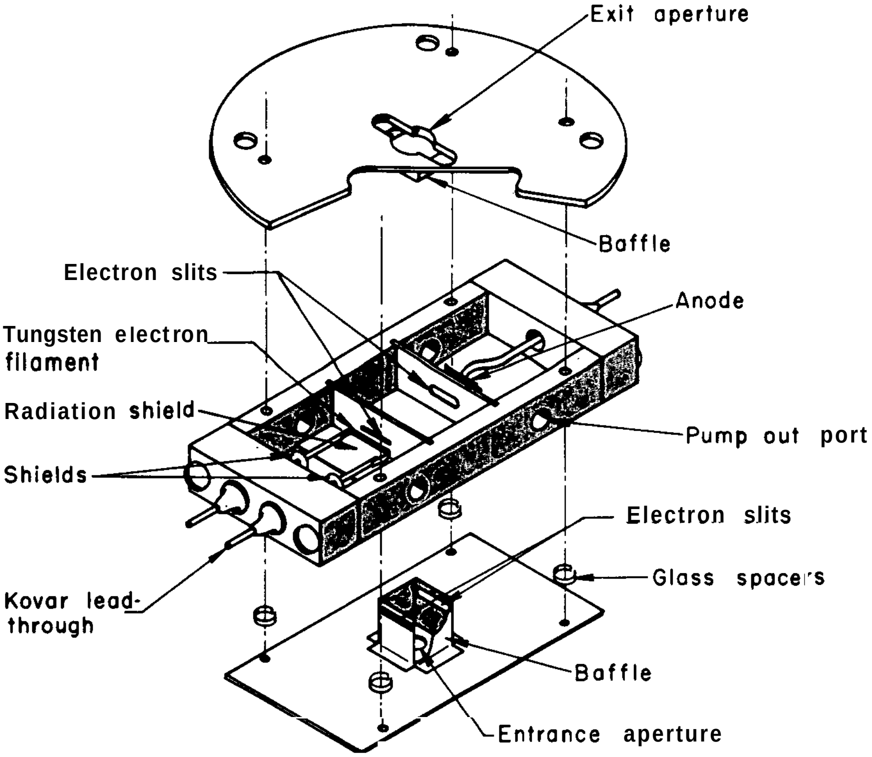

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Fig. 2. Ionization chamber.

the walls or from the hot electron filament. The chamber was provided with baffles and a "back door" that was larger than the "front door." In addition, it was in thermal isolation and was shielded from the hot filament. (For an interesting example of the effect of a hot filament in dissociation of gas molecules, see Kane's work on arsenic and red phosphorus.[11]) The ionization chamber was constructed of stainless steel, and all its interior surfaces were gold plated to minimize secondary electron emission.

The ionizing electrons were collimated by a remarkably efficacious external alnico V magnet with an effective field of only about 50 gauss. The electron slits were made progressively larger between the cathode and the anode to minimize electron-bombardment heating and to maximize the anode current. Shields were spot-welded to the filament leads to prevent electrical leakage caused by conductive deposits on the glass insulation. The electron emission was electronically regulated by controlling the temperature of the filament to maintain a constant anode current, which could be varied from 1 to 100 microamperes. The electrons were accelerated by applying a potential, continuously variable from negative values to 125 volts, between the filament and the closest slit. The voltage was read with two meters: a 150-volt full scale meter for the higher voltages, and a meter accurate to 0.5%, with a mirror to reduce parallax reading error, for the critical region of 15 volts or less. The entire ionization chamber was floated at the full accelerating voltage.

Sulfur Source

The sulfur source shown in Fig. 3 was developed for the purpose of providing a small well-collimated molecular beam obtained directly from the vapor in equilibrium with the condensed phase. The sulfur container, which was 1 in. long and had an inside diameter of 0.090 in., was made of aluminum to provide the thermal conductivity necessary for uniform temperature and to avoid any sulfur reactions. (The experience of Prins is that the only convenient materials with which sulfur will not react are aluminum and lithium glass.)[12] Restriction of the diameter of the effusion opening to 0.004 in. provided a ratio of areas of approximately 2×10^{-3}, so that there was reasonable assurance that the effusing vapor had equilibrated with the condensed phase. (The effect on sulfur vapor at moderate temperatures of a deviation from equilibrium conditions, as pointed out by Guthrie, Scott, and Waddington,[5] is to increase the percentage of S_8 in the vapor.) The length of the effusion channel was 0.008 in. But at the small angle to the normal subtended by the collimated beam, the angular distribution of molecules is essentially unchanged from that for an orifice of infinitesimal channel length.[13]

The bottom of the container was a tapered plug which had an iron-constantan thermocouple spot-welded into a slot, and was mounted on a separate flange by a 2-3/8-in.-long stainless steel and ceramic support rod. The stainless caps were attached to the ceramic by using the thermal expansion of the stainless steel to

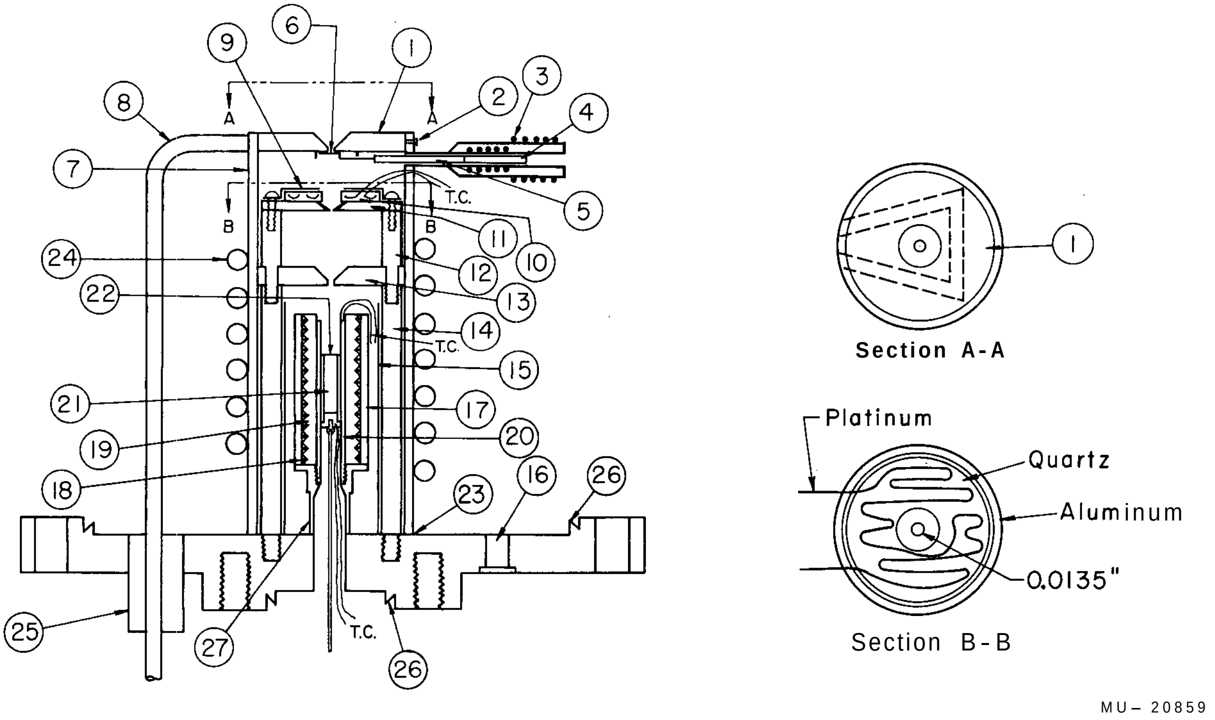

Fig. 3. Sulfur source (Identification on following sheet)

(1) 1/4-inch copper disc, 1/16-in. hole bored for passage of refrigerant

(2) Set screws to align disc (four)

(3) Coaxial solenoids

(4) 1/8 in. iron rod

(5) Stainless tube

(6) Shutter

(7) 1/16-in.-thick copper cylinder

(8) 1/4-in. copper tube for refrigeration

(9) Stiff aluminum foil to hold heater (attached under screws)

(10) Quartz sandwich heater containing Pt wire

(11) Aluminum disc with 13-1/2-mil collimating slit

(12) Stainless steel support rod (three)

(13) 1/4-in. copper disc with 1/8-in. hole (hard-soldered to jacket)

(14) Stainless steel support rod (three)

(15) Tantalum radiation shield

(16) Kovar lead-throughs (eleven)

(17) Ceramic cylinder

(18) Molybdenum wire

(19) Threaded ceramic cylinder

(20) Aluminum tube

(21) Aluminum container

(22) 4-mil hole in 8-mil-thick base

(23) Copper jacket touching base plate in only three places (each 1/2-in. long)

(24) Copper cooling coils soft-soldered to jacket

(25) Well for refrigeration coils

(26) Vacuum seal

(27) Stainless steel stool

achieve a quite tight shrink fit. Because the sulfur container was mounted on a separate plate, it could be removed without disturbing the rest of the source. The emf of the thermocouple, which was held at a 0°C reference temperature in an ice bath, was measured with a Rubicon potentiometer and galvanometer capable of easily detecting microvolt changes.

The heating unit had a large heat capacity to provide thermal stability, and contained a central aluminum tube to facilitate the attainment of a uniform temperature region as well as for the reasons given above. The actual heat capacity was not determined; but before the temperature of a dummy container reached 400° C during preliminary outgassing of the system, the initial nichrome heating element burned out. In fact, this occurrence raised the question whether there was good thermal contact between the tube and the container, which led to insertion of the iron-constantan thermocouple at the top edge of the 2-in.-aluminum tube. The stainless steel support stool was necked down to decrease heat leakage, and had pumpout holes to improve the outgassing character istics of the structure.

The copper jacket and two copper discs were refrigerated by pumping alcohol, cooled to below -50°C by solid carbon dioxide, through the top disc and through the coils soft-soldered to the jacket. The cold surfaces were to trap the sulfur that did not pass through the three collimating slits, and thus to prevent contributions to the molecular beam from sulfur at temperatures different from those that existed in the aluminum container. This alcohol refrigeration system is shown schematically in Fig. 4.

Initially, the heated aluminum slit was not included in the system and the lower copper disc had a 0.0135-in. hole. However, this hole became plugged by condensed sulfur quite quickly and was therefore enlarged to 1/8 in. and the heated aluminum disc with its 0.0135-in. hole was added for collimating purposes. The aluminum disc was heated by a platinum element encased in a quartz sandwich, and its temperature was measured by a spot-welded Pt-Pt-13% Rh thermocouple. The emf of this thermocouple and of the tube's thermocouple were measued with a "student" potentiometer without physical 0°C reference. The shutter, whose action depended upon the centering of the iron rod in whichever of the coaxial solenoids was energized, was developed by Werning at this Laboratory[14]. Ideally, the shutter should have been placed directly over the aluminum container opening, but this placement would have been extremely difficult.

To locate the sulfur source in such a way as to minimize the probability that the molecular sulfur beam would impinge upon the exit plate of the ionization chamber, the flanged plate upon which the source was mounted was first loosely attached to the flange on the bottom of the 6-in.-diameter cylinder. Than, the sulfur container and its supporting flanged plate were removed to permit insertion of a fairly rigid 0.0135-in.-diameter wire through the three source slits. The protruding portion of this wire was caused

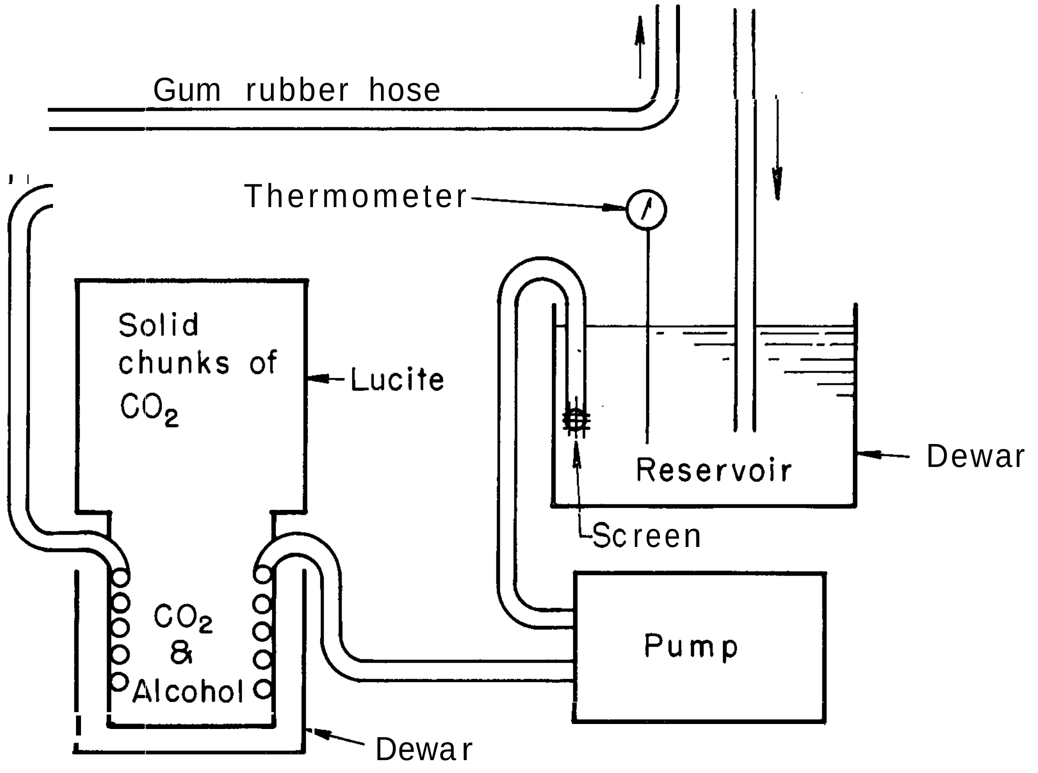

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Fig. 4. Alcohol refrigeration system.

to pass through the center of the entrance hole in the ionization chamber by movement of the entire source plate. The looseness of the bolts in their bolt holes was sufficient to permit this alignment because of the previous alignment and centering of the three source slits, and the centering of the ionization chamber within the 6-in. cylinder (made facile by virtue of the ductility of the copper tube to which the ionization chamber was attached). Rotating the aligning wire corrected for its eccentricity, and a sufficient length of wire passed beyond the entrance plate of the ionization chamber to reach the mass spectrometer's resolving slits.

SULFUR PURIFICATION

According to Bacon and Fanelli[15], the optimal method of purifying sulfur is by prolonged boiling with MgO. Prins[12] has found that if, following Bacon and Fanelli's procedure, the sulfur is vacuum distilled, its purity is further increased. As evidence of the purity, Prins has found that quenched plastic sulfur can exist in this metastable state at room temperature for as long as a year owing to the absence of nucleation centers. Parenthetically, it is unfortunate that Meyer and Go[16] were not aware of this stability of the metastable state, for they went to great lengths to perform an x-ray diffraction analysis of plastic sulfur as it was pulled from the liquid, a procedure they adopted because of the then well-known instability of the plastic state.

The sulfur used for this study, which had a minimum initial purity of 99.7% was kindly furnished by Stauffer Chemical Company. The procedure of Bacon and Fanelli was carefully followed, with all but the final 30-hour boiling done in liter boiling flasks whose necks were extended 12 in. Sulfur vapor would condense in the neck and could be refluxed by gentle heating. The final boiling was done in an open aluminum pot which was fitted with a long glass chimney. This glass chimney was sealed to the aluminum by a layer of asbestos under a coating of plaster of Paris to prevent escape of hot sulfur vapor. It was found that if the hot vapor was allowed to escape, it would ignite, whereas this problem was not present for cooled vapor.

