

Lawrence Berkeley National Laboratory

Recent Work

Title

SURFACE IONIZATION OF Na, K, Li, AND NaI ON TUNGSTEN, RHENIUM, AND PLATINUM-TUNGSTEN

Permalink

<https://escholarship.org/uc/item/8019353p>

Authors

Wilson, Kent R.
Ivan-etich, Richard J.

Publication Date

1964-08-25

University of California

Ernest O. Lawrence
Radiation Laboratory

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

SURFACE IONIZATION OF Na, Rb, LiI, AND NaI
ON TUNGSTEN, RHENIUM, AND
PLATINUM-TUNGSTEN

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Research and Development

UCRL-11606

UC-4 Chemistry
TID-4500 (3rd Ed.)

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

SURFACE IONIZATION OF Na, Rb, LiI, AND NaI ON
TUNGSTEN, RHENIUM, AND PLATINUM-TUNGSTEN

Kent R. Wilson
and
Richard J. Ivanetich

August 25, 1964

Printed in USA. Price \$2.00. Available from the Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U. S. Department of Commerce, Springfield, Virginia.

SURFACE IONIZATION OF Na, Rb, LiI, AND NaI ON
TUNGSTEN, RHENIUM, PLATINUM-TUNGSTEN

Contents

	Abstract	v
I.	Introduction	1
II.	Apparatus	3
III.	Experimental Procedure	5
	A. Filament Temperature Calibration	5
	B. Preparation for Runs	6
	C. Data Normalization	9
IV.	Experimental Results and Interpretation . . .	10
	A. Theory	10
	B. Rb	13
	C. Na and NaI	15
	D. Li and LiI	17
	E. Contamination	18
V.	Conclusions	20
	Acknowledgments	21
	References	22
	Figure Captions	25

SURFACE IONIZATION OF Na, Rb, LiI, AND NaI
ON TUNGSTEN, RHENIUM, AND PLATINUM-TUNGSTEN

Kent R. Wilson and Richard J. Ivanetich

Inorganic Materials Research Division
Lawrence Radiation Laboratory,
Department of Chemistry,
University of California
Berkeley, California

ABSTRACT

The ionization of Na, Rb, LiI, and NaI has been measured on tungsten, rhenium, and 92% platinum - 8% tungsten surfaces as a function of surface temperature. The results are compared with the predictions of the Saha-Langmuir equation, and deviations are discussed. The technique of differential surface ionization is shown to distinguish between Li and LiI and between Na and NaI. The role of surface contamination is discussed. Rhenium is shown to give more efficient surface ionization than tungsten for Na, NaI, and LiI.

I. INTRODUCTION

Surface ionization, the formation of ions at the surface of a substance from which atoms or molecules are evaporating, was discovered in 1923 (KIN 23, IVE 23) and has since been widely investigated (ZAN 59), yet many of its aspects are still imperfectly understood. One of the least understood aspects is differential surface ionization, the differentiation by various surfaces between chemical compounds yielding the same ions. While the ionization of alkali metal atoms on metals of high work function may be at least approximately understood on the basis of the Saha-Langmuir equation (ZAN 59), the ionization of alkali halide molecules (giving alkali metal ions) is found to vary greatly from one metal surface to another in a way which is not directly explicable in terms of the Saha-Langmuir equation.

The surface ionization of the alkali halides was first observed by Rodebush and Henry (ROD 32) and has been investigated by many authors on tungsten and tungsten oxide (COP 35, HEN 37, STA 38, JOH 39, ZIM 44, STA 48, ION 48, DAT 56b, ROB 59). The ionization of the alkali halides on tungsten is at least partially explicable in terms of a model in which the molecule dissociates and then the alkali atom independently ionizes (ROD 32). The formation of volatile halides or oxyhalides of the surface metal may play a role in the dissociation (KIN 61b). In this model, if the alkali halide dissociates easily, the ionization efficiency of an alkali halide as a function of temperature would be expected to be quite similar to that of the corresponding alkali metal.

The surface ionization of the alkali halides has also been studied on platinum and 92% platinum - 8% tungsten alloy (DAT 56b, ROB 59, DAT 64).

The ionization, or lack of it, on platinum (and platinum alloy) surfaces is not yet understood, but may be related to inhibited dissociation of the alkali halide molecules due to surface contamination.

Under the proper conditions, the alkali halides are only very inefficiently ionized on platinum surfaces which ionize the corresponding alkali metals much more efficiently. This is in contrast to tungsten and rhenium which ionize the alkali metals and their halides with almost equal efficiency. Thus a combination of a rhenium or tungsten filament with a platinum or platinum alloy filament can be used to measure quantitatively, and to distinguish between, fluxes of alkali atoms and alkali halide molecules striking the filaments at the same time. This technique of differential surface ionization, discovered by Datz and Taylor (DAT 56a, DAT 56b), has been of immense value in the study of chemical reactions with crossed molecular beams. It is because of this useful application to molecular beam studies that this investigation has been undertaken.

