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THE VAPORIZATION, THERMODYNAMICS, AND
PHASE BEHAVIOR OF URANIUM MONOSULFIDE

by

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THE VAPORIZATION, THERMODYNAMICS, AND PHASE BEHAVIOR OF URANIUM MONOSULFIDE

E. David Cater

ABSTRACT

Quantitative investigations of the vaporization of refractory inorganic sulfides are basic to the study of systematic trends in the thermodynamics of vaporization processes and of chemical bonding in gaseous molecules, because of the comparisons which can be made between their results and those for the corresponding oxides. The characterization of the fundamental properties of uranium monosulfide is of interest both from this basic standpoint and from that of its evaluation for possible applications in nuclear technology.

Uranium monosulfide of high purity was prepared by reaction of uranium metal with hydrogen sulfide and subsequent homogenization of the crude product by heating at approximately 2300°K in a tungsten crucible in high vacuum. Uranium samples of natural isotopic composition and of high enrichment in U^{235} were used, and sulfide samples of various compositions between $US_{0.80}$ and $US_{1.07}$ were synthesized.

The vaporization of these sulfides over the temperature range from 1840 to 2770°K was investigated by the effusion method. Samples were evaporated from inductively heated tungsten effusion cells, and known fractions of the total effusate were collected on platinum targets which were assayed for uranium by an α -counting technique. Chemical and X-ray analyses of the solid residues were performed. The composition of the vapor in the temperature range from 2100 to 2400°K was studied by means of a time-of-flight mass spectrometer.

Samples of other than one-to-one stoichiometry were found to decrease in volatility with time until the congruently evaporating composition $US_{1.00}$ was attained. The vapor in equilibrium with this solid composition was found to consist chiefly of the gaseous atoms U and S

with gaseous molecules US of less, though comparable, importance. At the highest temperatures of the spectrometric study the gaseous molecule US_2 was barely detectable.

The rate of effusion of uranium-containing species, measured in the target experiments, was expressed in terms of an "effective vapor pressure" P_E , which, when combined with the molecular weight 270.14, gives directly the rate of evaporation of stoichiometric US. An empirical equation fitted by the method of least squares to the data gave

$$\log P_E(\text{atm}) = -1.7382 + 3.127 \times \frac{10^4}{T} - 1.3181 \times \frac{10^8}{T^2} + 0.093776 \times \frac{10^{12}}{T^3} .$$

The observed volatility varied by a factor of 10^5 over the nine hundred degree temperature range, and was about one third that of uranium dioxide at 2300°K .

Combination of target and mass spectrometric data yielded the data requisite to a linear treatment of the logarithms of the partial pressures of the individual vapor species as a function of reciprocal temperature. By means of the second law the following values were obtained (both statistical standard deviations and estimated absolute errors are given).

For the reaction

For the reaction

The corresponding heat of dissociation of the gaseous molecule is 121 kcal/mole or 5.2 electron volts per molecule, not far less than for the corresponding gaseous monoxide.

The second law results were combined with published data for the elements to give absolute entropies at 2300°K for solid and gaseous US of 45.08 and 83.44 cal/deg-mole, respectively.

Theoretical considerations were employed to obtain the forms of equations expressing the changes of entropy and free energy for the reactions as functions of temperature and the constants were evaluated from the experimental data. The resulting equations for the free energies, which are not valid for extrapolation to low temperatures, are

$$\Delta F_T^{\circ}(\text{I}) \text{ (cal/mole)} = -7.65271 \times 10^6 - 1.2210 \times 10^3 T + 0.13212 T^2 \\ + 2.90655 \times 10^6 \log T + 6.8635 T \log T \quad ,$$

$$\Delta F_T^{\circ}(\text{II}) \text{ (cal/mole)} = -7.53833 \times 10^6 - 1.2232 \times 10^3 T + 0.132119 T^2 \\ + 2.90655 \times 10^6 \log T + 2.96503 T \log T \quad .$$

Other data obtained were the melting point of uranium monosulfide ($2735 \pm_{-5}^{+30}$ °K), its lattice parameter at room temperature (5.4903 ± 0.0002 Å), and its resistivity ($100 \pm 30 \times 10^{-6}$ ohm-cm). Schematic phase diagrams were drawn for the systems uranium-sulfur and uranium-oxygen-sulfur, and lattice parameters were obtained for uranium oxysulfide.

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I. INTRODUCTION

A. General Incentives for This Research

The test of any scientific theory must be the closeness of agreement between its predictions and experimental observation. Conversely, without a sufficiency of reliable experimental results available, the theorist is handicapped in any attempt to formulate principles for predicting the behavior of new systems. Present knowledge of quantitative aspects of chemical bonding, for example, is based largely on study of diatomic molecules of elements of low atomic number, either homonuclear or composed of oxygen and one of the regular subgroup elements. The commonly accepted fundamental theoretical treatment, that of the Schrödinger wave equation, has been able only qualitatively to predict spectra and bond energies, even for the simplest molecules, and it is reasonable to suppose that until the behavior of relatively simple systems is understood, the behavior of complex systems must remain only vaguely intelligible.

Thermochemical and mass spectrometric studies in recent years have shown that previously unsuspected gaseous molecules containing heavy metal atoms are rather common in the vapor in equilibrium with their solid compounds, and further that some of these molecules are of surprising complexity. To date, systematization of vaporization behavior and detection of trends, for example of dissociation energies, have been seriously hindered, not only by the considerable absence of pertinent data, but also by the poor reliability of many of those available. Only for homonuclear diatomic gases and the metal oxides have there been enough quantitative data to permit an approach

to a systematic survey of the thermodynamics of the vaporization processes and stabilities of the gaseous species.^(1,2)

Good thermochemical measurements in a large number of refractory systems of heavy metals are necessary both to provide stepping stones to simplification of the theory of chemical bonding and to enable formulation of empirical treatments for technological purposes. Clearly, no single experimental investigation can hope to provide more than a small contribution toward these goals. Each accurate characterization of a new molecule, on the other hand, is a definite advance in this direction. This study of the vaporization of uranium monosulfide was undertaken with these thoughts in mind.

B. Interest in Sulfide Systems in General

The current interest in refractory inorganic compounds has led to the study of binary systems involving such metals as aluminum, the lanthanides, titanium, zirconium, tantalum, molybdenum, tungsten, thorium, and uranium with the nonmetals of the oxygen, nitrogen, carbon, and halogen groups of the Periodic Table, and with boron. Of these substances, the sulfides have been studied the least, particularly with respect to vaporization. From a scientific standpoint, experiments with sulfides yielding thermodynamic data for the vaporization processes and determining the existence and properties of any gaseous molecules are of great interest, for the results of such experiments can be compared with those for the corresponding oxides, and the effects of the increased anion atomic number on bonding and thermodynamics of the vaporization process can be inferred and used to extend present theories as well as tabulations of data.

Herzberg⁽³⁾ lists in addition to the molecules HS and SO only twelve gaseous monosulfide molecules of formula MS, where M represents Mg, Ca, Sr, Ba, C, Si, Ge, Sn, Pb, Zn, Cd, or Hg, all elements of groups IIA, IVB, and IIB of the Periodic Table. The dissociation energies given were usually obtained by extrapolation of spectroscopic data and are somewhat uncertain, or else only upper limits are estimated.

Inghram and Drowart⁽⁴⁾ have tabulated the gaseous species determined in the vapor of the condensed phases studied mass spectrometrically to date. The solid sulfides listed are CdS, HgS, and ZnS. Goldfinger, Ackerman, and Jeunehomme⁽⁵⁾ found only the gaseous elements above these phases. Inghram and Drowart state that BaS and SrS give gaseous molecules of the same formulas, but do not include these in their table. The vapor pressures of the sulfides GeS,^(6,7) Ga₂S₂, ZnS, and CdS^(8,6) recently have been measured by transpiration methods. In general, the dissociation energies of the monosulfides are less by 20 to 80 kilocalories per mole than those of the corresponding monoxides. Reasoning by analogy with oxides leads to the expectation that the most stable gaseous monosulfides are those of tantalum, thorium, lanthanum, hafnium, zirconium, uranium, strontium, and yttrium.⁽²⁾

An opportunity certainly is present in the study of the vaporization of sulfides for providing good data in a field of high temperature chemistry relatively unexplored in previous work and uncluttered with the errors of previous workers. The choice of uranium monosulfide for the present research seemed particularly reasonable because of the likelihood of its forming gaseous molecules and because of the previous interest in the vaporization of uranium oxides and the availability of requisite materials and equipment at Argonne National Laboratory.

C. The Uranium-Sulfur System: Previous Studies

Five compounds having the formulas US₃, US₂, U₃S₅, U₂S₃, and US have been identified in the uranium-sulfur system, chiefly during three series of investigations in the last two decades; in addition, an oxy-sulfide, UOS, is known. Tables I and II list the reported physical and chemical properties of these compounds; some of the results of the present research are included.

Strotzer, Schneider, and Biltz⁽⁹⁾ studied the pressure produced in the dissociation of the trisulfide to give solid disulfide and gaseous sulfur. They also verified earlier findings on US₂ and U₂S₃. They assigned a formula U₄S₃ to a compound having a cubic structure of the

TABLE I
PROPERTIES OF THE URANIUM SULFIDES

Compound	US ₃	US ₂ - α (high-temp.)	US ₂ - β	US ₂ - γ (low-temp.)
Appearance	black, metallic luster	dark gray or black in powder	same as α	
Physico- Chemical Properties		U ₃ S ₅ on melting at 1680	Melted at 1560 on TiC M.P. $1850 \pm 200^\circ \text{C}$ $\alpha \rightleftharpoons \beta$ at 1150 to 1450 $^\circ \text{C}$ $\gamma \rightarrow \beta$ above 425 $^\circ \text{C}$	
Mol. mag. (cgs) sucept. (units)	2700×10^{-6}	3140×10^{-6}	3470×10^{-6}	3720×10^{-6}
Crystal Structure (parameter in Å)	monoclinic $a_0 = 5.40$ $b_0 = 3.90$ $c_0 = 18.26$ $\beta = 80^\circ 30'$ (USe ₃ - type)	tetragonal $a_0 = 10.27$ $c_0 = 6.31$	orthorhombic iso. w. ThS ₂ $a_0 = 4.13$ $b_0 = 7.12$ $c_0 = 8.48$	hexagonal $a_0 = 7.252$ $c_0 = 4.067$
Solid Solution?	None	probably small		
Vacuum Behavior	Dissociates to US ₂ (s) + S ₂ (g)	U ₃ S ₅ or U ₂ S ₃ (s). In graphite U ₂ S ₃ (s) + US (s) + carbide. Probably gaseous sulfide molecules, e.g. US ₂ (g).		

Compound	U ₃ S ₅	U ₂ S ₃	US	UOS
Appearance	blue-black powder	gray-metallic in bulk black powder	Bright metallic luster, gold or silver	black powder
Physico- Chemical Properties	M.P. 1850 (k) $\pm 100^\circ \text{C}$ some el. cond. M.P. <1800 $^\circ$ (p)	M.P. 1850 (k) $\pm 150^\circ \text{C}$ fair el. cond. M.P. <1800 $^\circ$ (p)	M.P. $2462^{+30}_{-5} \text{ }^\circ \text{C}$ Resistivity $100 \pm 30 \mu\text{-}\Omega \text{ cm.}$	
Mol. mag. (cgs) sucept. (units)	3740×10^{-6}	2630×10^{-6}	4600×10^{-6}	3010×10^{-6}
Crystal Structure (parameter in Å)	orthorhombic $a_0 = 7.42$ $b_0 = 8.08$ $c_0 = 11.72$	orthorhombic (Sb ₂ S ₃ type) $a_0 = 10.41$ $b_0 = 10.65^*$ $c_0 = 3.89$	cubic (NaCl-type) $a_0 = 5.4903 \pm .0002$	tetragonal (PbClF - type) $a_0 = 3.483$ $c_0 = 6.697$
Solid Solution?	probably small		Probably $0.96 \pm 0.01 \leq \text{S/U}$ $< 1.01 \pm 0.01$	yes $0 \geq \text{U}$ $0 \geq \text{S}$
Vacuum Behavior	In graphite U ₂ S ₃ + US (s) at 1600 $^\circ \text{C}$. Above 1750 $^\circ \text{C}$ US (s) + carbide. Probably form gaseous sulfide molecules.		Congruent vapor- ization to U + S + US + US ₂	Perhaps congruent vaporization. Probably elements, UO (g), UOS (g).

TABLE II
CHEMICAL REACTIONS OF THE URANIUM SULFIDES

Compound	US ₃	US ₂
Dil. acid	Easily soluble	Easily soluble. β -US ₂ most slowly attacked. H ₂ + H ₂ S formed.
Acetic acid	Soluble	Soluble
Alkalies and NH ₃		No reaction.
Oxidizing agents (aqueous)	Reacts	Reacts to form uranyl sulfate.
Hydrogen		Reduced to U ₃ S ₅ or U ₂ S ₃ at high temperatures.
Air	Oxidized to sulfur and uranyl sulfate on standing.	Surface oxidation at room temp. Forms UOS at 300°C. γ -US ₂ forms UO ₂ . Pyrophoric when ground.
Al		Reduced to U ₂ S ₃
Graphite		Reduced to lower sulfides and carbide.
Sulfur		Forms US ₃ in sealed tube.

Compound	U ₃ S ₅ U ₂ S ₃	US	UOS
Dil. acid	Slowly soluble. H ₂ + H ₂ S formed.	Slowly soluble. H ₂ + H ₂ S formed.	No reaction.
Acetic acid	No reaction.	No reaction.	No reaction.
Alkalies and NH ₃	No reaction.	No reaction.	No reaction.
Oxidizing agents (aqueous)	React to form uranyl sulfate.		Reacts to form uranyl sulfate.
Hydrogen			No reaction, even at 1000°C.
Air	No apparent reaction at room temp. Oxide formed at 300°C.	No reaction at room temp. Slow oxidation to UOS at 160°C. Pyrophoric on grinding.	
Al	Not reduced.		Reduced to US.
Graphite	Form US + carbide.	Forms carbide	Reduced to US + carbide
H ₂ S	Form US ₂ .	Forms US ₂	Forms US ₂ .

sodium chloride type, whose X-ray diffraction pattern was found by Zumbush⁽¹⁰⁾ to have weak lines, indicating the regular absence of a sulfur atom from the center of the unit cell. Their density measurements seemed to confirm the U_4S_3 formula.

Eastman, Brewer, Bromley, Gilles, and Lofgren^(11,12,13) prepared and studied the sulfides and oxysulfides of cerium, thorium, and uranium in a program of evaluating their possible use as crucible materials.⁽¹⁴⁾ Zachariasen^(15,16) performed the X-ray examinations of their materials. These authors found that the disulfide US_2 on being heated in vacuum loses sulfur and forms U_2S_3 in the condensed phase. They obtained no evidence for a compound of formula U_4S_3 , rather finding a sodium chloride-type cubic phase of formula US and the corresponding monosulfides of thorium and cerium. Two modifications of US_2 were found.⁽¹⁶⁾ The melting point of US_2 was found to be $1850 \pm 100^\circ C$; that of the gray metallic US was above $2000^\circ C$. They demonstrated the existence of the oxysulfide UOS ⁽¹³⁾ and determined its crystal structure.

Picon and Flahaut⁽¹⁷⁾ have discussed the previous studies on the uranium sulfides. They performed careful work which provided the crystal structures of the trisulfide and of a third modification of the disulfide, and verified those of the compounds U_2S_3 , US , and UOS . They prepared and characterized a new compound of formula U_3S_5 . Picon and Flahaut heated uranium disulfide in a graphite crucible in vacuum, observing loss of sulfur and the formation of a solid residue containing the lower sulfides U_3S_5 at $1530^\circ C$ after one hour, and of $U_3S_5 + U_2S_3 + US$ after $2\frac{1}{2}$ hours at $1700^\circ C$. The residue at $1700^\circ C$ contained appreciable amounts of carbide. The lower sulfides US (see below), U_2S_3 , and U_3S_5 were found to be conductors of electricity, the conductivity decreasing in that order.

Both Eastman et al.⁽¹²⁾ and Picon and Flahaut⁽¹⁷⁾ have reported measurements of the magnetic susceptibilities of these compounds and have discussed the nature of the chemical bonds in the solid sulfides in terms of the crystal structures and observed chemical, electrical, and

magnetic properties, as have Zachariasen⁽¹⁵⁾ and Fried and Zachariasen.⁽¹⁸⁾ Picon and Flahaut concluded that in all the compounds uranium is in the +4 state, with the electronic configuration $6d^2$ in the compounds US_2 , UOS , and US_3 , and $5f^2$ in the lower sulfides U_2S_3 , U_3S_5 , and US . In the lower sulfides the electrical conductivity is attributed to metallic bonding between the uranium ions by the electrons not required for bonding to the sulfide ions. In US_3 the existence of polysulfide groups accounts for the necessary sulfur bonds. Fried and Zachariasen pointed out that in the sesquisulfide U_2S_3 uranium behaves as a member of the molybdenum-tungsten group rather than as an actinide.

Uranium monosulfide is one of a rather large number of known compounds of formula MS , in which M may be a metal in any group of the Periodic Table except IA and IIIB (Ga, In, Tl). Of this larger number, some twenty monosulfides with the sodium chloride structure have been characterized, formed by the alkaline earth metals, manganese, and lead;^(19,20) yttrium, lanthanum, and the rare earth metals;^(21,22) uranium, thorium, and plutonium;⁽¹⁵⁾ and zirconium.⁽²³⁾ These compounds are refractory. The lanthanide monosulfides, for example, have melting points between 1940 and 2140°C;⁽²²⁾ US , reportedly between 2000 and 2200°C^(11,17) but shown in the present research to be about 2460°C; ThS , 2400 to 2450°C;⁽²⁴⁾ and CeS , $2450 \pm 100^\circ C$.⁽¹²⁾ Many exhibit a metallic luster and are conductors of electricity.

D. The Specific Purpose of this Research

The purposes of this research were to prepare and to study the phase behavior and vaporization of pure uranium monosulfide in order to determine whether there is a congruently vaporizing composition near $S/U = 1.00$; if such were found, to measure its volatility quantitatively, and, if possible, to infer the gaseous species and to determine their partial pressures as a function of temperature. Thereby their heats and entropies of vaporization and the dissociation energies of any gaseous molecules could be established. These ends have been

accomplished by combining results obtained from chemical and X-ray studies and from effusion experiments, utilizing both collection of effusate on targets and mass spectrometric techniques.

II. DATA OBTAINABLE FROM VAPORIZATION STUDIES

An investigation of the vaporization of a given substance, particularly of a refractory inorganic substance, can be of more fundamental importance than simply serving to measure the evaporation rate, for it can yield much valuable information about the thermodynamic nature of both the condensed phase or phases and of the gaseous species produced. By a study of the dependence upon temperature or on time at a fixed temperature of the vapor pressure or partial pressures of individual vapor species, especially if certain other data are available or can be estimated, enthalpy, entropy, and free energy changes for the vaporization process or processes, heats of formation of solid compounds and gaseous molecules, and dissociation energies, as well as a characterization of the phase relationships in the condensed material, can be obtained. The interrelationships deducible from thermodynamic "cycles" may permit the results from any one study to be applied to the elucidation of other systems. The understanding of the condensed phase behavior is requisite to the calculation of thermodynamic data from vapor pressure measurements.

The phase rule,

$$\underline{F} = \underline{C} - \underline{P} + 2 \quad ,$$

expresses the relationship between $\underline{F}$, the number of thermodynamic variables (degrees of freedom) which must be specified in order completely to define a system in a thermodynamic sense, and $\underline{C}$ and $\underline{P}$, respectively the number of components and the number of phases in equilibrium in the system. For a two-component system, for example, in order for the pressure to be defined at a given temperature in a closed container in which condensed material is in equilibrium with vapor, either there must be three phases present or else some additional restriction must be imposed on the system. Since the vapor constitutes one phase, either there must be two condensed phases, either solid or liquid or both, or else the overall composition of the

vapor must be the same as that of the condensed phase. The latter case constitutes a congruent vaporization process. Both situations are said to be univariant, because a change in one variable, e.g., the temperature, to a new, fixed value uniquely redefines the total pressure. A study of the vapor pressure or related rate of evaporation of a given substance with time at a given temperature, combined with chemical and X-ray diffraction analyses before and after the evaporation, permits a deduction of the behavior of the condensed phase involved, and thus renders meaningful any thermodynamic values obtainable from further vaporization studies with the same substance. The application of the phase rule to the vaporization of uranium monosulfide will be discussed in connection with the corresponding experimental results in later sections.

The thermodynamic values most directly obtainable from vapor pressure measurements are the changes of enthalpy and entropy accompanying a vaporization reaction, commonly termed the heat and entropy of vaporization. It is, of course, necessary that the vapor species produced in the evaporation be known in order that the reaction can be correctly written.

The equilibrium constant for any vaporization reaction at any temperature is related to the enthalpy and entropy changes, ΔH_T° and ΔS_T° , by the Clausius-Clapyron equation:

$$\log K = -\frac{\Delta H_T^\circ}{2.303 RT} + \frac{\Delta S_T^\circ}{2.303 R} \quad , \quad (1)$$

in which R is the molar gas constant and 2.303 is the natural logarithm of 10. The so-called second law determination of the heat and entropy of vaporization follows from the assumption that ΔH° and ΔS° are constant over the temperature range (usually a few hundred degrees) in which vapor pressures are measured. The equilibrium constant is expressed in the usual way as the product of partial pressures raised to the appropriate powers, and the average values of ΔH° and ΔS° over

the temperature range are obtained from the slope and intercept of a straight line through the data plotted as $\log K$ vs. $1/T$.

The assumption of constant enthalpy and entropy changes over the temperature range implies that at each temperature the heat capacities of the gaseous products are equal to those of the condensed phases, a situation virtually never realizable. If heat capacity data are available or can be estimated for reactants and products, it is possible to obtain values of ΔH_T° and ΔS_T° for each temperature, and to extrapolate them for tabulation purposes to suitable reference temperatures, usually 0°K or 298.16°K . For example, if the assumption is made, not that the heat capacities of gaseous and condensed phases are equal, but that the difference ΔC_p between them is constant, then

$$\Delta H_T^\circ = a + \Delta C_p T \quad ,$$

where a is a constant (sometimes called ΔH_0). In this case a plot of

$$\left(\log K - \frac{\Delta C_p}{R} \right) \text{ against } 1/T \text{ gives a straight line for which the equation is}$$

$$\log K - \frac{\Delta C_p}{R} \log T = \frac{a}{2.303 RT} + I \quad ,$$

where I is an integration constant from which the entropy change can be calculated. It is almost never possible to obtain ΔC_p accurately from vapor pressure data by fitting the best curve through experimental points plotted as indicated, because of the great sensitivity of the experimental curvature to small errors in temperature measurement, and the scatter of points that results.

Because the slopes of the various experimental plots are sensitive to small systematic errors in measured temperatures, and generally unexplainable errors seem to lurk even in careful high-temperature measurements of vapor pressure, it is advisable if possible to check the values determined by the second law method against a method based on the third law of thermodynamics. When the third law method is applicable, the calculated heats and entropies of vaporization may be more reliable than second law values because of a decreased sensitivity to errors in the calculated pressures. In essence, either absolute

entropies and heat capacities or else the free energy functions $(F_T^\circ - H_\theta^\circ)/T$ for the gases and condensed phases involved are used to calculate from each experimentally determined pressure a corresponding heat of vaporization ΔH_θ° at the reference temperature θ . The free energy functions are calculable from spectroscopic and heat capacity data, and knowledge of them is effectively the same as knowledge of the absolute entropies of the substances of interest at the temperatures T . Unfortunately, the standard tabulations of free energy functions [see for example references (25) and (26)] for high-temperature substances and those found in individual publications usually do not contain data applicable to the problem at hand, and one must often accept the second law values without third law confirmation. It is possible, however, to estimate free energy functions for a given compound with fair accuracy, if those for related compounds are known. Such semi-empirical estimates are frequently used to provide rough third law heats and entropies for use in determining whether second law values are reasonable.

III. THE EFFUSION METHOD FOR VAPORIZATION STUDIES

A. Principles of the Effusion Method

The most widely applicable method for the determination of vapor pressures of slightly volatile substances is the effusion method, which was employed in the present investigation. Consider a closed, inert, initially evacuated container, inside which a solid or liquid sample is in equilibrium with its vapor. The container is at a fixed, uniform temperature and is located in an evacuated space. The pressure inside the container is then the equilibrium vapor pressure, and if the vapor behaves ideally, one can show from kinetic theory that the number of each kind of molecule striking unit area of the container wall in unit time is $n\bar{c}/4$, where n is the density of the gas in molecules per unit volume and $\bar{c}$ is the average speed of the molecules. It was first demonstrated by Knudsen in 1909⁽²⁷⁾ that if the wall were thin enough and if a small enough opening were made in it, then under certain conditions, one could measure the pressure inside the container by measuring the number of molecules effusing through this orifice of known area without appreciably disturbing the equilibrium inside. Accordingly, the method is generally called by his name. In the classical Knudsen experiment a measurement is made of the rate of weight loss of the container, in which case the kinetic theory relates the partial pressure p of the vapor species of molecular weight M to the weight, W , of that species effusing in time t through an orifice of area a by the equation

$$p = \frac{W}{at} \sqrt{\frac{2\pi RT}{M}} \quad , \quad (2)$$

where T is the absolute temperature of the container and R is the ideal gas constant per mole. This result corresponds, of course, to expression of the pressure in terms of the rate of effusion, Z moles, of vapor as

$$p = \frac{Z}{at} \sqrt{2\pi MRT} \quad . \quad (3)$$

It is often more convenient, particularly in the investigation of systems at high temperature, to condense a known fraction of the

effusate on a suitably positioned and cooled target than to measure the actual weight loss of the container (hereinafter called the effusion cell or crucible). If the target is circular, of radius r , and is placed coaxial with the orifice at a distance d , if the target is large compared to the orifice, and if the other conditions listed below are met, then it can be shown⁽²⁸⁾ that the pressure p is related to the weight w gained by the target according to the equation

$$p = \frac{w}{at} \sqrt{\frac{2\pi RT}{M}} \left(\frac{r^2 + d^2}{r^2} \right) . \quad (4)$$

Evaluation of the constants for p in atmospheres, w in grams, a in cm^2 , t in seconds, and T in degrees Kelvin gives

$$p = 0.022557 \frac{w}{at} \sqrt{\frac{T}{M}} \left(\frac{r^2 + d^2}{r^2} \right) . \quad (5)$$

B. Experimental and Theoretical Requirements

The conditions limiting the validity of equations (2) and (3) as applied to an experimental investigation are here classified either as fundamental or practical, according to whether they may be attained only to the same degree in all experiments or to varying degrees depending on the experimental materials and techniques. The practical limitations are as follows:

- (a) The experimental sample must not react with the crucible material, or else the character of such reaction must be known and taken into consideration, e.g., if new vapor species are produced.
- (b) The residual pressure in the vacuum system must be low enough to preclude the scattering of the effusing vapor or reaction with the crucible charge by the residual gases present.
- (c) The effusion cell and sample must be at a known uniform temperature.
- (d) The molecular weights and relative abundances of the vapor species must be known.

- (e) The area of the evaporating surface and its location must be such that the saturation pressure is maintained within the effusion cell.
- (f) The orifice must be of the proper shape as described below, and be small enough that the saturation pressure is maintained within the effusion cell and that the temperature uniformity in its cavity is not disturbed.
- (g) The fraction of impinging molecules which sticks to the target must be known, and the walls of the vacuum system must condense and retain all effusate striking them, so that the target receives material only from the orifice.
- (h) If weight losses or gains by targets are to be determined directly by weighing, the volatility of the crucible itself must be known and allowance made for it.
- (i) The physical dimensions of the apparatus must be accurately known and allowance made for changes effected by temperature.

The means by which and the degree to which these various experimental requirements were met in the present investigation are discussed in appropriate places later in the text. A further statement regarding condition (f) should be made here, however. If a binary compound AB evaporates congruently to the gaseous atoms A and B, the observed effusion rates for A and B must always differ from those calculated from equation (3) and the equilibrium partial pressures expected in a closed container. At a given temperature the ratio of the average molecular velocities for any two vapor species A and B is given by the inverse ratio of the square roots of the molecular weights:

$$\bar{c}_A / \bar{c}_B = (M_B / M_A)^{1/2} \quad ,$$

and so, therefore, must be the effusion rates, provided the partial pressures remain equal. Now the specification that the solid composition remain fixed requires that the effusion rates of A and B be equal, with

the result that the partial pressures must adjust in the effusion cell to give a measured ratio

$$p_A/p_B = (M_A/M_B)^{\frac{1}{2}}, \quad (6)$$

whence

$$p_A = p_B (M_A/M_B)^{\frac{1}{2}}.$$

The equilibrium constant determined in an effusion experiment in which only the partial pressure of B is measured directly is then given by

$$K = p_B^2 (M_A/M_B)^{\frac{1}{2}}, \quad (7)$$

and the equilibrium partial pressure p_B^e to be expected in a closed vessel, or which would be obtained in a transpiration or rate of evaporation measurement from an unenclosed surface, is related to the partial pressure in the effusion cell by

$$p_B^e = p_B (M_A/M_B)^{\frac{1}{4}}. \quad (8)$$

Equilibrium conditions can be approached as nearly as desired in the effusion cell if the orifice is made smaller and smaller, but equations (6), (7), and (8) always must be kept in mind in treatment of the data.

The two chief fundamental limitations to the range and accuracy of pressure measurement by the Knudsen method relate to the assumption that the number of molecules leaving the orifice gives the pressure inside the crucible in accordance with formula (3). First of all, the pressure in the cell must be low enough that "free molecular flow" obtains, i.e., collisions between the gaseous molecules must be so infrequent that each molecule leaves through the orifice without affecting the trajectories of the others. Knudsen⁽²⁹⁾ in his experiments on the flow of gases through thin-edged orifices observed that hydrodynamic flow effects caused the mass of gas effusing from a region at a known pressure to be greater than that calculated from formula (3) when the pressure was above certain values. These values corresponded to a ratio of mean-free path to orifice diameter, λ/D , of about 10, and this

value of λ/D has often been quoted in the literature as the upper pressure limit of molecular effusion and thus of the effusion method for vapor pressures.

Subsequent experimental evidence^(30,31,32,33) gave mutually inconsistent information on the upper limit. Because of the complex way in which molecular sizes and intermolecular potentials enter, and in view of the inaccurately known effective collision diameters of actual molecules, it is not surprising that no theoretical treatment has yet been presented which accurately predicts the pressure at which departure from molecular flow should occur for a given gaseous species. Therefore the data from each individual set of measurements must be examined separately to detect upward curvature of a $\log K$ vs. $1/T$ plot at the higher pressures. Carlson⁽³⁴⁾ has given a method of plotting the data which gives a more sensitive test than does the $\log K$ plot itself.

If the data from a given investigation give evidence of a departure from molecular flow in its upper pressure region, at present it seems best to determine thermodynamic functions only from measurements at the lower pressures.

The second fundamental limitation (orifice shape) to the validity of pressure measurements by the effusion method will be discussed only briefly. If the effusion orifice has the form of a tube of finite length, there will be a corresponding probability that a molecule entering the orifice will strike its wall and, because such a collision results in a diffuse reflection, be returned to the cavity. It follows that the number of effusing molecules does not accurately represent the number entering the orifice, and so does not accurately give the pressure from equation (3). A theoretical treatment of the transmission probability for molecules passing by molecular flow through tubes of finite length should yield both the decrease in total flow from that expected for a thin-edged orifice and the distribution with angle of the effusing molecules. Clausing⁽³⁵⁾ performed the necessary calculations and

obtained integral equations whose approximate numerical solution yielded the factors by which the right side of equation (3) must be multiplied to give pressures from rates of effusion through orifices whose shapes are circular cylinders of various ratios of length to diameter.

The number of molecules emitted by molecular flow per unit time per unit solid angle in each direction above the orifice plane is described for an ideally thin-edged orifice by the "cosine law." This law, which also describes the intensity of radiation of light from a plane surface, the distribution of molecules emitted from a plane surface by free evaporation, and (usually) the directional probability of re-emission from a plane surface of molecules impinging upon the surface, may be written as

$$dz = Z_0 \frac{1}{\pi} dS_0 \cos \theta d\omega \quad . \quad (9)$$

For the present purpose dz represents the number of molecules leaving the orifice in unit time from the element of area dS_0 in an elementary solid angle $d\omega$ at the angle θ to the normal to the orifice plane at dS_0 . The total rate of emission from the entire orifice is Z_0 molecules per cm^2 per unit time. Integration of equation (9) shows that in a given time equal numbers of molecules pass through equal areas located anywhere on a large sphere tangent to the orifice. If, therefore, the orifice is ideally thin, it is necessary only to know the distance to and the angular orientation of a target anywhere above the orifice in order to calculate the fraction of the total effusate which strikes the target.

If the orifice has a finite thickness, the distribution of molecules effusing through it will no longer be given by the cosine law, because reflections from the orifice wall will change the distribution of molecules at large angles to the normal. The distribution in the forward direction, on the other hand, will be little affected for orifices shaped like short channels. Clausing⁽³⁵⁾ evaluated numerically the case for a short tube of circular cross section, whose length and diameter are equal, and obtained quantitative results verifying this expectation.

The most important result from the standpoint of the present investigation is that even for appreciable deviation from the ideal orifice shape in the effusion cell, a target located on the normal to the orifice plane at the center of the orifice should still give accurate pressures by means of formula (4), provided the target subtends a small angle (less than, say, 10 degrees) at the orifice. A careful analysis of these problems and a discussion of the published experimental investigations and attempts^(36,37) to treat theoretically the transmission probabilities of effusion cells themselves are to be found in Carlson's work.⁽³⁴⁾

Of the several conditions described in this section, the one most difficult to meet in an effusion study utilizing weight loss or target techniques is (d). For substances evaporating congruently by one process only, it is often possible to identify the process indirectly by judicious consideration of all possibilities in the light of available thermodynamic tabulations and the experimental evidence, particularly if static or transpiration techniques can be applied to measure the gas density. However, if two or more simultaneous evaporation reactions are occurring, it is necessary to employ more sophisticated experimental techniques, preferably techniques sensitive individually to the various reactions or species. For accurate determination of the total effusion rate, the classical methods continue to give the most reliable results.

C. The Mass Spectrometer Applied to Effusion Studies

1. Theory, Advantages, Technique, and Limitations

Because of the ability in principle simultaneously to identify and to determine concentrations of the various molecular species present in a gas or a vapor mixture, the mass spectrometer is an outstanding tool in the study of vaporization of solids. Its use has provided information on species of very low partial pressures and reliable numerical results when the third law method has been applicable. The

main experimental limitations to date have been in temperature measurement, nonuniformity, and the maximum temperatures available with present control systems, but the more fundamental limitation is the lack of knowledge of accurate ionization cross sections.

The use of the mass spectrometer as a detector for the molecular beam effusing from a Knudsen cell is basically as follows. The effusing molecules pass through collimating slits and some are ionized, usually by collision with an electron beam. The resulting ions are accelerated electrostatically as an ion beam from the ionization region into an evacuated space where the beam is resolved by magnetic deflection or drift time into components whose ions are characterized by different charge-to-mass ratios. Assume, for simplicity, that all ions are singly charged molecules or atoms which were formed in the effusate without changes in formula. Then the ion current I_i^+ due to the species of molecular weight M_i is related⁽³⁸⁾ to the partial pressure p_i of the corresponding molecules of kind i in the effusion cell at temperature T by the equation

$$I_i^+ T = G D_i \sigma_i p_i \quad . \quad (10)$$

Here G is a constant determined by the physical dimensions of the system and the ionizing electron beam intensity. D_i is the efficiency of the ion detector (commonly a secondary electron multiplier system) for ions of molecular weight M_i of a given molecular structure and the appropriate energy, and σ_i is the cross section or efficiency of ionization for molecules i when bombarded by electrons of the particular energy used. Measurement of I_i^+ at various source temperatures in principle permits evaluation of $d(\log p_i)/d(1/T)$ and so of $\Delta H_T^\circ(i)$, because the constants of equation (10) may be assumed to be independent of temperature and pressure.