The sulfur was filtered into the distillation apparatus, shown in Fig. 5, after this final boiling. This apparatus was evacuated

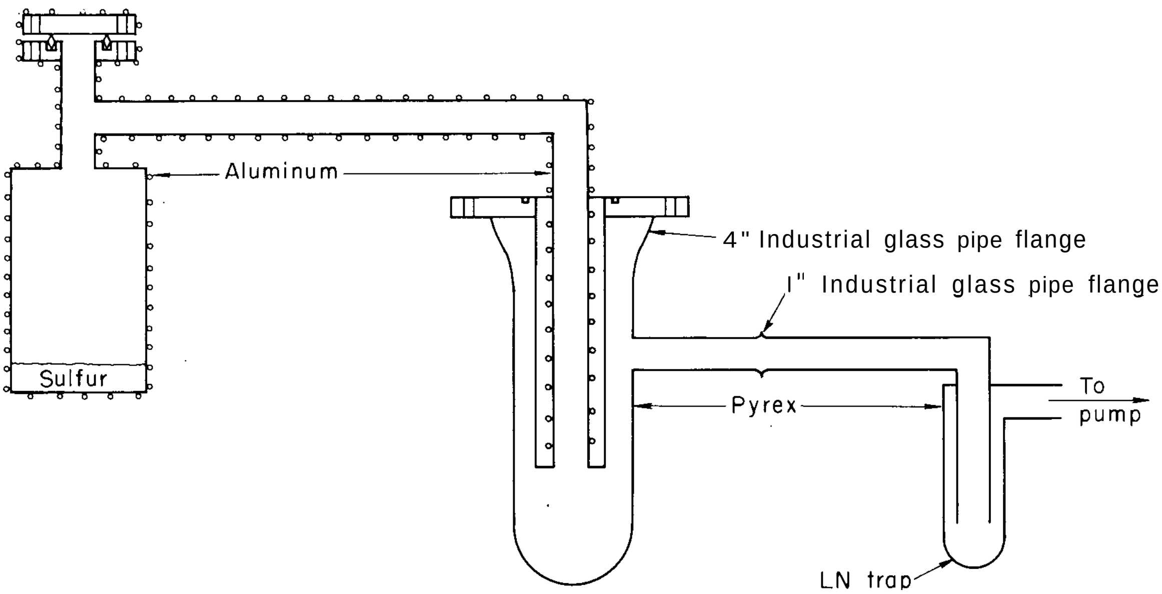


Fig. 5. Sulfur distillation apparatus.

to about 15 microns, then a slightly positive pressure of argon was introduced, and the system was sealed. The purified sulfur was left under argon for about two years, as it seemed desirable to defer the vacuum distillation until the highly purified sulfur was to be used. (experimental problems arose that were not quickly resolved).

EXPERIMENTAL TECHNIQUE

Preparation

The vacuum system was outgassed, with an empty container and the hot slit first heated to 200°C without cooling the copper discs and jacket, and then heated to 450°C with the copper cooled to prevent melting the soft-soldered connections. During this outgassing period, the envelope of the source, with the exception of the indium gasketed window, was heated to 200°C. The lowest pressure indicated by the VG1A ionization gauge was 7×10^{-8} mm of Hg, with pressures being more commonly on the 10^{-7} mm scale.

Purified sulfur was evaporated, condensed at 0°C, and tested for purity by pouring a small portion, which had been heated past the polymerization temperature, onto a transite table top and observing that it retained the dark brown color characteristic of plastic sulfur. When the sample was cool enough to touch, the plasticity was verified, but the handling caused it to transform into its stable structure. A previously outgassed container was filled from the bottom with this sulfur, and the tapered plug forced into it. The thermocouple was spot-welded in the slot in the plug, and the container was screwed onto the stainless steel and ceramic support rod. This rod was screwed into the flanged mounting plate of the container and the thermocouple leads were spot welded to Kovar lead-throughs soft soldered in the plate. The container was slid into the aluminum tube and its supporting plate was bolted to the mating portion of the source plate.

When the pressure in the system was low enough to permit turning on the electron filament, the external alnico V magnet was aligned to maximize the anode current. The net effect of this magnet was to increase the current to the anode by an order of magnitude at a given filament temperature when the electron energy was 75 volts, and by a greater amount when the electron energy was reduced to lower values. The collimated electron current to the anode was set at twenty microamps.

With the electron filament on, the source envelope heated to 200°C, and a pressure in the vacuum system of 10^{-6} mm of Hg or better, the sulfur container was heated to approximately 93°C and allowed to outgas at that temperature for 24 hours. During early work, large jumps of the pressure and of the sulfur ion currents were observed in the vicinity of 119°C, unless previously unheated sulfur was allowed to outgas thoroughly before it was melted. In order to see what was happening, a container of sulfur was heated rapidly in an evacuated bell jar, and it was observed that a "plug" of sulfur "climbed" out of the hole in the container, then "sat" on top of the container and bounced away from the hole and back over it several times. Each time the hole became unplugged a burst of vapor would come out and leave a white deposit on the walls of the bell jar. As the temperature was raised, the plug liquefied and spread out across the top of the container. When another container of sulfur was heated slowly, no plug appeared, and the deposit on the inside of the bell jar built up gradually.

The explanation of this phenomenon is that the first melting of sulfur occurs on its surface, and because this liquid wets the aluminum container walls, it forms a rather impervious barrier to the gas that is desorbed from the balance of the sulfur when it melts. Then, the gas expands and forces liquid sulfur out the hole, where it solidifies forming a plug. As this gas, augmented by sulfur vapor and gas desorbed from the container, builds up pressure, the plug acts like a valve, and the pressure required to actuate it is sufficiently large to cause the observed cyclic behavior which continues until most of the gas escapes.

To prevent evaporation of sulfur from the top of the container and to avoid premature loss of sample, it was essential that the sulfur be outgassed below its melting point. The criterion for adequate outgassing was the complete absence of irregular increases in the ion current and in the pressure when the temperature of the sulfur container passed through 119°C. A by-product of the plugging phenomenon was that its association with the melting of sulfur served to establish the accuracy of temperature measurements as ± 0.5° at 119°C.

The alcohol refrigeration system was turned on at least one hour before any data was taken, and the electronic components of the mass spectrometer were allowed to warm up for approximately 1 hour, with the ion accelerating potential set at 2 kv and the potential across the 16 stages of the electron multiplier at 2.3 kv (providing a current gain of approximately 10^5). During this warm up period, the hot slit was heated (its temperature was always at least 25°C greater than that of the container and was never less than 200°C).

Measurements

The effect of temperature on the ion currents of sulfur was observed under essentially static and also under dynamic conditions. For static measurements, time was allowed for the temperature of the sulfur to become fairly stable, whereas the dynamic conditions entailed a rate of temperature change varying from .25 to 4 deg. per minute. Measurements were also made, at constant temperature, of the dependence of the ion currents on the energy of the ionizing electrons.

Prior to all measurements, the mass spectrometer was focused by first manually increasing the electromagnet current to its maximum value and decreasing it to provide the magnetic field required to cause the $(S^{32})_8^+$ ions to strike the first stage of the multiplier. Then, this ion current was optimized by coincident adjustment of the drawing out, beam focusing, and receiver deflection voltages, and the magnetic field.

The reason for saturating the magnet before focusing the mass spectrometer was to cause the magnet to operate on the upper portion of its hysteresis curve, which was necessary to obtain reproducible ion currents. The influence on the ion currents of the previous history of the magnet was probably due to changes in the stray magnetic field which could conceivably affect the magnetic focusing of the ions, the gain of the electron multiplier, and the path of the ionizing electrons.

To obtain the "static" temperature dependence, time was allowed for the temperature of the sulfur to become fairly stabile, and the S_8^+ ion current was focused as described above. Then, in sequence, the S_7^+, S_6^+, S_5^+, S_4^+, S_3^+, and S_2^+ ion peaks were measured, the magnet was saturated, and the S_8^+ peak was remeasured. For each peak, focusing was accomplished by adjusting the magnetic field and receiver deflection voltage to optimize the $(S_x^{32})^+$ ion current, and measurements were made with the shutter open and closed, except when previous measurements had shown the "closed" peak to be zero. The time required to scan the spectrum in this fashion was usually about 15 minutes.

The procedure followed in observing the effect of changing temperature on sulfur ion currents was to heat the sulfur, allow its temperature to become stabile, and focus the mass spectrometer on a S_x^{32} ion peak. Then, the sulfur was cooled and heated while the emf of the Rubicon potentiometer was set for intervals of 2°C, and the temperature was recorded on the strip chart as the galvanometer light passed through zero. The shutter was closed about every 10° to determine the background peak. The ion peak was refocused, during a heating and cooling run, only when it became apparent that refocusing was essential. This procedure was repeated for each sulfur ion. The usual rate of temperature change was between 2 and 2.5° per minute. The energy of the ionizing electrons was 74 volts for both of these sets of measurements.

The electron energy dependence was also obtained for one S_x^{32} ion at a time, with periodic measurement of the background peak, and the ion current refocused as infrequently as drift of the mass spectrometer would permit. The time required to accumulate sufficient information for an appearance potential curve was of the order of 25 minutes, during which time the variation of temperature was usually less than 1° (the largest change was 2°C).

Throughout this work, the background ion currents, except for S_2^+ and S^+, were quite small. At the beginning of a day's measurements the background peaks would be less than the high-temperature 75-volt ion currents by at least an order of magnitude, and within an hour would decrease by another one or two orders of magnitude.

EXPERIMENTAL RESULTS

All the data reported were obtained with a single container of sulfur and except where noted are net ion currents (i.e. the difference between measurements made with the shutter open and closed). The "static" temperature dependence measurements are presented as ratios with respect to S_8^+: in the chronological order taken in Table II, and graphically in Figs. 6, 7, and 8. These ratios were calculated with respect to the first S_8^+ peak measurement, so that the last column in Table II is a measure of the reproducibility (or lack of it) of the S_8^+ ion current. The lines drawn to correlate the data in Figs. 6, 7, and 8 favor the higher values of the ratios. Because the maximum value of the S_8^+ ion current peak could be obtained more consistently than the maximum values of the lower mass ion current peaks, the scatter of the data would not be random. Another reason for choosing the higher values of the ratios is presented in the general discussion section.

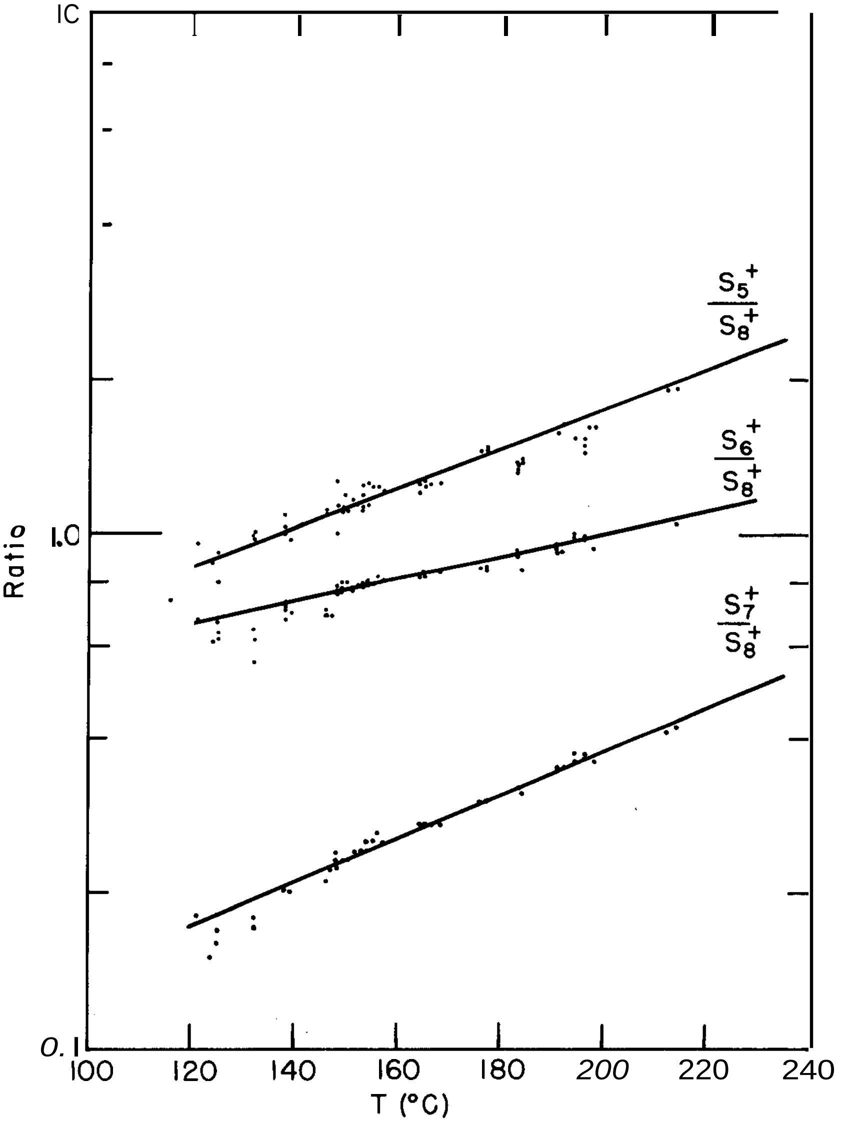
The measurements taken during heating and cooling, presented as logarithmic plots with respect to 1/T in Figs. 9 through 15, are only a fraction of those obtained. However, the measurements shown were those taken over the largest temperature range and generally had the best agreement between points obtained during heating and cooling. The electron energy dependence of the sulfur-ion currents is presented graphically in Figs. 16 through 22, and Figs. 23 and 24 are of the electron energy dependence of the background S_2^+ and Hg^{204} ion currents respectively (all of these ion currents have been normalized to 2000 at 74 ev).

Table II

S_x^+/S_8^+ Ratios

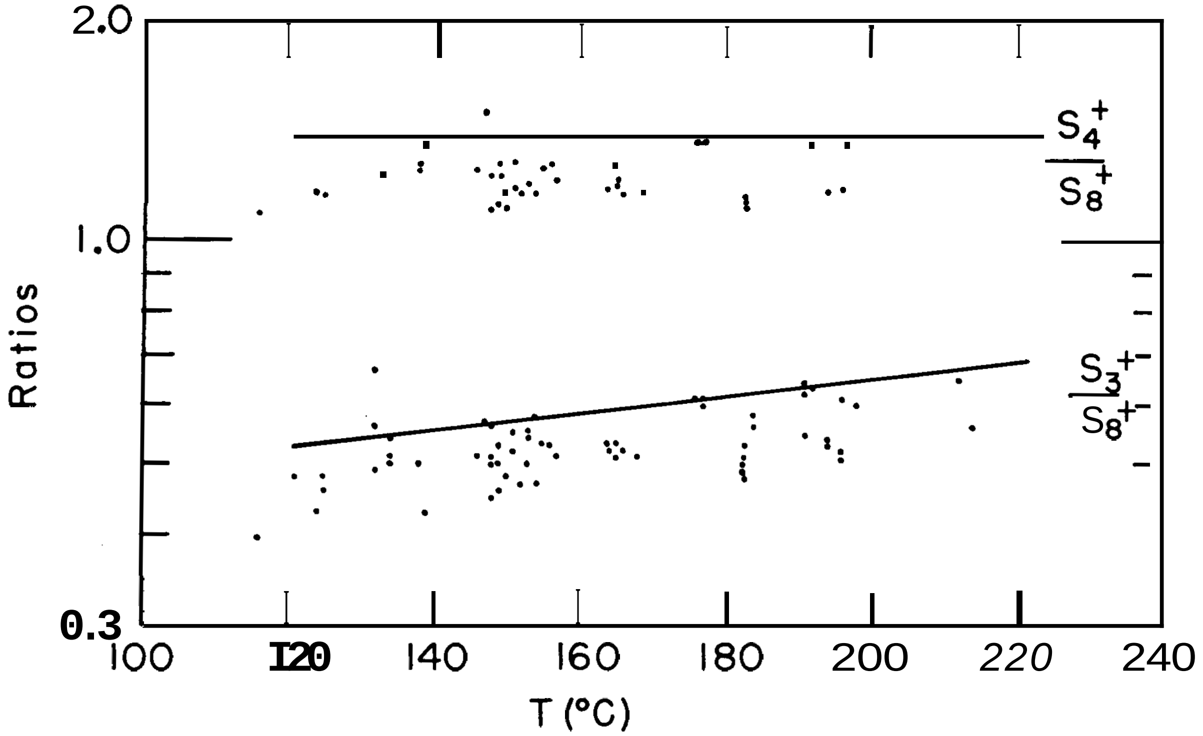
Temp	S_x^+						
(°C)	S_7^+	S_6^+	S_5^+	S_4^+	S_3^+	S_2^+	S_8^+
116	0.07	0.44	0.74	1.09	0.40	1.31	0.97
124	0.15	0.61	0.88	1.17	0.43	1.31	1.00
125	0.16	0.62	0.80	1.04	0.48	1.44	0.94
125	0.17	0.67	0.92	1.24	0.48	1.42	0.98
121	0.18	0.68	0.96	1.27	0.48	1.43	1.04
125	0.18	0.64	0.92	1.16	0.46	1.18	----
132	0.17	0.65	1.04	1.56	0.67	1.77	1.25
132	0.17	0.56	0.98	1.21	0.49	1.30	0.81
132	0.18	0.62	0.99	1.32	0.56	1.51	0.95
138	0.20	0.68	1.00	1.25	0.50	1.41	1.04
138	0.20	0.71	1.08	1.31	0.54	1.46	0.98
138	0.20	0.72	1.09	1.35	0.52	1.48	0.98
146	0.21	0.69	1.08	1.25	0.52	1.43	----
147	0.21	0.69	1.26	1.51	0.57	1.57	1.08
146	0.21	0.71	1.12	1.25	0.52	1.39	0.95
153	0.24	0.80	1.18	1.32	0.55	1.42	1.01
154	0.24	0.80	1.25	1.36	0.58	1.47	1.00
153	0.24	0.78	1.24	1.30	0.54	1.43	0.97
155	0.25	0.79	1.23	1.26	0.53	1.37	1.02
148	0.24	0.76	1.00	0.99	0.41	1.07	0.86
148	0.23	0.78	1.08	1.14	0.45	1.18	0.88
148	0.23	0.76	1.14	1.23	0.50	1.48	0.90
149	0.23	0.77	1.18	1.28	0.53	1.39	1.02
149	0.23	0.78	1.13	1.23	0.50	1.35	1.02
149	0.23	0.77	1.11	1.18	----	1.26	0.97
156	0.26	0.82	1.23	1.27	0.53	1.28	1.04
157	0.25	0.81	1.21	1.22	0.51	1.33	1.00
150	0.23	0.80	1.11	1.14	0.48	1.25	0.95
149	0.23	0.80	1.13	1.16	0.46	1.26	0.98
148	0.22	0.77	1.14	1.34	0.56	1.57	1.06

Temp	S_x^{+}						
(^{o}C)	S_7^{+}	S_6^{+}	S_5^{+}	S_4^{+}	S_3^{+}	S_2^{+}	S_8^{+}
151	0.23	0.77	1.17	1.28	0.55	1.45	1.06
151	0.23	0.78	1.14	1.22	0.52	1.38	1.02
153	0.24	0.78	1.13	1.23	0.50	1.35	1.00
164	0.27	0.83	1.25	1.26	0.52	1.40	1.01
164	0.26	0.82	1.20	1.21	0.53	1.34	0.99
165	0.27	0.82	1.23	1.22	0.51	1.35	1.00
154	0.25	0.79	1.13	1.16	0.47	1.26	0.95
152	0.24	0.79	1.14	1.19	0.47	1.32	1.00
165	0.27	0.84	1.27	1.25	0.53	1.34	1.06
166	0.27	0.84	1.25	1.19	0.52	1.35	1.01
168	0.27	0.84	1.26	1.20	0.51	1.34	1.01
139	0.20	0.70	0.97	1.09	0.43	1.24	0.96
138	0.20	0.73	1.04	1.27	0.50	1.30	0.98
176	0.30	0.86	1.45	1.37	0.61	1.61	1.04
177	0.30	0.85	1.45	1.36	0.60	1.55	1.01
177	0.30	0.86	1.46	1.37	0.61	1.55	1.00
184	0.31	0.85	1.38	1.22	0.56	1.39	0.83
184	0.31	0.85	1.39	1.30	0.58	1.50	1.04
183	0.32	0.91	1.36	1.17	0.53	1.37	1.01
183	0.32	0.92	1.37	1.14	0.51	1.34	1.02
183	0.32	0.91	1.34	1.13	0.50	1.26	0.99
183	0.32	0.93	1.35	1.10	0.49	1.22	1.01
183	0.32	0.92	1.33	1.11	0.48	1.23	1.00
194	0.36	1.00	1.53	1.20	0.54	1.35	1.08
196	0.36	0.99	1.48	1.17	0.52	1.27	1.02
196	0.37	0.98	1.44	1.13	0.51	1.24	1.00
194	0.37	0.99	1.54	1.16	0.53	1.34	1.05
192	0.35	0.93	1.63	1.42	0.63	1.52	1.03
191	0.35	0.93	1.57	1.37	0.62	1.48	1.00
198	0.36	0.94	1.62	1.33	0.60	1.47	0.97
191	0.35	0.94	1.66	1.39	0.64	1.56	1.02
196	0.36	0.99	1.69	1.39	0.61	1.50	1.06
191	0.35	0.96	1.56	1.25	0.55	1.30	----
212	0.41	1.04	1.91	1.47	0.65	1.60	1.01
214	0.42	1.05	1.92	1.46	0.56	----	----



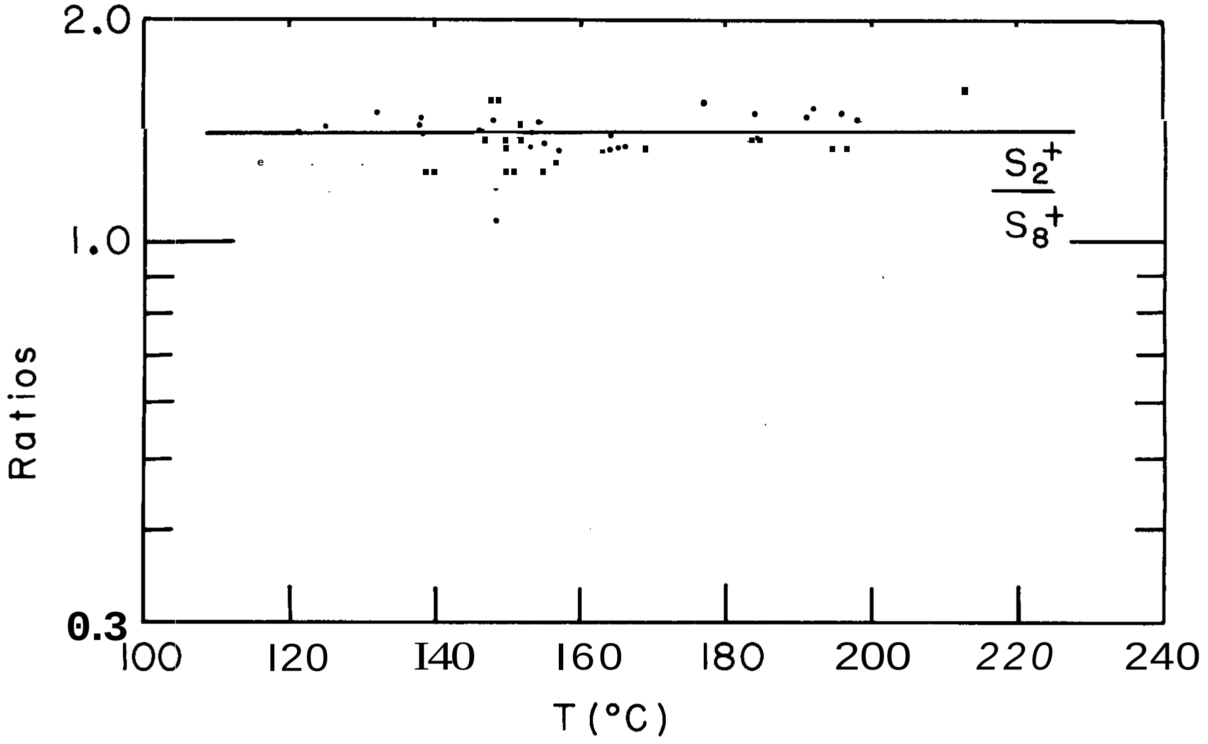
MU-20862

Fig. 6. Ratio of S_7^+/S_8^+, S_6^+/S_8^+, and S_5^+/S_8^+ as a function of temperature. Electron energy = 74 volts.



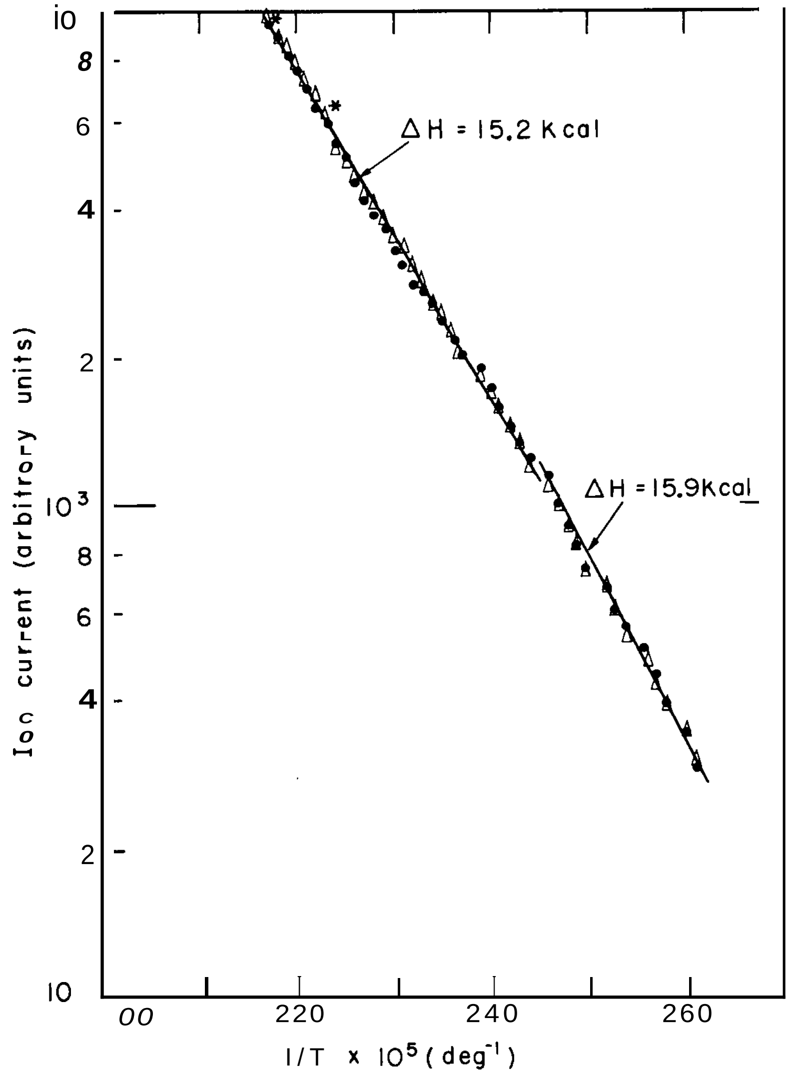
MU-20863

Fig. 7. Ratios of S_4^+/S_8^+ and S_3^+/S_8^+ as a function of temperature. Electron energy = 74 volts.



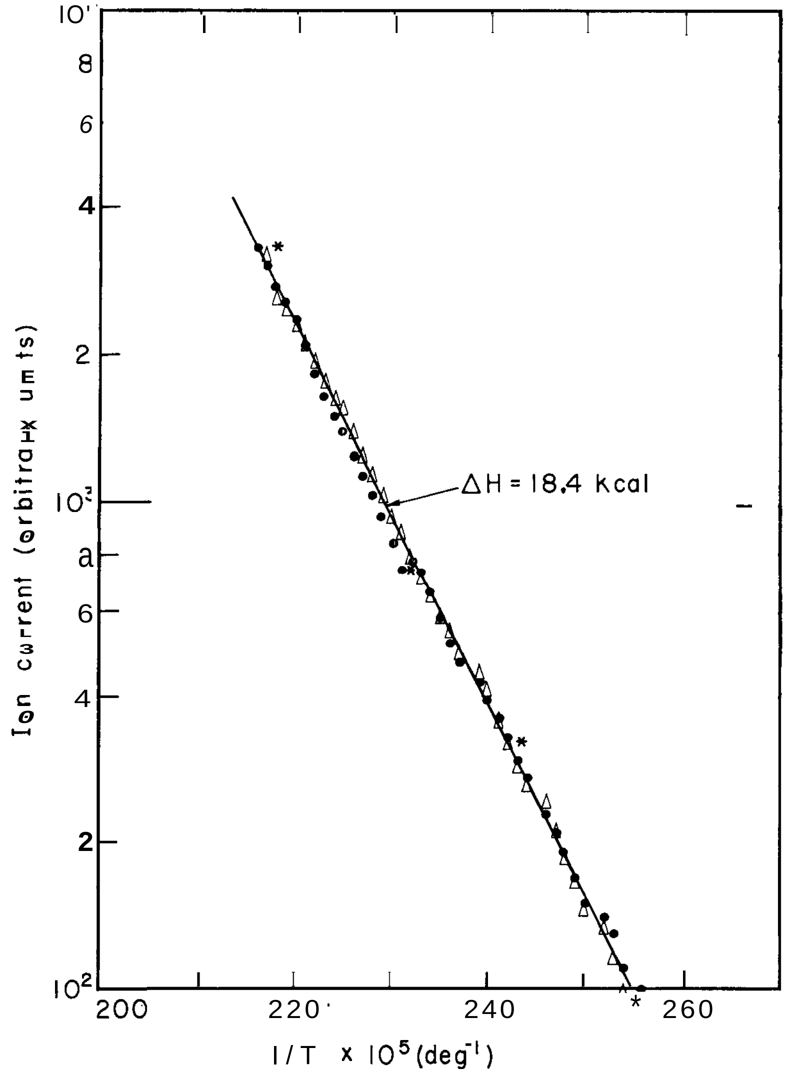
MU-20864

Fig. 8. Ratio of S_2^+/S_8^+ as a function of temperature. Electron energy = 74 volts.