In practice determination of absolute partial pressures involves several fundamental uncertainties over and above those already inherent in the effusion technique, chiefly those involving knowledge of ionization and detector efficiencies. Because of the complex geometry of the apparatus, in particular the width and location of molecular and electron beams, the constant G is generally evaluated by total evaporation at constant temperature of a sample of known mass and comparison of the mass loss with the total charge calculated by integration with time of the ion currents due to the observed species, or by measurement of the ion current from a standard substance, for example silver, of known vapor pressure. If the experimental material yields more than one gaseous species and in any case involving a standard, the relative ionization cross sections of all the species must be known (a situation almost never realized) or they must be estimated. A special case in which combination of total rate of effusion and mass spectrometric measurements enables an accurate determination of the cross sections is discussed below. It is generally assumed that ionization efficiencies of atoms are proportional to atomic radii and that the cross section for a molecule is an additive function of the cross sections of its constituent atoms.⁽³⁹⁾

Use of the electron multiplier detector introduces uncertainty in pressure measurements because its efficiency is not constant for ions of different mass and is affected by molecular structure at constant mass. These uncertainties are probably not so serious as those due to cross-section estimation. Other problems which must be treated include differentiation between primary ions and those formed by their dissociation or arising in other regions than the effusing beam in the ionization chamber, and effects due to molecules and ions in excited states. Uncertainties in the estimated relative cross sections and multiplier efficiencies are commonly reported to give uncertainties

in absolute pressures of a factor of two or three. In a recent survey Inghram and Drowart⁽⁴⁾ discussed these matters rather fully.

Most spectrometer studies of evaporation of solids have employed effusion cells heated by electron bombardment, and uncertainties and gradients in temperatures have led authors to regard the second law determination of heats as unreliable for this reason, even though good precision may have been attained.⁽⁴⁰⁾ Although it should be possible to eliminate these sources of error by improved technique, the second law determination of entropies from mass spectrometric data for systems containing more than one gaseous species or in which a reference standard substance is used for calibration must still yield numbers uncertain by R times the logarithm of the uncertainty in absolute pressure, or thus by ± 1 or 2 cal/deg-mole.

2. Combination of Mass Spectrometric and Absolute Rate of Effusion Measurements

Use of standard effusion technique, say in an effusate collection study, to determine the temperature dependence of the total volatility can be combined with use of the mass spectrometer to provide data of greater reliability than from the latter alone and results impossible by the former alone. For example, assume that some binary compound AB evaporates by the two processes

and

A precise effusion study in which the total rate of weight loss of solid AB is determined as a function of temperature would give at each temperature an "effective pressure" P_E calculated from equation (3) or (4):

$$P_E = p_{AB} + p_A \sqrt{\frac{M_{AB}}{M_A}} \quad (11)$$

Here p_{AB} and p_A represent the partial pressures of the AB molecules and A atoms in the effusion cell. The effective pressure P_E can be

determined to an accuracy of a few per cent at each temperature. Measurement in a mass spectrometer of the temperature dependence of the individual ion currents due to A^+ and AB^+ under conditions of constant ionization and acceleration would then provide all the data requisite to the calculation of the cross sections, σ , for A and AB, and thus to the calculations of their actual partial pressures over the temperature range studied. This method, when applicable, should provide a direct determination of the cross sections of vapor species which could not otherwise be obtained. For subsequent application elsewhere, the values so obtained would have to be adjusted for the detector efficiencies for the various ions.

In the more numerous cases in which the above treatment does not apply, it is still desirable to combine data from ordinary and mass spectrometric effusion experiments. The mere identification of species may enable solution of an otherwise "impossible" standard effusion study, and the independent determination of absolute vaporization rate serves as a check for gross errors in the mass spectrometrically estimated material balance.

IV. EXPERIMENTAL STUDY OF THE VAPORIZATION OF URANIUM MONOSULFIDE

A. Summary of Experimental Approach

Uranium monosulfide free of oxide contamination was prepared by reaction of finely divided uranium with hydrogen sulfide and subsequent homogenization of the reaction product by annealing and sublimation at high temperatures in vacuum. Samples of uranium monosulfide of other than stoichiometric composition were found to attain one-to-one stoichiometry on vacuum vaporization. The total rate of loss of uranium in vaporous species was determined as a function of temperature by the condensation, on platinum targets in a system of known geometry, of the vapor from tungsten effusion cells containing uranium monosulfide, and assay of these targets by α -counting. Vapor species were identified, and their relative concentrations as a function of temperature were obtained mass spectrometrically. The data were combined with the data on total volatility for calculation of partial pressures of the gaseous species U, S, and US. A second law determination of the enthalpy and entropy changes accompanying the processes

and

could then be made.

Theoretical considerations yielded the proper forms of non-linear equations, which were then fit to the data to give the entropies and free energies of vaporization as functions of temperature.

B. Preparation of Uranium Monosulfide

1. Method

Strotzer et al.⁽⁹⁾ prepared a uranium subsulfide, which they formulated as U_4S_3 , by reaction of the elements in a sealed, initially evacuated tube. Picon and Flahaut⁽¹⁷⁾ prepared the monosulfide US by aluminum reduction of the oxysulfide UOS, but their best preparations

were slightly sulfur poor and slightly contaminated with aluminum and residual oxysulfide. Eastman et al.⁽¹¹⁾ prepared US by reaction of solid disulfide, US_2 , with solid uranium hydride, UH_3 , and of gaseous hydrogen sulfide with solid UH_3 . This last method seemed to offer convenience and freedom from contamination and so was adopted for this research. The present technique and apparatus differ little from those of Eastman et al., except in the decomposition of the hydride before admission of H_2S and in the use of fused silica rather than of Pyrex for the reaction tube and of tungsten rather than of molybdenum for the annealing crucible. The procedure employed involved four steps, namely, (1) preparation of the hydride UH_3 , (2) its decomposition to give finely divided metal, (3) reaction of the metal with H_2S to give a mixture of metal and higher sulfide, and (4) heating this mixture to 1800 to 2100°C in a tungsten crucible in high vacuum to produce sintered, crystalline monosulfide.

2. Materials

Pure uranium metal, both of natural isotopic composition and enriched in U^{235} , was obtained from the Special Materials and Services Division of Argonne National Laboratory in the form of cylindrical rod of diameters $1/16$, $1/10$, and $1/8$ inch. Spectrographic analysis by the spectroscopy group of the Chemistry Division showed the natural uranium to contain only traces of metallic impurities, of which the most abundant were iron, silicon, copper, aluminum, and magnesium in the respective concentrations of 70, 60, 20, 10, and 10 parts per million. Most of the other metals detected were in amounts too small to measure. The enriched metal was not analyzed, but the sulfide produced from it contained even less foreign matter. The isotopic composition of the enriched uranium is given in a later section.

Hydrogen sulfide gas specified by the manufacturer to be 99.5 per cent pure was obtained in 4-inch cylinders from the Matheson Company of Joliet, Illinois. Mass spectrometric analysis by the

analytical chemistry group of the Chemistry Division at Argonne National Laboratory showed the tank H_2S to contain approximately 0.4 per cent carbon dioxide and 0.3 per cent carbon monoxide or nitrogen. No estimation of oxygen could be made because of the strong peak at mass 32 due to dissociation of H_2S under electron bombardment in the spectrometer. No other contaminants were detected. Two samples of the hydrogen sulfide were taken in a calibrated volume at a measured pressure, then flushed with argon through a solution of 0.1 N silver nitrate. Back titration of the excess silver and calculation of the absolute amount of sulfide sulfur precipitated gave for the tank gas 98.9 and 99.5 per cent H_2S .

The tank hydrogen (electrolytic) and argon (welding grade, 99.8%) used were not analyzed, but were passed through a Vycor tube containing uranium metal turnings maintained at about 600°C . This treatment should have removed quantitatively virtually any impurities except the inert gases.

3. Apparatus and Technique

The reaction apparatus is sketched in Figure 1. It consisted

FIGURE 1
APPARATUS FOR THE PREPARATION OF URANIUM MONOSULFIDE

of a bulb for containing gases, a fused silica reaction tube, a manometer for measuring gas pressure, the stopcocks required for admitting and handling the gases, and a pumping system including mercury diffusion and mechanical pumps. Uranium rod was electropolished in a bath composed by volume of 42 parts sulfuric acid, 6 parts glycerin, and 48 parts water to remove the oxide layer from the metal. In the meantime the fused silica reaction tube had been baked out under high vacuum at 800°C for several hours, then cooled and filled to atmospheric pressure with purified argon. The electropolished uranium was weighed, then dropped into the quickly opened and reclosed reaction tube, which was attached again to the line and re-evacuated. The system was flushed several times with purified hydrogen, with the evacuated reaction tube closed off at stopcocks 7 and 8. Then hydrogen at a measured pressure slightly less than atmospheric was closed off in the volume V_1 between stopcocks 5 and 9; the rest of the system was re-evacuated, and stopcock 4 was closed. Stopcocks 5 through 9 were opened and the pressure in the total volume V_2 to the right of stopcock 4 was read from the manometer. The procedure described was designed to eliminate oxygen and water vapor from the reaction line, both to prohibit contamination of the sulfide and obviate the induction period otherwise encountered before the reaction between uranium and hydrogen would proceed.⁽¹¹⁾ The furnace was then placed around the reaction tube and heated.

The hydriding reaction generally commenced as soon as the temperature reached 200°C. Sometimes the reaction seemed to proceed fastest with the furnace closed and the temperature between 175 and 300°C; sometimes, with the furnace at full power and open, so that one side of the reaction tube was at perhaps 600°C and the other much cooler. Sometimes either stopcock 7 or 8 was closed to decrease circulation and consequent cooling of the gas in the furnace. Once stopcocks 7 and 8 were both closed simultaneously with disastrous results. In all cases the hydriding reaction proceeded slowly and steadily to

completion, no further pressure change being observed on further heating after two to four hours with 2 to 4-gram uranium samples. The furnace was then removed and the pressure read when room temperature was attained in the reaction tube.

From the weight of uranium taken, the initial hydrogen pressure, and the pressure changes on expansion of hydrogen from V_1 to V_2 and due to reaction, the volumes of V_1 and V_2 could be calculated, as could the pressure of hydrogen sulfide in V_1 required to prepare sulfide of any composition from U to US_2 , according to the reactions

and

Agreement within a per cent for the values of V_1 and V_2 , respectively 1940 and 2210 cm^3 , was obtained in all preparation runs, indicating reproducible and quantitative formation of UH_3 .

The uranium hydride was decomposed upon evacuation of the system with the diffusion pump and the heating of the reaction tube. The subsequent reaction with hydrogen sulfide went most smoothly when the hydride was decomposed at temperatures below 300°C, for this procedure avoided formation of a sintered lump of metal powder.

The tank of hydrogen sulfide was connected to the reaction line through Tygon plastic tubing, a P_2O_5 trap (that was probably unnecessary), glass tubing with a mercury manometer on a side-arm, and stopcock 3. Because H_2S in this system slowly but continuously decreased in pressure, eventually producing a vacuum of about 30 cm Hg due to reaction with the mercury in the manometer and perhaps diffusion through or reaction with the Tygon, the procedure adopted for admitting the gas to the reaction line was as follows. During the hydriding time while stopcock 4 was still closed, the hydrogen sulfide line was evacuated through stopcock 3 several times and refilled above atmospheric pressure with H_2S , which pressure was maintained until after the gas had been admitted to V_1 . After the decomposition of the hydride,

the reaction tube was again cooled to room temperature with the system evacuated, stopcocks 7, 8, and 9 were closed, and H_2S was admitted to V_1 to the desired pressure through stopcocks 3 and 4. Stopcock 5 was then closed, the system re-evacuated, stopcock 4 closed, the furnace placed around the reaction tube and set for $550 \pm 50^\circ\text{C}$, and stopcocks 9, 8, 7, and 5 were opened, admitting H_2S to the hot, finely divided metal. The design of the reaction tube in principle causes the hot hydrogen formed in the reaction to rise up and out the side-arm, thus flushing more H_2S down to the hot zone through the re-entrant tube. Experience showed that the hot zone must be restricted to the bottom of the tube in order to obviate the dissociation of H_2S in the upper part of the tube, which would have been accompanied by deposition of sulfur on the walls and a sulfur-poor reaction product.

Because the stoichiometry of the sulfiding reaction maintains a constant number of moles of gas in the system, pressure change could not be used to follow the course of the reaction. To test for completion of the sulfiding, the reaction tube was cooled, then immersed in liquid nitrogen. If no white deposit of solid H_2S formed in a few minutes, it was assumed the sulfide had been made. The residual hydrogen was then pumped out and the vacuum was broken with purified argon. It was generally observed that a thin film of solid H_2S collected in cold trap II if cooled with liquid nitrogen during the final pump-out, but in no case was the rise in pressure on closing stopcock 1 and warming trap II to room temperature sufficient to warrant chasing the H_2S back into the reaction tube for further action. Because ordinarily the reaction proceeded quite slowly, it was found convenient to let it run overnight.

4. Homogenization and Annealing of Uranium Monosulfide

At the end of the above procedure the reaction tube contained a mixture whose X-ray powder¹ diffraction pattern showed lines of α -uranium and higher sulfides, but no monosulfide. Homogenization

of the crude reaction product was effected by heating it to about 2000 to 2200°C as described below. The tube was opened in an argon atmosphere in a drybox and the black, loosely sintered reaction product was crushed in an alumina mortar and transferred to the annealing crucible shown in Figure 2. The latter had been machined with carbide tools

FIGURE 2
TUNGSTEN CRUCIBLE FOR ANNEALING SULFIDE SAMPLES

from 3/4-inch diameter dense tungsten rod and was fitted with three legs of 1/8-inch tantalum rod, pointed at their ends, and with a tungsten lid containing a 1/16-inch diameter orifice.

In order to reduce the time that the highly reactive crude sulfide was exposed to air, the loaded annealing crucible was removed from the drybox in a Mason jar with a tightly screwed-down lid, which jar was opened adjacent to the vacuum line used for effusion measurements (see Figure 4). The crucible was placed on the beryllia kinematic

table, a water-jacketed fused silica condenser with no side arms and capped by an optical window was placed over it, and the line was evacuated as rapidly as possible without blowing powdered sulfide through the crucible orifice. When the pressure had dropped to 1×10^{-5} mm Hg, induction heating was begun. After the initial burst of occluded and adsorbed gas (presumably mostly argon) was eliminated below red heat, the temperature was increased as rapidly as was possible (and therefore quite slowly) without exceeding a pressure in the line of 2 or 3×10^{-4} mm. Final annealings were carried out at 1900 to 2200°C for periods from one-half to several hours. Pressure in the line was usually about 6×10^{-6} mm Hg in the final stage of an annealing.

At the end of this treatment, the samples of uranium monosulfide were sintered plugs, greatly decreased in bulk volume from the original crude powder, and had a gray metallic appearance with sometimes a slight yellow cast. The sintered material was crushed easily in an alumina mortar under argon in the drybox. On being ground in air, US samples emitted sparks and the odor of hydrogen sulfide, presumably by reaction with water in the atmosphere, and their X-ray diffraction patterns were slightly blurred. On the other hand, sintered US samples did not gain weight or change their powder diagrams merely on standing in air. As a precautionary measure, all samples not in use were stored in a desiccator that was evacuated and refilled with purified argon after each opening to the air. After annealings carried out at the highest temperatures and for the longest times, the underside of the lid of the annealing crucible was found to be coated, sometimes to about 1 mm thickness, with a crust of small US crystals of bright, highly reflective, silver-gray or yellowish metallic appearance. Interestingly, such deposits left the orifice clear, except in preparation P-17, whose product was found to contain appreciable oxysulfide contamination. X-ray diffraction and chemical analyses of the sulfide samples are described below.

Brief descriptions of the individual preparations are also given in a later section.

C. Analysis of Samples of Uranium Monosulfide

1. Chemical and Spectrographic Analyses

Sulfide sulfur was determined⁽⁴¹⁾ by measurement of the quantity of hydrogen sulfide evolved on treatment with 3.6 N sulfuric acid. The apparatus, illustrated schematically in Figure 3, was

FIGURE 3
APPARATUS FOR ANALYSIS OF SAMPLES
FOR SULFIDE CONTENT

essentially a closed flask fitted with a delivery tube to carry evolved H_2S into a second flask containing silver nitrate solution. The container for the acid was designed to insure quantitative recovery of the H_2S by preventing loss of small bubbles of gas up the acid entry tube. A sample of sulfide of weight between 15 and 100 mg was weighed to the nearest 0.01 mg in a small porcelain cup on a semimicro balance.

(In the earliest analyses the sample was weighed by difference from a weighing bottle, the sample being placed directly into the flask I.) The cup was placed in the round bottom flask I and the delivery tube immersed in the Erlenmeyer flask II, which contained an ammoniacal silver nitrate solution prepared by adding 85 ml H_2O and 15 ml concentrated ammonia to a 10-ml portion of standard 0.1 N AgNO_3 delivered from a calibrated pipet. Air was continuously passed through the system at a slow bubble rate to agitate the solution in I and to sweep evolved gases into the receiver. Approximately 150 ml of 1:10 sulfuric acid was admitted to I through the stopcock, and the solution in I was boiled vigorously to evolve all H_2S . The boiling was continued until steam passing through the solution in II had heated it, digesting the precipitated silver sulfide and causing it to coagulate. Experiments in which II was fitted with a two-hole stopper fitted with a delivery tube to carry any unabsorbed H_2S through a second silver nitrate solution showed quantitative absorption of the H_2S in II.

When the evolution and absorption of hydrogen sulfide was judged to be complete, the tip of the delivery tube was rinsed into II, and the contents of the flasks filtered hot into another flask. The precipitate was washed several times with hot water and this water was added to the filtrate. The filtrate, when cool, was made acid with 20 ml of concentrated nitric acid; then 3 ml of saturated ferric alum was added as indicator, and the solution was titrated to a sharp color change with standard 0.1 N potassium thiocyanate added from a calibrated 10-ml buret graduated in increments of 0.02 ml. The thiocyanate was standardized by titration against weighed quantities of primary standard silver nitrate dissolved in convenient volumes of water. The silver nitrate solution used in the absorber was standardized by titration against the thiocyanate solution.

Precision of the analysis was good, particularly considering the quantities of samples available and the possibility for loss of

hydrogen sulfide. In analysis of all but five of the last sixteen experimental samples for which duplicates were run, the sulfide contents obtained from all aliquot portions of a given sample lay within 0.5 per cent of the average. The maximum deviations from the average for the remaining five samples were between 1 and 3 per cent. In these cases the poorer precision was attributable to very small sample size or to nonhomogeneity due to two phases in the samples. For example the P-14(1) material contained excess uranium in the form of a few small globules whose malleability defied attempts to grind them up and thus distribute them through all portions of the solid. Kolthoff and Lingane⁽⁴²⁾ have shown that the titration itself is capable of accuracy to ± 0.1 per cent, but for the small quantities used in this work an endpoint error of 0.01 ml in the titration corresponded to an error of 0.28 per cent in the sulfide from a 50-mg sample of US.

Analysis for total sulfur was performed on some early sulfide samples by the analytical group of the Chemistry Division by a standard gravimetric procedure. The samples were dissolved and the sulfur was oxidized to sulfate by the action of bromine water and concentrated nitric acid. The sulfur was then precipitated and weighed as BaSO_4 .

No uranium analyses were performed on the later sulfide samples except for P-12(1), although they were obtained volumetrically by the analytical group of the Chemistry Division for some of the early materials which were not useable for volatility studies.

Serious oxygen contamination of samples of uranium monosulfide was observed only in early preparations in which a ceramic reaction tube was employed, and in preparation P-17. The oxygen was found to be present variously as the dioxide UO_2 in solid solution in the US or present as a second phase, or as uranium oxysulfide in a second phase. When the US was dissolved in the analysis for sulfide, any UOS present remained as a rather coarse, black, insoluble residue, in

accordance with previous observations of its solubility.⁽¹⁷⁾ Similarly, UO_2 did not dissolve, but yielded a very finely divided, brown solid, even though the X-ray pattern of the original monosulfide had indicated the presence of only one phase with a lattice parameter slightly less than pure US. The insoluble residues were filtered off onto tared, sintered-glass Gooch crucibles, dried at 110°C , and weighed. The dried material gave sharp (some of them beautifully sharp) X-ray diffraction patterns characteristic of UO_2 or UOS, respectively, or occasionally of both.

Sulfides of less than stoichiometric sulfur content gave acid-insoluble, granular residues of metallic appearance when examined microscopically, whose X-ray powder diffraction patterns agreed with that of α -uranium. These residues were also filtered off and weighed. The sulfide analyses and weights of insoluble material corresponded to sulfur-deficient monosulfide samples; only enough uranium went into solution to give an atomic ratio $\text{S}/\text{U} = 1.00$ in solution if the insoluble material was indeed pure uranium. Sulfur-rich samples dissolved completely if oxygen free.

Spectrographic analysis of sulfide samples showed only traces of metallic impurities. In the P-18 and P-19 sulfides used for vapor pressure measurements, for example, the only metals present in measurable concentrations and their amounts in parts per million were aluminum, 20; boron, 0.1; magnesium, 10; and silicon, 40, with an estimated accuracy of a factor of two.

2. X-Ray Diffraction Studies

All Samples of interest were characterized by powder diffraction patterns taken with copper $K\alpha$ radiation of wavelengths 1.54050 and 1.54434 Å for the α_1 and α_2 components, respectively, and North American Philips cameras of 11.47-cm diameter. The finely divided samples were usually contained in 0.2-mm diameter glass capillaries, but were sometimes stuck to the exterior of fine Pyrex glass fibers

with Duco cement or LePage's mucilage. Lattice parameters were obtained from the film measurements by the extrapolation procedure of Hess,⁽⁴³⁾ by means of a program written by Dr. Harry A. Eick and the IBM 650 computer at the University of Kansas. The quoted errors are statistical standard deviations obtained from the least-squares treatment of the measurements of the films. The lattice parameters obtained from the various monosulfide and oxysulfide samples studied are described at suitable places in later sections, and are summarized in Sections VB and VD.

D. Description of Individual Preparations

1. First Attempts to Prepare Uranium Monosulfide

Three attempts were made to prepare uranium monosulfide by forming the crude sulfide in a ceramic reaction tube by the procedure described previously and homogenizing it by heating the evacuated reaction tube at 1500°C in a silicon carbide element tube furnace, thus eliminating some handling of the sample. A Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) reaction tube sealed to a Pyrex standard taper joint and using a Mullite re-entrant tube was abandoned after sulfides prepared in it were found to be contaminated with uranium dioxide and oxysulfide, silicon, and aluminum. A recrystallized alumina (Morganite) tube using an O-ring vacuum seal and the same Mullite re-entrant tube was found unsuitable because of diffusion of oxygen into it at the high annealing temperature. Use of Morganite for the initial sulfiding, followed by homogenization in the tungsten annealing crucible gave better results, partly because of preferential vaporization of oxide impurities on annealing, but was still unsatisfactory. An attempt to eliminate the oxide impurity in one sulfide sample by aluminum reduction gave poor results because of difficulty in eliminating the excess aluminum from the product. Use of fused silica reaction and re-entrant tubes virtually eliminated oxygen contamination except where it could be blamed on imperfect purging of the hydrogen sulfide line. A platinum liner for

the quartz tube was used only twice because no contamination of the sulfides by silicon occurred in reactions employing the quartz tube alone. No discoloration of the tube by reaction with H_2S was observed.

2. Samples Used for Vaporization Studies

Table III summarizes the data on sulfides used for vaporization measurements. Brief descriptions of each preparation run and the analytical data for each sample follow. Each synthesis and its product was assigned a sequential number prefixed by the letter P (for preparation) and followed by a number in parentheses to indicate the number of times the material had been annealed in vacuum in the tungsten crucible. Thus for example P-13(1) indicates the product from the thirteenth synthesis of sulfide, and that this sulfide was heated once for homogenization. The number P-13(2) indicates the same material after it had been reground under argon and annealed a second time.

a. Preparation P-12(1)

This material, the first satisfactory sulfide, was synthesized in the quartz reaction tube lined with platinum. The sample was homogenized above 1600°C for 5.5 hours; during the final half hour the sample was held at 2080°C . Uranium, sulfide sulfur and total sulfur as gravimetric sulfate were determined. The analyses yielded an atomic ratio S/U of 1.01, with 0.47 per cent acid-insoluble material identified by X-ray diffraction to be UOS. The P-12(1) sulfide was used in vaporization series V-1.

b. Preparations P-13(1) and (2)

The P-13 preparation of uranium monosulfide was also effected with a platinum liner in the quartz reaction tube. The P-13(1) sample was homogenized by heating at 2030°C and then at 2100°C holding for one-half hour at each temperature. Sulfide analysis indicated 11.6 per cent sulfide sulfur with 1.1 per cent acid-insoluble material. The soluble part of the sample thus had the composition $\text{US}_{0.99}$. The P-13(1) X-ray pattern was not sharp and the $\alpha_1 - \alpha_2$ lines were not

TABLE III
DATA DESCRIBING SULFIDE SAMPLES

Sample Number	Annealing Conditions		Chemical Analysis				X-ray Results				Use of Sample	Remarks
	T, °C	time, hr	% S =	S/U uncorr. for insol. res.	% insoluble residue	S/U, soluble	insoluble residue phases	insoluble residue film no.	whole sample film no.	lattice parameter, Å		
P-12(1)	1600	5.5	11.92		0.47	1.01	UOS	3028	3026	5.4877 ± .0003	V-1	Total S (as BaSO ₄): 12.12% Total U (volumetric): 88.75% U sol. in dil. H ₂ SO ₄ : 87.21%
P-13(1)	2080	0.5										
	2100	0.5	11.6		1.1	0.99	UO ₂ α-U					Poor X-ray pattern
	(2) 1950	1.3	11.79		1.9	1.01	UO ₂ α-U	3525	3068	5.4896 ± .0006	V-3	
P-14(1)	1985	1.0	9.71	0.80	16.0	0.97	α-U	3119	3146	5.4723 ± .0004	V-2,5	Globules of U in sample
	2066	0.5						3431				
P-17(1)	2000	0.5	12.56		2.2	1.09	UOS	3254	3239	5.4862 ± .0002		Film shows higher sulfide lines
(2)	2140	0.5	12.19		2.2	1.06			3251			Orifice deposit formed; higher sulfide lines in film
(2-lhd)			12.31		11.0	1.19	UOS		3253			Looked like baked, gray enamel. Higher sulfide + UOS lines in film
(3)	2210	1.25	12.32		2.5	1.08	UOS	3267	3259	5.4885 ± .0004		Higher sulfide lines; orifice closed by deposit
(3-lhd)			12.19		est. 2 to 4	1.07	UOS		3260	5.4875 ± .0006		Shiny metallic; higher sulfide lines
P-18(1)	1900	2.5	11.07	0.93	2.9	0.96	α-U	3293	3274	est. 5.460		Poor X-ray pattern
(2)	2035	5.3	11.11	0.93	6.3	1.00	α-U		3278	est. 5.48		Poor X-ray pattern
	2100	1.0										
(2-lhd)			11.74	0.99	0.92	1.00	α-U		3279	5.4816 ± .0009		
(3)	2150	3.5	10.63	0.88	10.1	0.99	α-U	3308	3286	5.4857 ± .0005	V-11,12	Globules of U in sample
(3-lhd)			11.98	1.01	Zero	1.01	-	-	3287	5.4865 ± .0004	V-6,7,8 MS-2	Oxygen contamination observed mass spectrometrically
P-19(1)	2160	3.0	11.88	0.99	Zero	0.99	-	-	3321	5.4868 ± .0003		U ²³⁵ enriched; X-ray pattern fair
(1-lhd)			12.10	1.01	Zero	1.01	-	-	3322	5.4924 ± .0006	V-9,10, 13	U ²³⁵ enriched, X-ray pattern fair

separated at high angles. After a re-annealing at 1950°C for 80 minutes, the P-13(2) monosulfide gave a satisfactory X-ray pattern, and sulfide analysis indicated 11.79 per cent sulfide sulfur with 1.9 per cent insoluble material whose appearance and X-ray pattern identified it as a mixture of UO_2 and α -uranium. The atomic ratio of sulfur to uranium for the soluble portion of the sample was 1.01. The P-13(2) sulfide was used in vaporization series V-3.

c. Preparation P-14(1)

The P-14 monosulfide, with a deficiency of sulfur, was prepared in the quartz reaction tube. The crude material was homogenized at 1985°C for an hour followed by half an hour at 2066°C. The P-14(1) sulfide was a two-phase mixture containing very small, bright silver globules of material insoluble in sulfuric acid, identified as α -uranium by X-ray diffraction pattern. Sulfide analysis indicated a content of 9.71 per cent sulfide sulfur. The insoluble α -uranium was about 16.0 per cent by weight of the sample. The soluble portion of the sample thus had the formula $\text{US}_{0.97}$. The P-14(1) sulfide was used in vaporization series V-2 and V-5.

d. Preparations P-15 and 16

These materials were discarded because of accidents during their preparations.

e. Preparations P-17(1) to (3)

The sulfur-rich P-17 uranium monosulfide was contaminated with oxysulfide, presumably because of incomplete purging of the hydrogen sulfide line after it had been disassembled and reassembled. After the first homogenization, ending at 2000°C for half an hour, the P-17(1) sample gave an X-ray pattern chiefly containing lines due to US , but with very faint extra lines seemingly of higher sulfide and perhaps of UOS . The sulfide analysis gave 12.56 per cent sulfide sulfur and 2.2 per cent insoluble material whose X-ray pattern showed it to be UOS . The second annealing at 2140°C for 30 minutes yielded P-17(2) sulfide of 12.19 per cent sulfide sulfur and 2.2 per cent insoluble material.

A heavy deposit, designated P-17(2-lid), under the lid and in the orifice of the annealing crucible had the appearance of gray, baked enamel. Its analysis showed 12.31 per cent sulfide sulfur (one sample) and 11.0 per cent insoluble material. The X-ray pattern of the P-17(2-lid) material showed lines of US, together with UOS and higher sulfide lines of about half the intensity of the US lines.

The P-17(2) sulfide had an X-ray pattern characteristic of US, with the same barely visible lines as in P-17(1), except that none could be attributed to UOS. After a third annealing at 2210°C for 75 minutes, the orifice was completely plugged and the underside of the lid was covered with a shiny metallic deposit. The P-17(3) sulfide contained 12.32 per cent sulfide sulfur and 2.5 per cent insoluble material, again identified as UOS. Again the P-17(3) sulfide gave a powder pattern with lines identified as those of US and very faint lines due to higher sulfides.

The P-17(3-lid) material contained 12.19 per cent sulfide sulfur, with an estimated, though not weighed, 2 to 4 per cent insoluble material, again identified as UOS. The P-17(3-lid) X-ray pattern showed US lines and faint lines from higher sulfides.

The respective ratios S/U for the soluble parts of sulfides P-17(1), P-17(2), P-17(2-lid) and P-17(3) were 1.09, 1.06, 1.19, and 1.08, respectively. The P-17 monosulfide was not used for vaporization runs because of its orifice-clogging tendencies due, presumably, to the presence of UOS and higher sulfide of low thermal conductivity (compare the observations with the P-18 sulfide).

Table III summarizes the above observations, and they are mentioned again in the section discussing the system uranium-oxygen-sulfur. Lattice parameters of the acid-insoluble residue from the P-17(3) sulfide, the most precise obtained to date for UOS, are presented in the same section.

f. Preparations P-18(1) to (3)

The uranium monosulfide sample from preparation P-18 was sulfur-deficient initially. After homogenization at 1900°C for 2.5 hours followed by an hour at 1030°C, the P-18(1) sample analysis showed 11.07 per cent sulfide sulfur and 2.9 per cent acid-insoluble material whose X-ray diagram showed it to be α -uranium. The X-ray diagram of the P-18(1) sulfide was free of extra lines, but the pattern was not sharp. A light deposit under the lid was bright and metallic.

Re-annealing at 2035°C for 5.3 hours followed by an hour at 2100°C gave a heavy deposit under the lid, P-18(2-lid), but no orifice clogging occurred. The P-18(2) sulfide was found to contain 11.11 per cent sulfide sulfur, with 6.3 per cent acid-insoluble residue of α -uranium. Again the X-ray film was not sharp but was free of extra lines. The P-18(2-lid) sample contained 11.74 per cent sulfide sulfur with only 0.92 per cent insoluble material.

Re-annealing of the P-18(2) sulfide at 2150°C for 3.5 hours gave a very heavy, shiny metallic crust under the crucible lid without causing clogging of the orifice. The sintered plug of sample P-18(3) showed 10.63 per cent sulfide sulfur with 10 per cent insoluble matter, which latter material again gave the X-ray pattern of α -uranium. Some small, bright metal particles were found in the P-18(3) sample, which particles were malleable and so were not ground up with the rest. They were thus not included with the material in the X-ray sample. The P-18(3-lid) US contained 11.98 per cent sulfide sulfur with no detectable insoluble residue. The X-ray patterns of samples P-18(3) and (3-lid) contained no lines other than those of US.

The behavior of the P-18 sample on annealing was peculiar in that the material in the bottom of the crucible became progressively richer in the more volatile uranium while the presumably cooler lid collected sublimate of the less volatile monosulfide, whose composition approached a one-to-one stoichiometry. This behavior is discussed in connection with the results from

vaporization series V-11 and V-12, pages 78 - 79 . The ratios S/U for the soluble parts of samples P-18(1), P-18(2), P-18(2-lid), P-18(3), and P-18(3-lid) were, respectively, 0.96, 1.00, 1.00, 0.99, and 1.01. The P-18(3-lid) US was employed in effusion series V-6, V-7, and V-8, and in mass spectrometer experiment MS-2. The product from P-18(3), of overall ratio S/U = 0.88, was used in volatility vs. time studies V-11 and V-12.

g. Preparation P-19(1)

Uranium monosulfide was synthesized in preparation P-19 from enriched metal rod of isotopic composition 5.36 ± 0.05 per cent U^{238} , 0.436 ± 0.004 per cent U^{236} , 93.19 ± 0.05 per cent U^{235} , and 1.00 ± 0.01 per cent U^{234} . The corresponding atomic weight is 235.20. After homogenization at 2160°C for three hours, the P-19(1) product was found to contain 11.88 per cent sulfide sulfur and no detectable insoluble material. This sulfide content corresponds to the formula $US_{0.99}$. The heavy crust on the annealing crucible lid (but again not in the orifice) consisted of many small, brightly reflecting, silvery crystals. This sublimate, P-19(1-lid), contained 12.10 per cent sulfide sulfur ($US_{1.01}$) with no detectable insoluble material. The X-ray patterns from both samples were of moderate quality and contained only lines due to US. The P-19(1-lid) monosulfide was used for effusion series V-9, V-10, and V-13. The P-19(1) sulfide was used for the determination of the melting point of US.

3. Other Preparations

In preparation P-6, synthesis of uranium oxysulfide was attempted by passing a stream of hydrogen sulfide over uranium dioxide contained in a graphite boat in a fused silica tube maintained at 800 to 1050°C by a tube furnace. Analysis of the product for total sulfur as gravimetric sulfate gave 10.29 per cent sulfur, which, combined with the amount of uranium in the original UO_2 , gives the formula $UO_{1.03}S_{0.91}$ for the product. The X-ray diffraction pattern showed lines attributable

to UOS plus very faint lines from UO_2 . This X-ray film was used for comparison purposes until it was found that some of the insoluble residues from oxygen-contaminated sulfides gave sharper X-ray patterns of UOS. The lattice parameters obtained from the P-6 film are included in the discussion of the uranium-oxygen-sulfur system in a later section.

In Preparation P-7 an attempt was made to synthesize the disulfide, US_2 , by the method used for the monosulfide. The Morganite reaction tube was used. The product was not annealed, and the X-ray film showed lines due to higher sulfide and weaker ones attributed to UOS. Analysis of one sample gave 17.5 per cent sulfide sulfur, which corresponds to the formula $\text{US}_{1.57}\text{O}_\chi$, where χ may be guessed to be about 0.1. The X-ray pattern, which was not very sharp, thus probably corresponds to a mixture of the compounds U_3S_5 ($\text{US}_{1.667}$), U_2S_3 ($\text{US}_{1.50}$), and UOS. Lines not due to oxysulfide in this pattern were found to correspond to lines in all unannealed monosulfide samples, lines in patterns from the P-17 materials called "higher sulfide lines" above, and lines in the pattern from material described in the next paragraph.