MU-20976

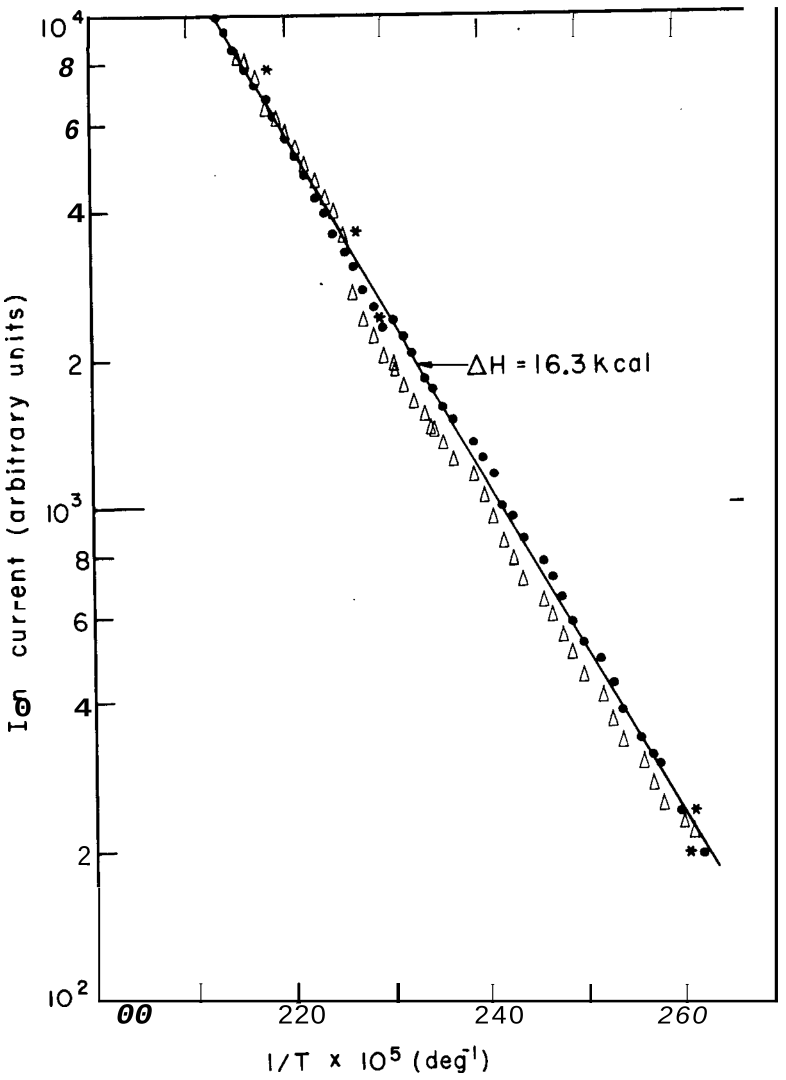
Fig. 9. **Log** of S_8^+ ion current vs 1/T.
A = heating
● = cooling
* = magnetic field adjusted
Electron energy = **74** volts.



MU- 20977

Fig. 10. Log of S_7^+ ion current vs 1/T.

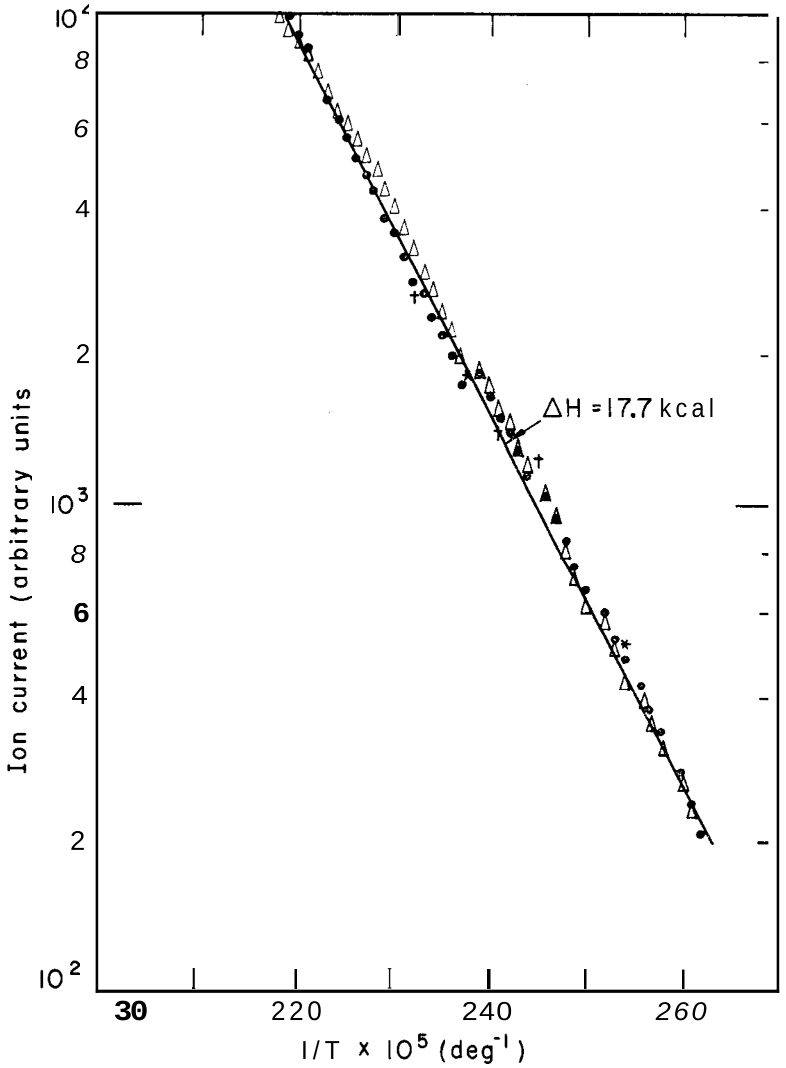
A = heating
● = cooling
* = magnetic field adjusted
Electron energy = 74 volts.



MU-20978

Fig. 11. Log of S_6^+ ion current vs 1/T.

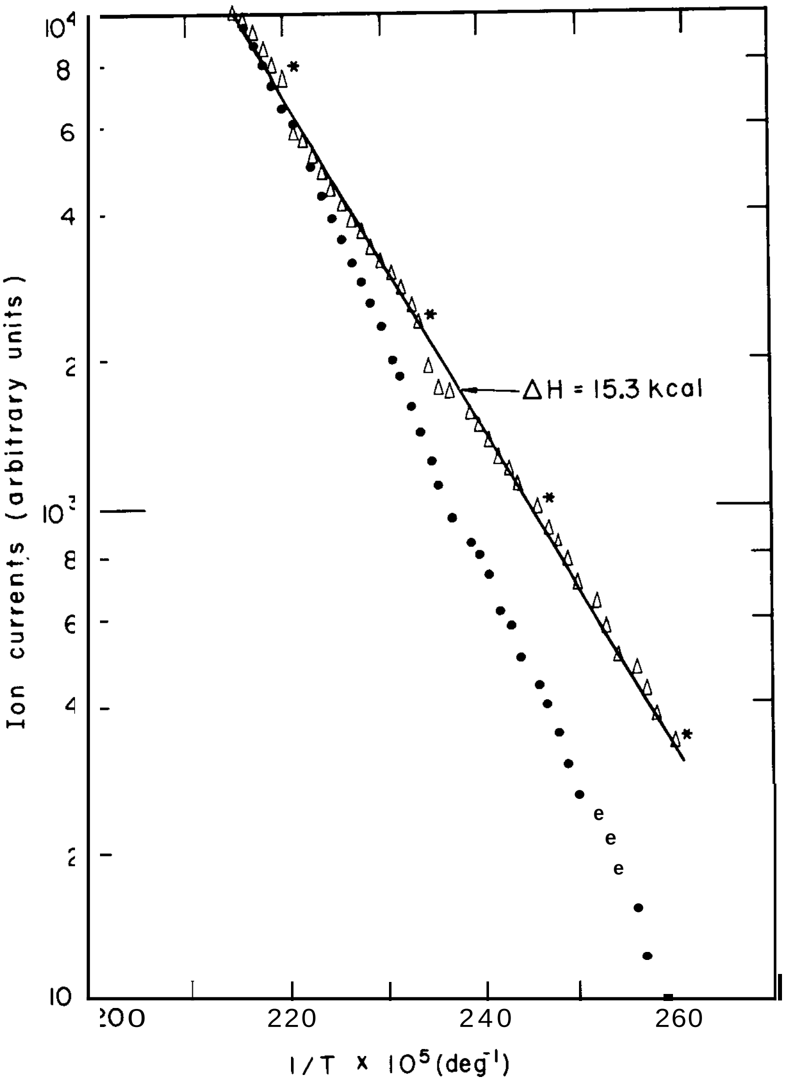
A = heating
● = cooling
✻ = magnetic field adjusted
Electron energy = 74 volts.



MU – 20979

Fig. 12. Log of S_5^+ ion current vs 1/T.

A = heating
● = cooling
* = magnetic field adjusted
Electron energy = 74 volts..



MU-20980

Fig. 13. Log of S_4^+ ion current vs 1/T.

A = heating
● = cooling
* = magnetic field adjusted
Electron energy = 74 volts.

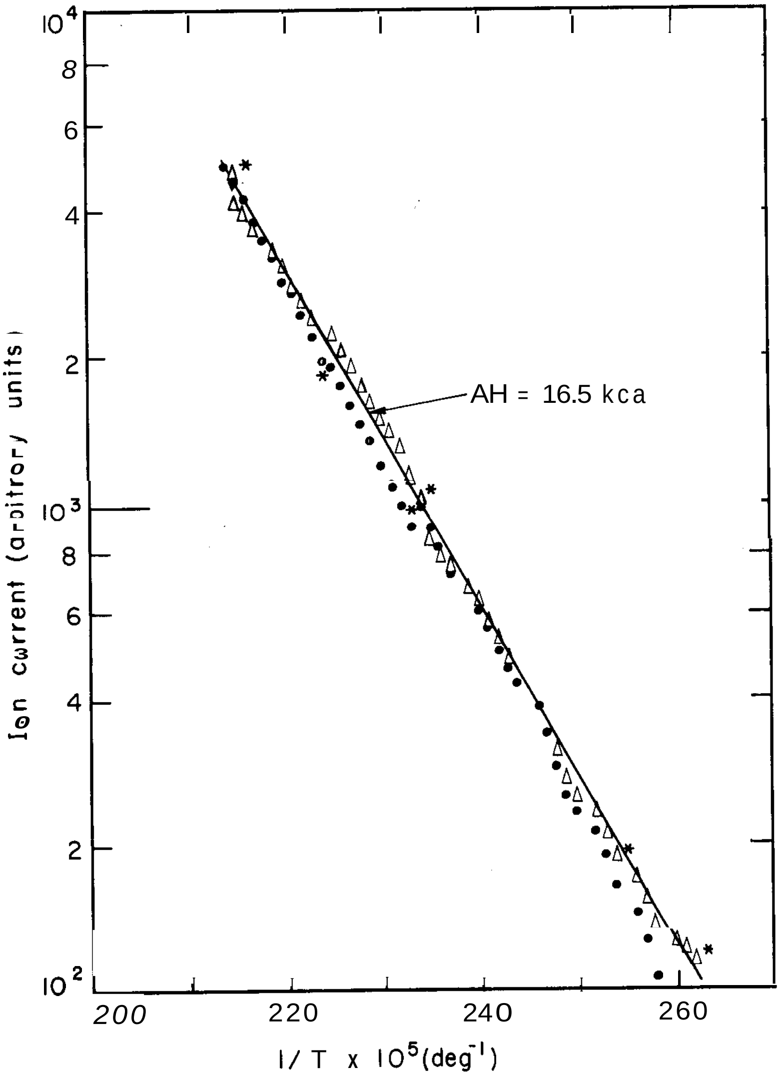
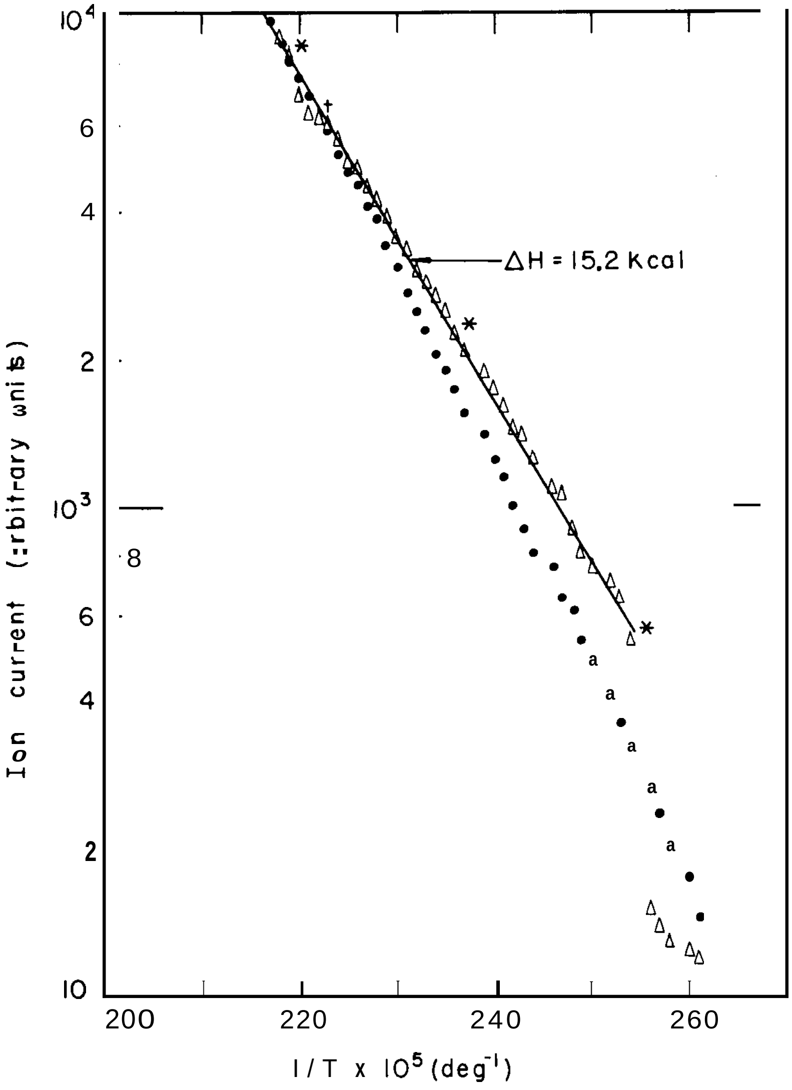


Fig. **14.** Log of S_3^+ ion current vs 1/T.

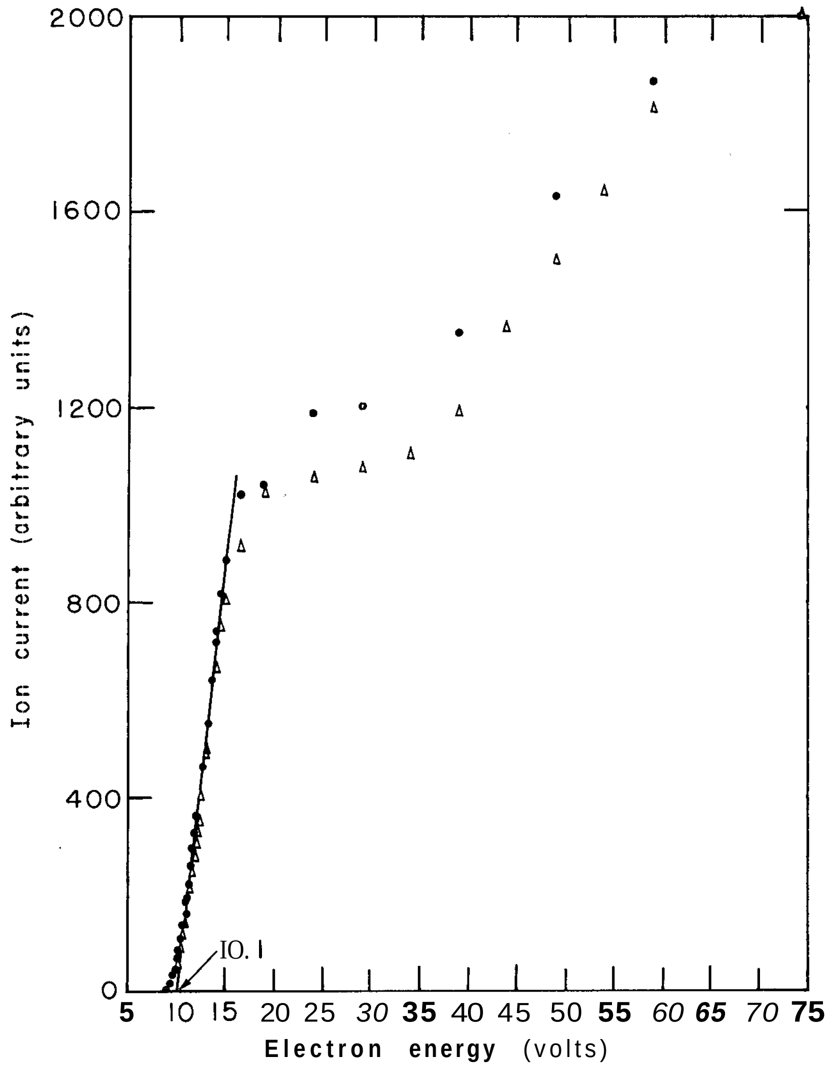
A = heating
● = cooling
* = magnetic field adjusted
Electron energy = 74 volts.



MU – 20982

Fig. 15. Log of S_2^+ ion current vs 1/T.

A = heating
● = cooling
* = magnetic field adjusted
Electron energy = 74 volts.

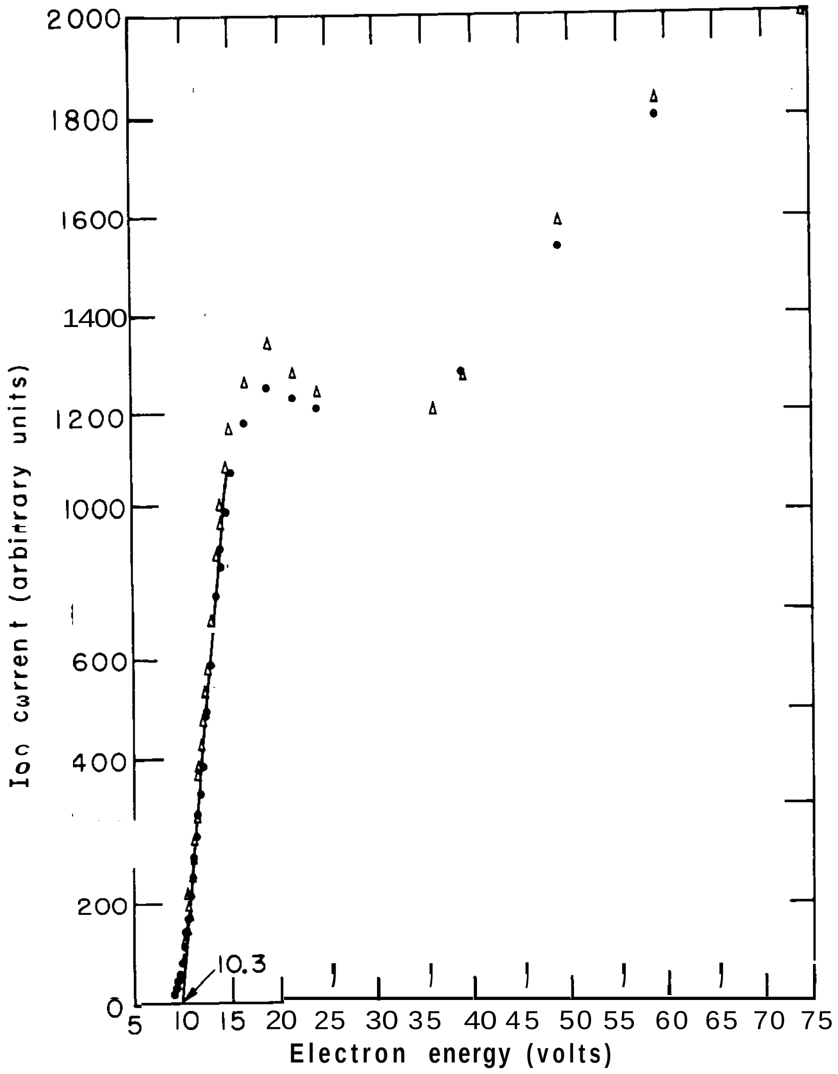


MU– 20865

Fig. 16. Normalized S_8^+ ion current as a function of electron energy.

A = 150°C

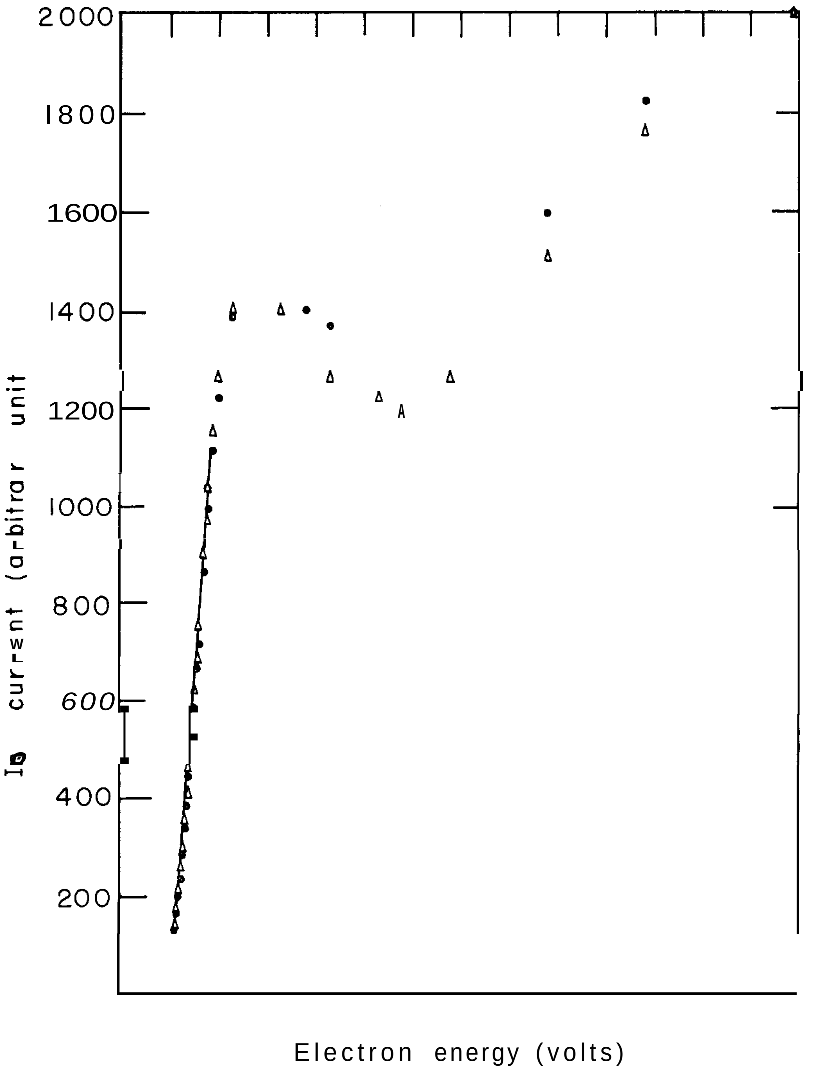
● = 195°C



MU- 20866

Fig. 17. Normalized S_7^+ ion current as a function of electron energy.

Δ = 150°C
● = 195°C

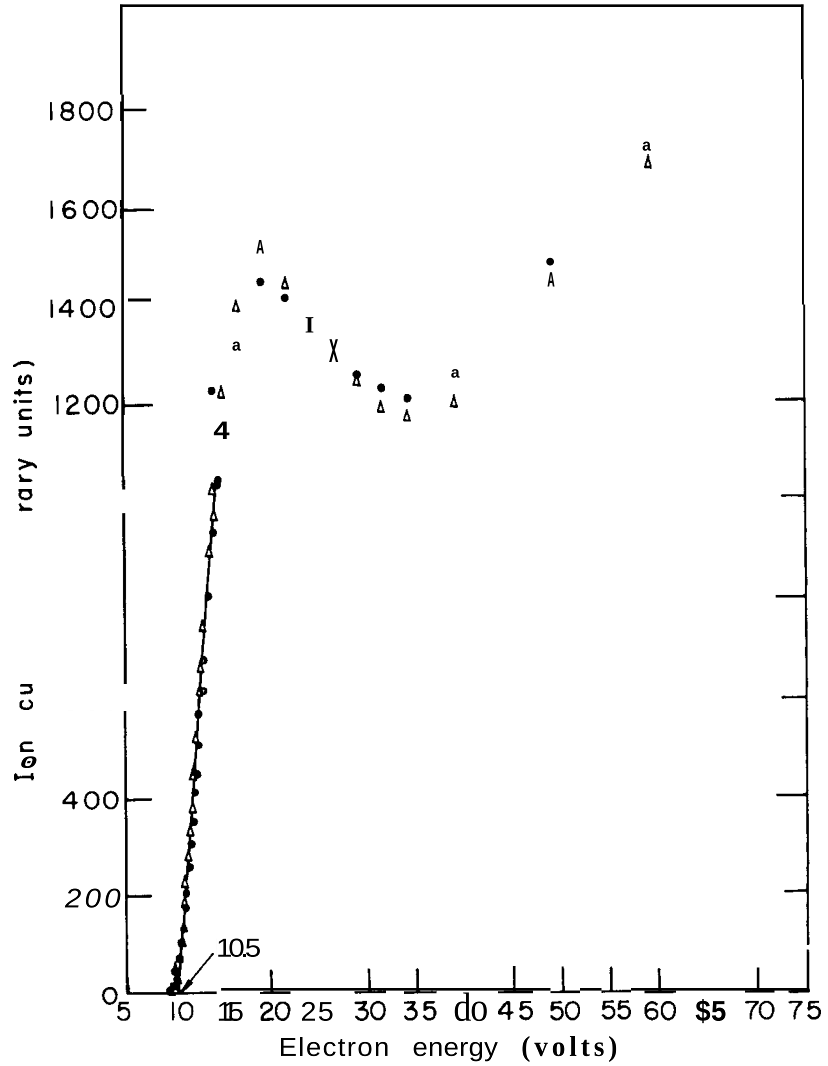


MU-20867

Fig. 18. Normalized S_6^+ ion current as a function of electron energy.

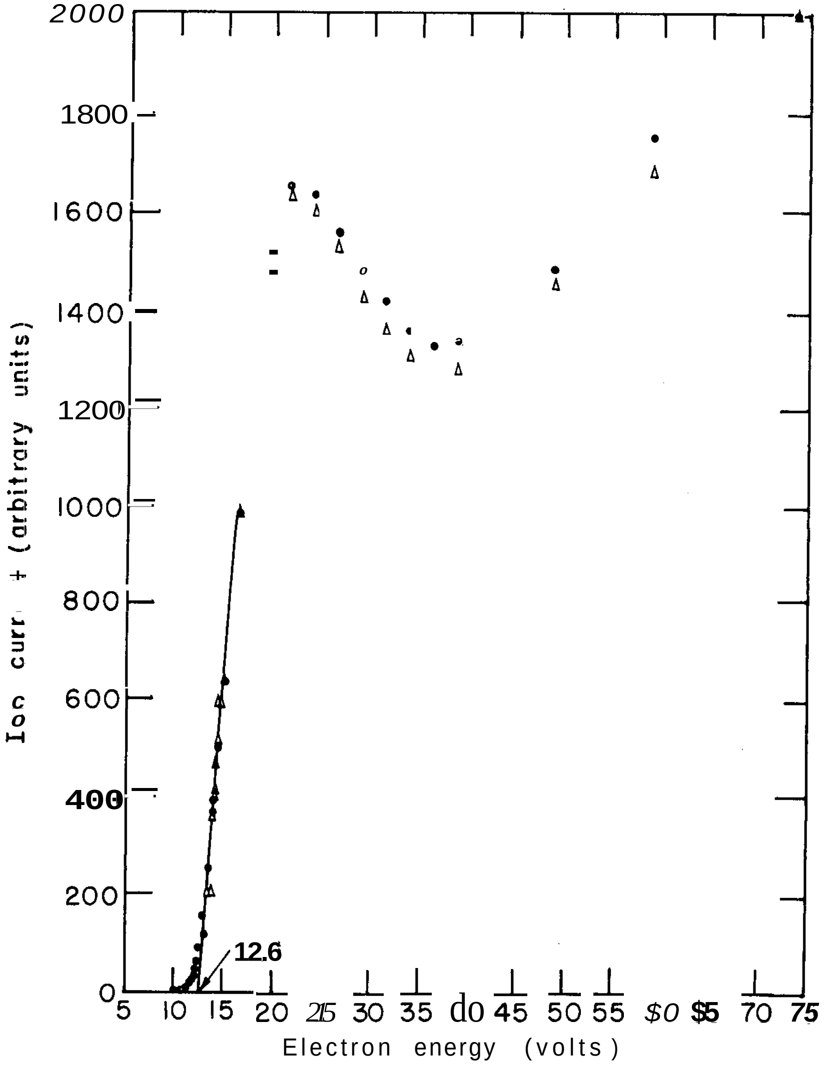
△ = 150°C

● = 195°C



MU-20868

Fig. 19. Normalized S_5^+ ion current as a function of electron energy.
Δ = 150°C
● = 195°C



MU-20869

Fig. 20. Normalized S_4^+ ion current as a function of electron energy.
△ = 150°C
● = 195°C