A one-pound lot of black, finely divided material, labeled only "uranium sulfide" and given the laboratory designation US_2 -1, was obtained from the Oak Ridge National Laboratory. The container was a polyethylene jar; a strong odor of hydrogen sulfide filled the jar. Gravimetric total sulfur analysis of the material US_2 -1 showed 18.4 per cent sulfur, corresponding to the formula $\text{US}_{1.68}$, very near to the composition of the compound U_2S_3 ($\text{US}_{1.667}$). The X-ray pattern was very light, with many lines fading out at the high angles, and contained neither US nor UOS lines. A large insoluble residue remained after the dissolution of this material, even in concentrated nitric acid. X-rays showed the insoluble residue to consist chiefly of UOS.

A portion of the US_2 -1 sample was heated in vacuum to about 1650°C for 1.2 hours in the annealing crucible. Deposits of sulfur

on the condenser wall resulted. The material from the annealing, $\text{US}_2\text{-1}$ (1), appeared to have been melted, and its fair X-ray pattern showed UOS to be a major constituent. Of the many other lines present, some seemed to match lines of the film from the original $\text{US}_2\text{-1}$ sample.

E. Effusion Studies

1. Apparatus

The apparatus used in effusion measurements with uranium monosulfide was essentially that used by Ackermann, Gilles, and Thorn⁽⁴⁴⁾ for studying the vapor pressure of uranium dioxide. It is sketched schematically in Figure 4. In its essentials the apparatus consists of a pumping system, an evacuated fused silica condenser, a support for the effusion cell, an optical window, and a device for presenting targets to the effusate. Pumping was effected by a divergent nozzle mercury vapor pump backed by a two-stage mercury vapor pump of the "Princeton" type, backed in turn by a Duoseal mechanical pump. A large-diameter Pyrex re-entrant trap cooled by liquid nitrogen was located between pumps and high-vacuum region. The residual pressure in the evacuated system was monitored by a cold-cathode ionization gage, and could be maintained at about 1×10^{-7} mm with the effusion cell cold. The effusion cell stood on a beryllia semikinematic table, supported in turn by a fused silica table designed to hold the beryllia table in position if it cracked from thermal shock. The fused silica table capped the upper end of a fused silica tube sealed by means of a quartz-to-Pyrex graded seal to the vacuum line above the optical window. Holes through the center of the two tables permitted measurement of the effusion cell temperature from below by means of an optical pyrometer. The effusion cell was surrounded by a water-jacketed, fused silica condenser at whose upper end were the target magazine, a magnetically operated fused silica shutter for controlling exposure times, and a magnetically operated tungsten push-rod for ejecting exposed targets into the Pyrex receiver. Power for heating the effusion cell

was supplied from a 20-kva Thermonic high-frequency generator to the coil of flattened copper tubing placed around the condenser.

FIGURE 4
APPARATUS FOR EFFUSION EXPERIMENTS

Figure 5 shows the cold finger that replaced the target magazine during series V-13. It held single platinum targets of 0.020-inch thickness, which were cooled by a flow of water in direct contact with the platinum.

FIGURE 5
HOLDER FOR SINGLE, WATER-COOLED TARGETS

Two effusion cells, shown schematically in Figure 6, were used in this research. Both were machined from partially sintered bars of compacted tungsten powder and sintered to their final density by induction heating to 2600°C in vacuum. During the sintering process the lids of both cells shrank onto their lower parts and could not be removed afterward. Effusion cell no. 1 had an orifice of approximately 1.7-mm diameter, which was originally sharp-edged. Repeated use of a tungsten wire of 0.040-inch diameter to scratch residues loose from the bottom and walls of the cavity after effusion experiments enlarged the diameter, rounded the edge somewhat, and rendered the orifice slightly out of round.

FIGURE 6
SINTERED-TUNGSTEN EFFUSION CELLS

Effusion cell no. 2 was produced from the bottom of an older effusion cell and a new lid. The lid with its orifice of approximately 0.8-mm diameter shrank more than anticipated and thus was of smaller diameter than the bottom. The orifice was initially in the form of a short right circular cylinder of length-to-diameter ratio about $1/7$. Use at temperatures of the order of 2500°C in series V-6, 7, and 13 caused the orifice to shrink slightly. Its hot lower edge shrank somewhat more than its cooler upper edge, so that the orifice walls sloped outward at about 10° from the axis. The edge suffered similarly to that of effusion cell no. 1. In an attempt to improve temperature measurement, the blackbody hole of effusion

cell no. 2 was bored out to a diameter of $1/8$ inch and a depth of $1/4$ inch. A tantalum disk with a 0.035-inch diameter hole through it was forced into the bottom of the blackbody hole, as shown in Figure 2.

2. Measurement of Dimensions

Equation (4) and thence (13) require the measurement of three linear dimensions for calculation of the "effective vapor pressure" of uranium monosulfide. These dimensions are the diameter of the orifice of the effusion cell, the distance from orifice to collimator for each experiment, and the diameters of the two collimators.

a. Measurement of Orifice Diameter

Orifice diameters for effusion series V-6 through V-13 were measured before and after each experiment by means of a microscope mounted on the moving stage of a micrometer slide comparator, Gaertner catalogue no. M340, serial no. 549P. The travel could be read directly to 0.001 mm on the vernier provided, and the instrument was certified by the National Bureau of Standards to be accurate to ± 0.001 mm throughout the 50-mm range of the micrometer. The effusion cells were mounted in a jig that was rotated beneath the microscope to give readings both ways along six separate and equally spaced diameters. In each setting the orifice was measured with the microscope travelling in both directions.

The arithmetic average of the total of twenty-four measurements was used for the calculation of the orifice area. The standard deviations amounted to 0.002 or 0.003 mm for both orifices of approximate diameters 1.7 and 0.8 mm, except that standard deviations of 0.008 and 0.004 mm were obtained in the measurements before and after series V-12. The errors in the average diameters were due chiefly to the small peripheral irregularities and slightly noncircular shapes of the sintered-tungsten orifices. In those cases in which small differences were found between orifice diameters measured before and

after a given experiment, the average of the two values was used. The use of effusion cell no. 2 at high temperatures led to decreases of the order of three per cent in the orifice diameter during each series of exposures. Correction for the shrinkage was applied to the measured diameters, as described in section IV, E7a.

The orifice diameters for preliminary experiments V-1 to V-5 were measured by means of a calibrated eyepiece scale in a Spencer Lens Company stereoscopic microscope. The effusion cells were mounted as described above. The standard deviations obtained were from 0.003 to 0.005 mm.

The orifice diameters are tabulated with other data from the individual experiments.

b. Measurement of Orifice-to-Collimator Distance

The distance from orifice to collimator was measured before each vaporization experiment by means of a cathetometer, Gaertner Scientific Company catalogue no. M901, serial no. 757. The scale could be read directly to 0.05 mm by means of a vernier, and readings were estimated to within 0.01 mm. The manufacturer specifies an accuracy of "about 0.003 mm in the graduation of the scale of the instrument."

The measurement was made after the apparatus had been assembled and evacuated for at least half an hour, so that the greased joints were well seated. The vacuum was broken, the receiver for exposed targets was removed, and the height of the lip of the collimator was determined. A small correction (about 0.02 cm) was applied to the observed height to correct the level of the lip of the slightly cocked collimator soldered to the bottom of the magazine to that of the center of the collimator above the orifice. The height of the collimator attached to the water-cooled target holder in experiment V-13 was measured at the bottom of the collimator ring, and the thickness of the ring, measured as described below, was added. The height of the top

of the effusion cell was measured by sighting through the water-jacketed fused silica condenser.

Each measurement was made four times and the standard deviation in the average of each measured height was from 0.001 to 0.002 cm. For a typical orifice-to-collimator distance of 11 cm, the resulting standard deviation amounted to about 0.02 per cent.

c. Measurement of Collimator Diameter

The diameters of the two collimators were measured by means of the traveling microscope described above. The lengths of three equally spaced diameters of the collimator of the target-holding magazine were measured. Each length was determined four times, with two traverses of the microscope in both directions. The average value with its standard deviation was found to be 19.0065 ± 0.0042 mm.

The lengths of six equally spaced diameters of the collimator ring of the water-cooled target holder were determined, with one traverse in each direction across each. The average diameter with its standard deviation was found to be 19.0229 ± 0.0039 mm. The thickness of the collimator ring was measured in six places by means of a micrometer caliper reading directly to 0.001 inch and estimated to the nearest 0.0001 inch. The average thickness with its standard deviation corresponded to 4.623 ± 0.002 mm.

3. Techniques Common to All Vaporization Experiments

a. Measurement of Temperature

Temperatures were measured by means of a Leeds and Northrup disappearing-filament optical pyrometer, serial number 709378. This pyrometer had been calibrated by the primary method of rotating sectors⁽⁴⁵⁾ by Dr. R. J. Thorn. The accuracy of the absolute temperatures measured with the pyrometer and this calibration should be within ± 2 degrees at 2300°C, as shown by comparison of the temperature scale defined by this pyrometer and its calibration with the temperature scales of the Bureau of Standards and similar laboratories of other

countries.⁽⁴⁶⁾ Because it often happens that small systematic differences exist in temperatures measured pyrometrically by two observers, each capable of equal precision, a comparison was made between temperatures read on a tungsten band lamp by the writer and by Dr. Thorn.

Groups of four readings were made alternately by each observer at each of seven temperatures between 1400 and 2400°C apparent, with two groups apiece at each temperature. At 1400°C the writer's values averaged 0.4° higher than Dr. Thorn's; at about 2300°, about 1.3° lower. There was a regular trend with increasing temperature, but the difference between the average values at each temperature was within the sum of the average deviations. The graph in Appendix A, Figure 18, was used to correct the writer's observed temperatures before the pyrometer correction was applied for the calculation of temperatures of effusion.

It should be noted that the temperatures reported in the tables and discussions for preliminary experiments V-1, V-2, V-3, and V-5 are in error by amounts from zero to about four degrees. The first calculations of the results of the effusion experiments were carried out before the eye intercomparison was effected. In these earlier calculations, experimental temperatures were corrected by means of a pyrometer calibration in which a filter transmissivity, later found to be slightly in error, had been used. The temperatures for the preliminary experiments listed above were not recalculated, because the small corrections which would result would not change the deductions from the experimental results. Further, they could not affect the final results of this research, because the final numerical conclusions are based only on experiments V-6 through V-13. Where comparisons are made between the later results and those from series V-1 to V-5, the uncorrected values from series V-6 through V-13 are used.

In preliminary experiments with each effusion cell, comparisons were made between temperatures in the cavity, measured from above, and in the blackbody hole, measured from below. For each case in which one or more annular shields were used to warm the orifice, the intercomparison was repeated. These preliminary intercomparisons covered the temperature ranges of the effusion experiments. During the effusion experiments temperatures were monitored from below, and the corresponding cavity temperatures were used in calculations of the vapor pressure. The temperature difference between top and bottom was found in each case to change approximately linearly with temperature, and linear least-squares treatments were used to calculate the cavity temperatures. Plots of the difference between top and bottom as a function of bottom temperature for the effusion cell and work coil arrangements for effusion experiments V-6 to V-13 are found in Figures 19 and 20 in Appendix A. The standard deviations in the calculated differences are indicated in the figures. These errors varied from 0.3 to 1.4 degrees over the temperature ranges and for the different effusion cells.

The greatest differences were found for effusion cell no. 2 with two shields on its top; for blackbody hole temperatures from 2300 to 2800°K the cavity was, respectively, from 21 to 24 degrees hotter. Late in the research it was discovered that adjustment of the coil height eliminated much of the difference. Thus for series V-13 the cavity of effusion cell no. 2 without shields was hotter by only 6 to 9 degrees, the correction decreasing from blackbody hole temperatures 1700 to 2500°K, respectively. For effusion cell no. 1 in series V-8, V-9, and V-10, differences increasing from 2 to 14 degrees were found for respective blackbody hole temperatures of 1700 to 2500°K. The cavity of effusion cell no. 1 was cooler than the blackbody hole, presumably because the heavy lower part of the crucible heated more efficiently than the lid. The cavity of effusion cell no. 2 was warmer than

the blackbody hole, presumably because the tantalum plug in the latter hole heated less efficiently than the surrounding tungsten.

Before and after each series of target exposures, the transmissivity of the window-prism combination was measured, so that corrections could be made for absorption of light by these objects and for any change due to coating of the window during an experiment. For this measurement the pedestal section of the vacuum system was cracked off from the pumping line and a series of measurements was made of apparent temperatures near 1150°C of the filament of a tungsten band lamp, directly and through window and/or prism. The correction for transmissivity, $\Delta \frac{1}{T}$, follows from Wien's law and is defined by the equation

$$\Delta \frac{1}{T} = \frac{1}{T_A} - \frac{1}{T} \quad , \quad (12)$$

in which T_A is the apparent temperature of the hot object viewed through the window and/or prism, and T is its true temperature. The quantity $\Delta \frac{1}{T}$ is approximately constant for all temperatures, and equation (12) was used to calculate true temperatures from apparent temperatures measured during the experiments. The determination of $\Delta \frac{1}{T}$ involved measurement of a relatively small temperature difference at about 1100°C and an extrapolation to a high temperature where the corresponding difference was several times as large. The resulting uncertainties in temperature corrections were calculated to be between ± 1 and ± 2 degrees for various determinations of $\Delta \frac{1}{T}$.

For those experiments in which the window transmissivity changed because the window became coated with sublimate, it was assumed that the change in $\Delta \frac{1}{T}$ was proportional to the thickness of the film on the window. The film thickness was assumed proportional to the product of the apparent total pressure and the time the shutter was open during an exposure. The pressure used in this calculation

at each temperature was obtained from the final vapor pressure curve. In no case did the decreased window transmissivity correspond to a change in apparent temperature of more than a few degrees.

The hot effusion cells remained at temperatures constant to $\pm 1^\circ$ over periods up to several hours, except during experiments in which rapid deposition of heavy metallic sublimates on the condenser wall occurred at high temperatures. The effective radiation shields so developed caused temperatures to drift upward unless the oscillator power was occasionally decreased. Constant temperatures were attained after the deposits reached what presumably was constant reflectivity, but a downward drift of temperature tended to set in later, perhaps because of absorption of power by the now heavy deposits or because of partial shielding of the effusion cell from the high-frequency field. Even in these cases readjustment of input power permitted maintenance of temperatures constant within $\pm 3^\circ$.

In all cases temperatures were measured in groups of four or six readings to permit determination of temperature with a precision of $\pm 1^\circ$ for each group, so that any real drift with time could be detected. Measurement was repeated frequently enough to give several such groups during an exposure. The arithmetic average of all temperatures was taken as the temperature of the exposure. The window was protected by the shutter except during temperature measurement.

b. Preparation of Targets and Their Assay for Uranium

Effusate from the effusion cells containing uranium monosulfide was collected by condensation on platinum targets. Each 15/16-inch diameter by 0.005-inch thick target was cleaned in hot nitric-sulfuric acid solution, then heated inductively in air at red heat for about 30 seconds. When cool, each target was mounted in a 1/8-inch thick aluminum ring (cassette) and held there by a stainless steel or phosphor bronze spring. The targets so mounted were stacked in the copper magazine soldered to the bottom of the liquid nitrogen container

at the top of the condenser. The angular fraction of the total effusate impinging on a target was defined by the stainless steel collimator supporting the stack.

Assay of each target for total uranium was performed by counting, in a parallel-plate counter of 51.4 ± 0.1 per cent efficiency, the number of α -particles per unit time emitted from the deposit. The weight of uranium present was then calculated from the known decay rate of uranium. For uranium of natural isotopic composition, Fleming, Ghiorso, and Cunningham⁽⁴⁷⁾ list the specific activity as $1.501 \pm 0.003 \times 10^6$ decays per minute per gram. For the enriched uranium used in Preparation P-19, the isotopic composition determined mass spectrometrically by the Special Materials and Services Division of Argonne combined with the half-lives listed by Strominger, Hollander, and Seaborg⁽⁴⁸⁾ gives a specific decay rate of $1.411 \pm 0.014 \times 10^8$ decays per minute per gram. Deposits on the targets were thin enough and activities low enough that self-absorption of emitted α -particles and coincidence effects were negligible. Except in the cases of very low activity, the counting of each target was continued until the statistical standard deviation of the total count was one per cent or less, where the standard deviation is given by the square root of the total number of counts. The total weight of uranium on the targets varied from 7.3×10^{-8} to 1.5×10^{-4} gram. The total activities on targets used for vapor pressure calculations varied from 5.3 to 7501 counts per minute.

c. Procedure for Volatility Measurements

The procedure followed during a given series of target exposures was as follows. The sample was weighed into the effusion cell, the targets loaded into the magazine, and the apparatus assembled and evacuated. When the joints were well seated, the vacuum was broken with helium, the receiver for exposed targets was removed from its joint, and the orifice-to-collimator distance was measured. The line was re-evacuated, the magazine Dewar was filled with liquid

nitrogen, and heating was begun when the residual pressure dropped below 10^{-6} mm Hg. The effusion cell was brought to the desired temperature and maintained there for a few minutes to attain a steady state. Then the collimator shutter was opened. The time, read from a Precision Scientific Company "Time-It" electrical timer with dial graduated to 0.01 minute, was noted, and the temperature was measured. When the desired exposure time had elapsed, the shutter was closed, the target was ejected, the next target fell into place, the temperature was adjusted to a new value, and the cycle was repeated. When a given series was concluded, the crucible was allowed to cool in the high vacuum for several hours before the vacuum was broken with helium or purified argon and the effusion cell removed for reweighing.

The temperatures at which targets were exposed gave exposures at successively increasing temperatures over the range of a given experiment, followed by a series at successively decreasing temperatures, followed, if possible, by another series at increasing temperatures, and so on until all targets had been exposed. This procedure gave unreproducible, time-dependent trends in target activities only in preliminary experiments V-2 and V-5, in which the composition of the solid was changing, and in experiment V-6, in which the sample was exhausted during the run. The data from the vaporization experiments are tabulated in all cases in order of exposure rather than in order of temperature, and only for experiments V-2 and V-5 (Figure 8) have the order of the vapor pressure points been numbered in order in plots of the experimental data.

4. Observations Concerning Interpretation of Volatility Data

a. Interaction of Sample and Effusion Cell

The material used for construction of effusion cells must have certain characteristics before good measurements can be made with it. Among these properties the most necessary are

nonreactivity, low volatility, and tightness with respect to leaking. The use of tungsten was indicated for the present research because of its low volatility, high melting point, and ability to be heated inductively.

Two experiments were performed to determine specifically whether or not reaction of tungsten and uranium monosulfide occurs. Samples of the preparation P-3 uranium monosulfide, which contained about 30 per cent uranium dioxide, were heated in a sintered-tungsten effusion cell to determine whether the total weight loss would be greater than the weight of initial sample plus the background weight loss of the crucible, which latter was determined separately. In the first experiment, the 58-mg sample was placed in the effusion cell and heated at about 2330°C for a total of eight hours. At the end of this time, the excess weight remaining in the crucible corresponded to 20 per cent of the initial sample weight. During the first 45 minutes of heating, 90 per cent of the total weight loss had been obtained. It appeared that the crucible had absorbed the remaining sample, which was eliminated from the effusion cell only by outgassing at temperatures approaching 2600°C.

In the second interaction experiment, a 53-mg sample was contained in a cup machined from dense tungsten rod placed in the same crucible. The crucible was heated for three hours at about 2230°C. At the end of the first hour the cup retained an excess weight corresponding only to 0.6 per cent of the initial sample, while the crucible proper retained another 1.9 per cent. After another two hours at the same temperature, the cup had not changed weight, and the excess weight of the crucible was still equivalent to 0.9 per cent of the original sample. It was concluded that the sample reacted to form a very small amount of residue less volatile than tungsten, which possibility seems unlikely, or else that the background weight loss to be expected was incorrectly determined, and so the sample really had evaporated without reaction with tungsten. In either case it is clear that no volatile reaction

products were formed to carry away excess tungsten or affect measurably the observed volatility of uranium monosulfide. Spectrographic analysis of a nitric acid solution of sublimate from the condenser wall, showed uranium and tungsten in the proportions expected if no reaction occurred.

The later mass spectrometric study of the vaporization of pure uranium monosulfide from a tungsten cell gave no evidence of formation of gaseous molecules containing tungsten.

b. Porosity of the Sintered-Tungsten Effusion Cells

The heating of uranium monosulfide samples in sintered-tungsten effusion cells quite often yielded heavy deposits on the fused silica condenser below the level of the effusion cell orifices. It had been observed that liquids, such as water, when placed in an effusion cell cavity were absorbed into its walls and bottom, apparently by capillary action. In vapor pressure measurements at relatively low temperatures in which US samples were heated in the sintered-tungsten cells, deposits were formed on the condenser only above orifice level, but at high temperatures deposits rapidly appeared opposite the crucible walls. It was thought, therefore, that the appearance of such deposits might indicate the presence of molten sample within the effusion cell. A study of the recorded observations showed that the deposits were formed in all experiments in which the maximum temperature exceeded 2485°K, that of the first part of series V-8, but were not formed when the maximum temperature was below 2475°K, that of exposures (1) and (2) of series V-13. The average of these temperatures, 2480°K (2207°C) may be compared with the value 2200°C reported by Picon and Flahaut⁽¹⁷⁾ as approximately the melting point of uranium monosulfide. Experiments which were performed to determine the melting point by more direct means are described in a later section. These later experiments demonstrated clearly that the melting point must be higher by 260° than 2200°C. The appearance of sublimate

opposite the effusion cell walls must therefore have been due to diffusion of gaseous species through them at some rate governed by the temperatures of the cells and the pressures inside them. The agreement of the "melting point" deduced from the appearance of sublimate with that reported by Picon and Flahaut must be regarded as fortuitous.

The question remains, whether or not the vapor pressure measurements were affected by the transfer of material through the walls of the effusion cells. Because a collection rather than a weight loss technique was used, only the material passing through the lid should have caused trouble. The agreement between the low-temperature data and those taken at higher temperatures, and between the data taken with effusion cell no. 2 with and without radiation shields on its top shows any effect to have been outside the experimental precision and hence undetected. A calculation from the data of vaporization experiment V-5, using the total weight loss, the weight loss expected from the target activities, corrected as required by the results of experiment V-3, and the areas of lid and total external surface of the effusion cell, showed that at maximum one could expect an increase of one per cent in the amount of uranium collected. Such a small amount would be expected to be masked by the experimental scatter, but might remain as a systematic error in the pressures.

c. Tests for Total Condensation of Vapor on the Targets

It is necessary, in the calculation of vapor pressures from amounts of effusate collected on targets, that any departure from total condensation of the effusate be taken into account. At the outset of this research, quantitative condensation was expected because of use of well-cleaned target surfaces and the relatively low target temperatures. Ackermann et al.⁽⁴⁴⁾ showed, for essentially the same apparatus used here, that the target temperature increased linearly with the temperature of the effusion cell, attaining about 825°K for a corresponding oven temperature of 2770°K, the maximum used in the

present research. The targets ought to have been somewhat cooler in the present case because backless cassettes were used to hold the targets, thereby permitting better radiation of target heat in the vertical direction. Any observed incomplete condensation might result either from re-evaporation of the deposit or noncondensation because of incomplete energy transfer (accommodation) between arriving molecules and target. (It might be impossible to distinguish experimentally between the two processes.) The former effect should be entirely negligible, since both uranium⁽⁴⁹⁾ and uranium monosulfide (the solid phases of which might result from condensation of the gaseous species involved here) at the experimental target temperatures have vapor pressures corresponding to evaporation rates many orders of magnitude lower than the observed arrival rates at the targets. It was thought that the second effect would be negligible in view of the metallic nature both of solid uranium and solid monosulfide.

Two experiments were performed to test for incomplete condensation. Holes were punched in the centers of two targets which were then mounted together in the same aluminum ring. The hole in the target nearest the effusion cell, the lower target, was $1/2$ inch in diameter; the hole in the upper target was $9/16$ inch. By this arrangement, some of the effusate could pass through these targets and strike the target next above in the stack in the magazine. If "bouncing" occurred from that target, most of the reflected molecules would pass back through the holes into the space below, but some would be reflected onto and stick to the upper perforated target, which could be analyzed for their presence by α -counting. For the first exposures of series V-10 and V-11, the target arrangements were as described; in V-11 an empty aluminum ring was included between the perforated and next higher targets, while in V-10 the rings containing these targets were in contact. Activity was detected in both cases on the upper perforated target. In experiment V-10 this target showed 0.5 count per minute,

0.6 per cent of the activity of the target above, and in V-11 also 0.5 count per minute, or 0.9 per cent. Since the cosine law governs the distribution of molecules bouncing from a target, a knowledge of the dimensions and spacing of the targets permits a calculation⁽⁵⁰⁾ of the fraction of the total number that should impinge on the upper perforated target. Calculations for the present cases showed that the perforated target received the fractions 0.28 in V-10, and 0.36 in V-11 of the total number of bouncing molecules. The observed target activities thus corresponded to 2.1 and 2.5 per cent bouncing in V-10 and V-11, at respective oven temperatures of 2344 and 2353°K.

The effects of bouncing were observed also after the mass spectrometric study of uranium monosulfide in the form of a deposit on the back of the plate holding the lower of the two beam-defining slits in the mass spectrometer. No quantitative estimate was made of the amount of bouncing in that case, and the temperatures of the two slit plates were unknown.

Two further kinds of evidence relating to completeness of condensation of vapor were obtained in experiments V-3 and V-13, respectively. In the former, described on pages 85 to 89, a comparison was made of the ratio of weight loss calculated from target activity to the total measured weight loss for an effusion cell containing, at different times, uranium monosulfide and uranium dioxide. The ratio for the monosulfide was 1.21 ± 0.03 , while that for the dioxide was 1.19 ± 0.01 . This agreement shows that within the experimental error the fraction of the vapor condensed from US was the same as that from UO_2 . Ackermann *et al.*⁽⁴⁴⁾ showed that, within a fraction of a per cent, complete condensation of UO_2 vapor was obtained in essentially the same apparatus. In experiment V-13, described on pages 96 to 99, vapor from a sample of uranium monosulfide contained in an effusion cell at temperatures from 2416 to 2724°K was collected on a series of platinum targets cooled directly by water

flowing across their backs. Within the experimental precision, the vapor pressures calculated from the α -activities of the deposits on these targets agreed with those from targets supported in the usual way in the magazine for comparable effusion cell temperatures in series V-6, V-7, and V-8.

The conclusion is that, although bouncing of effusate from the targets occurred to a detectable extent, and therefore constitutes a very small systematic error in the calculated vapor pressures, the experimental precision is not great enough to require allowance for it in the final calculations.

d. Accuracy of α -Counting as an Assay for Uranium on the Targets

Experiment V-4 was intended to show that the counting of α -particles could be considered a quantitative method of assay for uranium on targets. A fused silica condenser in the form of an inverted test tube of approximately 12-inch length was substituted for the usual condenser and magazine. The new condenser was cooled by water which flowed through a surrounding jacket. Effusion cell no. 1 containing uranium dioxide was twice heated at temperatures near 2420°K in this apparatus with successive 28 and 29-milligram weight losses, and the sublimates were dissolved from the condenser with concentrated nitric acid. The acid solutions were evaporated to convenient volumes, diluted to 100 ml in volumetric flasks, and an aliquot of one of them was evaporated to dryness and ignited to U_3O_8 in a platinum crucible and weighed. The weight of oxide obtained showed that at least 99 per cent of the vaporized UO_2 had been recovered in the nitric acid solution. Aliquots of 0.200 ml of both solutions were pipetted onto platinum targets and evaporated to dryness, and the rates of emission of α -particles from the residues were measured in the same parallel-plate α -counter used with the targets from effusion experiments. The results were about two per cent lower than expected, but

because a faulty pipetting technique had been used it was assumed the counts obtained accurately represented the amount of uranium on the plates. Ackermann et al.⁽⁴⁴⁾ found that uranium assay of targets by counting gave results in good agreement with those from a colorimetric technique.

5. Convention Chosen for the Expression of Results of Effusion Measurements

It is necessary to adopt some consistent manner of expressing the data from the effusion measurements to allow intercomparison of data from the different experiments. Further, the convention chosen should be conveniently obtainable from the raw data and involve a minimum of assumptions not directly related to the measurements.

One obvious choice involves the nature of the detection of the effusate, and thus of the amount of uranium collected on the targets. Another possibility involves the nature of the condensed phase from which the vapor arises, and thus the amount of uranium monosulfide evaporated. In any case, the chosen treatment differs from any other treatment only by multiplicative constants.

The convention chosen here was to calculate "effective vapor pressures," P_E , from the α -counting data for each experimental measurement by the assumption, for convenience, that the vapor had the average molecular weight 270.14, that of uranium monosulfide. The α -activities of the targets were converted to the equivalent weights of uranium monosulfide that would give rise to these activities, and these weights and the above molecular weight were inserted in the effusion equation (4) to obtain the values of P_E . It follows from equation (11) that the "effective pressure" P_E is related to the partial pressures p_U of uranium atoms and p_{US} of uranium monosulfide molecules by the equation

$$P_E = p_{US} + p_U \sqrt{M_{US}/M_U} \quad . \quad (13)$$

This choice of convention seems justified, firstly, because P_E is directly related to the rate of evaporation of uranium monosulfide through equation (2); it is shown in the next section that the congruently evaporating composition in the monosulfide phase is $US_{1.00}$. A second justification is that the "effective pressure" is a function easily compared with p_U and p_{US} in plots of data. Thirdly, because P_E amounts to a fair approximation of the total pressure in equilibrium with solid US, the plot of $\log P_E$ against $10^4/T$, such as in Figure 9, is a convenient reference for quick comparison of the total volatilities of uranium monosulfide and other refractory compounds.

6. Preliminary Vaporization Experiments

The experiments described in this section are those establishing the congruence of vaporization of monosulfide of the composition $US_{1.00}$ and relating to ideality of the effusion cell used. They are presented in what is hoped to be a logical order in terms of their aims and results, rather than chronologically. Vaporization experiments were given the designation V- followed by numbers indicating their chronological order. A tabulation of the overall conditions and results of the preliminary vaporization experiments is presented in Table IV.

a. Experiment V-1: Study of the Approach to Congruent Vaporization with an Initially Sulfur-rich Sample

The first vaporization experiment, series V-1, was designed to determine whether there is a congruently vaporizing composition in the uranium monosulfide phase by studying the volatility as a function of time at constant temperature. An initial 0.6022-gram sample of P-12(1) monosulfide was heated for a total of 610 minutes in the tungsten annealing crucible in vacuum at temperatures near 2417°K . The initial composition of the charge was $US_{1.01}$, with 0.47 per cent UOS contamination. The heating was interrupted, the crucible allowed to cool, and the vacuum was broken with helium after 42, 247, and 610 minutes at temperature, and the crucible weighed. The respective

TABLE IV
SUMMARY OF PRELIMINARY VAPORIZATION EXPERIMENTS

Series	V-1	V-2	V-3		V-5	V-11	V-12
Purpose	To test approach to congruence from $S/U > 1$	To test approach to congruence from $S/U < 1$ and measure $\log P$ vs. $1/T$	To examine ideality of the effusion cell		To confirm V-2 and extend temperature range	To test approach to congruence from $S/U < 1$ and check condensation on targets	Same as V-11
Initial Sample number	P-12 (1)	P-14 (1)	Part A P-13 (2)	Part B UO ₂	P-14 (1)	P-18 (3)	P-18 (3)
weight (mg)	602	115	76.9		169	408	452
S/U (soluble)	1.01	0.97	1.01		0.97	0.99	0.99
insol. res.	0.5% UOS	16.0% α -U	1.9% UO ₂ + α -U		16.0% α -U	10.1% α -U	10.1% α -U
a_0 (Å)	5.4877 $\pm$ 0.0003	5.4723 $\pm$ 0.0004	5.4896 $\pm$ 0.0006		5.4723 $\pm$ 0.0004	5.4857 $\pm$ 0.0005	5.4857 $\pm$ 0.0005
Effusion cell	Annealing crucible	number 1	number 1		number 1	number 1	number 1
Temperature Range (°K)	2417	2290 to 2540	2402 to 2428		2262 to 2576	2344 to 2364	2460 to 2488
Total wt. loss	1.8% in 42 min 7.1% in 247 min 17.1% in 610 min	96%	47.8%		69.5%	24.0%	61.7%
No targets	12	16	3	4	12	9	12
Sublimate on wall?	no	yes	no	no	yes	yes	yes
Final Sample no.	V-1		V-3		V-5	V-11	V-12
S/U (soluble)	~0.98	none				1.00	1.00
insol. res.	< 0.1%	obtained				6.0% α -U	W only
a_0 (Å)	5.4907 $\pm$ 0.0003		5.4904 $\pm$ 0.0004		5.4894 $\pm$ 0.0005	5.4896 $\pm$ 0.0004	5.4902 $\pm$ 0.0003
film no.	3042		3148		3165	3412	3422
Results and Remarks	Congruent vaporization was attained.	Two univariant vaporizations obs., from condensed phases U + US	Ratio of wt. loss calc. from target to that observed = 1.20. Target data believed to be reliable.		Same as V-2. Residue used for experiment MS-1, which showed some oxygen to be in sample.	Univariance due to condensed phases U + US observed after initially high volatility.	Same as V-11, followed by congruent vaporization.

accumulated weight losses corresponded to 1.8, 7.1, and 17.1 per cent of the initial sample weight. The three heatings were designated V-1(a), (b), and (c). An optical window was used in place of the target magazine in part V-1(a) to permit comparison of cavity temperature with the apparent temperature of the bottom of the crucible. The weight loss obtained in experiment V-1(a) was used to determine the proper lengths of exposures for targets in V-1(b) and (c).

In series V-1(b) and (c) a total of twelve targets was exposed, with individual exposures varying in duration from 15 to 56 minutes and spaced over the entire heating period. The targets were α -counted for times sufficient to give at least 5000 total counts; this value corresponds to a statistical standard deviation of ± 1.4 per cent of the total count. It was shown by a study of α -activity as a function of the period that the shutter was both closed and open while a given target was in place in the collimator, that the total α -activity on the targets must have been collected with the shutter open, hence during and not between the exposures. The data from series V-1 are presented in Table V, in which "effective pressures" P_E are calculated from the target activities and weight losses in accord with the previously outlined convention. In the last column are tabulated pressures normalized to the temperature 2417°K by use of equation (1), rewritten as

$$\frac{\log P_E(2417^\circ)}{\log P_E(T^\circ)} = - \frac{\Delta H_T^\circ(\text{effective})}{2.303 R} \left(\frac{10^4}{2417} - \frac{10^4}{T} \right) \quad (14)$$

Here the slope $[\Delta H_T^\circ(\text{effective})/2.303R]$ was taken to be 2.997, that given by equation (16) for the plot of $\log P_E$ vs. $10^4/T$ for the data of series V-6, V-8, V-9, V-10, V-13.

The table shows that for the experiments termed V-1(a) the total weight loss divided by the total time at temperature gave $w/t = 0.264$ mg/minute. In parts V-1(b) and (c) the respective values of w/t were 0.155 and 0.166 mg/minute. Neglecting for the moment the 6.8 per cent difference between the values for parts (b) and (c),

TABLE V
DATA FROM SERIES V-1

WEIGHT LOSS DATA						
Experiment	Weight Loss w (mg)	Time t(min)	T°K (cavity)	w/t (mg/min)	$P_E(\text{atm}) \times 10^5$	
(a)	11.1	42.0	2412	0.264	2.76	
(b)	31.8	205.0	2414	0.155	1.82	
(c)	60.4	363.0	2416	0.166	1.95	

TARGET DATA								
Exposure No.	Target No.	T°K (cavity)	Exposure Time (min)	Counts/min	cpm/min	Log P_E	Log P_E (normalized to 2417°K)	$P_E(\text{atm}) \times 10^5$ (normalized to 2417°K)
Part (b)								
1	8	*2414	16.31	43.22	2.65	-4.7532	-4.7429	1.808
2	14	2416	20.00	48.88	2.45	-4.7871	-4.7871	1.633
3	15	2414	34.00	79.19	2.33	-4.8091	-4.7937	1.608
4	16	2414	40.00	97.54	2.43	-4.7908	-4.7805	1.658
5	17	2414	56.00	134.97	2.41	-4.7944	-4.7841	1.644
							average	1.636 ± 0.011
Part (c)								
6	18	2416	15.00	38.50	2.57	-4.7663	-4.7663	1.713
7	19	2413	20.00	50.23	2.51	-4.7768	-4.7604	1.736
8	20	2416	20.00	51.65	2.58	-4.7646	-4.7646	1.720
9	21	2416	30.00	78.23	2.61	-4.7596	-4.7596	1.739
10	23	2417	25.00	67.89	2.72	-4.7422	-4.7473	1.789
11	24	2416	20.00	51.93	2.59	-4.7629	-4.7629	1.726
12	25	2418	25.00	65.90	2.62	-4.7578	-4.7681	1.706
							average	1.724 ± 0.005 (omit no. 23)

Orifice diameter: 1.688 ± 0.013 mm at room temperature
 1.704 mm at exposure temperature

Orifice to collimator distance: 9.07 cm

Collimator diameter: 1.9007 ± 0.0004 cm

and the corresponding difference between the average P_E for (b) and (c), the general behavior consisted of an initially high volatility falling off after two per cent weight loss (that is, after target number 8) to a constant value corresponding to $P_E = 1.70 \times 10^{-5}$ atm at 2417°K. The initially high volatility may be attributed to loss of oxygen-containing species (see section F below) and species containing the excess sulfur from the P-12(1) sample.

Analysis of the V-1(c) residue for sulfide sulfur gave 11.6 per cent, corresponding to the formula $US_{0.98}$. Less than 0.1 per cent insoluble material was detected. The sulfide analysis is believed

to have given low results. It was not until after this analysis that the small porcelain cups were used to weigh the solid sulfide and transfer it to the acid reaction flask, and small amounts of sulfide were found in the ground glass joint of the reaction flask at the end of this analysis. Further, it was found later that UOS contamination was encountered only in samples of atomic ratio of sulfur to uranium equal to or greater than unity. The lattice parameter, measured at room temperature, of the series V-1 residue after part (c) was found by film measurement to be $5.4907 \pm 0.0003 \text{ \AA}$.

The apparent discrepancy between the volatilities in series V-1(b) and (c) may now be discussed. Target 8, the first exposed in V-1(b), may probably be disregarded as giving high results, due to a still changing sample composition. The other four V-1(b) targets gave an average effective pressure P_E at 2417°K of $(1.636 \pm 0.011) \times 10^{-5} \text{ atm}$, and the individual exposures gave pressures lying within 1.7 per cent of this value. The weight loss gave $P_E = 1.82 \times 10^{-5} \text{ atm}$ from a Clausing factor of 0.421 for the orifice channel, an assumed constant temperature of 2417°K , and neglect of the material vaporized during warm-up and lost through the crack under the crucible lid. For V-1(c) the target activities gave an average value of $P_E = (1.724 \pm 0.005) \times 10^{-5} \text{ atm}$ (with target number 23 omitted), and all individual target values lay within 1.6 per cent of this value, except that from no. 23, which was 3.2 per cent high. The total weight loss in V-1(c) gave $P_E = 1.94 \times 10^{-5} \text{ atm}$.

There thus is a real difference in the pressures measured in V-1(b) and (c), the same difference being obtained from target data and from weight loss data. Equation (14) shows that a four-degree unrecognized temperature difference between the two series would yield the observed discrepancy. Such a temperature difference might have resulted from slightly different positioning of the crucible and support tables, such that different spots on the bare crucible bottom

were used for temperature measurement in the two series. In series V-1(b) the weight loss measurement leads to a prediction of a pressure 1.09 times that from target data; in V-1(c) the factor is 1.12. Part of the 10 per cent difference between weight loss and target may be attributed to loss of vapor from under the crucible lid. Perhaps a fraction of the difference is due to bouncing of molecules from the targets, as discussed previously. The value $P_E = 1.81 \times 10^{-5}$ atm taken from the final volatility data of series V-6 to 13 lies between the V-1 weight loss and target values, giving a satisfactory agreement.

The series V-1 observations may be summarized as follows. After an initially decreasing volatility during a change in composition of the condensed phase, the partial pressures of the vapor species in the crucible became constant at constant temperature and remained so until the end of the experiment. During the same interval, an appreciable fraction of the solid material was vaporized away. The final constancy of the volatility with time and the monophasic nature of the solid residue lead to a conclusion that the final overall composition of the effusing vapor was the same as that of the solid, which must therefore have been evaporating congruently. Uranium monosulfide containing a slight excess of sulfur is thus shown to lose sulfur preferentially until a congruently evaporating composition is reached, which composition appeared to be $US_{0.98}$ on the basis of sulfide analysis of the V-1 residue, but which later, more accurate analyses of other samples showed to be $US_{1.00}$.

b. Experiments V-11 and V-12: Study of the Approach to Congruent Vaporization with an Initially Uranium-saturated Sample

In series V-11 and V-12, samples of uranium monosulfide from preparation P-18(3) with the overall composition ratio $S/U = 0.88$ were heated in vacuum in effusion cell number 1 at temperatures near 2350 and 2470°K for total periods of 480 and 394 minutes, respectively,

with successive exposures of targets to the effusate. The purpose of these experiments was to study the volatility as a function of time, in order to establish whether congruent vaporization would be reached with an initial sample from the low-sulfur end of the monosulfide phase. The P-18(3) monosulfide was saturated with uranium, as was mentioned earlier.

Nine exposures were made during series V-11. The first exposure was of two targets arranged as described on page 63 for a "bouncing" experiment. After the third exposure, the vacuum was broken with helium and the effusion cell weighed. A weight loss corresponding to 10.2 per cent of the initial 408-mg sample was found after the first 169 minutes at temperature. After the ninth exposure, the effusion cell was reweighed, and the accumulated total weight loss was found to be 24.0 per cent of the initial sample weight for the 481 minutes at temperature. During experiment V-11, sublimates were deposited on the condenser wall both above the orifice and opposite and below the level of the effusion cell wall, with a sharp change in appearance just above orifice level.

The residue was loosened from the bottom and wall of the cell by means of a tungsten probe and removed through the orifice in the argon-filled drybox. It did not appear to have been melted, but was in the form of sintered, yellowish metallic lumps similar to those from sample annealings. The residue was ground in an alumina mortar in the argon atmosphere, and samples were taken for X-ray and chemical analyses. Sulfide analysis showed 11.14 per cent sulfide sulfur, corresponding to the formula $US_{0.93}$, with an insoluble residue amounting to 6.0 per cent of the total weight. The atomic ratio S/U for the soluble part of the sample was thus 1.00. The lattice parameter of the V-11 sulfide was $5.4896 \pm 0.0004 \text{ \AA}$. The insoluble residue gave the X-ray diffraction pattern of α -uranium.

The data obtained from target counting are presented in Table VI, in which, as before, "effective pressures" have been calculated from target activities by use of the molecular weight of US.

TABLE VI
DATA FROM SERIES V-11

Exp No	Target No	T°C (obs.)	$\frac{1}{T} \times 10^5$	T°K (cavity)	Exposure Time (min)	Counts min	Log P _E (obs.)	Log P _E (normalized to 2350.0°K, $10^4 T = 4.2553 \text{ deg}^{-1}$)	P _E (atm) × 10 ⁶
1	{ 1 2	2024.0	1.129	2352.7	80.00	65.21 51.16	-4.8823	-4.8968	12.68
2	3	2022.5	1.132	2350.5	40.00	43.93	-5.0156	-5.0186	9.59
3	4	2022.0	1.135	2350.1	40.00	42.76	-5.0273	-5.0226	9.38
4	5	2036.1	1.139	2365.0	40.00	50.50	-4.9537	-5.0351	9.22
5	6	2022.4	1.142	2350.9	40.00	42.65	-5.0284	-5.0326	9.28
6	7	2018.0	1.145	2347.5	50.00	49.72	-5.0590	-5.0418	9.02
7	8	2018.0	1.149	2346.7	53.00	53.30	-5.0542	-5.0357	9.21
8	10	2017.8	1.152	2346.6	60.00	58.23	-5.0697	-5.0506	8.90
9	12	2015.9	1.154	2344.8	50.00	45.41	-5.0986	-5.0695	8.52

Orifice Diameter: 1.747 ± 0.002 mm at room temperature
1.763 mm at exposure temperature

Orifice to collimator distance: 10.867 cm

Collimator diameter: 1.9007 ± 0.0004 cm

The pressures were normalized to the temperature of 2350°K as described under series V-1, and the normalized pressures are plotted against elapsed time in Figure 7.

FIGURE 7
VOLATILITY VS. TIME AT CONSTANT TEM-
PERATURE FOR URANIUM-SATURATED
US; SERIES V-11 AND V-12

In series V-12, twelve target exposures were obtained at temperatures near 2470°K, with an initial 452-mg portion of the P-18(3) sulfide. The effusion cell was cooled, removed from the vacuum line, and weighed after the third, seventh, and final exposures; accumulated sample weight losses of 13.7 per cent after 70 minutes, 37.3 per cent after 194 minutes, and 61.7 per cent after 395 minutes at temperature were found. The data, together with the pressures normalized to 2470°K, are tabulated in Table VII. In Figure 7 the normalized pressures are plotted with those of series V-11 as a function of accumulated time.

TABLE VII
DATA FROM SERIES V-12

Exp. No.	Target No.	T°C (obs.)	$\Delta \frac{1}{T} \times 10^5$	T°K (cavity)	t (min)	cpm	Log P _E (obs.)	Log P _E (normalized to 2470.0°K, $10^4/T = 4.0486$)	P _E (atm) $\times 10^5$
1	1	2139.4	1.156	2473.8	15.00	76.44	-4.3319	-4.3492	4.48
2	2	2128.6	1.159	2464.8	21.00	75.86	-4.4821	-4.4545	3.51
3	4	2129.5	1.162	2465.7	26.00	94.13	-4.4811	-4.4581	3.48
4	5	2137.2	1.165	2473.7	27.00	107.03	-4.4335	-4.4505	3.54
5	6	2134.2	1.169	2470.8	30.00	112.91	-4.4563	-4.4587	3.48
6	7	2132.8	1.171	2469.7	25.00	92.41	-4.4642	-4.4617	3.46
7	8	2152.8	1.172	2490.6	10.00	46.24	-4.3651	-4.4650	3.43
8	9	2134.5	1.176	2471.8	30.00	107.28	-4.4777	-4.4850	3.27
9	10	2134.8	1.179	2472.3	30.00	102.91	-4.4957	-4.5048	3.13
10	13	2128.9	1.182	2466.2	30.00	87.44	-4.5670	-4.5464	2.84
11	15	2126.6	1.185	2464.1	30.00	87.13	-4.5687	-4.5378	2.90
12	16	2125.3	1.190	2463.0	30.02	85.31	-4.5783	-4.5420	2.87

Orifice diameter: 1.752 ± 0.009 mm at room temperature
1.768 mm at exposure temperature

Orifice-to-collimator distance: 10.977 cm for exposures 1 to 3
11.073 cm for exposures 4 to 7
11.082 cm for exposures 8 to 12

Collimator diameter: 1.9007 ± 0.0004 cm

Again sublimate was observed on the condenser opposite the effusion cell wall. This sublimate had a silver-white metallic appearance, while that above the orifice but inside the water jacket was darker and more amorphous-looking. In the tops of the condenser side-arms the sublimate formed a bronze-colored mirror. After the final heating in series V-12 it was observed that the sublimate opposite the

effusion cell was completely soluble in concentrated nitric acid, whereas that above the orifice level always left a precipitate of free sulfur on dissolution. The appearance of sulfur on nitric acid treatment is a general characteristic of sulfides.

The V-12 residue was removed from the effusion cell in a manner similar to that for the V-11 residue. The residue, in the form of shiny gold flakes, seemed mostly to come from the cavity wall. Analysis of the residue following its crushing in the alumina mortar give 11.64 and 11.83 per cent sulfide sulfur for two samples, with 2.3 per cent insoluble residue in one analytical sample, and 0.3 per cent in the other. X-ray analysis showed the insoluble material to be metallic tungsten only; presumably it was present because a tungsten rod was used to scratch the residue from the sintered tungsten crucible. The analyses, when corrected for the weight of the insoluble tungsten, showed 11.87 and 11.91 per cent sulfur, indicating the formula $US_{1.00}$ in both cases. The lattice parameter of the V-12 residue was $5.4902 \pm 0.0003 \text{ \AA}$, and the X-ray film showed only US and tungsten lines.

The data from series V-12 in Figure 7 show an initially very high volatility which fell quite rapidly to a constant value at $P_E = 3.5 \times 10^{-5} \text{ atm}$ before the end of the first seventeen minutes. After vaporization of about thirty per cent of the sample, the volatility again decreased slowly until after perhaps a fifty per cent weight loss, when a second constant volatility at $P_E = 2.9 \times 10^{-5} \text{ atm}$ was reached. The data from series V-11 show qualitatively similar behavior, although at the lower temperature the second flat had not been reached by the end of the experiment.

Now the phase law requires that if condensed material in a two-component system at constant temperature is to have a unique pressure, either the vapor must have the same composition as the condensed phase, or there must be two condensed phases present. Since the composition of the solid phase changed during the time of the first

pressure flat, going from an overall atomic ratio, S/U, of 0.88 initially to 0.93 finally during series V-11, two condensed phases must have been present. Because the sample was initially uranium-saturated, and since no phases of less sulfur content than the US phase have been reported in the uranium-sulfur system, the inference is that one of the phases must have been liquid uranium. The other would thus have been the uranium-rich, solid monosulfide phase whose composition was that of the phase boundary at the temperature of each experiment. It seems not unlikely, in view of the analytical results for the V-11 residue, that this composition was $US_{1.00}$.

If this phase behavior is assumed to have been that which was observed, then one might expect the first constant pressure to correspond to that of pure liquid uranium plus that due to solid uranium monosulfide. From the data of Rauh and Thorn,⁽⁴⁹⁾ a vapor pressure of 1.6×10^{-4} atm for uranium at 2470°K, higher by a factor of two than P_E observed, may be calculated. [Use of the molecular weight 270.14 in the calculation of the "effective pressure" P_E introduces an error of less than seven per cent, even if the observed pressure were due wholly to $U(g)$.] The observed behavior is adequately explained by the observation that the sample surface must rapidly become depleted in uranium, because of its high volatility, so that the observed pressure is limited by the rate of diffusion of gaseous uranium through the solid sulfide mass.

The second pressure flat in the V-12 pressure-time curve must be due presumably to the congruent vaporization of solid, stoichiometric uranium monosulfide (the composition $US_{1.00}$ was established by the chemical analysis). If so, the "effective pressure," 2.9×10^{-5} atm, should be in agreement with the value found at 2470°K in later experiments in this research.

The final volatility found in series V-12 was lower than that calculated from equation (17) by 15 per cent, probably not a

serious discrepancy for the following reason. Most of the V-12 residue was found to have been deposited on the walls of the effusion cell, with a corresponding depletion of the evaporating area on the floor of the effusion cell cavity. Since the target "sees" only the floor of the cavity, depletion of sample there should decrease somewhat the quantity of effusate collected, because the presence of the orifice in the effusion cell precludes true vapor saturation. (It might be pointed out that unexplained discrepancies in pressures much larger than 10 per cent are often found in high-temperature vaporization studies.)

The final exposure in experiment V-11 gave a target activity corresponding to the calculated apparent pressure, 8.5×10^{-6} . The relative shapes of the V-11 and V-12 pressure-time curves seem to indicate a more rapid increase with increased temperature of the rate of evaporation of monosulfide, than of the rate of diffusion of gaseous uranium through the sintered, solid sulfide.

c. Discussion of the Annealing of Monosulfide

Sample P-18

An explanation of the behavior of monosulfide preparation P-18 during its successive annealings may now be set forth. It was observed that the residue in the bottom of the annealing crucible, already sulfur-deficient initially, became steadily poorer in sulfur, while deposits on the lower side of the lid approached the composition $US_{1.00}$.

Assume the lid to have been at a slightly lower temperature than the crucible cavity. Some of the vapor in the cavity would be expected to deposit there. The results of experiments V-11 and V-12 indicate that at the temperatures employed, the evaporating material during the P-18 annealings was probably a two-phase mixture of liquid uranium and solid monosulfide. Consider first the vapor from the uranium phase. As discussed in the above paragraphs, a diffusional process would prohibit the uranium from maintaining its saturation

vapor pressure in the crucible cavity. Any uranium condensing on the lid must then immediately re-evaporate, provided the partial pressure of uranium atoms in the cavity were also less than the saturation pressure at the temperature of the lid. At the same time some uranium atoms would be lost from the system by effusion through the orifice.

Now consider the case of evaporation from the monosulfide phase. This substance would be able to saturate the cavity with its vapor, and the cooler lid, though too hot to condense the vapor from the uranium phase, would be expected to collect a deposit of material vaporized from the monosulfide phase. Some of the atoms and molecules evaporating from the monosulfide phase would also escape through the orifice. The effective sink for loss of monosulfide vapor thus would consist of both orifice and lid, although the lid of course would condense only a fraction of the vapor from the monosulfide phase striking it.

So far nothing has been said about the species involved in the monosulfide vaporization. Mass spectrometric measurements, to be described later, showed that the species to be expected are gaseous uranium and sulfur atoms, and gaseous monosulfide molecules. The particular species involved, or whether or not the uranium and sulfur atoms recombine on the lid, do not affect the present interpretation.

It remains only to obtain a material balance for the overall process. The apparent enrichment in uranium of the residue in the bottom of the crucible cavity does not mean that the total amount of material in the cavity became relatively richer in uranium. Rather, the monosulfide phase in the bottom of the cavity must just have vaporized faster than the uranium phase, so that more units of formula "US" were lost to the lid and through the orifice in a given time than atoms from the uranium phase were lost through the orifice. Stated in another way, the rate of loss of uranium atoms through the orifice was exceeded by the combined rates of effusion and of condensation on the lid of the monosulfide vapor.

d. Experiments V-2 and V-5: Study of the Approach to
Congruent Vaporization with an Initially Uranium-
saturated Sample; First Attempt to Study Tempera-
ture Dependence of Pressure

In series V-2 and V-5, samples of monosulfide preparation P-14(1) of composition $US_{0.80}$ were heated in effusion cell no. 1 in vacuum at oven temperatures from 2262 to 2576°K, and targets were exposed to the effusate. For series V-2 an initial 114.5-mg sample was taken. The first four targets were exposed in experiment V-2(a) at temperatures from 2408 to 2435°K, then the effusion cell was allowed to cool, the vacuum was broken with helium, and the effusion cell was reweighed, a 35.4 per cent weight loss being observed.

Twelve more targets, two of them of fused silica instead of platinum, were exposed during series V-2(b) at temperatures from 2290 to 2540°K, but targets after the sixth exposure showed successively decreased α -activity on counting, with the final target having essentially a zero count per minute. The total weight loss amounted to 96 per cent of the initial sample weight and no residue could be obtained for analysis. Again, a heavy sublimate was obtained opposite the effusion cell wall, and the excess weight remaining in the effusion cell at the end of the experiment seemed to be due chiefly to material absorbed into the tungsten. The data from series V-2 are shown in Table VIII, and logarithms of "effective pressures" P_E , calculated as usual from a molecular weight 270.14 for the vapor, are plotted as a function of reciprocal temperature in Figure 8.

In series V-5 a sample of 169.4-mg weight was placed in the outgassed effusion cell, and essentially a duplicate of series V-2 was performed, except that the crucible was not heated to "dryness." Twelve exposures of platinum targets at effusion cell temperatures from 2262 to 2576°K were made. The first target was exposed during the entire warm-up to temperature, then for an additional 30 minutes

TABLE VIII
DATA FROM SERIES V-2

Exp. No.	Target No.	T°C (obs.)	T°K (cavity)	Exposure Time (min)	Counts, min	P _E (atm)	Log P _E	10 ⁴ T (deg ⁻¹)
1	2	2071.9	2408.6	25.00	41.41	1.468 × 10 ⁻⁵	-4.8332	4.1518
2	3	2093.2	2430.4	25.00	55.27	1.969 × 10 ⁻⁵	-4.7059	4.1145
3	4	2098.1	2435.9	26.00	57.79	1.981 × 10 ⁻⁵	-4.7030	4.1053
4	5	2097.4	2434.9	26.00	55.76	1.911 × 10 ⁻⁵	-4.7186	4.1069
5	6	2060.8	2396.4	34.00	45.99	1.200 × 10 ⁻⁵	-4.9207	4.1729
6	7	1960.3	2290.8	73.00	28.31	3.365 × 10 ⁻⁶	-5.4731	4.3653
7	9	2017.2	2350.7	62.00	47.29	6.703 × 10 ⁻⁶	-5.1737	4.2541
8	10	2072.1	2408.4	25.00	35.83	1.275 × 10 ⁻⁵	-4.8944	4.1521
9	24	2123.4	2462.0	15.00	35.32	2.118 × 10 ⁻⁵	-4.6741	4.0617
10	11	2161.8	2502.2	15.00	53.71	3.247 × 10 ⁻⁵	-4.4885	3.9964
11*	12	2108.1	2440.0	20.00	34.98	1.565 × 10 ⁻⁵	-4.8055	4.0883
12*	13	2036.8	2373.1	50.00	34.95	6.157 × 10 ⁻⁶	-5.2106	4.2134
13*	15	1981.4	2312.3	87.00	25.35	2.534 × 10 ⁻⁶	-5.5962	4.3247
14*	25	2098.9	2436.4	25.00	26.34	9.404 × 10 ⁻⁶	-5.0267	4.1044
15*	16	2142.0	2481.6	20.00	0.97	8.795 × 10 ⁻⁸	-7.0558	4.0297
16*	17	2190.4		15.00	not counted			

*Data not plotted in Figure 8.

Orifice diameter: 1.056 ± 0.007 mm at room temperature
1.672 mm at exposure temperature

Orifice to collimator distance: 10.284 cm for exposures 1 to 4
10.303 cm for exposures 5 to 16

Collimator diameter: 1.9007 ± 0.0004 cm

$$\frac{\Delta}{T} = 1.161 \times 10^{-5} \text{ deg}^{-1}$$

These data are represented by the symbol ○ in Figure 8.

FIGURE 8
VOLATILITY AS A FUNCTION
OF TEMPERATURE FOR
URANIUM-SATURATED US;
LOGARITHM OF "EFFECTIVE
PRESSURE" VS. RECIPROCAL
OF TEMPERATURE FOR
SERIES V-2, V-3, V-5, V-11,
AND V-12

at 2412°K to permit checking of total weight loss against the target count. After the second exposure, the effusion cell was allowed to cool, the vacuum was broken with helium, the effusion cell was reweighed, and the condenser sublimate, which again extended down past the level of the effusion cell, was dissolved off the wall with nitric and hydrofluoric acids. The weight loss amounted to 15.3 per cent of the initial sample weight.

The series was resumed and eleven more exposures were made. The first of this group of targets was exposed only during the rapid initial warm-up to temperature. The total weight loss amounted to 69.5 per cent. The residue was removed from the effusion cell through the orifice in the form of thin gold flakes only after vigorous scratching with a tungsten wire. It is not known whether the residue was located in the bottom of the cavity or on the walls as found after series V-12. From an X-ray diffraction pattern of the residue, with only US and light tungsten lines found on the film, the lattice parameter was found to be $a_0 = 5.4894 \pm 0.0005 \text{ \AA}$. The data from series V-5 are presented in Table IX, and "effective pressures," calculated with the use of the molecular weight of US for the vapor, are plotted with those of series V-2 in Figure 8.

The volatility behavior observed in series V-2 and V-5 should be analogous to that observed in series V-11 and V-12, except that the latter series were run at constant temperature. Qualitatively the observations are in agreement. The "effective pressure" P_E for the first V-5 target, which was exposed from the outset of heating, is quite high, presumably because of evaporation of uranium from the sample surface. The next eight exposures in series V-5 (except for the target exposed only during warm-up in the second part of series V-5) and the first four V-2 targets (the first of which was exposed beginning several minutes after temperature was reached) give lower pressures whose magnitudes presumably were limited by

TABLE IX
DATA FROM SERIES V-5

Exp. No.	Target No.	T°C (obs.)	T°K (cavity)	Exposure Time (min)	Counts, min	P _E (atm × 10 ⁵)	Log P _E	10 ⁴ /T (deg ⁻¹)
1	1*	2075.7	2412.0	30*	76.11	2.226	-4.6525	4.1459
2	2	2050.5	2385.6	30.00	41.6 ^a	1.213	-4.9163	4.1918
3	3**				2.27			
4	4	1933.2	2262.1	90.00	24.84	0.2345	-5.6298	4.4207
5	7	2011.6	2344.7	50.00	38.22	0.6613	-5.1796	4.2649
6	8	2107.7	2446.4	20.00	50.87	2.248	-4.6483	4.0876
7	9	2194.4	2535.2	10.00	66.02	5.939	-4.2263	3.9445
8	10	2161.2	2501.6	12.00	58.01	4.320	-4.3645	3.9974
9	11	2080.9	2417.4	20.00	38.34	1.684	-4.7737	4.1367
10	13	1979.4	2311.0	61.00	32.40	0.4502	-5.3408	4.3271
11	14	2141.6	2481.1	47.21	46.33	2.749	-4.5609	4.0305
12***	15	2172.4	2513.3	8.00	76.99***	3.885	-4.4106	3.9788
13***	16	2232.7	2576.2	5.30		7.313	-4.1359	3.8817

*Never covered by shutter; calculated pressure is therefore high.

**Never covered by shutter.

***Double exposure; counts divided between the two exposures according to time and slope.

Orifice diameter: 1.669 ± 0.004 mm at room temperature.

1.684 mm at exposure temperature

Orifice to collimator distance: 10.302 cm

$$\Delta \frac{1}{T} = 1.160 \times 10^{-5} \text{ deg}^{-1}$$

These data are represented by the symbol Δ in Figure 8.

diffusion of gaseous uranium through the solid sulfide mass. These data define a straight line given by the equation

$$\log P_E (\text{atm}) = - (2.950 \pm 0.036) \frac{10^4}{T} + (7.42 \pm 0.15) ,$$

where the standard deviations in slope and intercept from the linear least squares analysis are given. The next six V-2 points combined with the final three V-5 points indicate lower pressures, presumably due to congruently vaporizing US; the temperature dependence of the vapor pressure of US is given by the relationship

$$\log P_E (\text{atm}) = - (2.730 \pm 0.044) \frac{10^4}{T} + (6.44 \pm 0.18) , \quad (15)$$

which was obtained by least squares analysis with the standard deviations indicated. No further exposures were made in series V-5, and

The last six V-2 points (not shown in Figure 8) dropped off to zero pressure because of progressive decrease of amount of sample.

Were later data not available, one would conclude from the series V-2 and V-5 results that equation (15) gives the volatility of congruently evaporating US. If this were the case, then the values of P_E from the series V-11 and V-12 should lie on the same lines as those from series V-2 and V-5, and the lower line should coincide with that obtained in series V-6, 7, 8, 9, 10, and 13 described below. The data from series V-11 and V-12, and the indicated line from series V-6 to 13 are shown in Figure 8 for comparison. One immediately sees that neither set of later data gives the expected agreement with volatilities obtained in series V-2 and 5, although, as mentioned above, the data from series V-11 and V-12 and from series V-2 and V-5 showed the same qualitative behavior. The upper and lower points from series V-12 indicated pressures higher by 22 and 17 per cent than the pressures from the corresponding V-2 and V-5 lines.

If the processes are those assumed above, then good reasons for the discrepancies are not immediately obvious. One possible explanation is that both the V-2 and V-5 lines are low by reason of error in temperature measurement and the lower line is dropped even further and its slope decreased by reason of loss of vapor saturation due to sample depletion. Yet the agreement of data among the later experiments makes the temperature explanation seem distasteful. It is the writer's opinion that the observations in series V-2 and V-5 must be accepted on a qualitative basis only and thus can be neglected in the final quantitative calculations. The data from series V-6 to 13 stand as a coherent whole describing the vaporization of uranium monosulfide, and their internal agreement clearly outweighs any doubt cast upon them by the results of series V-2 and V-5.

e. Experiment V-3: Characterization of the Ideality of the Effusion Cells

Experiment V-3 was designed to permit comparison of observed weight loss with that calculated from target activity. Single targets were exposed to effusate from uranium monosulfide in experiments V-3(a), (b), and (c), and from uranium dioxide in V-3(d), (e), (f), and (g). For each determination the target, mounted as usual and held in the cooled magazine, was never protected from effusate by the shutter, and the effusion cell was weighed before and after each exposure. If the ideal effusion equations (2) and (4) describe the behavior adequately, then the weight, w , of material on each target should have been related to the total weight loss, W , by the formula

$$W = w \frac{r^2 + d^2}{r^2} \quad ,$$

in which as before r is the radius of the collimator and d the distance from orifice to collimator, and in which the same molecular weight is assumed for effusion cell sample and target deposit. Thus errors in measurement of orifice diameter, temperature, and exposure time could not affect the results. These experimental conditions were measured, however, so that pressures could be calculated as usual. In each heating the oscillator power was raised slowly over a period of about ten to fifteen minutes to maintain the residual pressure in the system below about 4×10^{-5} mm Hg. The power was then increased suddenly to raise the effusion cell temperature the final two or three hundred degrees in a few seconds. The time at maximum temperature could therefore be used to calculate the pressure within only a small error.

For exposures V-3(a), (b), and (c), an initial 76.9-mg sample was taken from preparation P-13(2) monosulfide of composition $US_{1.01}$. This material was contaminated with about 2 per cent uranium metal and dioxide. The residue from exposure V-3(c) had a lattice parameter at room temperature of $5.4904 \pm 0.0004 \overset{\circ}{\text{A}}$. The target deposits

from exposures V-3(a), (b), and (c) were assumed for calculation to have the molecular weight 270.14, that of US. The data are presented in Table X below, in which measured weight losses are compared with those calculated from target activity. The ratios of weight loss calculated to weight loss measured were 1.28, 1.18, and 1.17 for (a), (b), and (c), respectively.

TABLE X
COMPARISON OF WEIGHT LOSS AND TARGET DATA FOR
SERIES V-3

Target	T, °K	Exposure (min)	$\frac{r^2+d^2}{r^2}$	Target Activity, cpm	Weight loss, mg			
					Calc from Target	Observed	$\frac{W(\text{calc})}{W(\text{obs})}$	
US	a	2420	51	118.5	103.1	17.94	14.07	1.28
	b	2407	54	118.5	78.4	13.64	11.58	1.18
	c	2402	60	118.5	76.5	13.04	11.14	1.17
UO ₂	d	2414	18	118.2	87.9	15.26	12.52	1.22
	e	orifice clogged		118.2	75.9	13.17	9.20	1.43
	f	2428	20	118.2	126.2	21.90	18.68	1.17
	g	2412	20	118.2	93.5	16.23	13.72	<u>1.18</u>
	Average without (e)							1.20

The results of experiments V-3(a), (b), and (c) with monosulfide were unexpected, so that it was thought desirable to check with another substance of known vaporization process, from which target deposits of known molecular weight would be obtained. Uranium dioxide, whose vapor pressure⁽⁴⁴⁾ is comparable to that of US at the same temperatures, was chosen. The UO₂ samples were prepared by heating in the effusion cell in vacuum portions of oxide of composition UO_{2.048} obtained from the Argonne Special Materials and Services

Division. Ackermann⁽⁵¹⁾ has shown that such treatment reduces to UO_2 those uranium oxides richer in oxygen. It was necessary to reweigh the effusion cell and to remeasure its orifice after preparation of the dioxide, because the loss of the excess oxygen was accompanied by a slight enlargement of the orifice due to formation and vaporization of tungsten oxide. After experiment V-3(e), the orifice was found to be partially blocked by red-brown crystals of UO_2 of lengths approaching 1 mm; these crystals had formed on the slope back of the orifice and projected into the path of effusing molecules.

Two flat disks of tungsten of 0.005 inch thickness with holes $1/8$ inch in diameter in their centers were placed on top of the effusion cell to serve as radiation shields to warm the orifice for exposure V-3(f). The relative temperatures of cavity and blackbody hole were measured with the two shields in place. After exposure V-3(f), a slight deposit of UO_2 was found around the hole in the upper shield. For experiment V-3(g) only one such shield was used and it intercepted no vapor. A recomparison of the temperatures was also carried out for the single shield. The data obtained with uranium dioxide are included in Table X. The weight ratios found were 1.22, 1.17, and 1.18 for the three good measurements.

Table X shows that from the target activities there could be predicted an average of loss in weight greater by 20 per cent than that measured directly by weighing for experiments using both US and UO_2 . This result means that, relative to the distribution calculated from the cosine law, the number of molecules effusing in the forward direction, i.e., along the normal to the orifice plane, is enhanced over that effusing at larger angles to the normal. If, as is believed to be the case, the distribution of molecules in the forward direction was unchanged from that predicted by the cosine law, the twenty per cent deficiency in observed weight loss corresponds to the Clausing correction expected from an orifice shaped like a right circular cylinder whose

diameter is 5.0 times its length, or for an orifice of 1.70 mm diameter a length of 0.34 mm. The orifice of effusion cell no. 1 was not a right circular cylinder of length one-fifth its diameter. Before its initial use in series V-2, the top of the effusion cell was ground down until the edge of the orifice was sharp, though the orifice itself was slightly non-planar. Repeated use of tungsten rods to scratch samples of residue loose from the interior of the effusion cell had, by the end of series V-12, rounded the lip of the orifice to an effective length estimated to be at maximum only 0.12 mm. During series V-3, the actual orifice must have been much sharper-edged than that. One surmises that the effective length of the orifice inferred from series V-3 was due to the steep taper leading from cavity to orifice (see Figure 6). The total rate of arrival of molecules of effusate at the target, which subtended an angle of about 5° at the orifice, should have been negligibly affected by the degree of nonideality of the orifice used, and the pressures calculated from target data for the later experiments should suffer any errors only for other reasons.

The high ratio of exposure V-3(e) must have resulted from an effectively channeled orifice resulting from the deposition of the crystals on its lower edge, and this datum therefore may be discarded. The reason for the deviation of the V-3(a) result by seven per cent from the average is not known. Elimination of excess sulfur and oxygen-containing species from the oxide-contaminated monosulfide during the first exposure would have raised the result by less than one per cent, even if the excess sulfur were lost in the form of US_2 molecules.

The agreement between results obtained with monosulfide and dioxide permits the following conclusions to be deduced by analogy with the known behavior of the dioxide. Reaction of US with the container material to produce volatile products and bouncing of uranium-containing molecules from the targets were negligible within

the precision of the measurement. Formation of volatile reaction products containing tungsten would have increased the total weight loss, W_{obs} . Bouncing would have decreased the calculated weight loss, W_{calc} . Had either process occurred, the ratio $W_{\text{obs}}/W_{\text{calc}}$ would have been less in the experiments with the sulfide than with the oxide. If, however, bouncing had occurred simultaneously with the formation of nonvolatile reaction products which contained both tungsten and uranium, the ratio $W_{\text{obs}}/W_{\text{calc}}$ might still have been equal for the sulfide and oxide experiments. No evidence was ever found to indicate formation of such a nonvolatile material.

The use of uranium dioxide in experiments V-3(d), (f), and (g) provided the data requisite to calculation of the vapor pressures of UO_2 at the experimental temperatures. These pressures were calculated for the purposes of comparing them with those obtained by Ackermann, Gilles, and Thorn (AGT);⁽⁴⁴⁾ to check the agreement obtainable by independent observers using similar effusion techniques in the study of the vapor pressure of the same compound. The data from experiments V-3(d), (f), and (g) were compared with the tabulation⁽⁵¹⁾ of the individual experimental pressures of AGT's series B-4 and 8, which series included the V-3 temperatures. The V-3 pressures agreed with those of AGT within the experimental precision of AGT's data.

7. The Determination of the Temperature Dependence of the Total Effusion Rate

The preliminary experiments described above established the existence of a congruently vaporizing composition $\text{US}_{1.00}$ in the uranium monosulfide phase. The following experiments were performed to determine the quantitative relation between its volatility and temperature. Table XI contains a summary of the experimental conditions and observations from these experiments.