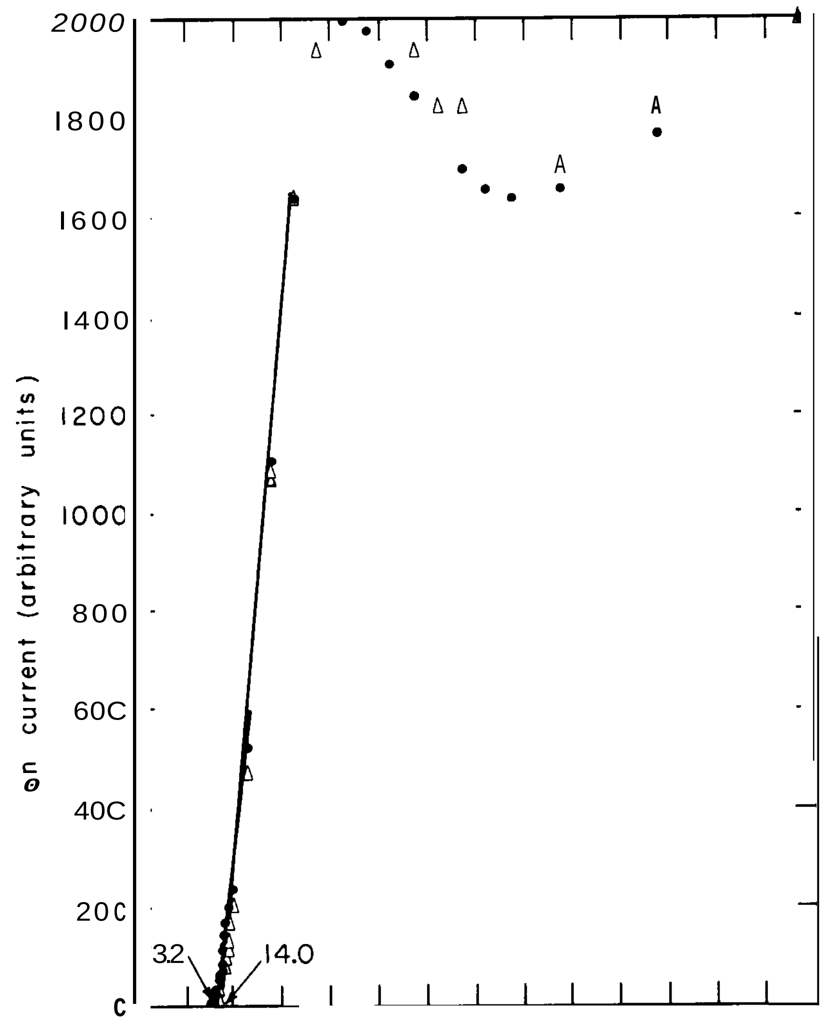
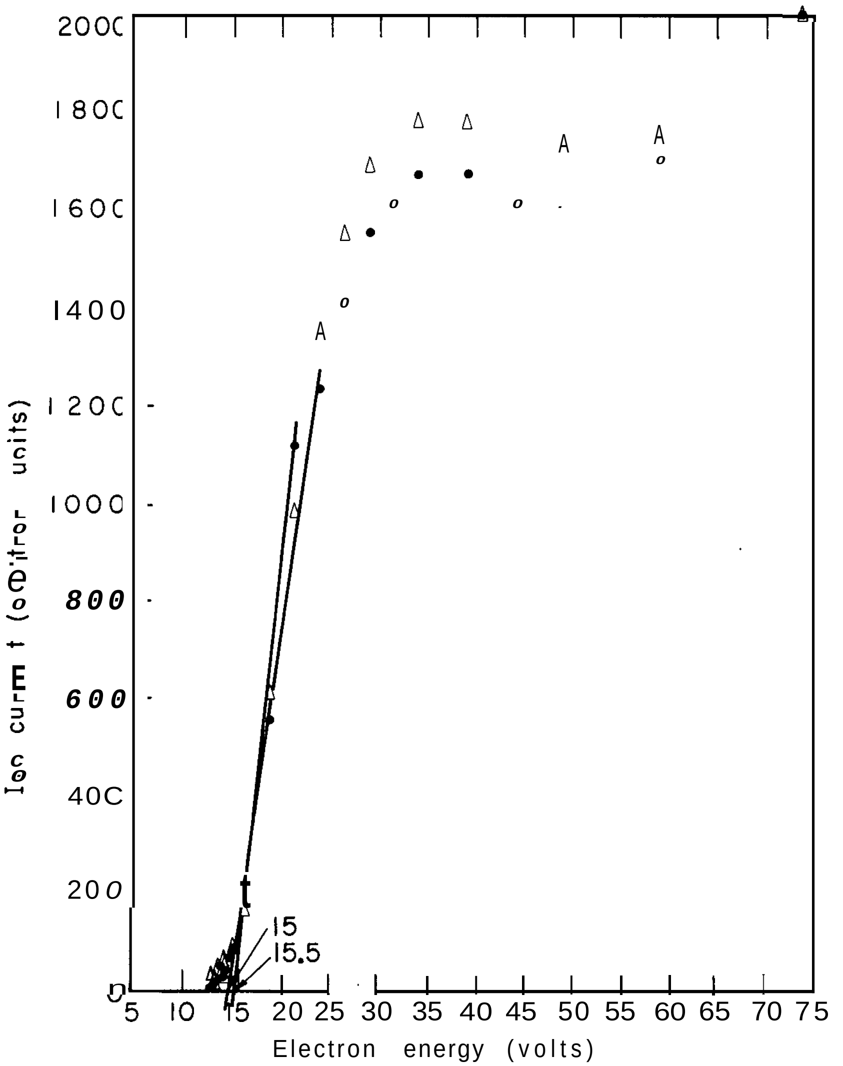
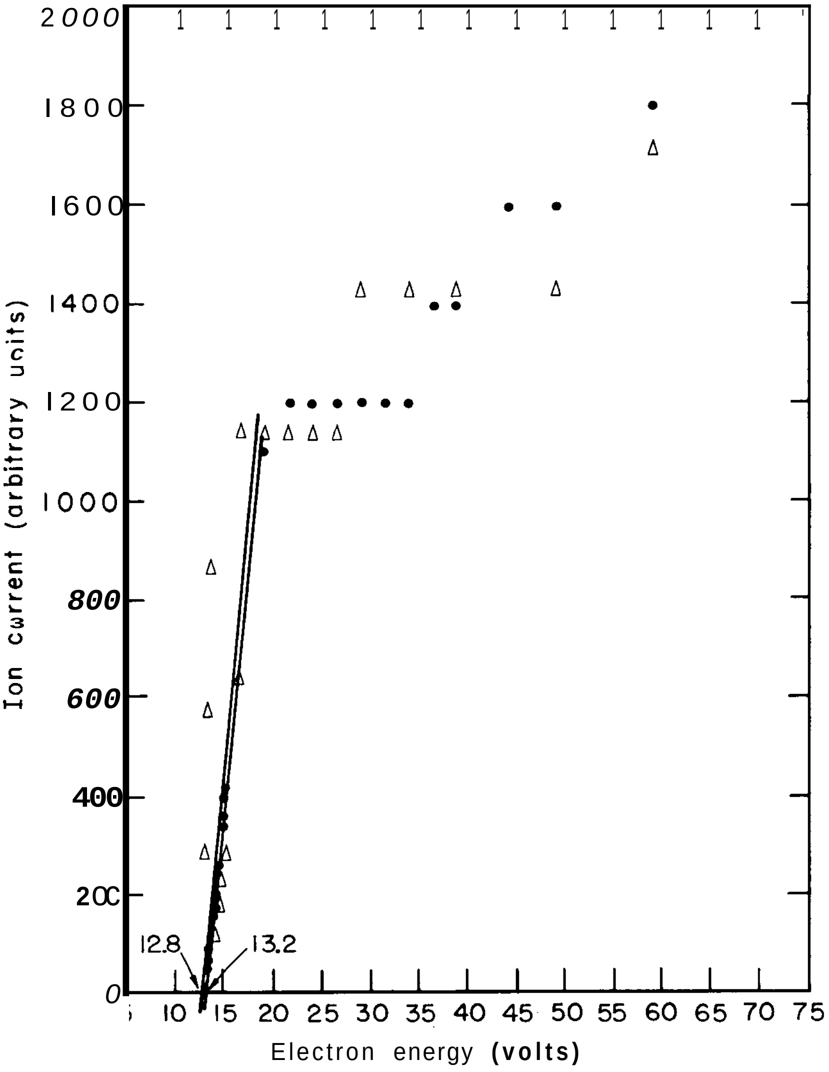


Fig. 21. Normalized S_3^+ ion current **as** a function of electron energy.
A = 150°C
● = 195°C



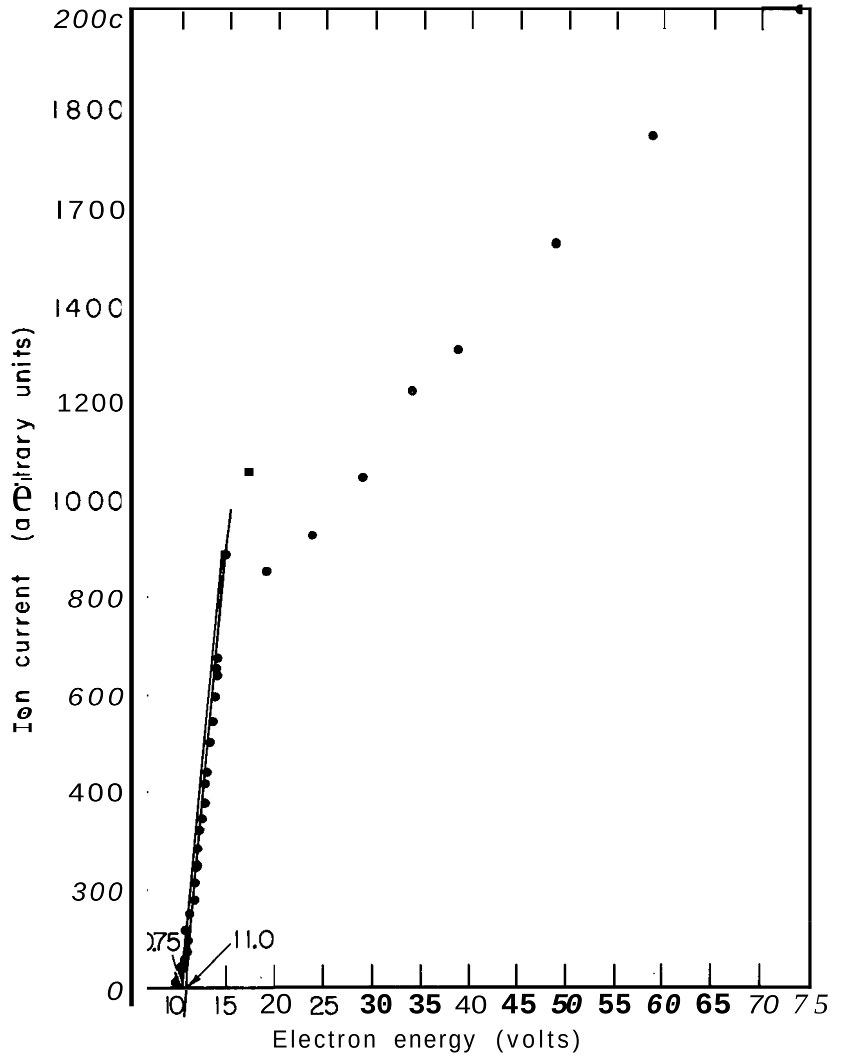
MU-20871

Fig. 22. Normalized S_2^+ ion current as a function of electron energy.
A = 150°C
● = 195°C



MU-20872

Fig. 23. Normalized background S_2^+ ion current as a function of electron energy.



MU– 20873

Fig. 24. Normalized Hg^{204} ion current as a function of electron energy.

It was not possible to obtain all the data without interruption, and there were some variations in conditions between different days and even during a given day's measurements. In most cases the hot slit and container were not allowed to cool to room temperature and were kept at approximately 70°C after the cooling system had been turned off, to encourage overnight outgassing. However, on one occasion, the cooling system was left on between runs on two successive days and neither the hot slit nor the sulfur container was heated; and, on another, the CO_2 trap for the diffusion pump was warmed to return the trapped mercury to the pump boiler between two days' measurements. In addition, although during the initial runs the ion gauge pressure readings were high on the 10^{-7} mm scale, during the final runs, the pressure readings were low on the 10^{-7} mm scale. Further, during the initial portion of the run made one day after the cooling system had been left on overnight, no sulfur ion currents could be found until the container temperature was 190°C. Then the S_8^+ peak suddenly appeared, rapidly increased by a factor of two, decreased almost to its initial value, and finally stabilized at approximately 1-1/2 times its first value. However, even this last occurrence had only a temporary effect on the ratios, and none of the other factors had an effect that could be distinguished from the usual scatter of data. Therefore, the data reported have not been segregated according to these differences.

During earlier work, it was observed that the S_7^+/S_8^+ ratio became essentially zero (less than 0.01) at sulfur temperatures in the vicinity of 90°C when the sulfur had not been previously melted, and the effusion orifice was 0.010 in. in diameter. At no time during any portion of this work were mass peaks observed that would correspond to a sulfur molecule containing more than eight atoms. On several occasions the mass-spectrometer sensitivity was increased and the higher-mass spectrum was carefully scanned, so that an ion current smaller than the S_8^+ ion current by several orders of magnitude would have been observed. A large ion current was observed at mass 32, but the difference between the readings obtained with the shutter open and closed was always quite small, and therefore the size of the S_{32}^+ peak was too uncertain to report.

DISCUSSION OF RESULTS

Molecular Species in Sulfur Vapor

The major enigma encountered in interpreting these data results from the ability of the ionizing electrons to fragment a molecule. A typical fragmentation reaction is

$$e^- + X_8 \longrightarrow X_7^+ + X + 2e^-, \qquad (1)$$

and there is no a priori reason to disregard any of the analgous reactions. In fact, as is the case with some hydrocarbons, ionization without fragmentation may never be observed. In addition, there is the possibility of molecular (or ionic) additions. For example, the H_3^+ ion has been observed. Thus, the existence or absence of an ion peak does not in itself answer the question, "Is the neutral molecule there?"

A method of avoiding the ambiguity induced by these reactions is to introduce known quantities of each component of a mixture of gases independently for calibration purposes. Then, with this information, analysis of data obtained from the mixture would be straightforward. However, in this study separation of each component of the mixture of molecules was not possible, so that it was necessary to obtain all of the information presented in Fig. 6 through 23, in order to determine the qualitative composition of sulfur vapor.

There is strong evidence for the existence of an S_8 molecule. Since no molecule containing more than eight atoms was observed, it does not seem likely that the large S_8^+ ion currents could result from fragmentation of molecules containing more than eight atoms. Also, because the low vapor pressure of sulfur in the ionization chamber would not be conducive to the occurrence of addition reactions, there is little probability that an appreciable number of ions would be formed by this process. In addition, since S_8 exists in the solid and the liquid, it would be quite surprising if it were not also found in the vapor.

Since it was observed that the S_7^+/S_8^+ ratio approaches zero at temperatures below the sulfur melting point, the entire S_7^+ ion peak can be attributed to ionization of S_7 molecules. Supporting evidence for S_7 not resulting from fragmentation of S_8 is that the temperature dependence of the S_7^+ ion differs from that of S_8^+ (See Figs. 6, 9 and 10) and that the appearance potentials of the two ions are essentially identical. If S_7^+ originated from fragmentation of S_8, it would have the same temperature dependence, and its appearance potential would reflect the energy of the fragmentation reaction by being greater than that of S_8^+. The possibility that a molecule containing more than eight atoms is a parent for the S_7^+ ion is quite slight, because the S_7^+/S_8^+ ratio increases with temperature (Fig. 6) and if a molecule containing more than eight atoms existed, its importance would be expected to decrease as the temperature increased, so that if S_7^+ derived from such a molecule, the temperature dependence of the S_7^+/S_8^+ ratio would be opposite to that observed.

There is also adequate evidence for the existence of an S_6 molecule in the equilibrium vapor. The slope of the S_6^+/S_8^+ ratio as a function of temperature (Fig. 6), and the fact that the appearance potential of S_6^+ is approximately the same as that of S_8^+ indicates that S_6^+ does not result only from fragmentation of S_8. The coincidence of the S_6^+ appearance potential with that of S_7^+ is evidence that the total S_6^+ ion current cannot be attributed to fragmentation reactions. Also, in order to attribute the total S_6^+ ion current to fragmentation of S_8 and S_7, it would be necessary that fragmentation of S_7 to yield S_6^+ be several times as probable as ionization of S_7, which does not seem likely, particularly when the corresponding fragmentation of S_8 to S_7^+ is not observed. In addition, the fact that solid allotropic sulfur has been identified as S_6 by Donohue et al.[17] adds credibility to the existence of an S_6 molecule in the vapor.

Because the appearance potential of S_5^+ is approximately the same as that of S_8^+, S_7^+, and S_6^+; and because it is improbable that the marked increase with temperature of the S_5^+/S_8^+ ratio is due to fragmentation of S_7 and S_6, it appears that there also exists an S_5 molecule in sulfur vapor. In addition, the observation that the heat of vaporization of S_5^+ is 17.7-kcal (Fig. 12), even though a large portion of this ion current arises from fragmentation of S_8 (15.5-kcal), supports the argument for the existence of a S_5 molecule.

Although the existence of S_4, S_3, and S_2 molecules cannot be disproven, the data quite strongly suggest that they are not present in appreciable concentrations in the equilibrium vapor below 214°C. The temperature dependence of the ratios of the ions corresponding to these molecules can be quite easily explained in terms of fragmentation of S_7, S_6, and S_5, and the higher appearance potentials for the S_4^+, S_3^+, and S_2^+ ions, in addition to their apparent heats of vaporization being nearly identical with that of S_8, are rather conclusive evidence for the belief that these lighter ions appear solely as a result of fragmentation reactions. The value of -5.122 for log K given by Stull and Sinke[18] for S_2 leads to a calculated pressure of S_2 three orders of magnitude less than for S_8 at 500°K, which is consistent with the statement that S_2 is not present in appreciable concentrations below 214°C.