TABLE XI
SUMMARY OF EXPERIMENTS MEASURING TOTAL RATE OF EFFUSION

Series	V-6	V-7	V-8	V-9, V-10	V-13
Initial Sample number	P-18(3-lid)	same as V-6	same as V-6	P-19(1-lid)	same as V-9
weight	129.7 mg	202.9 mg	126.3 mg	130.9 mg	164.3 mg
S/U _o	1.01			1.01	
a ₀ (Å)	5.4865 ± 0.0004			5.4924 ± 0.0006	
Effusion Cell	number 2 with 2 shields on top	number 2 with 2 shields on top	number 1 no shields	number 1 no shields	number 2 no shields
Temperature Range (°K)	2442 to 2646	2449 to 2772	2303 to 2536	1840 to 2374	2414 to 2727
Weight loss	96.2%	58.8%	73.0%	25.1%	20.2%
No. targets	13	9	7	9 in V-9 13 in V-10	8
Sublimate on Wall?	yes	yes	yes	no	yes
Final Sample number	none obtained	V-7	V-8	V-10	V-13(8)
a ₀ (Å)		5.4901 ± 0.0002	5.4908 ± 0.0002	5.4942 ± 0.0010	5.4915 ± 0.0004
film no.		3309	3310	3383	3450
Remarks	Volatility dropped to zero during run because of sample depletion.	Only four good exposures be- cause shields slipped and orifice clogged during run.		Isotopically enriched uranium sulfide used. Bouncing experiment performed during V-10, exposure (1). Poor X-ray pattern.	Isotopically enriched uranium sulfide used. Targets cooled directly by water. Residue af- ter exposure (5) had a ₀ = 5.4906 ± 0.0002 (film no. 3439).

a. Series V-6 and V-7

Effusion experiments V-6 and V-7 were undertaken to extend to higher temperatures and pressures the data of series V-2 and V-5, which at that time were thought to have yielded reliable data for the vaporization of congruently vaporizing uranium monosulfide. In both series V-6 and V-7, samples of preparation P-18(3-lid) monosulfide of composition $US_{1.01}$ were employed in effusion cell number 2 with two annular radiation shields of 0.001-inch tungsten sheet laid on its top. The data are presented in Table XII in which, as usual, the molecular weight of US for the vapor was assumed in calculating the "effective pressures" P_E . The values of the logarithm of P_E are plotted against the reciprocal of temperature in Figure 9. In experiment V-6, a 129.7-mg sample was used, and thirteen targets were exposed at effusion cell temperatures from 2442 to 2646°K. At the end of the series, the observed weight loss was equivalent to 96.2 per cent of the original sample weight. Target activities for the ninth through thirteenth exposures fell off steadily to near zero, and data from these targets are included in Table XII, but have been omitted from Figure 9.

Before series V-7 was carried out, the effusion cell was not re-outgassed. A 202.9-mg sample of the P-18(3-lid) monosulfide was used and nine targets were exposed at temperatures from 2449 to 2772°K. The weight loss corresponded to 58.8 per cent of the initial sample. The lattice parameter of the residue from experiment V-7 was $5.4901 \pm 0.0002 \text{ \AA}^\circ$.

During series V-7 one of the radiation shields on top of the effusion cell shifted slightly, so that a deposit of effusate built up on its edge. After the series was ended, observation showed that the orifice was almost obscured by the deposit which extended down into it. Target activities from exposures 3, 4, 5, 6 and 9 were quite low, presumably because of the reduced orifice area. Exposures 1, 2, 7, and 8 gave activities in fair agreement with those from series V-6.

TABLE XII
DATA FROM SERIES V-6

Exposure No.	Target No.	T (°C) (obs.)	$(\Delta I/T) \times 10^5$	T (°K) (cavity)	Exposure time (min)	Counts/min	Orifice** diam. (mm)	P_E (atm.)	Log P_E	$10^4/T$ (deg ⁻¹)
1	1	2140.0	1.120	2507.3	17.00	19.96	0.842	4.826×10^{-5}	-4.3164	3.9883
2	2	2138.2	1.120	2505.4	21.00	24.13	0.841	4.734×10^{-5}	-4.3247	3.9913
3	3	2138.0	1.120	2505.2	20.00	22.20	0.840	4.586×10^{-5}	-4.3385	3.9917
4	4	2191.8	1.120	2561.9	15.00	30.64	0.838	8.562×10^{-5}	-4.0675	3.9034
5	5	2194.5	1.120	2564.7	20.00	41.84	0.837	8.799×10^{-5}	-4.0556	3.8990
6	6	2248.3	1.120	2621.0	15.00	63.98	0.836	1.819×10^{-4}	-3.7403	3.8153
7	8	2272.3	1.120	2646.2	12.00	63.70	0.835	2.282×10^{-4}	-3.6417	3.7790
8	9	2256.7	1.120	2629.9	15.00	62.29	0.834	1.783×10^{-4}	-3.7487	3.8025
9*	10	2218.8	1.120	2589.8	20.00	50.76	0.832	1.086×10^{-4}	-3.9641	3.8611
10*	13	2174.8	1.120	2543.9	30.00	35.12	0.828	5.017×10^{-5}	-4.2995	3.9308
11*	14	2124.9	1.120	2491.3	56.00	10.92	0.827	8.288×10^{-6}	-5.0815	4.0140
12*	15	2079.8	1.120	2443.3	60.00	4.82	0.824	3.669×10^{-6}	-5.4354	4.0928
13*	18	2229.2	1.120	2601.2	20.00	1.02	0.822	2.24×10^{-6}	-5.6492	3.8444

*Not plotted in Figures 9 and 10.

**At exposure temperature

Orifice diameter at room temperature: before Series V-6, 0.835 ± 0.002 mm
after Series V-6, 0.813 ± 0.002 mm

Orifice to collimator distance: 11.045 cm

The data from series V-6 are represented by the symbol 0 in Figures 9 and 10.

DATA FROM SERIES V-7

1	1	2166.4	1.126	2535.4	25.00	38.82	0.817	6.422×10^{-5}	-4.1923	3.9441
2	2	2118.5	1.132	2485.2	50.00	44.22	0.810	3.683×10^{-5}	-4.4339	4.0238
3*	3	2084.5	1.135	2449.4	60.00	19.0	0.801	1.34×10^{-5}	-4.873	4.0824
4*	4	2229.5	1.146	2603.2	14.00	12.0	0.798	3.76×10^{-5}	-4.425	3.8414
5*	5	2300.6	1.160	2678.6	6.00	10.3	0.797	7.66×10^{-5}	-4.116	3.7333
6*	6	2332.9	1.174	2713.8	5.05	13.2	0.796	1.17×10^{-4}	-3.932	3.6849
7	7	2387.0	1.203	2772.5	5.00	46.96	0.794	8.867×10^{-4}	-3.0522	3.6069
8	9	2357.4	1.223	2743.1	5.05	80.57	0.793	7.286×10^{-4}	-3.1375	3.6455
9	11	2219.9	1.235	2599.1	16.00	33.20	0.790	9.30×10^{-5}	-4.032	3.8475

*Not plotted in Figures 9 and 10.

Orifice diameter at room temperature: before Series V-7, 0.813 ± 0.002 mm
after Series V-7, 0.781 ± 0.002 mm

Orifice to collimator distance: 10.711 cm

The data from series V-7 are represented by the symbol x in Figures 9 and 10.

FIGURE 9
VOLATILITY OF URANIUM MONOSULFIDE AS A FUNCTION OF
TEMPERATURE; DATA FROM SERIES V-6, V-7, V-8, V-9
V-10, AND V-13

Apparently, then, the orifice deposit did not form until after the second exposure, and thermal shock and its own weight must have caused the deposit to drop into the cavity during exposures 7 and 8. Only the data from exposures 1, 2, 7, and 8, are shown in Figure 9.

During both series V-6 and V-7, sublimates formed on the condenser opposite the effusion cell. The orifice shrank a total of three per cent in diameter during the two series. It was therefore necessary to correct the diameter somewhat for each exposure in order to make pressure calculations. The rate of shrinkage must have depended on both temperature and time, and for the small correction

required it was thought adequate to assume that the shrinkage occurred at a rate proportional to the product of temperature and time at each temperature. The corrected orifice diameters are indicated in Table XII.

A small change in the window transmissivity which occurred during series V-7, was distributed among the individual target exposures as described on page 56. Figure 9 shows the data from series V-6 and V-7 to lie along the line determined by least squares treatment of the data from experiments V-6, 8, 9, 10, and 13.

b. Series V-8

Series V-8 was performed with monosulfide of formula $US_{1.01}$ from the P-18(3-lid) sample in effusion cell no. 1. The temperature range covered was from 2303 to 2536°K, approximately that of series V-5 and overlapping the good measurements of series V-6 by thirty degrees. The initial sample weighed 126.3 mg, seven targets were exposed, and the weight loss corresponded to 73.0 per cent of the original sample. The residue had a lattice parameter of $5.4908 \pm 0.0002 \text{ \AA}$. Condensate on the condenser opposite the crucible wall again was found. The data are listed in Table XIII and the values of $\log P_E$ are plotted against $10^4/T$ in Figure 9.

TABLE XIII
DATA FROM SERIES V-8

Exp. No.	Target No.	T (°C) (obs.)	$(\Delta \frac{1}{T}) \times 10^5$	T (°K) (cavity)	Exposure Time (min)	Counts/min	$P_E (10^{-5} \text{ atm})$	$\log P_E$	$10^4/T \text{ (deg}^{-1}\text{)}$
1	1	2144.1	1.237	2483.3	11.00	49.05	4.202	-4.3765	4.0270
2	2	2108.7	1.239	2446.3	20.00	58.91	2.756	-4.5598	4.0878
3	3	1973.0	1.240	2303.2	70.00	36.80	0.4771	-5.3214	4.3418
4	4	2044.2	1.241	2377.9	36.00	47.56	1.219	-4.9141	4.2055
5	5	1922.5	1.245	2249.1	106.00	26.43	0.2235	-5.6507	4.4468
6	6	2194.1	1.249	2536.0	7.00	52.32	7.118	-4.1476	3.9433
7	8	2112.1	1.250	2450.4	35.00	102.80	2.749	-4.5608	4.0810

Orifice diameter: $1.731 \pm 0.002 \text{ mm}$ at room temperature
 1.747 mm at experimental temperatures

Orifice to collimator distance: 11.002 cm

Collimator diameter: $1.9007 \pm 0.0004 \text{ cm}$

These data are represented by the symbol $\square$ in Figures 9 and 10.

c. Series V-9 and V-10

The ranges of temperatures and pressures used for sublimation studies were extended downward by the use of isotopically enriched monosulfide, sample P-19(1-lid) of formula $US_{1.01}$, whose specific activity, due chiefly to enrichment in U^{234} content, was $1.411 \pm 0.014 \times 10^8$ decays per minute per gram of uranium. An initial sample of 130.9 mg was used for series V-9, nine targets were exposed at effusion cell temperatures from 1861 to 2320°K, and the total weight loss corresponded to 14.5 per cent of the initial sample weight. All condensate on the condenser was above the orifice level.

Series V-10 was a continuation of series V-9, and was performed two weeks later with the same effusion cell and charge. In the meantime the effusion cell had been stored in a purified argon atmosphere. Thirteen exposures were made, the first of which was of a double target arranged as described previously for a bouncing experiment. The temperature range was from 1840 to 2374°K. The accumulated weight loss during series V-9 and 10 amounted to 25.1 per cent of the initial sample weight. Again no visible deposit formed on the condenser opposite the effusion cell wall.

The 85-mg residue from series V-10 was divided into two portions and analyzed for sulfide content. The two samples contained 12.07 and 12.52% sulfide sulfur, corresponding to an average formula $US_{1.03}$. No insoluble material was detected. The apparent deviation from one-to-one stoichiometry is not surprising, in view of the poor analytical precision. The lattice parameter of the V-10 residue was $5.4943 \pm 0.0010 \text{ \AA}$. Table XIV shows the data from series V-9 and 10, and the $\log P_E$ values are plotted in Figure 9. The temperature range overlapped by forty degrees that of series V-8 in which sulfide of natural isotopic content was used. Figure 9 shows good agreement among the data from series V-9 and V-10 and those of previous experiments.

TABLE XIV
DATA FROM SERIES V-9 AND V-10

Exp. No.	Target No.	T (°C) (obs.)	T (°K) (cavity)	Exposure Time (min)	Counts/min	P _E (atm)	Log P _E	10 ⁴ /T (deg ⁻¹)
SERIES V-9								
1	9	1997.2	2320.1	10.40	661.7	5.986 × 10 ⁻⁶	-5.2229	4.3101
2	11	1803.2	2113.4	20.00	69.48	3.120 × 10 ⁻⁷	-6.5058	4.7317
3	12	1606.2	1908.4	88.00	9.85	9.54 × 10 ⁻⁹	-8.0205	5.2399
4	13	1558.6	1861.3	110.00	5.26	4.03 × 10 ⁻⁹	-8.3949	5.3726
5	15	1694.1	1995.3	40.10	20.01	4.353 × 10 ⁻⁸	-7.3612	5.0117
6	16	1852.9	2166.3	15.00	110.1	6.674 × 10 ⁻⁷	-6.1756	4.6162
7	18	1953.3	2273.6	10.14	356.4	3.273 × 10 ⁻⁶	-5.4850	4.3983
8	19	1649.4	1951.1	60.00	12.16	1.748 × 10 ⁻⁸	-7.7573	5.1254
9	20	1744.6	2050.8	25.25	31.15	1.093 × 10 ⁻⁷	-6.9614	4.8761
SERIES V-10								
1	{ 1 2 }	2020.4	2344.5	15.00	{ 691.0 566.7 }	7.722 × 10 ⁻⁶	-5.1123	4.2653
2	3	2017.7	2341.7	10.08	856.0	7.815 × 10 ⁻⁶	-5.1071	4.2704
3	4	1923.7	2241.9	15.04	355.6	2.129 × 10 ⁻⁶	-5.6717	4.4604
4	5	1822.7	2134.1	25.00	118.2	4.155 × 10 ⁻⁷	-6.3814	4.6859
5	6	1680.8	1982.1	60.10	22.10	3.144 × 10 ⁻⁸	-7.5067	5.0451
6	7	1537.1	1840.2	310.00	9.05	2.38 × 10 ⁻⁹	-8.6232	5.4343
7	8	1721.2	2025.9	50.10	42.77	7.312 × 10 ⁻⁸	-7.1359	4.9361
8	10	1621.3	1923.3	120.00	15.58	1.083 × 10 ⁻⁸	-7.9654	5.1993
9	12	1874.6	2189.3	15.00	165.1	9.802 × 10 ⁻⁷	-6.0087	4.5676
10	14	1978.3	2300.1	10.10	536.5	4.845 × 10 ⁻⁶	-5.3147	4.3476
11	15	2049.0	2374.5	10.00	1264.2	1.171 × 10 ⁻⁵	-4.9314	4.2115
12	16	1896.4	2215.6	15.00	246.8	1.472 × 10 ⁻⁶	-5.8320	4.5135
13	17	1768.9	2076.6	30.00	58.28	1.685 × 10 ⁻⁷	-6.7734	4.8156
Orifice Diameter: 1.751 ± 0.003 mm at room temperature 1.765 mm at exposure temperatures								
Orifice to collimator distance: 10.913 Series V-9 10.769 Series V-10								
Collimator diameter: 1.9007 ± 0.0004 cm								
$\Delta \frac{1}{T} = 1.075 \times 10^{-5} \text{ deg}^{-1}$								
These data are represented by the symbol Δ in Figures 9 and 10.								

d. Series V-13

Series V-13 was undertaken to provide more data at high temperatures and to determine whether an appreciable increase in the amount condensed would result from lower target temperatures. The cold finger shown in Figure 5 was substituted for the target magazine previously used. In the new apparatus, single platinum targets of 0.020-inch thickness were cooled by a flow of water across their backs, so that their temperatures remained several hundred degrees cooler

than those of targets in the previously used magazine. The initial charge of monosulfide from sample P-19(1-lid) weighed 164.3 mg and was placed in effusion cell no. 2. Eight targets were exposed at crucible temperatures from 2416 to 2724°K. No radiation shields were placed on the effusion cell. After each exposure, the effusion cell was permitted to cool in vacuum for a minimum of 1.7 hours, after which time the vacuum was broken with purified argon, the exposed target removed, and a new one inserted. The distance from orifice to collimator was measured for exposures 1, 5, 6, and 8. The effusion cell was reweighed after exposures 4, 5, and 8 and the total weight loss at the end was 20.2 per cent of the initial sample weight. A small amount of residue was removed from the effusion cell after exposure 5 for X-ray diffraction analysis. The resulting lattice parameter was $5.4906 \pm 0.0002 \text{ \AA}$. The residue at the end of series V-13 had a parameter $5.4915 \pm 0.0004 \text{ \AA}$. The orifice diameter was measured before exposure number 1 and after numbers 5 and 8. Shrinkage of about four per cent occurred in the diameter during the series, and corrections for this effect and for changing window transmissivity were performed as before. The data are recorded in Table XV and the points are plotted in Figure 9. The pressures obtained in experiment V-13 were in agreement with those from series V-6 to 10.

Sublimate did not form on the condenser opposite the effusion cell wall during exposures 1 and 2 at 2475 and 2474°K, respectively, but was found after exposure 3 at 2525°K and all subsequent exposures. These sublimates were much lighter than those observed previously, no doubt because of the shorter exposure times occasioned by the use of isotopically enriched sulfide.

In the discussion of series V-12, mention was made of use of concentrated nitric acid to test for sulfur in the condenser wall deposit. After series V-12 no sulfur was found opposite the wall of the effusion cell, and it was concluded that only uranium had been lost

TABLE XV
DATA FROM SERIES V-13

Exp. No.	T (°C) (obs.)	$(\Delta \frac{1}{T}) \times 10^5$	T(°K) (cavity)	Exposure time (min)	Counts/min	Orifice diameter (mm)*	Orifice to collimator** (cm)	P_E (atm $\times 10^5$)	Log P_E	$10^4/T$ (deg ⁻¹)
1	2122.6	1.094	2473.1	20.00	1667.9	0.883	11.625	3.661	-4.4364	4.0435
2	2121.2	1.096	2471.8	22.00	1691.2	0.875	11.625	3.434	-4.4642	4.0457
3	2170.5	1.098	2523.1	16.00	2067.4	0.875	11.625	5.821	-4.2343	3.9633
4	2227.6	1.099	2582.4	12.00	2836.7	0.873	11.625	10.86	-3.9643	3.8724
5	2317.1	1.100	2675.0	9.00	5138.4	0.871	11.630	26.86	-3.5709	3.7383
6	2172.9	1.102	2525.9	15.00	1902.8	0.864	11.626	5.884	-4.2303	3.9590
7	2366.8	1.103	2726.6	8.00	7501.4	0.860	11.626	45.60	-3.3410	3.6675
8	2065.3	1.105	2413.7	20.00	830.5	0.853	11.632	1.932	-4.7140	4.1430

*At temperature of exposure

**Corrected for expansion of effusion cell

Orifice diameter at room temperature: before series, 0.887 ± 0.003 mm
after exposure No. 5, 0.871 ± 0.003 mm
at end of series, 0.853 ± 0.002 mm

Orifice-to-collimator distance at room temperature: before series, 11.651 cm
before No. 5, 11.656 cm
before No. 6, 11.652 cm
before No. 8, 11.658 cm

Collimator diameter: 1.9023 ± 0.0004 cm

These data are represented by the symbol $\otimes$ in Figures 9 and 10.

through the wall. Similar tests with the sublimates from experiment V-13 were inconclusive, because of the lightness of the sublimates opposite the wall, although sulfur was definitely found above the orifice level. A considerable portion of the residue after series V-13 was found to be deposited on the underside of the effusion cell lid, but all was well back of the orifice.

8. Treatment and Discussion of the Data from Absolute Effusion Rate Measurements

a. Calculation of "Effective Vapor Pressures"

Details of the calculation of "effective pressures" from the target data via equation (5) should here be enumerated. The constant 0.022557 in equation (5) was evaluated from the tabulation of physical constants of Rossini et al.⁽⁵²⁾

The weight w_U , in grams of the uranium of natural isotopic composition on a target, is related to the activity by the equation

$$w_U = \text{cpm} \times \frac{1}{0.515} \times \frac{10^{-6}}{1.501} = 1.294 \times 10^{-6} \text{ cpm},$$

where cpm is the number of counts per minute registered in the counter of fractional counting efficiency 0.515,* and 1.501×10^6 is the number of α -decays per minute per gram of uranium. The corresponding weight, w_{US} , of uranium monosulfide is given by $w_U M_{US}/M_U$ or, numerically,

$$w_{US} = 1.468 \times 10^{-6} \text{ cpm}.$$

For the experiments in which isotopically enriched uranium was used, the specific activity of 1.411×10^8 decays per minute per gram and the decreased atomic weight of uranium led to the corresponding formula

$$w_{US} = 1.562 \times 10^{-8} \text{ cpm}.$$

*The efficiency of the α -counter was, more accurately, 0.514 ± 0.001 , as obtained from Mr. Robert Buchanan of the Chemistry Division after the calculations had been completed. No correction was applied to the data because the value used was within the quoted error.

Equation (5) reduces to the following when the molecular weight 270.14 of uranium monosulfide and the relations between cpm and weight of the target deposits are inserted:

for natural uranium,

$$P_E(\text{atm}) = 2.015 \times 10^{-9} \frac{\text{cpm}}{\text{at}} T^{1/2} [1 + (d^2/r^2)];$$

for enriched uranium,

$$P_E(\text{atm}) = 2.144 \times 10^{-11} \frac{\text{cpm}}{\text{at}} T^{1/2} [1 + (d^2/r^2)].$$

Orifice diameters measured at room temperature were corrected for the expansion due to temperature by use of the value $4.6 \times 10^{-6} \text{ deg}^{-1}$ given by Hoyt⁽⁵⁴⁾ for the mean linear coefficient of thermal expansion of tungsten between 20 and 2000°C, and as described previously for permanent changes incurred during each experiment. Orifice diameters both at room and experimental temperatures are listed with the other data from each experiment.

The procedures for measurement of exposure time and temperature have been described in previous sections.

The precision indicated elsewhere in the measurement of the orifice-to-collimator distance d , is deceptive from the standpoint of stating accurately the value of d during a given target exposure. The increase in the length of the effusion cell was calculated to be about 0.3 mm at 2000 to 2400°C. The beryllia kinematic table also must have expanded somewhat, for it attained red heat from radiation from the hot effusion cell. On the other hand, the shrinkage of the copper magazine on being cooled with liquid nitrogen gave a measured change in the collimator level of 0.59 mm with the effusion cell cold. This latter effect must have been less in the presence of a hot effusion cell, for radiation from the crucible was sufficient to raise target temperatures several hundred degrees. For calculation of the "effective pressures" the room-temperature orifice-to-collimator distances tabulated with the other experimental data were used. The resulting error

is a small, systematic one, tending to raise the measured pressures at high temperatures more than those at lower temperatures. Probably ± 0.02 cm is a reasonable estimate of the corresponding uncertainty in the orifice-to-collimator distance, an error of about ± 0.2 per cent.

A change in the diameter of the stainless steel collimator at the experimental temperatures must have occurred for similar reasons. Calculations showed that at liquid nitrogen temperature the expected decrease in diameter was 0.06 mm, and at 800°C the increase was 0.2 mm. The actual temperature was probably nearer room temperature than either of these extremes, and the room-temperature value was used in the calculations of pressure. The estimated uncertainty due to this systematic error is ± 0.1 mm, approximately 0.5 per cent.

In experiment V-13, in which the collimator ring was tightened down against the water-cooled platinum targets with sufficient pressure to effect a vacuum-tight seal, the errors in height and diameter due to temperature effects are believed to be negligible. The expansion of the crucible length was taken into account in the calculation of the pressures from the series V-13 data.

b. The Plot of $\log P_E$ vs. $10^4/T$

Figure 9 shows the value of the logarithm of the "effective vapor pressure," $\log P_E$, calculated from the data of series V-6, 7, 8, 9, 10, and 13 plotted at the respective values of reciprocal temperature, $10^4/T$. The mass spectrometric studies to be described in the next section showed that uranium monosulfide vaporizes by two reactions, so that the effusing uranium was in the form both of atoms and US molecules. Therefore calculation of the thermodynamics involved must be deferred until those experiments have been described. The target

data considered alone, however, will be examined here for evaluation of internal consistency and overall accuracy, and from the standpoint of obtaining a representation of them for later use.

Inspection of Figure 9 shows that the plotted data do not deviate greatly from a straight line, and a least squares treatment of them gives the linear equation

$$\log P_E(\text{atm}) = -(3.008 \pm 0.010) \frac{10^4}{T} + (7.714 \pm 0.045) ,$$

in which the standard deviations of slope and intercept are given. Analysis of the residuals of the experimental points showed that those from the four series V-7 points were seven to twelve times the standard deviations in the calculated values of $\log P_E$ at their respective temperatures. This observation, in addition to the uncertainty of the experimental conditions during experiment V-7, makes it seem reasonable to exclude these data from further consideration, and they are omitted from the following treatment. A linear least squares treatment of the remaining data gives the equation

$$\log P_E(\text{atm}) = (-2.997 \pm 0.009) \frac{10^4}{T} + (7.666 \pm 0.038) , \quad (16)$$

in which again the statistical standard deviations are given. This is the equation of the line drawn through the points in Figure 9.

The standard deviations in the calculated values of $\log P_E$ lie between ± 0.004 and ± 0.010 over the entire temperature range. These standard deviations correspond to uncertainties in the calculated pressures of between only ± 1 and ± 3 per cent over the nine-hundred-degree temperature range. In Figure 10a the residuals from this treatment, $\log P_E$ (calculated - $\log P_E$ (observed)), are plotted against $10^4/T$, and the standard deviations in the calculated values of $\log P_E$ are indicated by vertical lines at three values of $10^4/T$. A temperature-dependent trend in the residuals is evident, and this trend

corresponds except at the ends to a slight, continuous decrease with increasing temperature of the absolute value of the slope of the curve in Figure 9, that is, a downward curvature with increasing temperature.

FIGURE 10
RESIDUALS OF EXPERIMENTAL POINTS FROM LINEAR AND
FOUR-PARAMETER CURVES FIT TO THE DATA
OF FIGURE 9

An empirical fit to the data by means of a four-parameter least squares treatment gave the equation

$$\begin{aligned} \log P_E(\text{atm}) = & -1.7382 + 3.1274 \frac{10^4}{T} - 1.3181 \frac{10^8}{T^2} \\ & + 0.09378 \frac{10^{12}}{T^3} ; \end{aligned} \quad (17)$$

no errors were calculated for the parameters. The residuals from the four-parameter treatment are plotted against $10^4/T$ in Figure 10b. Comparison of Figures 10a and b shows equation (17) gives the better fit of the data in the middle and lower portions of the temperature range, and the overall distribution of the residuals is slightly changed.

The standard deviations of the calculated values of $\log P_E$ were not determined for the four-parameter equation (17), but inspection of Figures 10a and b indicates they should be slightly smaller than those for equation (16).

The inverse cubic curve departs from the linear by having a slope continuously decreasing in absolute value with increasing temperature. The greatest difference between the two lines occurs at the highest temperatures, where the inverse cubic equation predicts values lower by 0.03 in the logarithm of the pressure, or by seven per cent in the pressure. The experimental scatter is seen to be sinusoidal about either of the calculated curves. For series V-6, V-8, V-9, V-10, and V-13, thirty-six per cent of the observed pressures lie within two per cent of the values calculated from equation (17), sixty-four per cent of the points lie within six per cent of the calculated values, ninety per cent lie within ten per cent of the calculated values, and all points lie within thirteen per cent of the calculated pressures.

The existence of curvature is not surprising, particularly in view of the wide temperature range, and might result from one or more of several sources. One would expect a downward curvature from heat capacity effects, an upward curvature if the pressure limit of molecular effusion were exceeded, and a decrease in slope corresponding to the heat of fusion if the melting point of the sample were included in the temperature range. The nature of the plotted dependent variable, $\log P_E$, which apart from constants is the logarithm of the sum of the partial pressures of all the uranium-containing species, is such as to produce a slight upward curvature, provided that for the individual processes there are linear dependences of $\log p$ on $1/T$. Because the observed curvature is slight, and the dependence of $\log P_E$ on $1/T$ is related only in a complicated way to the thermodynamics of the individual vaporization processes, further thermodynamic

treatment of the effusion data along is unwarranted, but an analysis of the experimental precision and several conclusions from the general appearance of Figures 9 and 10 remain to be set forth.

c. Analysis of Errors in the Measured "Effective Pressures"

One should be able to show from the errors of the various experimentally determined quantities whether or not the scatter in the data plotted in Figures 9 and 10 can be ascribed solely to random errors in the measurements, or whether or not there were other factors involved. The predictable scatter in the data is of two kinds: firstly, the scatter within a given experimental series, and, secondly, the systematic differences between data from the various series. It is convenient to evaluate both sets of errors in one package and to compare the expected and observed magnitudes of the residuals of the experimental points. This evaluation may best be done by considering the errors involved in one representative datum, and that chosen for treatment was exposure no. 4 from series V-8 at 2378°K, for which $10^4/T = 4.2055$.

The observed scatter arises from two sources: firstly, the random errors in the second term in the equation for P_E :

$$P_E = [\text{constants}] \times \left(\frac{\text{cpm} \sqrt{T}}{\rho^2 t} \right) ,$$

in which ρ represents the orifice diameter, and, secondly, the displacement of the experimental points above and below the $\log P_E$ vs. $10^4/T$ line due to errors $\Delta \frac{10^4}{T}$ in the reciprocal temperature.

Consider the second effect. For an error ΔT in the temperature the corresponding displacement amounts to $\Delta \frac{10^4}{T} \times \text{slope} \cong \text{slope} \times (\Delta T/T^2) 10^4$. The estimated standard deviation in measured temperatures is ± 2 degrees, as previously discussed. From the slope of equation (16), one calculates at the temperature 2378°K of

exposure V-8(4) an expected uncertainty in $\log P_E$ of ± 0.011 . The corresponding multiplicative uncertainty in P_E is 1.026; the expected standard deviation in P_E resulting from the uncertainty in $10^4/T$ is thus $\pm 2.6\%$.

The various values and measured or estimated standard deviations for the experimental quantities for exposure V-8(4) are the following: $\text{cpm} = 47.56 \pm 0.48$; $\sqrt{T} = 48.77 \pm 0.018$; $\rho^2 = 2.397 \pm 0.0125$; $t = 36.00 \pm 0.02$. Using the theory of propagation of errors⁽⁵³⁾, one calculates that

$$P_E = [\text{constants}] \times (26.9 \pm 0.31).$$

The contributions to the standard deviation by the errors in the individual quantities may be seen from an intermediate result in the calculation:

$$\begin{aligned}
 (\text{standard deviation})^2 = & \underbrace{1.0 \times 10^{-4}}_{\sqrt{T}} + \underbrace{740 \times 10^{-4}}_{\text{cpm}} + \underbrace{200 \times 10^{-4}}_{\rho^2} \\
 & + \underbrace{2.1 \times 10^{-4}}_t.
 \end{aligned}$$

The part of the random distribution of the residuals due to these factors is thus 1.15 per cent, and the expected standard deviation in $\log P_E$ is $\log(1.0115) = 0.0050$.

Combining the two parts of the calculated standard deviation, one has for exposure V-8(4),

$$\text{Std. dev. in } \log P_E = \pm \sqrt{(0.011)^2 + (0.005)^2} = \pm 0.012.$$

In the neighborhood of $10^4/T = 4.2$, one expects about three-fourths of the points to lie within ± 0.012 of the value of $\log P_E$ obtained from equation (17). Examination of Figure 10b shows that this criterion is satisfied for the points from series V-8, but that the data from series V-9 and V-10 have larger residuals than expected. Almost all the residuals for values of $10^4/T$ from 4.0 to 5.0 lie in a band of width

about 0.02, so that in this region the scatter of the points is well within the predicted value, although there is a systematic displacement from the empirically fitted curve of equation (17).

At higher temperatures the probable scatter expected among data from different series should be about twice that near $10^4/T = 4.2$ because of the doubled per cent standard deviation in the diameter of the smaller orifice of effusion cell no. 2 and the larger error in the correction from blackbody to cavity temperature. The scatter within an experiment should be greater because the shorter exposure times increase slightly the uncertainty in the measurement of temperature and of exposure time. The wide scatter at the lowest temperatures is not understood.

It is concluded that there are no random experimental errors unaccounted for in the measurement of total rate of effusion, except at the extremes of the temperature range.

Similar treatments involving the effect of the estimated errors in the absolute values of the temperature, orifice-to-collimator distance, and decay rates gave these additional standard deviations in the absolute value of $\log P_E$: ± 0.011 due to the additional uncertainty in $10^4/T$; ± 0.001 due to the uncertainty in $[1 + (d^2/r^2)]$; ± 0.001 due to the uncertainty in the specific activity of natural uranium; and ± 0.002 due to the uncertainty in the specific activity of the isotopically enriched uranium. The estimated standard deviation in the absolute value of $\log P_E$ resulting from the combination of these errors and those due to random error in the measurements was ± 0.017 .

The corresponding estimated standard deviation in the measurement of the absolute value of the "effective vapor pressure" of uranium monosulfide was ± 4 per cent.

d. Conclusions Based on Figures 9 and 10

The following statements may be made concerning the general appearance of Figures 9 and 10. Firstly, there is no discrepancy

between results obtained with the two separate effusion cells, whose orifice areas differed by a factor of four. This observation means that the equilibrium pressure was that measured, and that the effect of temperature inhomogeneities in the effusion cells was eliminated by the use of the cavity temperatures, even though the actual temperature distributions were quite different for the two cells. Secondly, apart from the two highest points from series V-7, which may be disregarded because of experimental difficulties, there is no indication that the pressure limit of molecular effusion was reached. The data from the entire temperature range ought therefore to be valid for use in the calculation of thermodynamic functions or rates of evaporation. Figure 9 shows that the maximum pressures in this study were of the order of a fraction of a millimeter, so that one would not be surprised if the beginnings of departure from molecular flow had been observed.

At the time the effusion data were first analyzed, the melting point of uranium monosulfide had not yet been determined as described in section VC, and the literature value of 2200°C appeared to be confirmed by loss of sample through effusion cell walls above that temperature. An attempt to fit the points of Figure 9 with two straight lines whose intersection would be near the supposed melting temperature was moderately successful when the points from series V-7 and those at the three lowest and the third and fifth highest remaining temperatures were omitted. The variation with temperature of the residuals seemed to be eliminated, but the two lines crossed at a value of $10^4/T$ corresponding to about 2100, rather than at the expected value of 2200°C . This treatment was abandoned when the melting point was later found to be at the very top of the temperature range of the vaporization studies, because there remained no theoretical basis for forcing a fit of two straight lines to the data.

The "effective vapor pressure" of uranium monosulfide, P_E , gives the total rate of vaporization of uranium-containing species from the solid, and so can be directly compared with the vapor pressures of uranium metal and uranium dioxide. At all temperatures in the range of Figure 9 uranium monosulfide is less volatile than either uranium metal or dioxide. At 2300°K the respective pressures in atmospheres for the three substances are: US, $P_E = 4.41 \times 10^{-6}$; UO_2 , 1.33×10^{-5} [(44), total volatility]; U, 3.56×10^{-5} atm(49).

F. Mass Spectrometric Study of the Vaporization of Uranium Monosulfide

Two series of experiments, in which the vapor composition above solid uranium monosulfide was studied by means of a Bendix Aviation Corporation Model 12-101 time-of-flight mass spectrometer(55), were performed. The writer is indebted to Mr. E. G. Rauh, who was kind enough to employ US as a working substance while adapting and adjusting the machine for use in high-temperature vaporization studies, and who both aided the writer to make and himself made many of the observations. The effusion cell with its supports and associated heating filaments and radiation shielding were designed and fabricated by Mr. R. C. Sadler.

1. Apparatus

a. Time-of-Flight Mass Spectrometer

The principle of mass separation in a time-of-flight spectrometer is that singly charged ions of different masses M (in atomic mass units) when given the same energy by acceleration through the same potential difference have velocities inversely proportional to $\sqrt{M}$. Thus, for two species 1 and 2 the relative times, τ , required after acceleration to traverse a fixed distance are related by the equation

$$\tau_1/\tau_2 = \sqrt{M_1/M_2} \quad . \quad (18)$$

In the Bendix spectrometer the effusing molecular beam is directed vertically into the ionization region, where it is intersected by a

horizontal electron beam. The ions that result are accelerated electrostatically in a direction normal to the plane of molecular and electron beams. The beam of ionizing electrons is applied for 0.3 microsecond, at the end of which time the accelerating potential is applied for about 1.5 microseconds, and the cycle is repeated 10,000 times per second. The ion current is detected by an electron multiplier system and can be displayed as a function of drift time on an oscilloscope screen.