Quantitative Composition of Sulfur Vapor

In addition to the ambiguity resulting from fragmentation reactions, the quantitative interpretation of mass spectrometric data is complicated by the facts that the probability of ionizing a molecule (ionization cross section) is not the same for all molecules, and that the secondary emission of the first dynode of the electron multiplier, in our case, was dependent upon the velocity of the impinging ions. With a constant accelerating voltage, the velocity of an ion is mass dependent and, therefore, so is the gain of the electron multiplier. (See Ingraham and Hayden[19] for a full discussion of factors affecting the gain of an electron multiplier.)

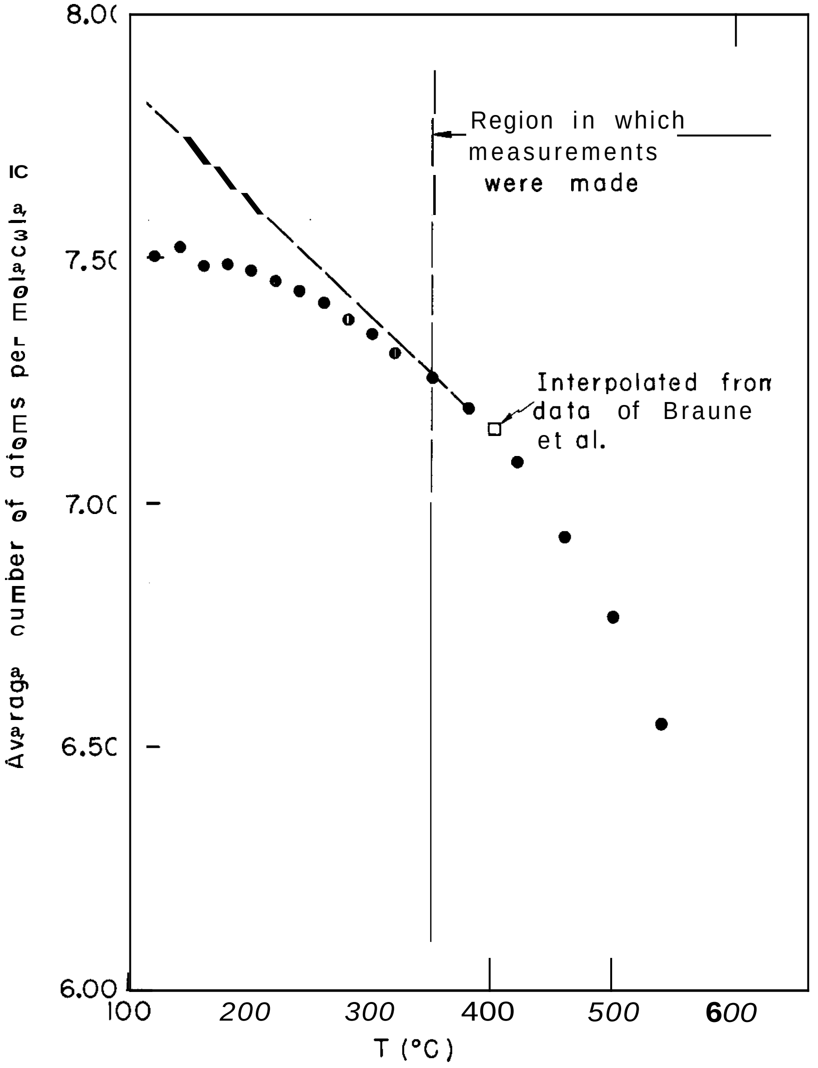
In the absence of calibration information, it is desirable to attempt to determine the quantitative composition of sulfur vapor by combining these data with the results of other workers. Unfortunately, the vapor density measurements by Braune et al.,[4] the partial pressures of S_8 calculated from the thermodynamic functions given by Guthrie et al.,[5] and the vapor-pressure measurements by West and Menzies[6] represent the totality of the usable available information.

As the vapor density measurements by Braune et al. were not extended below 350°C, the lower temperature partial pressures that they reported for S_8, S_6, S_4 and S_2 were obtained by extrapolation. In order to obtain values of the vapor density at low temperatures, it was necessary to recalculate their date to give $\bar{n}$ (the average number of atoms per molecule) as a function of temperature, which is presented in Fig. 25. That $\bar{n}$ appears to approach 7.5 instead of 8.0 is most likely a result of neglecting the presence of S_7 and S_5. Therefore, $\bar{n}$ was extrapolated from 350°C as shown by the dashed line. This extrapolation does not provide accurate low-temperature values for $\bar{n}$, but does provide an upper limit. The partial pressures of S_8 from Guthrie et al., which do not provide new information, as they are based on the work of Braune et al., are presented along with the vapor pressures from West and Menzies in Fig. 26.

If it is assumed that the ionization cross section is proportional to the number of atoms per molecule (i.e. equals the geometric cross section), and that the gain of the electron multiplier is also proportional to the number of atoms per molecule, these two effects cancel each other and the ratio of S_7^+ to S_8^+ is equal to the ratio of the neutral molecules. Then, the information in Figs. 25 and 26 can be combined with the S_7^+/S_8^+ ratios to calculate the composition of equilibrium sulfur vapor from the following four equations:

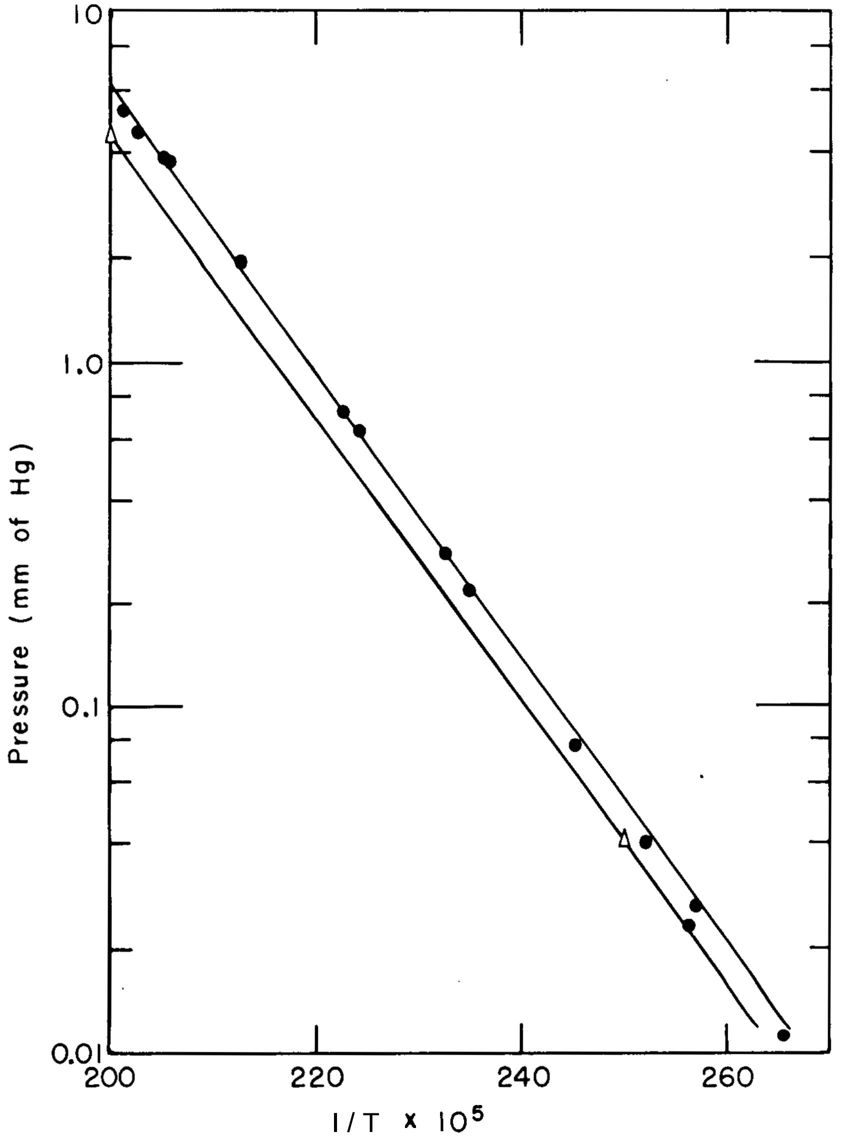
$$a + b + c + d = 1.00 \qquad (2)$$

$$8a + 7b + 6c + 5d = \bar{n} \qquad (3)$$



MU- 20983

Fig. 25. Average number of atoms per molecule, $\bar{n}$, as a function of temperature.



MU- 20874

Fig. 26. Log of vapor pressure as a function of 1/T.

A = S_8 vapor pressure (Guthrie et al)
● = Total sulfur vapor pressure (West and Menzies)

$$\frac{b}{a} = S_7^+/S_8^+ \tag{4}$$

$$a = P_{S_8}/P_{\text{total}} \tag{5}$$

(a, b, c, and d are the fractions of S_8, S_7, S_6, and S_5 respectively). The data necessary for calculating the composition at 120, 150, 175, and 200°C is compiled in Table III.

Table III

Data for Calculation of Sulfur Vapor Composition

Temperature (°C)	$\frac{S_7^+}{S_8^+}$	$\frac{S_6^+}{S_8^+}$	$\frac{S_5^+}{S_8^+}$	$\bar{n}$ Av. no. atoms / molecule	P_{S_8} (mm)	P_{total} (mm)
120	.16	.67	.86	7.80	.028	.037
150	.24	.80	1.19	7.73	.15	.20
175	.31	.90	1.48	7.67	.50	.66
200	.38	1.00	1.76	7.61	1.60	2.20

However, when the 200° value of 0.73 for "a" from Eq. (5) was combined with the 0.38 S_7^+/S_8^+ ratio according to Eq. (4), b was calculated as 0.28, which conflicts with Eq. (2). Another contradiction was observed when b, c, and d were set equal to 0.27, 0.0 and 0.0 respectively to not conflict with Eq. (2), as the value calculated for $\bar{n}$ by Eq. (3) is 7.73.

This inconsistency among the data in Table III, and with the qualitative evidence for the existence of S_6 and S_5, is probably due partially to inaccuracy in the partial pressure of S_8, which was obtained by assuming that the vapor consisted of S_8 and S_6 only.

Also, that the values of "a" from Eq. (5) at 120, 150, 175 and 200°C are 0.76, 0.75, 0.76 and 0.73 shows amazing consistency, which is incompatible with the expectation of a decreasing percentage of S_8 with increasing temperature. Admittedly, the values of $\bar{n}$ given in Table III are not precise, but since these values are an upper limit, any attempt to adjust $\bar{n}$ to remove the contradiction would be indefensible. Therefore, it was decided to attempt to arrive at the quantitative composition of sulfur vapor without recourse to Eq. (5). If first S_5, then S_6, is assumed equal to zero, Eqs. (2), (3), and (4) should provide upper limits to the actual percentages of S_5 and S_6, and lower limits as well as upper limits for the fractions of S_8 and S_7. Calculations made on this basis yielded the disconcerting results that when S_5 was set equal to zero, S_6 was amazingly constant at 4%, 4%, 6%, and 6% at 120, 150, 175, and 200°C, and when S_6 was set equal to zero, the corresponding values for S_5 were 3%, 3%, 3%, and 5%.

That such results are incompatible with both the experimental evidence and the expected behavior for S_6 and S_5 is evident, and so the assumptions upon which Eq. (4) is based were scrutinized and the relationship was rewritten as

$$b/a = C\ S_7^+/S_8^+, \qquad (4a)$$

where C is a constant that could be determined experimentally. In the absence of specific knowledge of the value of C, it was quite arbitrarily set equal to 1/2, and, with first S_5 and then S_6 assumed equal to zero, but this time using Eqs. (2), (3) and (4a), calculations were again made for the composition of sulfur vapor at 120, 150, 175, and 200°C. The results obtained by this calculation, which appear reasonable, are given in Table IV.

Table IV

Composition of sulfur vapor from Eq. (2), (3), and (4a)

Temperature (°C)	$S_5=0$			$S_6=0$		
	S_8 (%)	S_7 (%)	S_6 (%)	S_8 (%)	S_7 (%)	S_5 (%)
120	86.5	6.9	6.6	88.6	7.1	4.3
150	81.6	9.8	8.6	84.3	10.1	5.6
175	77.5	12.0	10.5	80.7	12.5	6.8
200	73.5	14.0	12.5	77.2	14.7	8.1

However, the physical significance of $C = 1/2$, is that the ionization cross section of S_7 is much larger than that of S_8, or the electron multiplier is much more efficient for S_7 than S_8, or both of these. Since there is no basis for either phenomenon, even though the assumption of $C = 1/2$ results in a reasonably consistent composition for sulfur vapor, the lack of plausibility of this assumption does not permit the end to justify the means.

The other possibility for arriving at the quantitative composition of sulfur vapor is to estimate the fraction of the S_6^+ and S_5^+ ion currents attributable to fragmentation reactions. If it is assumed that, since little or no S_7^+ arises from fragmentation of S_8, none of the S_6^+ ions occur as a result of fragmentation of S_7, the maximum percentage of S_6^+ that is due to fragmentation of S_8 is 67. On this basis, the S_6^+/S_8^+ ratio can be written as

$$S_6^+/S_8^+ = (c + 0.67a)/a \quad , \qquad (6)$$

which yields c = 0.33a at 200°C. This result, combined with the data in Table III by Eqs. (2), (3), and (4), and on the assumption of $S_5 = 0$, leads to $\bar{\bar{n}} = 7.33$, which is even lower than the value obtained by the extrapolation of Braune et al., and would be still lower if a nonzero value of S_5 were used. This inconsistency is analogous to the straw that broke the camel's back.

Because it does not appear possible to combine the results of this work with those of other studies of sulfur vapor without either having contradictions or having to make dubious assumptions, the final effort to establish the quantitative composition is totally based on the data obtained during this work. In order to solve for the four unknowns, a, b, c, and d, Eqs. (2), (4), and (6) must be augmented by a fourth relationship. As Eq. (6) provides a lower limit to the nonfragmentation portion of the S_6^+ ion current, an analogous relationship for S_5 would not be inconsistent.

The S_5^+ ratio can be written as

$$S_5^+/S_8^+ = (d + Aa + Bb + Cc)/a \quad , \qquad (7)$$

where A is the fraction of S_8 fragmenting to yield S_5^+, and B and C have analogous definitions with respect to S_7 and S_6. If d is assumed equal to zero at 120°C, which is consistent with the derivation of (6), and C is equal to zero for the same reasons the S_7 fragmentation to yield S_6^+ was neglected, and it is assumed that the fraction of S_5^+ that results from fragmentation of S_7 is the same as that assumed for S_6^+ deriving from S_8, it is possible to use the 120° data to evaluate A.

This calculation for A and the above assumptions for B and C result in values of 0.75, 0.67, and 0.0 for these three constants, and Eq. (7) becomes

$$S_5^+/S_8^+ = (d + 0.75a + 0.67b)/a \quad . \qquad (7a)$$

The results obtained by using Eqs. (2), (4), (6), and (7a) to calculate the composition of sulfur vapor are presented in Table V. Also included are values for $\bar{\bar{n}}$ obtained by Eq. (3).

Table V

Composition of sulfur vapor from Eqs. (2), (4), (6), (7a), and (3)

Temperature ($^\circ$C)	S_8 (%)	S_7 (%)	S_6 (%)	S_5 (%)	$\bar{\bar{n}}$ $\frac{\text{Av.no.atoms}}{\text{molecule}}$
120	86	14	0[a]	0[a]	7.86
150	60	15	8	17	7.18
175	49	15	11	25	6.88
200	41	15	13	31	6.66

[a] Assumed Value

Unfortunately, the results presented in Table V only serve to further illustrate the fundamental conflicts that arise. The constancy of the S_7 percentage is not indicative of these data, and the values of $\bar{\bar{n}}$ and of the percentage of S_8 are not within the maximum error of external data.

The most plausable quantitative composition of sulfur vapor is that given in Table IV, where the actual percentages of S_6 and S_5 are probably about one half of the values presented. These compositions do not seriously conflict with external data and are indicative of the results of this work.