In the apparatus used the ion current was applied to the vertical deflection plates of a Tektronix Model 545 oscilloscope equipped with a Model 53/54C two-channel preamplifier, whose horizontal sweep was triggered at the end of each accelerating pulse. Thus the entire mass spectrum from mass 1 to 6000, or any chosen portion thereof, could be displayed on the oscilloscope screen as ion current intensity vs. time of flight. Drift times of ions of interest were measured by comparing them with that of one of the isotopes of mercury, present in the background spectrum because a mercury diffusion pump was used to evacuate the system.

Determination of the ionic mass followed from equation (18). Two counting circuits operating from two auxiliary anodes at the detector were gated electronically to measure the currents due to ions of any two chosen masses, the counts or their ratio being displayed on the control panel lights. In practice, the two counters were set to the same sensitivity on one mass peak, then set on the peaks of interest and several counts of the ratio of the two currents taken. The gates were then switched to measure the inverse ratio and the ratios I_1^+/I_2^+ for the two settings were averaged. It can be shown that for constant counter sensitivities the average value so obtained is relatively insensitive to slight differences in sensitivity of the two counting circuits. On the other hand, if the sensitivity of one counter relative

to the sensitivity of the other changes by a small amount between the two ratio counts, relatively larger errors in the average value of I_1^+/I_2^+ are encountered.

The limit of mass resolution at high masses of a time-of-flight mass spectrometer is set by the finite width of the initial molecular beam, the presence in it of nonvertical velocity components, and the finite length of the accelerating pulse. In the mass region between 200 and 300, that of interest in this research, resolution was good enough to yield easy visual observation of adjacent mass peaks and nonoverlapping of peaks two mass units apart for counting purposes.

b. Effusion Cell

The effusion cell employed was machined from copper-impregnated tungsten obtained from North American Phillips Company. The copper was removed in vacuum by induction heating to 2600°C; a small shrinkage in dimensions resulted. The orifice had the form of a cylindrical channel, 1 mm in diameter and 4 mm in length, which extended nearly to the level of the topmost of the several tantalum radiation shields above the effusion cell to minimize bouncing in the source region and to permit easy loading of the charge through the orifice after the cell was outgassed. Radiation shields also surrounded the sides and bottom of the cell. A magnetically operated shutter was located between the two stainless steel collimating slits which separated the effusion cell and the ionization region. Temperatures could be measured from above by sighting an optical pyrometer through the collimating slits onto the orifice, or from below by sighting on the blackbody hole drilled into the crucible bottom.

2. Experiments

a. Experiment MS-1

In the first attempt to characterize the vaporization of uranium monosulfide by use of the mass spectrometer, the

experimental sample was the residue from the series V-5 effusion experiment. This approximately 25-mg sample had been stored in an initially argon-filled drybox for several weeks; although some air had probably leaked into the box, the sample was still shiny and metallic-looking. It was crushed easily in a boron carbide mortar under argon in the re-purged drybox and funneled through the orifice of the spectrometer effusion cell, which had been outgassed inductively at 2600°C in high vacuum by induction heating, and, surrounded by its shields, had been reheated at about 2200°C by electron bombardment in the spectrometer until the background mass spectrum was free of peaks due to residual vapors except in the region of low masses.

Experiment MS-1 was considered a preliminary one for identification of species and testing of the heating unit and spectrometer circuitry. Temperatures were measured with an optical pyrometer sighted on the blackbody hole. No correction to cavity temperature was attempted, and the window and prism transmissivities were estimated but not measured. Temperatures reported are therefore known only within perhaps $\pm 10^\circ$ and probably correspond to somewhat higher cavity temperatures.

The effusion cell was brought slowly to temperature and the appearance and disappearance of various mass peaks were observed. The initial background consisted chiefly of peaks at masses $18(\text{H}_2\text{O}^+)$, $28(\text{N}_2^+)$, $32(\text{O}_2^+)$, 102, 120, and 134 (probably hydrocarbons), and 198 to 203(Hg^+). At about 1400°C a peak at mass 40, identified as due to A^+ , was quite intense and could be eliminated by closing the shutter over the orifice. The peak at mass 32, probably O_2^+ , was about as intense. These peaks decreased rapidly to background level.

At higher temperatures peaks for the masses 238, 254, 270, and 286, presumably due to U^+ , UO^+ , UO_2^+ or US^+ and UOS^+ (not UO_3^+ because of the reducing conditions), respectively, appeared,

their presence or absence being controllable by means of the shutter. All appeared to be primary peaks, fading together as the ionizing electron energy was reduced to zero, and reappearing at about the same potential as well as could be detected from visual observation. After about 90 minutes at temperatures increasing from 1700 to 2100°C, the ion current intensities were in the approximate ratios of 8:20:8:1 for the peaks at masses 238, 254, 270, and 286. Then the peaks at mass 254(UO^+) and 286(UOS^+) faded rapidly, so that their intensities could no longer be measured after 30 more minutes. The peak at mass 270 diminished relative to that at 238 but remained of appreciable relative intensity. The peaks due to oxygen-containing species were found to reappear each time the effusion cell was permitted to cool down (for example at the end of the day's observations) and then was reheated, even though the residual pressure in the spectrometer commonly decreased to below 1×10^{-7} mm Hg on cooling of the cell. In successive reappearances, the oxide peaks were relatively less intense and disappeared more rapidly.

When the temperature was raised to about 2220°C, the maximum obtainable without losing control, a peak at mass 272 became discernible and remained so. The peak at mass 32 was prominent in the background hash, but did change intensity slightly with the position of the shutter. The peak at mass 34, due to H_2S formed by reaction of effusate and residual water vapor, was quite prominent and fragmented easily to give a peak at 33 and an increased intensity at mass 32.

The major species above the uranium monosulfide sample therefore appeared to be U, S, and US. No masses above 286 were found, nor were any peaks attributable to tungsten-containing species. The peak at mass 270 with its less intense companion at 272 must be due to the ion US^+ ; if these were due to the ion UO_2^+ , the 272 peak due to the ion $\text{U}^{238}\text{O}_2^{17+}$ would be too faint to see, whereas that due to the ion $\text{U}^{238}\text{S}^{34+}$ should be 4.2 per cent as intense as the peak at

mass 270 due to the ion $\text{U}^{238}\text{S}^{32+}$. An attempt to measure the ratio I_{272}^+/I_{270}^+ gave a value somewhat below 0.02, probably low because of low multiplier sensitivity to the very weak ion current at mass 272. The disappearance of the ions UO^+ and UOS^+ from the spectrum and the diminution of the peak at mass 270, presumably by elimination of the species giving rise to UO_2^+ on reaching temperature, also argue for absence of further oxygen in the US under study. The ratio I_{270}^+/I_{238}^+ was found to increase about five per cent as the energy of the ionizing electrons was increased from 20 to 100 volts. Clearly, then, the uranium atoms are primary species, since if they were due chiefly to fragmentation there should have been a decrease with increased energy of the ratio I_{270}^+/I_{238}^+ .

Portions of the observed mass spectrum photographed from the oscilloscope screen with a Polaroid Land Camera are presented in Figure 11. Shown at (A) is the region from mass 198 to 300;

(A) MASS REGION 198-270

(B) MASS REGION 238-272

(C) MASS REGION 270-272

FIGURE 11
MASS SPECTRA OBTAINED FROM THE VAPORIZATION OF
URANIUM MONOSULFIDE; PHOTOGRAPHS OF OSCILLOSCOPE
PATTERNS OBTAINED WITH THE TIME-OF-FLIGHT
MASS SPECTROMETER

the peaks are at masses 198-203 (Hg^+), 238 (U^+), and 270-272 (US^+). At 2200°C, the pressure in the effusion cell due to gaseous US molecules and U atoms was about 3.6×10^{-5} atm or 2.7×10^{-2} mm Hg. The residual pressure in the spectrometer was about 5×10^{-6} mm Hg, as read from an ionization gage. The comparable ion intensities due to the gaseous species Hg and U + US in the ionization region are to be expected from the geometry of the system. Figure (B) shows the region of masses 238 to 272 in greater detail; the isotopic compositions of U and US are apparent, as is the weak peak at mass 254 due to UO^+ . Figure (C) is an expanded view of the region around mass 270, showing the US isotopic composition. The ordinates are ion currents in arbitrary units; the abscissae, time of flight. The 270-272 separation was, for example, $0.10 \mu \text{ sec}$.

An attempt to obtain accurate ratios of intensities for the various peaks in experiment MS-1 was defeated by instability in the counter circuits and drift of the gating times. Approximate ratios were obtained, however, which showed that the ratio I_{270}^+/I_{238}^+ was in the range 0.5 to 0.7 between 1900 and 2200°C.

After experiment MS-1, a small amount of sintered, gold-colored uranium monosulfide was left in the bottom of the effusion cell. This material was scratched loose with a tungsten rod in an argon atmosphere and loaded without grinding into a capillary for X-ray exposure. The sharp but spotty pattern showed only lines due to US and tungsten. The lattice parameter was found by film measurement to be $5.4901 \pm 0.0002 \text{ \AA}$. Data from experiment MS-1 are summarized in Table XVI.

TABLE XVI
SUMMARY OF MASS SPECTROMETRIC OBSERVATIONS

Observation	Experiment MS-1	Experiment MS-2
US sample taken	V-5 residue, ~25 mg	P-18 (3-lid), 80 mg
Temperature range	to 2220°C	to 2150°C
Species on initial warmup	U, UO, UO ₂ , US, UOS	U, UO, UO ₂ , US, UOS
Primary species	U, S, US	U, S, US, US ₂
I_{270}^+ / I_{238}^+	approximately 0.5 to 0.7 in the range 1900 to 2200°C	Varied regularly from 0.48 to 0.65 from 1885 to 2130°C with a scatter $\pm 10\%$.
I_{32}^+ / I_{238}^+	not measured	0.15 ± 0.05
Electron energy	20 to 100 ev	20 and 50 ev
Residue: Lattice parameter	$a_0 = 5.4901 \pm 0.0003 \text{ \AA}$	$a_0 = 5.4923 \pm 0.0011 \text{ \AA}$
Film number	3227	3381

b. Experiment MS-2

Before and during the second mass spectrometric study, many of the electronic difficulties in the instrument and its external ground connection were alleviated. Larger multiplier plates were installed for greater sensitivity. The ratio of ion currents due to the ions US^+ and U^+ was measured as a function of temperature and a new ion at mass 302, identified as US_2^+ , was observed.

Prior to introduction of the sample, the effusion cell and shields were outgassed, and an intercomparison was made of temperatures of the orifice and blackbody hole and apparent surface temperature on the effusion cell bottom, with the effusion source in the spectrometer. It was found that the blackbody hole temperature varied approximately linearly from thirty to sixty degrees below that measured in the orifice over the temperature range. Considerable difficulty was experienced in focusing the pyrometer through the slits on the partially hidden orifice and on the very small blackbody hole. Experimental temperatures were read on the bottom of the cell just to the

side of the blackbody hole with good reproducibility and then corrected to the corresponding orifice temperatures by the aforementioned inter-comparison. The standard deviation in the correction from bottom to orifice temperatures varied from ± 3 to ± 6 degrees over the range from 1800 to 2150°C. Anticipating the value given below for the slope of the plot vs. $1/T$ of $\log I_{270}^+/I_{238}^+$, namely -0.320×10^4 , one sees that an error of 6 degrees in temperature at 2000°C causes a shift of the experimental point above or below the line of $6 \times 0.320 \times 10^4 / (2273)^2 = 0.0037$. This effect about equals the statistical standard deviation in the calculated values of $\log I_{270}^+/I_{238}^+$ at the middle of the temperature range.

The experimental sample for experiment MS-2 was an 80-mg portion of monosulfide sample P-18(3-lid), the same material used in experiments V-6, V-7, and V-8. Measurements were made on a number of days over a four-week period while Mr. Rauh's work on the spectrometer circuitry continued. Observation of the spectrum during initial warm-up of the effusion cell showed again the peaks due the ions UO^+ and UOS^+ , which behaved as described previously. Once for a brief period during experiment MS-2, a weak peak, whose intensity was independent of shutter position, due to UOS^+ was observed; presumably this peak resulted from a deposit in the ionization region or from a reaction there between effusate and oxygen or water vapor.

The ion current ratios I_{270}^+/I_{238}^+ reported below were recorded on several days. The experimental ratios and the corresponding temperatures are tabulated in Table XVII, are plotted as $\log I_{270}^+/I_{238}^+$ vs. $10^4/T$ in Figure 12, and discussed in section 3 below. It is noteworthy that the results for points taken with both 50 and 20-volt ionizing electrons and during a considerable period of time are in agreement within the precision. During the final day's measurements the values of the ratio I_{270}^+/I_{238}^+ for the last six measurements

TABLE XVII
DATA FROM EXPERIMENT MS-2

Series	T(°K)	Ion Current Ratios for US^{270} and U^{238}		
		I_{270}^+/I_{238}^+	$10^4/T(^{\circ}K^{-1})$	$\text{Log } I_{270}^+/I_{238}^+$
(a) 50 volts	2283	0.496	4.380	-0.305
	2382	0.618	4.196	-0.209
	2206	0.487	4.533	-0.312
	2385	0.673	4.193	-0.172
	2206	0.470	4.533	-0.328
	2334	0.606	4.284	-0.218
	2281	0.514	4.384	-0.289
	2343	0.568	4.268	-0.246
	2403	0.668	4.161	-0.175
	2373	0.636	4.214	-0.197
(b) 50 volts	2367	0.629	4.225	-0.201
	2367	0.623	4.225	-0.206
	2373	0.615	4.214	-0.211
	2323	0.581	4.305	-0.236
	2254	0.504	4.437	-0.298
	2194	0.495	4.558	-0.305
	2169	0.480	4.610	-0.319
	2253	0.528	4.439	-0.277
	2298	0.585	4.352	-0.233
	2351	0.634	4.253	-0.198
(c) 50 volts	2394	0.673	4.177	-0.172
	2381	0.630	4.200	-0.201
	2381	0.585	4.200	-0.233
	2381	0.641	4.200	-0.193
	2376	0.571	4.209	-0.243
	2376	0.580	4.209	-0.237
	2280	0.482	4.386	-0.317
	2280	0.492	4.386	-0.308
	2280	0.535	4.386	-0.272
	2280	0.490	4.386	-0.310
(d) 20 volts	2248	0.530	4.448	-0.276
	2242	0.531	4.460	-0.275
	2242	0.487	4.460	-0.312
	2158	0.461	4.634	-0.336
	2158	0.493	4.634	-0.307
	2248	0.501	4.448	-0.300

The data are fit by the linear least squares equation

$$\text{Log } \frac{I_{270}^+}{I_{238}^+} = -(0.320 \pm 0.028) \times (10^4/T) + (1.137 \pm 0.122) \quad . \quad (20)$$

Standard deviations are given.

FIGURE 12
MASS SPECTROMETRIC STUDY OF THE VAPORIZATION OF
URANIUM MONOSULFIDE; LOGARITHM OF THE RATIO
OF ION CURRENTS DUE TO US^{270} AND U^{238}
VS. RECIPROCAL OF TEMPERATURE

(not shown) were well below the previous values. When the heating unit was disassembled, the effusion cell cavity was found to be empty of sample except for a deposit of about a milligram on the underside of the lid.

At temperatures near 2100°C a peak at mass 302, corresponding to US_2^+ , was observed, apparently due to a primary species, of intensity estimated visually to be about one-tenth that of the peak at mass 272 due to US^{34} . The indication is that the molecule US_2 is one of the vaporization products of uranium monosulfide, probably by way of the reaction

which, according to the estimated ion current intensity, accounts for a few tenths of a per cent of the total volatility. Failure to observe this peak during experiment MS-1 may perhaps be attributable to use of a less sensitive multiplier system in that experiment.

Three measurements of the ratio of the ion currents due to the ions S^+ and U^+ were obtained while the spectrometer circuitry was still unstable. Because of the high background at mass 32, the ratios used were I_{32}^+/I_{18}^+ (shutter open), I_{32}^+/I_{18}^+ (shutter closed), and I_{32}^+/I_{238}^+ (shutter open). From the three ratios one can calculate I_{32}^+/I_{238}^+ , the ratio of sulfur and uranium ion currents from the effusate, assuming the I_{18}^+ current to be due to noneffusing background species only. The results gave values of 0.096, 0.194, and 0.161, whose average is 0.150. This last value is used in the following section to estimate the cross-section ratio for the gaseous species U and US.

At the conclusion of experiment MS-2, X-ray diffraction patterns of the residue deposited under the effusion cell lid and of two sublimate deposits were obtained. The residue was in the form of a clump of small, shiny crystals. Its film showed only lines of uranium monosulfide and tungsten, the latter probably because a tungsten rod was used to scratch the deposit loose from the tungsten lid. The US lattice parameter was found to be $5.4923 \pm 0.0011 \text{ \AA}$ by measurement of the film, whose lines were not sharp.

The top radiation shield collected a crust inside its circular opening at a level slightly above the orifice; this crust was soluble in dilute sulfuric acid except for a slight solid residue. The crust gave X-ray diffraction lines of US ($a_0 = 5.4871 \pm 0.0004 \text{ \AA}$), barely detectable tungsten lines, and weak but sharp lines due to uranium oxysulfide.

The lower stainless steel plate containing the first collimating slit was coated with a black, amorphous-looking deposit which gave the X-ray diffraction pattern of US and a more complex phase which was neither U nor UOS, but was perhaps a product of reaction between sublimate, either sulfide or oxygen-bearing species, with the slit material. The upper side of the lower slit plate was covered with

a light, smooth deposit showing clearly the shadow of the opened shutter. It may be inferred from this observation that bouncing of effusate from the upper slit plate occurred.

3. Discussion of Results of Mass Spectrometric Studies

A tabular summary of experiments MS-1 and MS-2 is presented in Table XVI. Gaseous species identified for the first time were US, US₂, and UOS. In view of the stability of the US molecule (its dissociation energy is 5.2 ev, as shown below) and the existence of molecular US₂, it seems likely that there exist gaseous monosulfide molecules in the vapors of other monosulfides, for example those of the compounds ThS, CeS, LaS, and PuS. Similarly one can discount neither the possibility of disulfide or other higher sulfide molecules above the phases US₂, U₂S₃, U₃S₅, or US₃ under experimentally realizable conditions, nor of analogous molecules above higher sulfide phases of other metals. The vapor above uranium oxysulfide can be expected to contain molecules, for example of UO and UOS.

In Figure 12 the values of $\log I_{270}^+/I_{238}^+$ taken from Table XVII have been plotted against reciprocal temperature. If values of ΔH_T° for the two reactions

and

are constant over the range of temperatures included, it follows that a linear curve drawn through the points of Figure 12 should have a slope $\underline{s}$ given by the equation

$$2.303R \times 10^4 \underline{s} = \frac{1}{2} \Delta H_T^\circ (\text{II}) - \Delta H_T^\circ (\text{I}) \quad , \quad (19)$$

because, since I^+T is proportional to the partial pressure of a given species, a plot of $\log (I^+T)$ vs. $1/T$ for (I) gives a slope $-\Delta H_T^\circ (\text{I})/2.303R$,

and for (II), $-\Delta H_T^\circ(\text{II})/(2)2.303R$. Least squares analysis of the data gives

$$\log I_{270}^+/I_{238}^+ = -(0.3203 \pm 0.0281) \frac{10^4}{T} + (1.137 \pm 0.122) \quad , \quad (20)$$

where the statistical standard deviations in slope and intercept are given. The slope corresponds to

$$\frac{1}{2} \Delta H_T^\circ(\text{II}) - \Delta H_T^\circ(\text{I}) = -(14.6 \pm 1.2) \text{ kcal/mole} \quad .$$

The standard deviations in the calculated values of $\log I_{270}^+/I_{238}^+$ vary from ± 0.004 at $10^4/T = 4.35$ to ± 0.008 at both $10^4/T = 4.1$ and 4.6 . These standard deviations correspond to errors in the calculated ion current ratios of, respectively, 0.9 and 1.9 per cent. Thirty-eight per cent of the individually measured ratios were within three per cent of the calculated values, seventy-four per cent of the measured points lay within six per cent of the calculated values, and all experimental points had residuals corresponding to less than 12 per cent of the calculated ion current ratios.

The eight per cent standard deviation in the slope is less serious than so large a percentage error might seem to indicate on first glance, because it corresponds to only one kilocalorie in absolute value. Since the slope of the plot of $\log I_{270}^+/I_{238}^+$ vs. $10^4/T$ is essentially just the difference between the heats of vaporization of solid US to atoms and to molecules, it follows from the later calculations that the error here yields less than a per cent error in the heats for the individual reactions. Such precision is as good as is usually obtained with more expensive, conventional mass spectrometers.

No attempt was made during experiment MS-2 to determine absolute ion currents; only their ratios were measured. Therefore the treatment on page 25 cannot be used for the uranium monosulfide data, and the mass spectrometric data must be combined with the target data through use of ionization cross-section ratios to derive heats and entropies for processes I and II. Few data are available for use in

estimation of cross sections of heavy atoms and their molecules. The experimental value 0.150 ± 0.050 for I_{32}^+/I_{238}^+ may be combined with the pressure ratio $p_S/p_U = \sqrt{M_S/M_U} = 0.367$ to give for the experimental conditions of experimental MS-2,

$$\frac{\sigma_S}{\sigma_U} = \frac{I_{32}^+}{I_{238}^+} \frac{p_U}{p_S} = 0.41 \pm 0.14 \quad .$$

Assuming $\sigma_{US} = \sigma_U + \sigma_S$ and assuming the multiplier efficiencies for U^+ , US^+ , and S^+ to be included, one finds

$$\frac{\sigma_{US}}{\sigma_U} = 1 + \frac{\sigma_S}{\sigma_U} = 1.41 \quad ,$$

with an unestimated uncertainty. This value will be used in the following section for the calculation of absolute partial pressures and resultant thermodynamic quantities, and the errors involved in its use will be discussed there.

The effective temperature of evaporation of the sample in experiment MS-2 is known to perhaps $\pm 30^\circ$. The error due to the intercomparison of temperatures of the cavity and bottom surface is outweighed by the uncertainty due to the thirty to sixty-degree difference in temperatures measured in orifice and blackbody hole. Presumably the evaporating surface was nearer the former temperature than the latter, but use of the long orifice channel renders it impossible to say what point in the cavity is represented by the observed orifice temperature and to what temperature each ratio I_{270}^+/I_{238}^+ belonged. The slope of the plot of $\log I_{270}^+/I_{238}^+$ vs. $10^4/T$ should be affected relatively slightly by the temperature gradient, which comprises a systematic error, but the imprecise knowledge of the temperature corresponding to a given value of I_{270}^+/I_{238}^+ renders absolute partial pressures, and therefore entropy changes deduced therefrom, somewhat uncertain. Appropriate numbers are given in the following section.

V. TREATMENT AND DISCUSSION OF EXPERIMENTAL RESULTS

A. Partial Pressures from and Thermodynamics of the Vaporization of Uranium Monosulfide

1. Calculations with an Assumed Cross-Section Ratio

$$\underline{\sigma_{US}/\sigma_U = 1.41}$$

The measurements of absolute effusion rates were correlated in the following way with the mass spectrometric results for the calculation of partial pressures of uranium atoms and uranium monosulfide molecules in equilibrium with solid uranium monosulfide, and the heats and entropies of the two vaporization reactions. Equation (20) was accepted as the best representation of the data from experiment MS-2, and ion current ratios I_{US}^+/I_U^+ were calculated from it for each of the values of $10^4/T$ in the range of the mass spectrometric observations at which an "effective pressure" P_E had been obtained by target exposure. Equation (20) was corrected by addition to the right hand side of 0.0212, the logarithm of 1.05, to account for the isotopes of uranium and sulfur other than 238 and 32, respectively. From the calculated values of I_{US}^+/I_U^+ , the assumed cross-section ratio $\sigma_{US}/\sigma_U = 1.41$, and the experimental values of $\log P_E$, the logarithms of the partial pressures p_{US} and p_U were obtained by the use of an IBM 610 computer.

The equations used in these calculations were derived as follows. From equation (10) it follows that at any temperature

$$\frac{p_{US}}{p_U} \frac{\sigma_{US}}{\sigma_U} = \frac{I_{US}^+}{I_U^+} .$$

Rearrangement and substitution into equation (13) gives, after another rearrangement,

$$p_U = \frac{\frac{\sigma_{US}}{\sigma_U} P_E}{\frac{I_{US}^+}{I_U^+} + \frac{\sigma_{US}}{\sigma_U} \sqrt{\frac{M_{US}}{M_U}}} . \quad (21)$$

Hence

$$\log p_U = \log \frac{\sigma_{US}}{\sigma_U} + \log P_E - \log \left(\frac{I_{US}^+}{I_U^+} + \frac{\sigma_{US}}{\sigma_U} \sqrt{\frac{M_{US}}{M_U}} \right) \quad (22)$$

and

$$\log p_{US} = \log p_U + \log \frac{I_{US}^+}{I_U^+} - \log \frac{\sigma_{US}}{\sigma_U} \quad (23)$$

The data from the calculations are presented in Table XVIII for the fifteen target data at values of $10^4/T$ between 4.13 and 4.69 (T between 2416 and 2134°K). The logarithms of the individual partial pressures together with those of P_E are plotted against the reciprocal

TABLE XVIII
PARTIAL PRESSURES OF GASEOUS URANIUM AND
URANIUM MONOSULFIDE FROM COMBINED
EFFUSION RATE AND MASS SPECTROMETRIC
MEASUREMENTS

Series and ex- posure number	$\frac{10^4}{T}$ (°K ⁻¹)	$\log P_E$ (atm)	I_{US}^+/I_U^+ [corrected Eq. (20)]	$\log p_U$ (atm)	$\log p_{US}$ (atm)
V-13(8)	4.1430	-4.7140	0.6778	-4.9032	-5.2213
V-8(4)	4.2055	-4.9141	0.6473	-5.0972	-5.4353
V-10(11)	4.2115	-4.9314	0.6444	-5.1139	-5.4539
V-10(1)	4.2653	-5.1123	0.6194	-5.2897	-5.6470
V-10(2)	4.2704	-5.1071	0.6170	-5.2840	-5.6429
V-9(1)	4.3101	-5.2229	0.5992	-5.3962	-5.7678
V-8(3)	4.3418	-5.3214	0.5854	-5.4918	-5.8736
V-10(10)	4.3476	-5.3147	0.5829	-5.4846	-5.8682
V-9(7)	4.3983	-5.4850	0.5615	-5.6504	-6.0503
V-8(5)	4.4462	-5.6507	0.5420	-5.8120	-6.2272
V-10(3)	4.4604	-5.6717	0.5364	-5.8318	-6.2515
V-10(12)	4.5135	-5.8320	0.5158	-5.9877	-6.4244
V-10(9)	4.5676	-6.0087	0.4956	-6.1600	-6.6141
V-9(6)	4.6162	-6.1756	0.4781	-6.3231	-6.7927
V-10(4)	4.6859	-6.3814	0.4542	-6.5236	-7.0156

Assumed cross-section ratio $\sigma_{US}/\sigma_U = 1.41$

of the temperature in Figure 13. A linear least squares treatments for the plots of $\log p_U$ and $\log p_{US}$ vs. $10^4/T$ gave the lines drawn through the points, and the corresponding equations:

$$\log p_{US}(\text{atm}) = -(3.2839 \pm 0.0221) \frac{10^4}{T} + (8.3828 \pm 0.0971). \quad (24)$$

and

$$\log p_U(\text{atm}) = -(2.9636 \pm 0.0221) \frac{10^4}{T} + (7.3739 \pm 0.0971). \quad (25)$$

The standard deviations of slopes and intercepts are given.

FIGURE 13
APPORTIONMENT OF TOTAL VOLATILITY BETWEEN GASEOUS U
AND US; LOGARITHMS OF OBSERVED "EFFECTIVE PRESSURES"
AND OF PARTIAL PRESSURES OF U AND US CALCULATED
FROM COMBINED MASS SPECTROMETRIC AND TOTAL
EFFUSION RATE MEASUREMENTS VS. RECIPROCAL
OF TEMPERATURE

The changes of enthalpy and entropy accompanying the sublimation of uranium monosulfide to gaseous US molecules [reaction (I)] at an average temperature 2300°K are just the slope and intercept of the line given by equation (24) multiplied by 2.303R, or, where the

statistical standard deviations are given,

$$\Delta H_{2300}^{\circ} \text{ (I)} = 150.3 \pm 1.0 \text{ kcal/mole}$$

$$\Delta S_{2300}^{\circ} \text{ (I)} = 38.36 \pm 0.44 \text{ cal/deg-mole.}$$

Reference to equation (7) shows that for vaporization of solid US to the gaseous elements [reaction (II)] the heat of vaporization is the slope of the line given by equation (25) multiplied by $2 \times 2.303R$ and the entropy of vaporization is $2 \times 2.303R$ (intercept - $\frac{1}{2} \log \sqrt{M_S/M_U}$). Again including the statistical standard deviations, there are obtained

$$\Delta H_{2300}^{\circ} \text{ (II)} = 271.2 \pm 2.0 \text{ kcal/mole}$$

$$\Delta S_{2300}^{\circ} \text{ (II)} = 65.49 \pm 0.88 \text{ cal/deg-mole.}$$

2. Examination of the Validity of the Treatment

a. Internal Consistency of the Calculated Results

It is now necessary to examine the assumptions underlying the calculations in the preceding section and the experimental values used in order to estimate the degree to which their results are valid. The experimental quantities employed were the values of P_E , I_{US}^+/I_U^+ , and σ_{US}/σ_U at each temperature. It was tacitly assumed that the vaporization to gaseous US_2 molecules detected in experiment MS-2 contributed only insignificantly to the total volatility. The change in the equilibrium constant $p_U p_S$ resulting from use of uranium of decreased atomic weight was ignored. It was also assumed that the enthalpy and entropy changes for reactions (I) and (II) were constant over the temperature range of the mass spectrometric observations, and that $\log I_{US}^+/I_U^+$ varied linearly with $1/T$ in the same range. We shall examine the assumptions first, then consider errors in the results due to errors in the experimental quantities.

The vaporization of solid uranium monosulfide to gaseous disulfide molecules according to reaction (III) was estimated to contribute at most a few tenths of a per cent of the total volatility at the highest temperature in experiment MS-2, and so may indeed be considered negligible for the present calculations. It seems probable

that even at the maximum temperatures of the target experiments reaction (III) was unimportant with respect to reactions (I) and (II) in terms of the observed volatility.

A test of the assumptions of linear dependence on $1/T$ of $\log I_{US}^+/I_U^+$ and of ΔH° and ΔS° for reactions (I) and (II) is essentially a test of the mutual consistency of equations (20), (24), and (25) and of the measurements of absolute effusion rate as represented, say, by equation (17). The same test should show whether it was reasonable to use values of $\log P_E$ from the individual target data for the above calculations of partial pressures, rather than using smoothed values taken from equation (17). These tests are essentially independent of absolute errors in σ_{US}/σ_U , P_E , and I_{US}^+/I_U^+ . Choosing the values 3.8 and 5.2 for $10^4/T$, both approximately 200° outside the temperature range of the mass spectrometric measurements, and the value 4.4 inside that range, one calculates the values in Table XIX for P_E , respectively via equation (17) and a combination of equations (24), (25), and (13). The values of $\log P_E$ calculated from the combined equations (13), (24), and (25) are shown in Figure 9.

TABLE XIX
COMPARISON OF "EFFECTIVE PRESSURES," P_E , FROM
TOTAL EFFUSION RATE MEASUREMENT (A) AND
COMBINED MASS SPECTROMETRIC AND
TARGET DATA (B)

$\frac{10^4}{T}$ ($^\circ K^{-1}$)	(A) by equation (17)		(B) by equations (13), (24) and (25)		$\frac{P_E(B)}{P_E(A)}$	$\log P_E(B)$ - $\log P_E(A)$
	$\log P_E$	$P_E(\text{atm})$	$\log P_E$	$P_E(\text{atm})$		
3.8	-3.742	1.81×10^{-4}	-3.661	2.18×10^{-4}	1.20	0.081
4.4	-5.508	3.11×10^{-6}	-5.501	3.16×10^{-6}	1.02	0.007
5.2	-7.932	1.17×10^{-8}	-7.928	1.18×10^{-8}	1.01	0.004

Inspection of Table XIX shows excellent agreement for the values of the "effective pressure" at the two lower temperatures and adequate agreement at the highest. The residuals shown in Figure 10b indicate that equation (17) gives a slightly poorer fit to the experimental points at $10^4/T$ near 4.4 than does the treatment utilizing the mass spectrometric measurements. This situation arises because the individual effusion data in this temperature range were used in the latter treatment. The close agreement at $10^4/T = 5.2$ shows that over this range ΔH° and ΔS° for processes (I) and (II) are indeed virtually constant.

The twenty per cent difference in the calculated "effective pressures" at $10^4/T = 3.8$ is attributable to two causes. First, as mentioned elsewhere, if $\log p_U$ and $\log p_{US}$ are assumed linearly dependent on $1/T$, then a plot of $\log P_E$ calculated from extrapolated values of p_U and p_{US} must show an upward curvature with increasing temperature. Second, heat capacity effects should cause, as observed, a downward curvature of the measured $\log P_E$ vs. $10^4/T$ line. That the discrepancy is small at $10^4/T = 3.8$ indicates only a slight departure from constancy of ΔH_T° and ΔS_T° with increasing temperature, so that again the linear treatment is justified in the absence of knowledge for solid US of either the heat capacity or the absolute entropy at some temperature in the experimental range or, what is the same thing, of the free energy functions.

b. The Effect of Errors in the Chosen Cross-section Ratio

Consider now the effect on the derived partial pressures and thermodynamic values of errors in the three sets of experimental values used to calculate them. The most precisely determined was the total rate of effusion expressed heretofore as the "effective pressure." The discussion in Section IV E8 of the errors involved in the measurement of P_E and the agreement between the values extrapolated from the above treatment of a limited set of the experimental

points and the values measured over a wide temperature range establish that these data are those on which further calculations must be based.

The effects of the use of an incorrect cross-section ratio will now be discussed. The value 1.41, that used in the calculations above, was obtained from indirect measurement in the spectrometer of the ion current ratio I_{32}^+/I_{238}^+ in experiment MS-2 and the assumption that $\sigma_{US} = \sigma_U + \sigma_S$. Because the value 1.41 is uncertain by an unknown amount, it is essential that the effect of an error of any given size be estimated. An approximation to this effect is obtained by differentiation with respect to σ_{US}/σ_U of the various functions of interest. For convenience let $\sigma_{US}/\sigma_U = \Sigma$.

(1) Effect on Partial Pressures of Errors in Cross-section Ratio

Partial differentiation of equation (22) with respect to the cross-section ratio Σ gives

$$\frac{\partial \log p_U}{\partial \Sigma} = \frac{1}{2.303} \frac{1}{\Sigma^2 \frac{I_U^+}{I_{US}^+} \sqrt{\frac{M_{US}}{M_U}} + \Sigma}, \quad (26)$$

since the "effective pressure" and ion current ratio do not depend on Σ . Similar differentiation of equation (23) gives

$$\frac{\partial \log p_{US}}{\partial \Sigma} = \frac{\partial \log p_U}{\partial \Sigma} - \frac{1}{2.303\Sigma}. \quad (27)$$

One calculates that $I_U^+/I_{US}^+ = 1.9$ at $10^4/T = 4.4$. Substitution of this value and $\Sigma = 1.41$ into equations (26) and (27) gives

$$\left(\frac{\partial \log p_U}{\partial \Sigma} \right)_{\Sigma = 1.41} = 0.08 \quad (28)$$

and

$$\left(\frac{\partial \log p_{US}}{\partial \Sigma} \right)_{\Sigma = 1.41} = -0.22. \quad (29)$$

If Σ was chosen too low by 1.00, a factor of 71 per cent of its chosen value, equations (28) and (29) indicate, respectively, that the calculated

values of p_U is too low by about a factor of 1.2 and p_{US} is too high by about a factor of 1.7.

(2) Effect on ΔH_T° of Errors in Cross-section Ratio

If it is assumed that the heats and entropies of vaporization of solid US by reactions (I) and (II) are constant over the range of temperatures of the mass spectrometric measurements, then from equation (1), which applies to the vaporization to the elements,

$$\Delta H_{T_1 \text{ to } T_2}^\circ (\text{II}) = 4.606R (T_2 - T_1) [\log p_U(T_1) - \log p_U(T_2)] \quad (30)$$

Differentiation with respect to Σ gives

$$\frac{\partial \Delta H_{T_1 \text{ to } T_2}^\circ (\text{II})}{\partial \Sigma} = 4.606R (T_2 - T_1) \left[\frac{\partial \log p_U(T_1)}{\partial \Sigma} - \frac{\partial \log p_U(T_2)}{\partial \Sigma} \right] \quad (31)$$

Numerical evaluation of equation (26) for I_{US}^+/I_U^+ at $10^4/T = 4.2$ and 4.8 ($T = 2381$ and 2083°K) and substitution into equation (31) gives

$$\frac{\partial \Delta H_{2300}^\circ (\text{II})}{\partial \Sigma} = \frac{3.4 \times 10^3}{4.4\Sigma^2 + 1.2\Sigma + 1}$$

Evaluation for $\Sigma = 1.41$ gives 0.30 kilocalorie per mole for the error in $\Delta H_{2300}^\circ(\text{II})$ per unit error in Σ . A similar treatment of the heat of sublimation to gaseous US gives the general equation

$$\frac{\partial \Delta H_{T_1 \text{ to } T_2}^\circ (\text{I})}{\partial \Sigma} = 2.303R (T_2 - T_1) \left[\frac{\partial \log p_{US}(T_1)}{\partial \Sigma} - \frac{\partial \log p_{US}(T_2)}{\partial \Sigma} \right],$$

and the specific formula for temperatures between 2381 and 2083°K is

$$\frac{\partial \Delta H_{2300}^\circ (\text{I})}{\partial \Sigma} = \frac{344}{\Sigma^2 + 0.25\Sigma + 0.20}$$

Evaluation for $\Sigma = 1.41$ gives for the error in $\Delta H_{2300}^\circ(\text{I})$ a value of 0.14 kilocalorie per mole per unit error in Σ . If the chosen cross-section ratio was low by a factor of two, the heats are incorrect only by a fraction of a per cent, providing the approximations used are valid. A comparison of this result with heats calculated by the use of different cross-section ratios will be found below.

(3) Effect on ΔS_T° of Errors in Cross-section Ratio

To obtain the effect of errors in the cross-section ratio on the entropy changes on vaporization of uranium monosulfide, let us first combine equations (1) and (7), writing thence for the vaporization to the elements

$$\log p_U = -\frac{\Delta H_T^\circ(\text{II})}{2 \times 2.303R} \frac{1}{T} + \frac{\Delta S_T^\circ(\text{II})}{2 \times 2.303R} - \frac{1}{2} \log \sqrt{\frac{M_{\text{US}}}{M_U}}, \quad (32)$$

and for the sublimation to gaseous US,

$$\log p_{\text{US}} = -\frac{\Delta H_T^\circ(\text{I})}{2.303R} \frac{1}{T} + \frac{\Delta S_T^\circ(\text{I})}{2.303R}.$$

Differentiation gives

$$\frac{\partial \Delta S_T^\circ(\text{II})}{\partial \Sigma} = \frac{1}{T} \frac{\partial \Delta H_T^\circ(\text{II})}{\partial \Sigma} + 2 \times 2.303R \frac{\partial \log p_U}{\partial \Sigma},$$

and

$$\frac{\partial \Delta S_T^\circ(\text{I})}{\partial \Sigma} = \frac{1}{T} \frac{\partial \Delta H_T^\circ(\text{I})}{\partial \Sigma} + 2.303R \frac{\partial \log p_{\text{US}}}{\partial \Sigma}.$$

Evaluation at $10^4/T = 4.4$, using the values $I_{\text{US}}^+/I_U^+ = 1.9$ and $\Sigma = 1.41$, gives the following results:

$$\frac{\partial \Delta S_T^\circ(\text{II})}{\partial \Sigma} = 0.87 \text{ cal/deg-mole/unit change in } \Sigma,$$

and

$$\frac{\partial \Delta S_T^\circ(\text{I})}{\partial \Sigma} = 0.49 \text{ cal/deg-mole/unit change in } \Sigma.$$

The errors in ΔS_T° for both reactions caused by an error of 1.00 in the chosen cross-section ratio thus appear to be about equal to the statistical standard deviations obtained from the linear least squares treatments. It should be noted that somewhat different errors are estimated from the present treatment for different values of Σ taken as starting points.

(4) Summary of the Effect of Errors in the Assumed Cross-section Ratio

To give a better idea of the effect of errors in the assumed value of the cross-section ratio, recalculations of the partial pressures and the heats and entropies were performed, using the ratios $\Sigma = \sigma_{US}/\sigma_U = 1.70$ and 2.82 . The effect of doubling the ratio is indicated in Table XX. The estimations above predict smaller changes in the case of ΔH° than those from the recalculations. Both calculations for ΔS° give the same result. The changes for reaction (II), not listed in the table, are virtually the same percentagewise as those for reaction (I).

TABLE XX
EFFECT OF CHOICE OF CROSS-SECTION RATIO
ON THE THERMODYNAMICS OF VAPORIZATION
OF URANIUM MONOSULFIDE

σ_{US}/σ_U	$\Delta H_{2300}^\circ(I)$ (kcal/mole)	$\Delta S_{2300}^\circ(I)$ (cal/deg-mole)	pUS(atm) at 2378°K
1.41	150.2 ± 1.0	38.4 ± 0.4	3.7×10^{-6}
1.70	150.8 ± 1.0	38.3 ± 0.4	3.5×10^{-6}
2.82	151.9 ± 1.0	38.0 ± 0.4	2.2×10^{-6}

The values for the heats and entropies given on page 127 are accepted as those obtainable from the second law from the present research, because, although the cross-section ratio is uncertain by an unknown amount, little difference is found in the values calculated from different assumed ratios within a factor of two of 1.41.

The partial pressures of uranium atoms and US molecules in equilibrium with solid US are relatively more sensitive to the assumed values of σ_{US}/σ_U , but their sum is, within six per cent, independent of these values at all temperatures. The final evaluation is given following the next section.

c. The Effect on Derived Quantities of Errors in the Ion Current Ratio

The determination of the temperature dependence of the ion current ratio I_{270}^+/I_{238}^+ was accomplished with fair precision, and the reproducibility appeared to be limited only by the spectrometer circuitry. The real question concerning the reliability of these data is, as was previously mentioned, as to what temperature a given ion current ratio ought to be assigned. An estimated uncertainty of $\pm 30^\circ$ was assigned in Section IV F3 to the orifice temperature as representative of the equilibrium giving rise to a particular ion current ratio. The corresponding error in the logarithm of the ratio at 2300°K is given by the product of the slope of Figure 12 and the uncertainty in the reciprocal temperature, $10^4/T$. The uncertainty in $\log I_{270}^+/I_{238}^+$ is thus 0.018, and that in the ratio itself amounts to about ± 5 per cent of the absolute value over the temperature range of the mass spectrometric measurements.

First, consider the effect of this uncertainty on the values obtained for the partial pressures of uranium and uranium monosulfide. From equation (22), the previously estimated error in the absolute value of $\log P_E$, the above uncertainty in I_{270}^+/I_{238}^+ , the neglect of the uncertainty in the cross section ratio, and the average value 0.56 for I_{270}^+/I_{238}^+ , one finds an uncertainty in $\log p_U$ of ± 0.022 . The corresponding uncertainty in the absolute value of the partial pressure of uranium atoms, apart from the uncertainty due to that in σ_{US}/σ_U , is ± 4 per cent. The error in the partial pressure of uranium monosulfide molecules is the same in absolute value at each temperature as that for the partial pressure of uranium atoms, but it is larger percentage-wise. At 2300°K the calculated ratio p_U/p_{US} is 2.46, so that the uncertainty in p_{US} is ± 10 per cent.

If the heats of vaporization are assumed constant over the temperature range from T_1 to T_2 for the mass spectrometric measurements, then for the reaction yielding gaseous atoms $\Delta H_T^\circ(\text{II})$ is

given by equation (30). The errors in T_1 and T_2 are of the same magnitude; the systematic errors, those of by far the largest magnitude, are in the same direction at all temperatures, and the same situation obtains for the pressures, so that the uncertainty in ΔH_T° is small but difficult to evaluate. Probably an error of ± 1 per cent is a generous guess for either of the vaporization processes.

The error in the entropy change for the reaction yielding atoms may be estimated from the above values and equation (32). The result is an error of ± 1.23 cal/deg-mole, or about ± 2 per cent. For the entropy of sublimation to gaseous monosulfide molecules a similar calculation yields uncertainties of ± 0.7 cal/deg-mole, or ± 2 per cent.

d. Summary of Errors in the Second Law Heats and Entropies of Vaporization

The values for the entropy and enthalpy changes for the processes by which uranium monosulfide vaporizes are given below, along with estimated uncertainties obtained from a combination in the root-mean-square fashion of all those described previously. For the reaction

there are obtained

$$\Delta H_{2300}^\circ(\text{I}) = 150.3 \pm 2.1 \text{ kcal/mole}$$

and

$$\Delta S_{2300}^\circ(\text{I}) = 38.4 \pm 0.6 \text{ cal/deg-mole} \quad .$$

For the reaction

there are obtained

$$\Delta H_{2300}^\circ(\text{II}) = 271.2 \pm 4.0 \text{ kcal/mole}$$

and

$$\Delta S_{2300}^\circ(\text{II}) = 65.5 \pm 1.6 \text{ cal/deg-mole} \quad .$$

3. Summary of the Thermodynamics of Uranium Monosulfide

a. Additions to the Second Law Treatment

Various thermodynamic quantities related to uranium monosulfide and its vaporization processes are summarized in Table XXI.

TABLE XXI
SUMMARY OF THE THERMODYNAMICS OF URANIUM MONOSULFIDE

Major Vaporization Processes:

Second Law Values:

Quantity	Value	Statistical Standard Deviation	Estimated Absolute Uncertainty
$\Delta H_{2300}^{\circ} (\text{I})$	150.3 kcal/mole	± 1.0	± 2.1
$\Delta H_{2300}^{\circ} (\text{II})$	271.2 kcal/mole	± 2.0	± 4.0
$\Delta S_{2300}^{\circ} (\text{I})$	38.36 cal/deg-mole	± 0.44	± 0.6
$\Delta S_{2300}^{\circ} (\text{II})$	65.49 cal/deg-mole	± 0.88	± 1.6

Values obtained from Second Law Data and Published (26) Data for the Elements:

$$\begin{aligned} S_{2300}^{\circ} (\text{US,s}) &= 45.08 \text{ cal/deg-mole} \\ S_{2300}^{\circ} (\text{US,g}) &= 83.44 \text{ cal/deg-mole} \end{aligned}$$

Free energy of formation from the gaseous elements:

$$\Delta F_{f,2300}^{\circ} (\text{US,s}) = -256.2 \text{ kcal/mole}$$

Heat of dissociation of gaseous US:

$$\Delta H_{2300}^{\circ} = 121 \text{ kcal/mole or } 5.2 \text{ electron volts/molecule}$$

Equations Derived from the Above Data and Theoretical Considerations Regarding the Forms to be Used. (Equations are valid for T between 1800 and 2800°K):

$$\begin{aligned} \Delta F_T^{\circ} (\text{I}) (\text{cal/mole}) &= -7.65271 \times 10^6 - 1.2210 \times 10^3 T + 0.13212 T^2 \\ &\quad + 2.90655 \times 10^6 \log T + 6.8635 T \log T \end{aligned}$$

$$\begin{aligned} \Delta F_T^{\circ} (\text{II}) (\text{cal/mole}) &= -7.53833 \times 10^6 - 1.2232 \times 10^3 T \\ &\quad + 0.132119 T^2 + 2.90655 \times 10^6 \log T + 0.29650 T \log T \end{aligned}$$

$$\begin{aligned} \Delta S_T^{\circ} (\text{I}) (\text{cal/deg-mole}) &= 1218.01 - 0.264238 T - \frac{1.26225 \times 10^6}{T} \\ &\quad - 6.8635 \log T \end{aligned}$$

$$\begin{aligned} \Delta S_T^{\circ} (\text{II}) (\text{cal/deg-mole}) &= 1223.06 - 0.264238 T - \frac{1.26225 \times 10^6}{T} \\ &\quad - 0.29650 \log T \end{aligned}$$

The second law heats and entropies derived previously have been combined with the published data for the elements⁽²⁶⁾ to give the absolute entropies of solid and gaseous US at 2300°K, a temperature near the middle of the range of the mass spectrometric measurements. The tabulated temperature dependences of the quantities are derived below.

A rough calculation by the third law method was carried out to check the reliability of the second law treatment. Free energy functions for solid uranium monosulfide were estimated as the sum of those for uranium and two-thirds the difference between those for uranium and uranium dioxide⁽⁵⁶⁾ extrapolated to the appropriate temperatures. Calculation of ΔH_{298}° (II) using these free energy functions and the partial pressures of uranium atoms in Table VIII gave an average of 272 kcal/mole with less than 0.2 per cent change with temperature over the temperature range of the mass spectrometric measurements. This result is taken as evidence that the calculated pressures are accurate, and the second law treatment of the data valid. An average heat capacity for solid uranium monosulfide of $5.9R$ combined with the second law value of ΔH_{2300}° (II) and the published data⁽²⁶⁾ for gaseous U and S would give this value of ΔH_{298}° (II).

In another calculation, the absolute entropy of solid uranium monosulfide at 2300°K, determined from the entropies of the gaseous elements and ΔS_{2300}° (II), was combined with the high temperature form of the Debye equation for the entropy of crystalline solids,⁽⁵⁷⁾ and the heat capacity was calculated from the characteristic temperature Θ so determined. The result indicated that if solid US behaves as a Debye solid, then its heat capacity is that of a classical diatomic solid, namely, $6R$. Assuming the validity of this value, the second law value of ΔH_{2300}° (II), and the data for the gaseous elements, one obtains the corresponding value at room temperature: ΔH_{298}° (II) = 273 kcal/mole. This result agrees with the rough third law value. The heat capacities calculated in these two treatments are somewhat lower than one might have expected a priori.

Assuming $\Delta H_{298}^{\circ}(\text{II}) = 273 \text{ kcal/mole}$, one calculates from the data given by Stull and Sinke⁽²⁶⁾ for the elements the corresponding heat of formation from rhombic sulfur and solid uranium at 298°K, $\Delta H_f^{\circ}(\text{US}, \text{s}) = -99 \text{ kcal/mole}$. This value is based on the value 3.6 e.v. for the dissociation energy of gaseous S_2 . If the value 4.4 e.v.⁽⁵⁹⁾ for the dissociation energy is used, $\Delta H_f^{\circ}(\text{US}, \text{s}) = -90 \text{ kcal/mole}$. These values may be compared with the calorimetrically determined heat of formation at 298°K of -118 kcal/mole for cerium monosulfide⁽¹²⁾ and the estimated value $-120 \pm 5 \text{ kcal/mole}$ reported for thorium monosulfide.⁽¹¹⁾

The absolute entropy of solid uranium monosulfide at 2300°K, namely, 45.08 cal/deg-mole, is about twice that of such refractory metals as tungsten, tantalum, and molybdenum. The metallic nature of US and its entropy thus imply that sulfur in US behaves somewhat as an alloying "metal," so that Kopp's rule is obeyed.

The absolute entropy of gaseous US at 2300°K is that of the solid plus the entropy change accompanying the sublimation to this species, or 83.44 cal/deg-mole. If gaseous US is assumed to behave ideally, then, neglecting electronic contributions, the temperature dependence of the entropy is $(9/2)R \ln T$, and

$$S_T^{\circ}(\text{US}, \text{g}) = \text{Constant} + (9/2)R \ln T.$$

Evaluation of the constant at 2300°K gives

$$S_T^{\circ}(\text{US}, \text{g}) = 14.22 + (9/2)R \ln T. \quad (33)$$

The free energy of formation of solid uranium monosulfide from the gaseous, monatomic elements is the negative of the free energy of vaporization, or

$$\Delta F_f^{\circ} = -\Delta H_T^{\circ}(\text{II}) + T\Delta S_T^{\circ}(\text{II}).$$

At 2300°K, therefore,

$$\Delta F_f^{\circ} = -256.2 \text{ kcal/mole}.$$

b. Temperature Dependences of the Thermodynamic Quantities

It was shown in Section V A2a that extrapolation of the linear equations (24) and (25) gives calculated "effective pressures" larger by twenty per cent at 2632°K than those calculated from equation (17). It is desirable to extend the treatment of the data to obtain the dependence on temperature of the thermodynamics of the two vaporization processes (I) and (II). Any such treatment should preferably have some theoretical basis rather than being purely empirical, and in view of the quality of the experimental data, the treatment should be based upon them rather than upon estimated quantities. The following derivation accepts the second law values for the entropies of vaporization at the selected reference temperature 2300°K and the partial pressures p_U and p_{US} given by equations (24) and (25) for the same temperature, then uses theoretical considerations to obtain reasonable forms for equations whose parameters are determined from the measurements of total effusion rate.

For a Debye solid composed of two atoms per formula weight, the contribution to the entropy by the lattice vibrations at constant volume is given⁽⁵⁷⁾ by the expression

$$S_V \cong 6R \left\{ \frac{4}{3} - \ln \frac{\Theta}{T} + \frac{1}{40} \left(\frac{\Theta}{T} \right)^2 + \dots \right\} \quad (34)$$

To evaluate the contribution from lattice expansion, one recalls that

$$C_P - C_V = (9\alpha^2/\beta) VT \quad , \quad (35)$$

in which α is the linear coefficient of thermal expansion and β is the compressibility. Grüneisen⁽⁵⁸⁾ has shown that the quantity

$$\gamma = 3\alpha V / C_V \beta$$

is independent of the temperature, so that

$$C_P = C_V + 3C_V \gamma \alpha T \quad .$$

The entropy of the crystalline solid may therefore be written as

$$S^\circ = \int \frac{C_P}{T} dT = \int \frac{C_V}{T} dT = 3\gamma \int \alpha C_V dT = S_V + 3\gamma \alpha \int C_V dT \quad ,$$

because the assumption can be made that α is independent of temperature at relatively high temperatures. Since

$$\int C_V dT = E ,$$

it follows that for high temperatures [see reference (57)]

$$S_T^\circ = 6R \left\{ \frac{4}{3} - \ln \frac{\Theta}{T} + \frac{1}{40} \left(\frac{\Theta}{T} \right)^2 \right\} + 3\alpha\gamma \left\{ 6RT \left[1 + \frac{1}{20} \left(\frac{\Theta}{T} \right)^2 \right] \right\} , \quad (36)$$

which is of the form

$$S_T^\circ = A + 6R \ln T + BT + \frac{C}{T} + \frac{D}{T^2} . \quad (37)$$

In the treatment mentioned above Θ was found to be of the order of 200° , so that the term in $1/T^2$ can be dropped from equation (37) for the present treatment at temperatures near and above 2000°K .

For solid uranium monosulfide the difference in entropy at some temperature T and at the reference temperature 2300°K follows from equation (37) as

$$S_T^\circ(\text{US}, s) - S_{2300}^\circ(\text{US}, s) = 6R(\ln T - \ln 2300) + B(T - 2300) + C \left(\frac{1}{T} - \frac{1}{2300} \right) ,$$

whence, since $S_{2300}^\circ(\text{US}, s) = 83.44 \text{ cal/deg-mole}$,

$$S_T^\circ(\text{US}, s) = -47.21 + 6R \ln T + B(T - 2300) + C \left(\frac{1}{T} - \frac{1}{2300} \right) . \quad (38)$$

The entropy data listed by Stull and Sinke⁽²⁶⁾ for gaseous monatomic sulfur and uranium were found to be represented within $0.01 \text{ cal/deg-mole}$ by the equations

$$S_T^\circ(\text{S}, g) = 10.994 + 2.5910 R \ln T \quad (39)$$

and

$$S_T^\circ(\text{U}, g) = 8.275 + 2.3442 R \ln T . \quad (40)$$

The entropy of vaporization of uranium monosulfide to the gaseous elements is therefore given as a function of temperature by combination of equations (38), (39), and (40) as

$$\Delta S_T^\circ(\text{II}) = 66.479 - 0.0648R \ln T - B(T - 2300) - C \left(\frac{1}{T} - \frac{1}{2300} \right) . \quad (41)$$

The entropy of vaporization to molecular US is given as a function of temperature by the difference between equations (33) and (38), whence

$$\Delta S_T^\circ (\text{I}) = 61.43 - \frac{3}{2} R \ln T = B(T - 2300) - C \left(\frac{1}{T} - \frac{1}{2300} \right) \quad (42)$$

The variation with temperature of the free energies of vaporization follows from the relationship

$$S = - \left(\frac{\partial F}{\partial T} \right)_P ,$$

which, upon integration, yields for a reaction at two temperatures, T_1 and T_2

$$\Delta F_{T_2}^\circ - \Delta F_{T_1}^\circ = - \int_{T_1}^{T_2} \Delta S^\circ dT \quad (43)$$

Subtraction of equation (42) from equation (41) and integration via equation (43) gives

$$\begin{aligned} & [\Delta F_{T_2}^\circ (\text{II}) - \Delta F_{T_1}^\circ (\text{II})] - [\Delta F_{T_2}^\circ (\text{I}) - \Delta F_{T_1}^\circ (\text{I})] \\ & = (-5.049 - 1.4352R)(T_2 - T_1) - 1.4352R(T_2 \ln T_2 - T_1 \ln T_1) \end{aligned}$$

The definitions of the standard free energy changes:

$$\begin{aligned} \Delta F_T^\circ (\text{I}) &= -RT \ln p_{\text{US}} \\ \Delta F_T^\circ (\text{II}) &= -2RT \ln p_{\text{U}} - RT \ln \sqrt{M_{\text{S}}/M_{\text{U}}} \end{aligned} \quad (44)$$

evaluated at $T_1 = 2300^\circ\text{K}$, combine with equation (47) to give

$$\Delta F_T^\circ (\text{II}) - \Delta F_T^\circ (\text{I}) = 11.43755 \times 10^4 - 2.197 T - 6.56700 T \log T,$$

and the corresponding equation in the partial pressures,

$$2 \log p_{\text{U}} - \log p_{\text{US}} = 0.91550 + 1.43520 \log T - 2.49964 \times \frac{10^4}{T} \quad (45)$$

Equation (45) relates the ratio $p_{\text{U}}^2/p_{\text{US}}$ to the temperature, and is based on the experimental observations of this research, the tabulation by Stull and Sinke⁽²⁶⁾ of the properties of the gaseous elements, and the assumption that gaseous US behaves as an ideal diatomic molecule with a negligible electronic contribution to its entropy, but is independent of any assumptions regarding the nature of

solid US. Combination of equation (45) with the definition of the "effective pressure" P_E , equation (13), gives the equations for the partial pressures of the gaseous species at any temperature T :

$$p_U = \frac{1}{2} [-X(M_{US}/M_U)^{1/2} + (X^2 M_{US}/M_U + 4XP_E)^{1/2}] \quad (46)$$

and

$$p_{US} = p_U^2/X \quad , \quad (47)$$

where $\log X$ is the right hand side of equation (45).

The form of the equations to be used to express the free energies of vaporization, hence the individual partial pressures rather than a ratio of them, as analytical functions of temperature may be derived from equations (41) and (42) and include the constants B and C of those equations. The constants, however, are related by linear equations involving functions of the temperature and the partial pressures, and so can be derived from the experimental data. Equation (42) if integrated in the manner of equation (43) gives for the sublimation of uranium monosulfide to gaseous US molecules

$$\begin{aligned} \Delta F_{T_2}^\circ(I) - \Delta F_{T_1}^\circ(I) = & -(61.43 + 1.5R)(T_2 - T_1) + 1.5R(T_2 \ln T_2 - T_1 \ln T_1) \\ & + B \left\{ \frac{T_2^2 - T_1^2}{2} - 2300 (T_2 - T_1) \right\} \\ & + C \left\{ \ln \frac{T_2}{T_1} - \frac{1}{2300} (T_2 - T_1) \right\} \quad . \quad (48) \end{aligned}$$

Rearrangement and substitution of equation (44) into equation (48), gives, when $T_1 = 2300^\circ K$,

$$\begin{aligned} B + C [\ln T - (T/2300) - 6.74066] 2/(T - 2300)^2 = & 2/(T - 2300)^2 \\ [-RT \ln p_{US} - 1.5RT \ln T + 64.4108 (T - 2300) - 8972.41] \quad . \quad (49) \end{aligned}$$

Inspection shows equation (49) has the form

$$B + C Y(T) = Z(T, p_{US}) \quad . \quad (50)$$

The individual partial pressures were evaluated from the experimental "effective pressure" at each temperature by use of an IBM 610 digital computer. The values of $\ln p_{US}$ obtained were then used to evaluate Y and Z for each temperature, and a linear least squares treatment gave, respectively, the slope and intercept

$$B = 0.26424 \pm 0.0459$$

and

$$C = (1.2623 \pm 0.2428) \times 10^6$$

When these constants were substituted into equations (49) and (42), the following equations for the sublimation of uranium monosulfide to US molecules were obtained:

$$\Delta F_T^\circ(\text{I}) = -7.65271 \times 10^6 - 1.2210 \times 10^3 T + 0.13212 T^2 + 2.90655 \times 10^6 \log T + 6.8635 T \log T, \quad (51)$$

$$\Delta S_T^\circ(\text{I}) = 1218.01 - 0.26424 T - \frac{1.26225 \times 10^6}{T} - 6.8635 \log T. \quad (52)$$

From equations (51) and (41) and the equation on page 141 for $\Delta F_T^\circ(\text{II}) - \Delta F_T^\circ(\text{I})$, one obtains

$$\Delta F_T^\circ(\text{II}) = -7.53833 \times 10^6 - 1.2232 \times 10^3 T + 0.132119 T^2 + 2.90655 \times 10^6 \log T + 0.29650 T \log T \quad (53)$$

and

$$\Delta S_T^\circ(\text{II}) = 1223.06 - 0.264234 T - 2.96503 \log T - \frac{1.26225 \times 10^6}{T}. \quad (54)$$

Equations (51) to (54) should be considered interpolation formulas to be used in the temperature range from 1800 to 2800°K. They do not give reasonable values, for example, at 298°K. It is to be recalled that the high-temperature form of the Debye equation and a constant coefficient of thermal expansion of solid uranium monosulfide were assumed in the derivations, and both assumptions hold only for $T \gg \theta$.

The partial pressure of diatomic sulfur molecules, S_2 , in the vapor above uranium monosulfide was shown by calculation to be less than one per cent that of sulfur atoms at 2700°K and less than one-tenth of a per cent at 1900°K. For these calculations the equilibrium constants given by Stull and Sinke⁽²⁶⁾ for the dissociation of S_2 were modified in accordance with a different dissociation energy. Stull and Sinke used the value 3.6 e.v., but later reviews⁽⁵⁹⁾ suggest that 4.4 e.v. is more nearly correct.

B. X-Ray Results and Phase Relationships in the System Uranium-Sulfur

1. The Lattice Parameter of Uranium Monosulfide

In Table XXII are presented the lattice parameters, measured at room temperature, of the various samples of interest. For the residues from vaporization experiments, omitting the V-10 and MS-2 residues, the average value is $a_0 = 5.4903 \pm 0.0002 \text{ \AA}$. The corresponding density at room temperature is 10.84 gm/cm^3 . This value is accepted as the lattice parameter of pure, stoichiometric uranium monosulfide, and is believed to be more reliable than those for the US

TABLE XXII
LATTICE PARAMETERS OF URANIUM MONOSULFIDE SAMPLES

Sample	$a_0(\text{\AA})$ $\pm$ Std. dev.	Remarks	Film No.
Vaporization Residues:			
V-1	5.4907 ± 0.0003	US _{0.98}	3042
V-3	5.4904 ± 0.0004		3148
V-5	5.4894 ± 0.0005		3165
V-7	5.4901 ± 0.0002		3309
V-8	5.4908 ± 0.0002		3310
V-10	5.4942 ± 0.0010 (EDC)	Poor pattern	3383
	5.4894 ± 0.0012 (ES)	US _{1.03}	
V-11	5.4896 ± 0.0004	US _{1.00} with 6.0% excess α -U present	3412
V-12	5.4902 ± 0.0003	US _{1.00}	3422
V-13(5)	5.4906 ± 0.0002	Deposit under lid	3439
V-13(8)	5.4915 ± 0.0004		3450
MS-1	5.4901 ± 0.0003		3227
MS-2	5.4923 ± 0.0011 (EDC)	Deposit under lid	3381
	5.4871 ± 0.0008 (ES)	Poor pattern	
Average (omit V-10, MS-2)	5.4903 ± 0.0002		
Preparations used in Vaporization Experiments:			
P-12(1)	5.4877 ± 0.0003	US _{1.01} ; 0.4% UOS in sample	3026
P-13(2)	5.4896 ± 0.0006	US _{1.01} ; 1.9% UO ₂ + α -U in sample	3068
P-14(1)	5.4723 ± 0.0004	US _{0.97} ; 16% excess α -U in sample	3116
P-18(3)	5.4865 ± 0.0004	US _{0.99} ; 10.1% excess α -U in sample	3286
P-18(3-lid)	5.4857 ± 0.0005	US _{1.01}	3287
P-19(1-lid)	5.4924 ± 0.0006	US _{1.01}	3322

preparations and those reported previously by Zumbush,⁽¹⁰⁾ Zachariasen,⁽¹⁵⁾ and Picon and Flahaut.⁽¹⁷⁾

The value $5.49_4 \text{ \AA}$ found by Zumbush for Strotzer's⁽⁹⁾ ideal composition U_4S_3 is of doubtful value because no subsequent investigator has been able to duplicate the work. The value $5.484 \pm 0.002 \text{ \AA}$ given by Zachariasen for material prepared by Eastman et al.⁽¹¹⁾ may be for nonstoichiometric or oxygen-contaminated US. A search of the war-time Metallurgical Project literature disclosed that the sample studied had the composition $\text{US}_{1.13}$, but that "the main constituent of this sample is US."⁽⁶⁰⁾ No statement was made concerning the remainder of the sample. The value $5.486 \pm 0.01 \text{ \AA}$ found by Picon and Flahaut refers to sulfide slightly poor in sulfur and probably containing small amounts of oxysulfide and perhaps carbide.

The lattice parameters obtained from the films taken of the V-10 and MS-2 residues are of questionable accuracy. The films were poor and the back reflection lines broad and indistinct. Mrs. Elizabeth Sherry of the X-ray laboratory of the Chemistry Division measured these films and obtained the parameters 5.4871 ± 0.0008 and $5.4899 \pm 0.0012 \text{ \AA}$ for the MS-2 and V-10 residues, respectively. The wide discrepancies in the parameters found by the writer and Mrs. Sherry indicate that neither set of values is likely to be correct, and that these parameters were legitimately omitted from the average for the vaporization residues.

The lattice parameters found for the samples of monosulfide from the preparations are seen to vary rather widely. Some variation is to be expected because of the different compositions of, and amounts and kinds of contamination in, the individual samples. The effect on the lattice parameters of different temperatures of annealing and other experimental conditions is unknown. The extent of solid solution in the uranium monosulfide phase and in the $\text{US-UO}_2\text{-UOS}$

system is discussed in later sections. The vaporization residues had more nearly uniform compositions and so must have given more reliable lattice parameters.

2. The Solid Solution Range of the Uranium Monosulfide Phase

The existence of a homogeneity range in the US phase has been considered by previous authors. Strotzer, et al. and Zumbush^(9,10) found that the X-ray pattern of a sulfide of overall composition $US_{0.33}$ showed lines due to metallic uranium, while that of $US_{1.06}$ showed lines of higher sulfide in addition to those of the US phase. Further, they found the lattice parameter of the US phase to be constant within the precision of the measurements, but they pointed out that their data only show that any homogeneity range must be narrower than corresponding to $US_{0.33}$ - $US_{1.06}$. For sulfide of composition $US_{0.75}$ a number of very weak lines in the X-ray pattern were identified by position and relative intensity as due to periodic absence of sulfur atoms from the central position in the NaCl-type unit cell. This defect structure would be expected to permit an appreciable homogeneity range.

No subsequent worker has found evidence for the composition U_4S_3 , and Picon and Flahaut⁽¹⁷⁾ gave other instances of the disagreement between Strotzer and Zumbush's X-ray and chemical analyses with those of Eastman et al.⁽¹¹⁾ and of Picon and Flahaut.

Picon and Flahaut found monosulfide phase lattice parameters from 5.45 to 5.486 Å with corresponding variation in the composition from 9.10 to 11.40 per cent sulfur (theoretical for US is 11.87). Density measurements showed the low-sulfur solid solutions to be due to absence of sulfur atoms rather than to the presence in the lattice of excess uranium atoms. These authors were unable to obtain the weak Debye-Scherrer lines of Strotzer's U_4S_3 .

The present research was not designed specifically to study the homogeneity range of the US phase, but information from various experimental results permits a more quantitative discussion than those

given by previous authors. Some pertinent data from previous tables are listed in Table XXIII. The individual samples have been more fully described in previous sections. It must be remembered that the X-ray measurements were performed at room temperature, and the results obtained may not be truly representative of the behavior at temperatures of 2000°C and above. The compositions indicated were deduced from analyses for sulfide sulfur and weights of insoluble residues, and are believed accurate to an estimated 0.5 per cent.

TABLE XXIII
DATA RELATING TO THE HOMOGENEITY RANGE OF THE US PHASE

Sample	Overall Composition S/U	Insoluble Residue		Soluble Portion of Sample S/U	Lattice Parameter (Å)	Remarks
		Per cent	Phase			
P-14(1)	0.80	16.0	-U	0.97	5.4723 ± 0.0004	Particles of U in bulk solid
P-18(1)	0.93	2.9	-U	0.96	est. 5.460 ± 0.005	X-ray pattern poor
P-18(2)	0.93	6.3	-U	1.00	est. 5.480 ± 0.005	X-ray pattern poor
P-18(2-lid)	0.99	0.9	-U	1.00	5.4816 ± 0.0005	
P-18(3)	0.88	10.1	-U	0.99	5.4857 ± 0.0005	Particles of U in bulk solid
P-19(1)	0.99	zero	-	0.99	5.4868 ± 0.0003	
V-11	0.93	6.0	-U	1.00	5.4896 ± 0.0004	
V-12	1.00	zero	-	1.00	5.4902 ± 0.0003	
P-18(3-lid)	1.01	zero	-	1.01	5.4857 ± 0.0005	
P-17(3)		2.5	UOS	1.07	5.4885 ± 0.0004	Higher sulfide present

Of the samples listed in the table only P-14(1) and P-18(1) exhibited both ratios of sulfur to uranium in the soluble part of the sample and lattice parameters appreciably lower than most. These sulfides represent the lowest sulfur compositions and lattice parameters attributable to the uranium monosulfide phases of the samples used in this research. The assumption here is that the uranium atoms in the solid solution went into aqueous solution on treatment with acid, whereas the insoluble uranium was present as a second phase in the bulk solid. Such behavior is reasonable if the sulfur-defect structure deduced by Picon and Flahaut is accepted, for then all the uranium atoms in the solid solution are chemically equivalent and should behave

alike. Uranium metal, on the other hand, is known to be attacked only slowly by dilute acid. In the case of sample P-14(1) the excess uranium amounted to sixteen per cent by weight of the whole sample, and was at least partly coagulated into small globules. These globules were malleable and so resisted grinding, were not thoroughly mixed with finely divided monosulfide phase, and were not detected in the X-ray pattern. The excess uranium in sample P-18(1) amounted only to three per cent of the total weight and so either did not agglomerate or else did so in very small particles that were either unnoticed or ignored when the notebook record of the grinding of sample P-18(1) was written. It would not be unusual if a second phase present to only three per cent went undetected in an X-ray powder diffraction pattern.

If, then, $US_{0.96}$ is indeed the low-sulfur boundary composition, one must suggest reasons why samples P-18(2) and V-11 of overall ratio $S/U = 0.93$ did not exhibit solid solution behavior in their X-ray and chemical analyses, and why sample P-18(3) of ratio $S/U = 0.88$ did exhibit such behavior, but gave a solid solution composition different from those from samples P-14(1) and P-18(1).