Appearance Potentials

The appearance potential data, Figs. 16 through 24, are relatively unambiguous. From the Hg^{204} appearance potential of 10.75 to 11.0 ev (Fig. 24) it is possible to state that the contact potentials are +0.5 ±0.2 ev, and thus corrections can be made to obtain the ionization potentials of the sulfur ions. The two intercepts extrapolated from the straight-line portion of the Hg^{204} appearance-potential plot serve to fix the error, caused by the uncertainty of the exact position of the extrapolating line, as ± 0.15 ev. The larger uncertainty of the extrapolation for the S_3^+ and S_2^+ appearance potentials is probably due to the difficulty encountered in maintaining proper focusing of these low mass ion-current peaks.

The ion currents were normalized to preclude dependence of the appearance potential on the absolute magnitude of the current. When nonnormalized ion currents were plotted as a function of the electron energy, the data obtained at 150° did not coincide with those taken at 195°, and the corresponding appearance potentials differed by approximately 0.3 ev. Although a plot of log i versus the electron energy provides a steeper slope of the intercept line than a linear plot, there is the disadvantage in use of the log i plot of not being able to extrapolate to zero ion current. And, since the contact potential correction actually includes errors resulting from inaccuracies inherent in the method used, the essential requirement is that only systematic errors be introduced, and it is believed that this was achieved. In fact, during earlier work, the appearance potential of Hg was determined to be 10.3 ev and the sulfur appearance potentials were all lower than those reported here by a corresponding amount.

The differences between the appearance potentials of S_8^+, S_7^+, S_6^+, and S_5^+ are virtually within the probable extrapolation error, so that evidently all four of these ions have essentially the same appearance potential, which can be expressed as 10.3 ± 0.2 ev. Correcting for the contact potentials, and adding the uncertainties, gives an ionization potential of 9.8 ± 0.4 ev, which is 0.5 ev less than the 10.3 ev first ionization potential accepted for atomic sulfur.[20]

The appearance potentials for S_4^+, S_3^+, and S_2^+ of 12.6, 13.2 to 14.0, and 15 to 15.5 ev respectively, cannot be converted into ionization potentials without knowledge of the energies required for fragmentation. It was hoped that since the background S_2^+ ion probably resulted principally from ionization of a S_2 molecule, it would be possible to determine the fragmentation energy portion of the appearance potential of the net S_2^+ ion peak. Unfortunately, the appearance potential of 12.8 to 13.2 ev for the background S_2^+ ion is quite uncertain, and even though there is evidently a real difference between this appearance potential and that of the net S_2^+ ion, a value of more than 3 ev (approximately 72 kcal) would represent an extraordinary fragmentation energy and must therefore reflect a nonrandom error.

A nonrandom error would result if the energy of the electrons that ionized the background S_2 molecules was different from the energy of the electrons that produced the net S_2^+ ions. And, because the S_2 background molecules most likely originated from thermal dissociation of larger molecules at the hot filament, these molecules could be ionized by electrons that had not been affected by the negative drawing out voltage, and which therefore would have more energy. As noted previously, the higher appearance potentials of S_4^+, S_3^+, and S_2^+ were most useful for establishing that these ions result from fragmentation reactions, although the magnitude of the differences from 10.3 ev may also be attributable to formation of these ions by thermal dissociation.

Heats of Vaporization

The heat of vaporization of S_8, as determined from the slopes of the plot of log i versus 1/T in Fig. 9, is 15.2 to 15.9 kcal. The data could not be fitted by a single straight line, but the degree of reproducibility of the experimental measurements would make useless more sophisticated treatments--such as fitting the points with a curve and determining the slope of tangents to the curve. On the basis of the differences in the heats obtained from the two slopes, an error limit of ± 0.35 kcal would be appropriate, but results obtained by calculations for other heating and cooling curves were sufficiently divergent that to report $\Delta H = 15.5 \pm 2$ kcal is not pessimistic. The value of ΔH obtained from the slope of Guthrie et al's S_8 vapor pressure data[5] is 18.5 kcal, from West and Menzies' total vapor pressure data[6] is 19 kcal, and from Stull and Sinke[18], by third law calculations, is 20 kcal at 400°K and 16.7 kcal at 500°K. The low value of the heat of vaporization obtained from Fig. 9 could be due to some essentially constant contributions to the molecular beam from an extraneous source. This possibility is discussed in more detail in the next section.

The 18.4-kcal heat of vaporization for S_7 (Fig. 10) is somewhat higher than heats obtained from other cooling and heating curves for S_7^+, but the over-all reproducibility was rather good, so that 18 ± 1 kcal represents these data quite well. That the heat of vaporization of S_7 is higher than that of S_8 is precisely what is to be expected for a species that becomes more important as the temperature is increased. The absolute magnitude of the heat is not certain, but its relationship to the S_8 heat is probably accurate.

The heats of vaporization of S_6 and S_5 from Figs. 11 and 12, and the attendant uncertainty deduced from all the cooling and heating curves, are 16.3 ± 2 kcal and 17.7 ± 1 kcal. These values can only be construed as lower limits, because of the unknown fragmentation contributions to the measured ion currents.

That the S_4 and the S_2 heats of 15.3 and 15.2 kcal (Figs. 13 and 15) are well within the accuracy of the 15.5 kcal S_8 heat indicates that these ions arise primarily from fragmentation of S_8. The slightly higher value of 16.5 kcal for S_3 is probably due to contributions from fragmentation of the other three neutral molecules. Therefore, these heats cannot be construed as heats of vaporization for the respective neutral molecules.

GENERAL DISCUSSION

This Work

The most disconcerting aspect of this work was the inconsistency of the absolute values of the ion currents and the irregular behavior of the S_x^+/S_8^+ ratios. Although the values of the ion currents at a given temperature would generally become constant one to two hours after a day's measurements were begun, when the same temperature was reproduced on a subsequent day, the constant values the ion currents reached would be almost invariably lower. For example, the S_8^+ peak heights, which showed a downward trend throughout this series of measurements, normally would decrease during a run to a stabile level that would be as little as 2/3 of the initial level, although there was one day during which the peak heights increased and two days during which they did not change. The S_8^+ peak heights consistently decreased between each day's measurements, with the greatest decrease (by a factor of 1/2) occurring at the beginning of one of the days during which the peak heights remained constant, and following the cooling system's being kept in operation overnight.

The S_x^+/S_8^+ ratios, which were calculated in order to normalize all peaks with respect to the S_8^+ peak, did not show any consistent increase or decrease, but did vary from day to day. For example, the low S_5^+/S_8^+ ratios between 183 and 196° (Fig. 6) were almost all obtained on one day, while the higher values in the same temperature range were obtained on the preceding day and on the following day. To investigate any trend in the ratios, the temperature of the sulfur source was kept constant for several hours on the days just preceding and just following the cooling system's being left on overnight, but all the values of these ratios coincided within the accuracy of the measurements.

A lack of reproducibility was characteristic of all the measurements made during this study. It was expected that the fragmentation pattern for S_8 could be obtained from the values of the ion currents at approximately 90°, as the vapor should be predominantly S_8 at this temperature, but even though these data were useful for determining that the S_7^+/S_8^+ ratio approached zero, the variation of the S_5^+/S_8^+ ratio from 0.62 to 1.24 and of the S_6^+/S_8^+ ratio from 0.21 to 0.45 made any fragmentation assignments impossible.

A probable explanation for some of the lack of reproducibility is that a portion of the molecular sulfur beam entering the ionization chamber did not come directly from the sulfur container. These molecules could have come from an anthill-like deposit of sulfur that was found on the bottom of the copper disc closest to the sulfur container when the source was dismantled at the conclusion of this work. The anthill was approximately 3/8 in. high and 5/8 in. in diameter, and its hole diameter was about 1/16 in. The position of this sulfur deposit together with the geometry of the slits, would make the probability very low that a molecule would evaporate from the anthill and enter the ionization chamber without impinging on a cold copper surface. However, the observation that the level of the ion currents generally decreased for several hours at the beginning of each day's run, and that no decrease was observed during the day after the cooling system had been in operation overnight, strongly suggests that there was an appreciable probability that a sulfur molecule could impinge on the cold copper and be reflected.

As the reflected portion of the molecular beam that effused from the sulfur container would contribute, to the sulfur vapor within the source, the magnitude of this background pressure would be dependent upon the temperature of the container, as well as upon the size and temperature of the deposit and upon the length of time the cooling system had been in operation.

The existence of a second source of sulfur vapor within the oven-slit system would not, however, explain the over-all decrease in the levels of the ion currents with time. Nor does it seem likely that growth of the anthill could account for this decrease, as a 1/16 in. hole would have a negligible collimating effect compared with that of the 0.0135-in.-diameter hole of the hot slit. Also, the anomalous behavior described previously--that is, that no ion current was observed until the temperature of the sulfur container had reached 184° at the beginning of one run--is most likely attributable to complete plugging of the copper slit by the sulfur deposit. Therefore, it does not appear that the size of the hole decreased with the regularity required to explain the consistent decrease in the level of the ion currents.

The most plausible explanation for an over-all decrease is that the first dynode of the electron multiplier became contaminated by sulfur and that the gain of the multiplier decreased as the degree of contamination increased. Because of the coincidence of the cooling and heating points (Figs. 9 through 15), it appears that the rate of contamination of the first dynode could not be rapid. (This coincidence of the heating and cooling data also served to indicate that the temperature measurements were reproducible and that thermal and chemical equilibrium were attained.)

The existence of a secondary sulfur source and a continuous decrease of the gain of the electron multiplier provide an explanation for the observed behavior of the levels of the ion currents. The irregularity of the S_x^+/S_8^+ ratios in the work reported here, can be attributed to the affects of the secondary sulfur source. However, the variations of the ratios between samples are not explained.

The lack of reproducibility did not affect the qualitative interpretation of these data, but did seriously hamper attempts to present quantitative information. By obtaining cooling-and-heating and appearance-potential data consecutively, and by choosing the higher values of the ratios to represent these data so as to minimize the inclusion of contributions from the low temperature sulfur vapor within the source, some of the effects of the lack of reproducibility were excluded.

Other Work

The only work that appears unquestionable is that of West and Menzies, and it was a pleasure to read their article and learn of their painstaking efforts.

The thermodynamic functions from Guthrie et al. which are based on the assumptions of Braune et al. that only S_8 and S_6 exist in appreciable quantities below 300° C, require recalculation because of the evidence presented here for the existence of S_7 and S_5 molecules.

The vapor density measurements made by Braune et al. appear to be quite good, so that the limiting factor in their accuracy is probably the extrapolation required of virtually all of their data in order to obtain vapor densities for the saturated vapor. As noted previously, the values of $\bar{n}$ obtained by calculations based on their extrapolation below the temperatures at which they made their experimental measurement require re-evaluation.

The mass spectrometric work of Bradt et al. was not designed to provide information about the composition of sulfur vapor, and the disagreement between their appearance potential work and results of this investigation is almost within the mutual experimental errors. Since the conditions under which this work was performed virtually eliminated contributions from the ionization chamber, and since the results more nearly correspond to the first ionization potential of sulfur, it is believed that the 9.8 ± 0.4 ev appearance potential obtained here for S_8^+ is the more accurate value.

The conclusions of Goldfinger et al. concerning the nature of stable neutral sulfur species do not appear to be substantiated by their experimental findings. Their data could as easily be interpreted as random scatter as showing "the shift of the ionic intensities toward lower molecular species" as a result of increasing the temperature of the upper portion of their two-temperature tube. Also, the predominance of the S_2^+ ion current (columns IV through VI, Table I) strongly suggests that their observed ion currents were more indicative of sulfur vapor partially equilibrated with the electron filament than of sulfur vapor effusing from their two-temperature tube. If their statements (quoted in the introduction to this work) that fragmentation reactions did not provide the major portion of the ion currents they observed are used as a basis for calculating $\bar{n}$ from their ion currents, the disagreement with all vapor-density measurements is really violent.

Their conclusion that a neutral S_9 molecule exists appears to be based on a single observation of a small S_9^+ ion current when the high vapor pressure of sulfur in their ionization chamber would be quite conducive to the occurrence of addition reactions, and disagrees with the observations of Bradt et al. and this work.

General

The information that odd numbered molecules exist in sulfur vapor is an unexpected result of this work. There is no apparent reason for assuming that only even numbered molecules exist, although the presence of S_7 and S_5, and presumably at higher temperatures of S_3, certainly complicates the picture of sulfur vapor. It would appear that S_7, S_6, and S_5 are ring molecules for several reasons. Rings are to be expected unless the strain energy of a ring structure plus the product of the temperature and the entropy change for ring opening is comparable to the energy of an S-S bond. The energy of a sulfur-sulfur bond is of the order of 50-60 kcal (the difference between ΔH_S of 8S to $S_8(g)$ and of 8S to 8S (g) times 1/8.) The entropy of ring opening cannot amount to more than a few cal. mole^{-1} deg^{-1}, and at 500°K the contribution of an entropy difference of even 10 cal. mole^{-1} deg^{-1} to a reaction free energy is only 5 kcal. Unless the strain energy of a ring is 40 or more kcal, a ring molecule must be more stable than the corresponding straight chain molecule. For hydrocarbons strain energies are small for rings of five or more members, so that strain energy should also be small for sulfur rings of five or more members and ring molecules should be expected to be more stable than linear molecules for temperatures in the range studied in this work.

Since rhombic sulfur is known to contain eight numbered, rings and, Donohue et al have found a solid modification of sulfur that contains S_6 rings, there is direct evidence that both S_8 and S_6 rings exist. The fact that appearance potentials for the four ions S_5^+, S_6^+, S_7^+, and S_8^+ are identical to within experimental error suggests that the ions are produced by reaction with molecules of similar stabilities toward simple ionization. S_8 (gas) is known to be a ring; the implication is that S_5, S_6, and S_7 may also be ring molecules.

The complete absence of S_9 or higher molecular weight molecules in the vapor is probably because S_8 is the vaporizing species, with S_7, S_6, and S_5 resulting from S_8 dissociation, (The observations that the S_7^+/S_8^+ ratio approached zero were made when the sulfur vapor had not equilibrated with the condensed phase.) It would be quite interesting to study sulfur vapor evaporating under Langmuir conditions at a temperature at which the equilibrium concentration of S_7 is appreciable, in order to determine whether or not S_7 arises from dissociation of S_8 or from direct evaporation,, The largest orifice used during this study was 0,010 in. in diameter, which did not produce significantly different S_7/S_8 ratios. In order to use a sufficiently large orifice to investigate the evaporating species, it would be necessary to have a much larger sample of sulfur and a means of removing all "secondary" sulfur. The sulfur source used for this study could not be adapted for use with larger molecular beams, since even if the shutter were placed directly over the effusion hole, the vapor pressure of sulfur within the source would be so large that it would undoubtedly eclipse the effusing vapor.

CONCLUSIONS

The results of this study lead to the conclusion that sulfur vapor in equilibrium with the condensed phase, in the temperature range of 120 to 210° C, contains appreciable quantities of S_8, S_7, S_6, and S_5 molecules only. It appears that all four of these molecules are ring shaped rather than linear, and that S_7, S_6, and S_5 most likely result from dissociation of S_8, which is evidently the vaporizing species. It was not possible to establish the quantitative composition of the vapor, but upper limits were obtained for S_8 and S_7 at 120°C of 86% and 14% respectively.

The ionization potentials of S_8, S_7, S_6, and S_5 appear to be identical and are equal to 9.8 0.4 ev. It was not possible to determine absolute values of the heats of vaporization, but the results indicate that the heat of vaporization of S_7 is 2.5 kcal greater than that of S_8 at 120°C to 210°C.

Information was also obtained that sulfur vapor impinging on a -50°C copper surface apparently has a finite probability of being reflected,

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