The vaporization experiments series V-2 and V-5 and series V-11 and V-12 confirmed the diphasic nature of sulfide samples P-14(1) and P-18(3), respectively. The analyses of the V-11 residue and of the P-18(2) and P-18(2-lid) sample indicate that at the high temperatures the sulfur-deficient uranium monosulfide solid solution is dissociated into two phases, presumably liquid uranium and stoichiometric US . In those cases, namely, the annealings which produced samples P-14(1) and P-18(3), in which there was sufficient liquid uranium present for it to agglomerate into separate particles, there was also a sufficiency either of liquid or vaporous uranium to retain saturation of the uranium monosulfide phase with uranium. In experiments V-11 and in annealing P-18(2), on the other hand, the amounts of the uranium phase apparently were not sufficient to maintain a saturated

monosulfide phase. It might be mentioned that of all the sulfide analyses performed by the writer, with the apparatus and procedure described in Section IV c, excellent precision (average deviations between 0.0 and 0.3 per cent of the average) was obtained except for the V-10 residue (previously discussed) and in the cases of the P-14(1), P-18(3), and V-11 samples. In these cases the respective average deviations from the average sulfide content, expressed as per cent of the average value, were 1.8 per cent for four determinations, 2.4 per cent for three determinations, and 1.4 per cent for five determinations. In each case the poor analytical precision can be attributed to presence of a separate uranium phase unevenly distributed throughout the bulk solid. In the V-11 case the uranium particles were not noticed at the time the sample was treated, and so must have been smaller than for the other two samples.

The data pertinent to estimation of the maximum sulfur content of the uranium monosulfide phase are few and quickly summarized. The monosulfide samples of atomic ratio sulfur-to-uranium greater than unity were preparations P-12(1), P-18(3-lid) and P-19(1-lid), all of composition $US_{1.01}$, the residue from series V-10 ($US_{1.03}$ according to the analysis), and the products from the various annealing in preparation P-17. Of these samples P-12(1) and those from P-17 were contaminated with uranium oxysulfide. The analysis of the V-10 residue is believed to have given erroneous results as previously discussed, and its composition is thought to have been $US_{1.00}$. Only the preparation P-17 samples gave X-ray diffraction patterns showing lines of higher sulfide phases. Because a few per cent of a second phase must be present for it to appear in the X-ray powder diffraction pattern of a given solid, one cannot deduce from X-ray evidence whether higher sulfide was or was not present in the samples of composition $US_{1.01}$. Because in preparations P-18 and P-19 deposits on the underside of the lid of the annealing crucible had this composition, it seems not unlikely

that $US_{1.01}$ lies in the monosulfide phase composition range. On the other hand, the upper limit to the monosulfide phase must be at a sulfur content less than $US_{1.07}$ for the lines from the higher sulfide to have been visible in the film from the P-17(3) sample. The presence of UOS probably did not greatly affect the equilibrium between the US and higher sulfide phases.

From the above and previous discussions the following conclusions may be drawn:

- (1) Uranium monosulfide exhibits solid solution at room temperature, at least over the composition range $0.96 \pm 0.01 \leq S/U \leq 1.01 \pm 0.01$
- (2) The sulfur-poor solid solution separates at elevated temperatures into two phases, liquid uranium and solid monosulfide, probably of composition $US_{1.00}$.
- (3) Uranium monosulfide samples of other than stoichiometric composition pass to stoichiometric $US_{1.00}$ on being heated in vacuum.

X-ray diffraction equipment capable of operating at temperatures above the melting point of uranium (1133°C) with samples maintained both in vacuum, and in both inert and sulfur or hydrogen sulfide atmospheres would be most helpful in elucidating more precisely the phase behavior of uranium monosulfide.

3. The Pressure-composition Diagram for the System Uranium-Sulfur

Figure 14 is a schematic pressure-composition diagram for the uranium sulfides at some temperature above the melting point of uranium. The vaporization behavior in the region S/U from 0.80 to 1.01 was investigated in the present research. The region S/U from 0 to 0.80 is drawn upon the assumption that there is essentially zero solubility of sulfur in uranium. The region at S/U greater than 1.01 is based on previous observations^(9,11,17) that, on vaporization, the higher sulfides pass to successively lower sulfur content in the

condensed phase. No solid solution range is pictured for the compounds U_2S_3 or U_3S_5 because none has been indicated by previous investigators. The small solubility range shown near US_2 is discussed in the next section. A small solid solubility is indicated near $S/U = 1.00$, although, as has been discussed earlier, it is likely that at the temperatures of the vaporization experiments the sulfur-deficient monosulfide solid solution dissociates to form $US_{1.00}$ and liquid uranium.

FIGURE 14
SCHEMATIC PRESSURE-COMPOSITION DIAGRAM
FOR THE SYSTEM URANIUM-SULFUR

4. A Possible Temperature-composition Diagram for the System Uranium-Sulfur

Figure 15 shows a schematic melting-point diagram for the uranium-sulfur system under its equilibrium partial pressures as drawn in an attempt to correlate the data of previous investigators^(9,11,17) and the present research. This diagram is one of several which could be drawn within the bounds of the incomplete information available at the present time.

FIGURE 15
A POSSIBLE SCHEMATIC TEMPERATURE-COMPOSITION
DIAGRAM FOR THE SYSTEM URANIUM-SULFUR

The behavior shown in the composition region from uranium to $\text{US}_{1.01}$ is based on discussions in other sections of this report. The phases U_2S_3 and U_3S_5 are shown without solid solution regions because the previous workers have not indicated any to exist.

The solid solution range shown for the disulfide is based on the indication of Picon and Flahaut⁽¹⁷⁾ that the three modifications of the disulfide may have slightly different compositions.

That the disulfide melts congruently is perhaps no more probable than that it melts incongruently. The former behavior is indicated here on the assumption that the observations of Picon and Flahaut may be better in accord with eutectic behavior between US_2 and U_3S_5 .

The incongruent melting of uranium trisulfide appears to be a reasonable guess. Strotzer et al.⁽⁹⁾ showed by static pressure

measurements that there is probably no solid solubility region around US_3 .

The indicated melting points for all sulfides except the monosulfide may be considerably in error because of oxygen contamination of the materials of the previous workers.

C. Some Physical Properties of Uranium Monosulfide

1. The Color and Mechanical Properties of Uranium Monosulfide

The annealed samples of uranium monosulfide dealt with in this research all exhibited a metallic luster if contaminated with less than about ten per cent oxygen-containing impurities. Their color varied from gray to silver and gold, and the pure materials ordinarily were slightly grayer than metallic silver and had a slight yellow tint. The appearance did not change appreciably on standing in the air; for instance, small pieces of the gold-colored residue from series V-5 were untarnished after a year's exposure to the laboratory atmosphere. When finely ground, the monosulfide appeared almost black to the unaided eye, but under magnification or strong light it showed its bright, metallic luster.

Uranium monosulfide was found to be quite brittle and was easily crushed when ground by hand in small alumina, agate, and boron carbide mortars.

2. The Melting Point of Uranium Monosulfide

Two types of evidence leading to possible estimates of the melting point of uranium monosulfide have been described earlier. These were the observation of the approximate temperature at which material began to diffuse through the wall of the sintered tungsten effusion cells and an apparent sharp, though slight, change in slope of the apparent total vapor pressure curve. The first observation, if due to the melting of uranium monosulfide, gave 2478°K as the melting point; the second gave approximately 2373°K . Previous authors have reported

that the melting point is well above 2273°K (2000°C)⁽⁹⁾ and that it is approximately 2473°K (2200°C).⁽¹⁷⁾ Proper interpretation of the vapor pressure data requires a knowledge of whether or not the sample melted in the range of temperatures investigated.

Two experiments were performed to determine the melting point. In the first, a small piece of the residue from series V-12 was heated on a tungsten strip in a Pyrex apparatus containing helium at a pressure of approximately 2 mm Hg. Heating was effected by the passage of an electric current through the strip, and the apparent temperatures of strip and US sample were monitored by means of an optical pyrometer. The temperature was slowly increased until the sample was seen to begin to melt. Then the temperature was quickly lowered to stop the melting, increased again to a lower temperature than before and maintained there for a few minutes to determine whether the sample would melt at the new temperature. Subsequent temperature changes were made as required by each previous result. From the observations one can set rather wide limits to the melting point. The upper limit is the lowest temperature of the filament at which melting occurred, namely, an apparent temperature of about 2412°C , which when corrected for an estimated transmissivity of the window and emissivity of the tungsten filament gives about 2750°C . The lower limit is the temperature of the coldest part of the solid sample when melting began, or an apparent 2107°C . Assuming a conservative emissivity of 0.5 for the sample and an estimated window transmissivity, one sets the lower limit to the melting point at 2340°C .

A more precise determination of the melting point of uranium monosulfide was carried out by heating a sample in the annealing crucible in vacuum for several minutes at a series of predetermined temperatures, and examining the residue after each heating, after the crucible had been allowed to cool and was removed from the vacuum line. The window placed at the top of the evacuated condenser received

an appreciable deposit of effusate, even in the short time the shutter was opened to permit measurement of the cavity temperature, so that experimental temperatures were measured on the crucible bottom. An intercomparison between cavity temperature and that of the crucible bottom was effected subsequently.

The monosulfide used was obtained by re-annealing the finely ground P-19(1) sulfide. This process gave a sintered plug shaped to fit the bottom of the crucible cavity but of smaller diameter. There were two kinds of observations by which one could determine whether melting had occurred in any given heating. First inspection of the residues showed that when the melting temperature was not attained, the sample retained its shape and did not stick to the crucible surface. In those cases in which melting definitely occurred, the re-solidified monosulfide was in the form of a smooth, highly reflecting, concave meniscus that completely covered the bottom of the cavity, but was easily broken loose from it. After the first melting of the sample, the solidified material was broken into several pieces with well-defined edges, so that when the pieces were subsequently reheated any change in their shapes was easily detected.

The second kind of evidence indicating melting was obtained by observation of the orifice with the optical pyrometer. When melting occurred, it was found that the previously essentially structureless orifice image developed a tiny dark spot in its center. The dark spot spread until it occupied most of the orifice. The apparent temperature of the spot was more than a hundred degrees lower than that of the cavity before melting occurred. The spot appeared to be a reflection of the orifice in the concave surface of the melt, and it danced about when the vacuum line was gently shaken. When the temperature was lowered below the melting point, the black spot disappeared, leaving again only a slight suggestion of nonuniformity in the view through the orifice.

The observations are summarized in Table XXIV, in which the observed temperatures are those of the bottom surface corrected for the transmissivity of window and prism.

TABLE XXIV
DETERMINATION OF MELTING POINT OF URANIUM MONOSULFIDE

Experiment	Obs. bottom temp, °C	Corrected apparent bottom temp, °K	Corrected cavity temp, °K	Remarks
1	2031	2384	2665	Residue not melted.
2	2088	2445	2742	Dark spot observed. Residue melted.
3	2055	2410	2698	Residue not melted.
4	2090	2448	2745	Dark spot observed. Residue melted.
5	2074, drift- ing to 2085	2430, drift- ing to 2442	2723 to 2738	Residue partially melted.
Chosen value for the melting point: 2735^{+30}_{-5} °K				

From the table it is seen that a reasonable estimate of the apparent melting point in vacuum of pure, stoichiometric uranium monosulfide is $2735 \pm 5^\circ\text{K}$. This value should be considered a lower limit, because the observation of the dark spot in the cavity, probably on the surface of the molten monosulfide, indicates that true blackbody conditions did not obtain when the sample was molten, and so to a lesser extent probably not during the intercomparison of cavity and bottom surface temperatures. Because the dark spot was not observed with either a solid sample or empty crucible, it is likely that departure from blackbody conditions in these cases was small, and the given melting point is probably low by twenty or thirty degrees at most. Hence the melting point may better be given as 2735^{+30}_{-5} °K. The melting point of uranium monosulfide is seen to lie at the very top of the temperature range in which the vapor pressure measurements

were taken, and so does not enter into treatment of the vapor pressure data. The much lower melting point of 2473°K given by Picon and Flahaut⁽¹⁷⁾ is probably low by reason of contamination of their monosulfide by oxysulfide and aluminum. It has been reported⁽¹³⁾ that the melting points of mixtures of the cerium sulfides Ce_2S_3 and Ce_3S_4 with cerium oxysulfide, $\text{Ce}_2\text{O}_2\text{S}$, are lower by 200 to 400° than those of the pure sulfides. The estimates of the melting point of uranium monosulfide from the two kinds of indirect evidence cited at the beginning of this section are dismissed as being incorrect interpretations of the experimental observations.

3. The Electrical Resistivity of Uranium Monosulfide

The resistivity of solid uranium monosulfide was determined by measurement of the potential difference developed across a small slug of the sulfide of known dimensions when a current was passed through it. The circuit used is shown in Figure 16.

FIGURE 16

CIRCUIT USED FOR MEASUREMENT OF THE RESISTIVITY OF URANIUM MONOSULFIDE

The experimental sample was a fragment of re-solidified melt broken free from the annealing crucible after one of the heatings in the melting point determination. The sample, though slightly curved, was

approximately the shape of a rectangular parallelepiped of length 2.5 mm, width 1.02 mm, and thickness 0.71 mm, as measured with a microscope with eyepiece scale.

The sample was held between two copper strips which carried the current to the sample, and each of which was fastened to the face of a small Lucite block. Good contact was assured by screws which squeezed the blocks together, thus tightening the copper strips down against the ends of the piece of sulfide. Current through the sample was provided by a 1.5-volt dry cell in series with a milliammeter, a 5000-ohm rheostat for controlling the current, and a one-ohm standard resistor. Two pointed tungsten probes made contact with the face of the sulfide sample at points separated along its length by 1.51 mm. The potential difference across the standard one-ohm resistor was measured by means of a Rubicon portable potentiometer, and the value of the current was calculated by Ohm's law from the resistance and potential difference. The potential difference between the tungsten electrodes was measured by means of a Leeds and Northrup type K-2 potentiometer equipped with a suspension galvanometer. The resistance of the sample was calculated by Ohm's law from the current and this potential difference. The resistivity was obtained by multiplying the resistance by the cross section of the sample, then dividing by the distance between the tungsten probes. The data are presented in Table XXV.

With only 2.00 milliamperes of current through the sample and the K-2 potentiometer set on zero voltage, a residual deflection of the galvanometer was still observed in the direction indicating the potentiometer setting was too high. This deflection, which corresponded to an estimated 1 to 3×10^{-6} volt, presumably was due to different contact potentials at the two tungsten electrodes, probably because one or

both was not quantitatively freed of oxide before use. The measured potential differences were therefore low, and the resistivities calculated from them were low by perhaps as much as 30 per cent.

TABLE XXV
DETERMINATION OF THE RESISTIVITY OF URANIUM MONOSULFIDE

Potential across 1-ohm resistor (mv)	Potential across sample (volts)	Calculated Current (ma)	Resistance of sample, Ω (ohms $\times 10^3$)	Resistivity, Ω -cm (ohm-cm $\times 10^4$)
1.998	<0*	2.00	-	-
4.123	9×10^{-6}	4.12	2.18	1.0
6.346	9×10^{-6}	6.35	1.41	0.7
6.39	1.6×10^{-5}	6.39	2.50	1.2
6.40	1.5×10^{-5}	6.40	2.34	1.1
			Average	1.0 ± 0.1

*Galvanometer would not zero. See discussion.

The value chosen for the resistivity of uranium monosulfide at room temperature is $(100 \pm 30) \times 10^{-6}$ ohm-centimeter, where the error is that estimated as the maximum due to the observed contact potential. This value, $100 \pm 30 \mu\Omega$ -cm, may be compared with the value $90 \mu\Omega$ -cm reported by Eastman *et al.*⁽¹²⁾ for cerium monosulfide. Resistivities at room temperature of some other elements and alloys taken for comparison from the *Handbook of Chemistry and Physics*⁽⁶¹⁾ are:

Substance	Cu	Hg	Si	W	Chromel	Nichrome
Resistivity ($\mu\Omega$ -cm)	1.7	96	58	5.5	70-110	100

Substance	Graphite
Resistivity ($\mu\Omega$ -cm)	800

A crude experiment was performed to test the sign of the temperature coefficient of the resistivity of uranium monosulfide. The hot, fused silica, target-protection shutter in the effusion apparatus commonly acquired a shiny, metallic mirror of sublimate during vaporization experiments. The leads from a multimeter equipped with

a resistance-measuring circuit were clipped to opposite ends of the shutter and the resistance of the semitransparent, gold-colored deposit after series V-9 was measured in air. Then a heat lamp was placed above the shutter and the resistance of the thin film was measured continuously with the lamp alternately on and off.

The initial resistance was 290 ohms. After the lamp was turned on the first time, the resistance increased steadily to 350 ohms, at which it remained constant except for small fluctuations. When the lamp was turned off, the resistance again increased, until a constant value of 440 ohms was attained. Thereafter when the lamp was turned on, the resistance decreased to a reproducible minimum of 380 ohms. When the lamp was turned off, the resistance increased to a reproducible maximum of 500 ohms.

The results were inconclusive. An increase of resistance with increasing temperature is characteristic of metallic conductors, but the initial increase of resistance with temperature of the US film might have been the result of oxidation of the sample. The subsequent decrease of resistance with increasing temperature is a behavior characteristic of semiconductors, but may have been characteristic of an oxidized US film, rather than a pure one. The final appearance of the mirror on the shutter was only slightly, if at all, different from the initial appearance.

4. Optical Properties of Thin Films of Uranium Monosulfide

Deposition of vapor from uranium monosulfide yielded films of various thicknesses on platinum targets and on two fused silica targets included with the platinum ones in series V-2. The α -activities of visible deposits corresponded to amounts of uranium from 5×10^{-7} to 1.7×10^{-4} gram. If the deposits were uranium monosulfide with the density calculated from the lattice parameter, the corresponding thicknesses of the visible deposits were from 1.8×10^{-9} to 6.3×10^{-7} centimeter. The majority of the targets with low activities were

gold-colored, while blue-gray and blue were the most common colors of the heavier deposits. The weights of uranium, thicknesses calculated as for uranium monosulfide, and colors of the deposits on platinum are listed in Table XXVI.

TABLE XXVI
COLOR OF THIN FILMS ON PLATINUM OF
EFFUSATE FROM URANIUM MONOSULFIDE

Wt. uranium in deposit (micrograms)	Thickness (Å)	Color
less than 0.5	less than 1.8	invisible
0.5 to 50	1.8 to 180	gold
50 to 60	180 to 220	gold to red-gold
60 to 70	220 to 260	brownish-gold, brown, red, purple, blue-gray
70 to 80	260 to 290	red-gold, blue, or gray-blue
80 to 90	290 to 330	blue
90 to 100	330 to 370	blue, gray, or golden brown
100 to 170	370 to 630	blue-gray to charcoal-gray

The two fused silica targets had deposits containing, respectively, 36 and 48 micrograms of uranium. They were metallic gray in appearance, in contrast to the gold color of metal targets containing the same deposit thicknesses. One of the fused silica targets had not been properly centered in the collimator when exposed, and its aluminum cassette showed a gold-colored deposit where the vapor had impinged.

The absorption spectrum of the deposit on one of the fused silica targets was measured in the infrared, visible, and ultraviolet regions by means of a Cary double-beam recording spectrophotometer. A clean fused silica target was placed in the reference beam. No absorption peaks were found between 2000 and 26,000 Å, the range of wavelengths scanned.

Whether the deposits on the targets were really pure monosulfide or were somewhat oxidized from exposure to the air is not known.

D. The System Uranium-Oxygen-Sulfur

1. Interaction of the Phases US and UO₂

The similarity of the X-ray patterns of uranium dioxide and uranium monosulfide was first observed by Strotzer et al.⁽⁹⁾ In both cases the uranium atoms are arranged in a face-centered lattice, and the lattice parameters are comparable, that of UO₂ being 5.4698 Å and that of US, 5.4903 Å. One might expect at least limited ranges of solid solubility of oxygen in US and sulfur in UO₂ although they should not be large because of the differing anion sizes and anion lattice positions in the fluorite-type oxide structure and sodium chloride-type sulfide structure. The major features of the powder patterns are the same for the two compounds but there are differences in relative intensities of several pairs of lines due to the effect of differing anion positions and atomic numbers. For example, in the US pattern the 200 line is stronger than the adjacent 111 line, the 420 line is stronger than the adjacent 331 line, and the 622 line is stronger than the neighboring 533 line. These relative intensities are reversed in the UO₂ pattern.

In the early attempts to prepare the monosulfide for the present research, extensive oxygen contamination was encountered, as has been described in earlier sections. The X-ray powder diffraction films of the impure samples were of varying degrees of sharpness and showed the patterns of uranium monosulfide, dioxide, and oxysulfide in various combinations and ratios of intensity.

The first preparation, P-1, was effected in the Mulite reaction tube, and its X-ray films showed strong lines attributable to US, with weaker UO₂ and UOS patterns. The US and UO₂ lines were sharp; those of UOS at the higher angles were blurred. Analysis for sulfur

and uranium soluble in dilute acid, for total sulfur (gravimetrically) and uranium, and for the amount of residue left after acid treatment, gave the following approximate composition of the P-1 material: US, 72 per cent; UO_2 , 19 per cent; UOS, 9 per cent.

The product from synthesis P-2, in which the Mullite tube was again used, was shown by a limited chemical analysis to contain about 50 per cent monosulfide. X-ray analysis showed the remainder of the sample to be chiefly dioxide, with a small percentage of oxysulfide. The oxygen-containing phases were preferentially located near the surface of the sample, as though they had been formed to some extent at least by reaction with the Mullite or with oxygen diffusing through it. Severe discoloration of the Mullite occurred.

The third preparation, P-3, was effected in a recrystallized alumina reaction tube. Chemical analysis showed the product to contain about 80 per cent monosulfide. X-rays identified the remainder as dioxide and a very small amount of oxysulfide. The dioxide was concentrated preferentially in the center of the sintered sample, as though it had been formed from oxygen present in the reaction gases and had been later preferentially vaporized from the surface.

The films showed the diffraction patterns due to UO_2 and US to be quite sharp for all three preparations, while the UOS patterns, of appreciable intensity only in the film of the P-1 product, were not well defined. Measurement gave the respective lattice parameters 5.4692 Å and 5.4862 Å for the dioxide and monosulfide phases in the P-2 product. Side-by-side visual film comparison indicated the same parameters for the P-1 and P-3 materials. It is to be noted that this parameter for UO_2 is the same as that for the pure material, whereas the US parameter is lower than that for the pure, solid samples obtained as residues in the later vaporization experiments. One wonders if the lower monosulfide parameter does not result from the presence of oxygen in solid solution in the impure samples

In subsequent preparations in which the alumina reaction tube was used, the products of synthesis were annealed in the tungsten annealing crucible. In general, the X-ray patterns from these materials were of poor quality, perhaps as a result of temperature gradients in the crucible. A visual study of the X-ray films showed that the lattice parameters of the monosulfide varied from about 5.486 to 5.488 Å and that relative intensities of the lines described above varied somewhat from those expected for pure US. The samples contained up to about ten per cent insoluble material, and those containing sulfur in the ratio $S/U > 1$ were contaminated with UOS rather than or else in combination with UO_2 . The insoluble residue from the sulfur-deficient preparation P-11(1) contained both α -uranium and dioxide.

Lattice parameters of the later monosulfide preparations taken as initial samples for the vaporization experiments were also lower than those of their residues. Of these later preparations P-12(1) and P-13(2) were slightly oxygenated as shown by chemical analyses which yielded acid-insoluble dioxide and oxysulfide precipitates. Products P-18(3), P-18(3-lid), P-19(1), and P-19(1-lid) were found to be free of oxygen, as revealed by chemical and X-ray analyses, but the P-18(3 lid) material was shown mass spectrometrically to contain at least traces of oxygen. Similarly, the residue from vaporization experiment V-5 had a slightly low parameter, 5.4894 ± 0.0005 Å, and was shown mass spectrometrically to contain traces of oxygen. The mass spectrometric studies, on the other hand, showed that samples freed of oxygen by vacuum heating picked up oxygen again on cooling, even in the evacuated spectrometer. Therefore one must ask the question, "If trace contamination by oxygen could lower the lattice parameters of pure uranium monosulfide samples, then why did not the later vaporization residues have lower lattice parameters?" The answer is not immediately obvious.

From these observations it seems reasonable to conclude that uranium dioxide dissolves almost no sulfur in solid solution, whereas the monosulfide can probably take up a small amount of oxygen when heated in contact with dioxide or oxysulfide. The lattice parameter of the monosulfide decreases in the presence of oxygen in the solid phase, a behavior opposite to that found by Samsonov and Popova⁽²⁴⁾ for thorium monosulfide. A more detailed statement concerning the UOS phase is presented in the next paragraph. The overall phase relationships involving UO_2 , US, and UOS are discussed in Section C below. A means of studying quantitatively the UO_2 -US interaction is presented in the Section VI.

2. The Uranium Oxysulfide Phase

Experimental results from this and previous research indicate the possibility of a solid solution range in the uranium oxysulfide phase. Lattice parameters for this tetragonal phase were reported by Zachariasen⁽¹⁵⁾ and by Picon and Flahaut.⁽¹⁷⁾ Film measurement gave lattice parameters for three experimental samples of UOS encountered in the present research. The indices for the lines as given in a wartime report by Zachariasen⁽⁶²⁾ were used in the calculations of the UOS parameters in this research.

The lines due to UOS in the diffraction pattern of preparation P-1 were measured after the lines due to US and UO_2 had been identified. The pattern from the preparation P-6 sample of composition $\text{UO}_{1.03}\text{S}_{0.91}$ contained weak UO_2 and strong UOS lines; the latter set was measured. This sample was obtained by reaction of hydrogen sulfide with uranium dioxide contained in a graphite boat at 1050°C . None of the high-angle oxysulfide lines in these patterns was sharp. The X-ray diffraction patterns of UOS samples obtained as insoluble residues from sulfide analyses of later preparations were of good quality, with good resolution in the back reflection region. The best

of these films, that from the insoluble residue from preparation P-17(3), was measured. The P-17(3) sulfide had the composition $US_{1.07}$ and contained 2.5 per cent UOS.

The five sets of lattice parameters are listed in Table XXVII. Analysis of the calculations for the film from the P-17(3-insoluble) UOS showed that the fit of several lines was poor when calculated from the indices listed by Zachariasen.⁽⁶²⁾ The parameters reported for this sample were obtained by omitting all lines of questionable index. The calculation of intensities for the high-angle lines to enable proper indexing had not been performed at the time of this writing, and the parameters would probably be changed in the last digit if re-indexing were carried out.

TABLE XXVII
LATTICE PARAMETERS OF URANIUM OXYSULFIDE

Sample	$a_0(\text{\AA})$	$c_0(\text{\AA})$	Investigator	Remarks
	3.843 ± 0.001	6.694 ± 0.001	Zachariasen ⁽¹⁵⁾	Sample prepared by Eastman <i>et al.</i> ⁽¹³⁾
	3.843	6.671	Picon and Flahaut ⁽¹⁷⁾	
P-1	3.842 ± 0.002	6.672 ± 0.002	This research	Film 2896. This sample contained 72% US, 19% UO_2 and 9% UOS.
P-6	3.843 ± 0.001	6.688 ± 0.002	This research	Film 2961. Overall composition of this sample was $UO_{1.03}S_{0.91}$ and very faint UO_2 lines were present.
P-17(3-insol)	3.8428 ± 0.0002	6.6967 ± 0.0003	This research	Film 3267. Excellent pattern, from acid-insoluble residue of sample of composition $US_{1.07}$ with 2.5% UOS contamination.

One sees from the table that, whereas all values of the parameter a_0 are equal, c_0 varies from 6.671 to 6.697 $\text{\AA}$. The structure type of UOS is that of $PbFCl$, space group $P_4/nmm-D_{4h}^7$.

Zachariasen gives the following atomic positions:

2 U in $(\frac{1}{2}, 0, 0.200 \pm 0.006)$; $(0, \frac{1}{2}, -0.200 \pm 0.006)$.

2 O in $(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, 0)$.

2 S in $(\frac{1}{2}, 0, 0.638)$; $(0, \frac{1}{2}, -0.638)$.

The oxygen atoms are seen to be located in a series of parallel planes, with the individual atoms at the corners and at the centers of the ends of the unit cells, which form rectangular prisms, each of whose height is c_0 and whose square ends have edges of length a_0 . The uranium and sulfur atoms are placed alternately along lines parallel to the c_0 axis and lying in the long faces of the prisms. For an oxysulfide preparation deficient in sulfur, but not oxygen, one would not be surprised to find a decrease in c_0 but not in a_0 .

From the conditions of formation, the P-6 oxysulfide would be expected to be sulfur deficient and oxygen saturated, while the P-17(3-insoluble) oxysulfide would be expected to be sulfur saturated and oxygen deficient. The constancy of the parameter a_0 probably indicates that the layers of oxygen atoms at the ends of the unit cell are filled in all cases. The variation of the parameter c_0 probably then indicates a range of solubility for sulfur and/or some replacement of sulfur atoms by oxygen atoms. The value obtained from the X-ray pattern of the P-17(3-insoluble) sample should then correspond to that of oxysulfide of maximum sulfur content. Since this value is the largest in the table and only slightly larger than that found by Zachariasen, the "best values" for the lattice parameters of uranium oxysulfide of maximum sulfur content are believed to be

$$a_0 = 3.4828 \pm 0.0002 \text{ \AA}$$

and

$$c_0 = 6.6967 \pm 0.0003 \text{ \AA} .$$

Although the present research does not establish the exact value of the upper sulfur content of the UOS phase, it seems likely that it is the stoichiometric UOS.

3. A Phase Diagram for the System Uranium-Oxygen-Sulfur

The phase relationships in the regions of the system uranium-oxygen-sulfur exemplified by various materials in this research are summarized in the phase diagram Figure 17.

FIGURE 17
SCHEMATIC PHASE DIAGRAM FOR THE SYSTEM
URANIUM-OXYGEN-SULFUR

In most cases the experimental samples were uranium monosulfides containing excess uranium or sulfur or contaminated with oxygen-containing phases, or a combination of these. The relative proportions of the phases in the samples were usually unknown, as was the extent of oxygen solubility in solid monosulfide; for these reasons the diagram is only schematic. Many of the samples were quenched from high annealing temperatures, so that the diagram does not

necessarily represent the phase equilibria obtaining at some unique temperature. Those materials not specifically described in Section IV, D were obtained in early attempts at preparation of the monosulfide. The phases present in each sample were identified by their X-ray diffraction patterns, either in the starting materials or after the monosulfide phase had been dissolved away with dilute acid.

The phases present in each portion of the diagram were identified in the samples listed on the diagram by the key letters. The important observations defining the phase diagram and corresponding to these key letters are as follows:

(A) and (B): Monosulfide phases with atomic ratios S/U less than 1.00 were found in samples containing uranium metal and/or dioxide, but not oxysulfide.

(C) and (D): Uranium oxysulfide was inferred to have a variable oxygen content such that $O/U \geq 1$ and a variable sulfur content such that $O/S \geq 1$, as was discussed in the preceding section.

(E), (G), and (H): The uranium oxysulfide phase was present only with monosulfide samples having the atomic ratio $S/U \geq 1$.

(A), (B), (D), and (E): Uranium dioxide appeared on visual intercomparison of X-ray films to have a fixed lattice parameter and so no appreciable solid solubility region.

(F) and (G): Uranium monosulfide seemed to have a solubility range for oxygen, uranium, and perhaps for sulfur, as discussed in preceding sections.

(H) and (I): Uranium oxysulfide but not dioxide was found in samples containing one or more higher sulfide phases.

(I): X-ray patterns from higher sulfide phases were not analyzed, and the lines in this part of the diagram are only guesses.

(J), (K), and (L): The solid solubility range in the oxygen-free uranium monosulfide phase is discussed in a previous section.

VI. SUGGESTIONS FOR FURTHER RESEARCH

A. Regarding the System Uranium-Sulfur

Investigation of the vaporization of the higher sulfides of uranium should be carried out by means both of effusion techniques and transpiration techniques using both inert gas and such gases as hydrogen sulfide, sulfur vapor, and carbon disulfide. In addition, mass spectrometric examination of the vapor from these compounds should be performed. The results from both pure sulfides and mixtures of them should disclose the vapor species and their relative abundances, as well as the vapor pressures and thermodynamics of vaporization and formation of the various phases.

B. Regarding the System Uranium-Oxygen-Sulfur

The formation of solid solutions by uranium dioxide and uranium monosulfide and the extent of the mutual solubility might be studied by an X-ray technique combined with chemical analysis. The different relative intensities of three pairs of lines in the powder patterns of the dioxide and monosulfide is probably due to the effect on the structure factors of the different anion positions, numbers, and atomic numbers. A calculation should show whether a gradual introduction of oxygen atoms in the dioxide positions into the monosulfide lattice would lead to a sufficient change in the relative intensities to be detectable for fairly small concentrations. If so, then mixtures of the oxide and sulfide could be annealed in vacuum and an X-ray diffractometer used to study changes in intensity and position of these lines.

Chemical analysis for sulfide content by evolution of hydrogen sulfide gives an insoluble precipitate of the oxide contaminants, as was described, but it is necessary to determine whether the oxygen in solid solution behaves differently in this respect than does that present in a separate dioxide phase.

C. Regarding a New Technique for the Determination of Relative Importances of Vapor Species

A new technique which seems to offer a means in certain cases of determining absolutely the relative amounts of vapor species is the condensation of the vapor on hot, rather than cold, targets. In the case, for example, of uranium monosulfide, in which there are two processes supplying almost all the vapor, if the targets intercepting the vapor were made of tungsten and heated to 1500 to 1800°K, then if the lifetime for re-evaporation or bouncing of the uranium atoms were small compared to that for reaction with sulfur atoms at the target, it should be possible to retain only the uranium monosulfide molecules on the targets. Comparison of target activity with that from cold targets at the same effusion cell temperature would then give by difference the proportions of U and US in the vapor.

A series of targets at different temperatures collecting vapor from an effusion cell at a fixed temperature would give the data necessary to make a plot of target activity per unit exposure time vs. target temperature. The shape of the curve should tell immediately whether the method is applicable to uranium sulfide; if applicable, the curve should show decreasing activity with increasing target temperature as less and less uranium is condensed, followed by a flat corresponding to condensation of US molecules but not U atoms, followed by decreasing activity due to noncondensation of an increasing percentage of the molecules.

The probable efficacy of this technique for the investigation of another system is shown by the re-examination⁽¹⁾ of the work of Erway and Seifert⁽⁶³⁾ on the vaporization of beryllia, in the light of a subsequent mass spectrometric study by Chupka et al.⁽⁶⁴⁾ The indication is that the beryllium arriving in the form of gaseous BeO and its polymers condensed on the hot targets used by Erway and Seifert, but that arriving in the form of beryllium atoms re-evaporated and so was not measured.

D. Regarding the Distribution in Angle of Molecules Effusing
from a Knudsen Cell

A suggested new technique for the determination of the distribution in angle of the numbers of molecules effusing from a circular orifice in a Knudsen cell involves condensation of the vapor inside a cylindrical condenser, such as the one used in experiment V-4, and the assay of segments of the condenser for total amount of condensate. In the case of experiment V-4, the condenser could easily have been sawed into rings, each of which had subtended an accurately measurable angle at the orifice, and the condensate on each ring could then have been removed by nitric acid and its amount determined gravimetrically, colorimetrically, or by α -counting. If necessary, the interior of the condenser could be sprayed with lacquer to insure that the condensate was not shaken loose in the sawing operation.

For an extended investigation it might be more convenient to use a presegmented condenser made of a stack of metal rings, sealed vacuum tight with aluminum gaskets. In this case, of course, the effusion cell would have to be heated otherwise than by induction with the coil outside the condenser.

A wide variety of orifice shapes and of working substances could be used with a minimum of inconvenience, high accuracy of analysis, and with relatively trouble-free performance of the simple apparatus.

VII. APPENDIX

Data for Correction of Observed Temperatures

Figure 18 is a plot of corrections to be applied to uncorrected temperatures read by the author with Leeds and Northrup pyrometer, serial number 709378, in order to use the calibration by R. J. Thorn to obtain true temperatures.

FIGURE 18
COMPARISON OF PYROMETER READINGS
BY EDC AND RJT

Figures 19 and 20 show, respectively, the differences between orifice and blackbody hole temperatures for effusion cells nos. 1 and 2, plotted against the blackbody hole temperatures. The temperatures used to plot these two figures were corrected for the observer's eye, the pyrometer scale, and the transmissivities of interposed windows and shutters.

FIGURE 19
INTERCOMPARISON OF CAVITY AND BLACKBODY
HOLE TEMPERATURES FOR EFFUSION CELL NO. 1

FIGURE 20
INTERCOMPARISON OF CAVITY AND BLACKBODY
HOLE TEMPERATURES FOR EFFUSION CELL NO. 2
IN TWO EXPERIMENTAL ARRANGEMENTS

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