In this laboratory we have used differential surface ionization to distinguish Na from NaBr and NaI, K from KCl, KBr and KI, Rb from RbBr and RbI and Cs from CsCl, CsBr, and CsI in the course of studies of chemical reactions with crossed molecular beams (KWE 60, HER 61a, HER 61b, KIN 61a, KWE 61, NOR 61, HER 62, WIL 62, NOR 63, KWE 64, WIL 64a, WIL 64b, WIL 64d, WIL 64e). That the technique actually distinguishes K atoms from KBr and KI molecules in the experiments has been elegantly demonstrated by Herm, Gordon and Herschbach through use of an inhomogeneous magnetic field (HER 64).

As is indicated in Section IV, Re has a considerably higher ionization efficiency than W for Li and Na and their halides. In this

laboratory we have successfully used it to detect Li, Na, K, Rb, Cs, LiI, NaBr, NaI, KBr, RbBr, RbI, CsBr, and CsI.

II. APPARATUS

The Test Stand, used in the experiments, is described in detail elsewhere (WIL 64b), and only a cursory description will be given here.

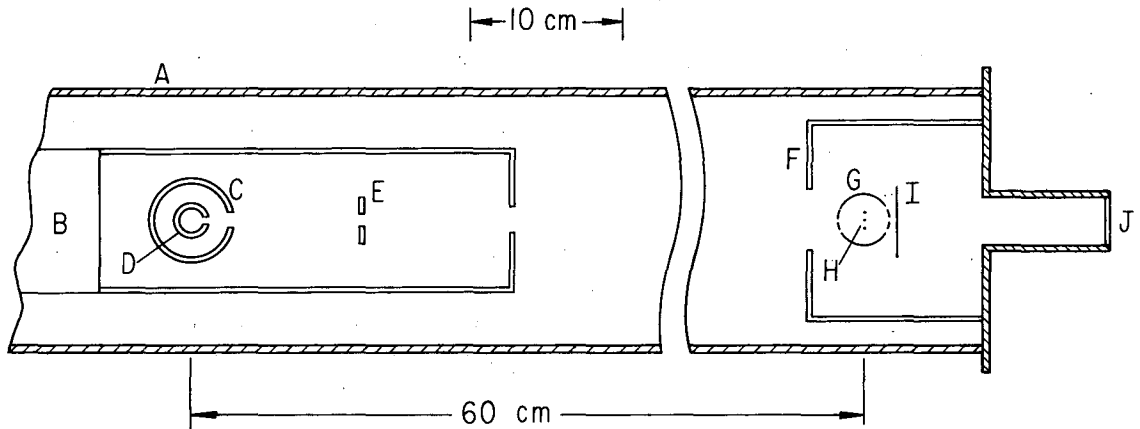
As shown in Fig. 1, the apparatus has three parts: a vacuum system, an oven system, and a detector system.

The vacuum system consists of a baffled six inch diffusion pump, a liquid nitrogen trap with large surface area, and a vacuum chamber largely built from six inch glass sewer pipe.

Molecular beams of the alkali metals and their halides are produced by a direct resistance oven heated by a current of several hundred amperes. The oven is made of two pieces of gold-plated stainless steel which unscrew so that an alumina crucible containing the beam material may be placed inside. A water-cooled cold shield surrounds the oven. A liquid nitrogen cooled shield prevents all but a narrow beam of molecules from reaching the detector. Condenser plates provide a small electric field which sweeps out any electrons or ions in the beam.

The detector contains four filaments. Three vertical filaments of W, Re and 92% Pt - 8% W alloy are used for surface ionization. A horizontal W filament is used for temperature calibration.

The W filaments are 0.010 cm (0.004 inch) diameter, of high purity and undoped with alkali metals, obtained from the Lamp Metals and Component Department, General Electric Company, 21800 Tungsten Road, Cleveland 17, Ohio. The Re filament is 0.0076 cm (0.003 inch) diameter from the Rembar Company, 67 Main Street, Dobbs Ferry, N. Y. (agents for



MU-29374

Fig. 1. Test stand, outline drawing. (A) Vacuum envelope, (B) liquid nitrogen trap around oven, (C) water-cooled oven shield, (D) direct resistance oven, (E) beam flag and collimator, (F) water-cooled detector shield, (G) surface ionization detector ion collector, (H) surface ionization filaments, (I) horizontal temperature calibration filament, (J) quartz window for temperature calibration. (The slit sizes are exaggerated for clarity.)

Chase Copper and Brass Co., Waterbury 20, Conn.). The 92% Pt - 8% W filament is 0.0076 cm (0.003 inch) diameter, available as alloy No. 479 from the Sigmund Cohn Corp., Mount Vernon, N. Y. The platinum alloy is used instead of pure platinum because of its superior mechanical strength at high temperature.

The filaments are surrounded by an ion collector with snouts extending forward and backward (not shown in Fig. 1) which subtends almost all the solid angle as seen from the filaments. A quartz window is included so that the filaments may be viewed for temperature calibration. The filament heating currents are accurately measured with Weston 931 ammeters.

The ion currents are measured on an Applied Physics model 31 vibrating reed electrometer and recorded by a Leeds and Northrup Speedomax G recorder.

III. EXPERIMENTAL PROCEDURE

A. Filament Temperature Calibration

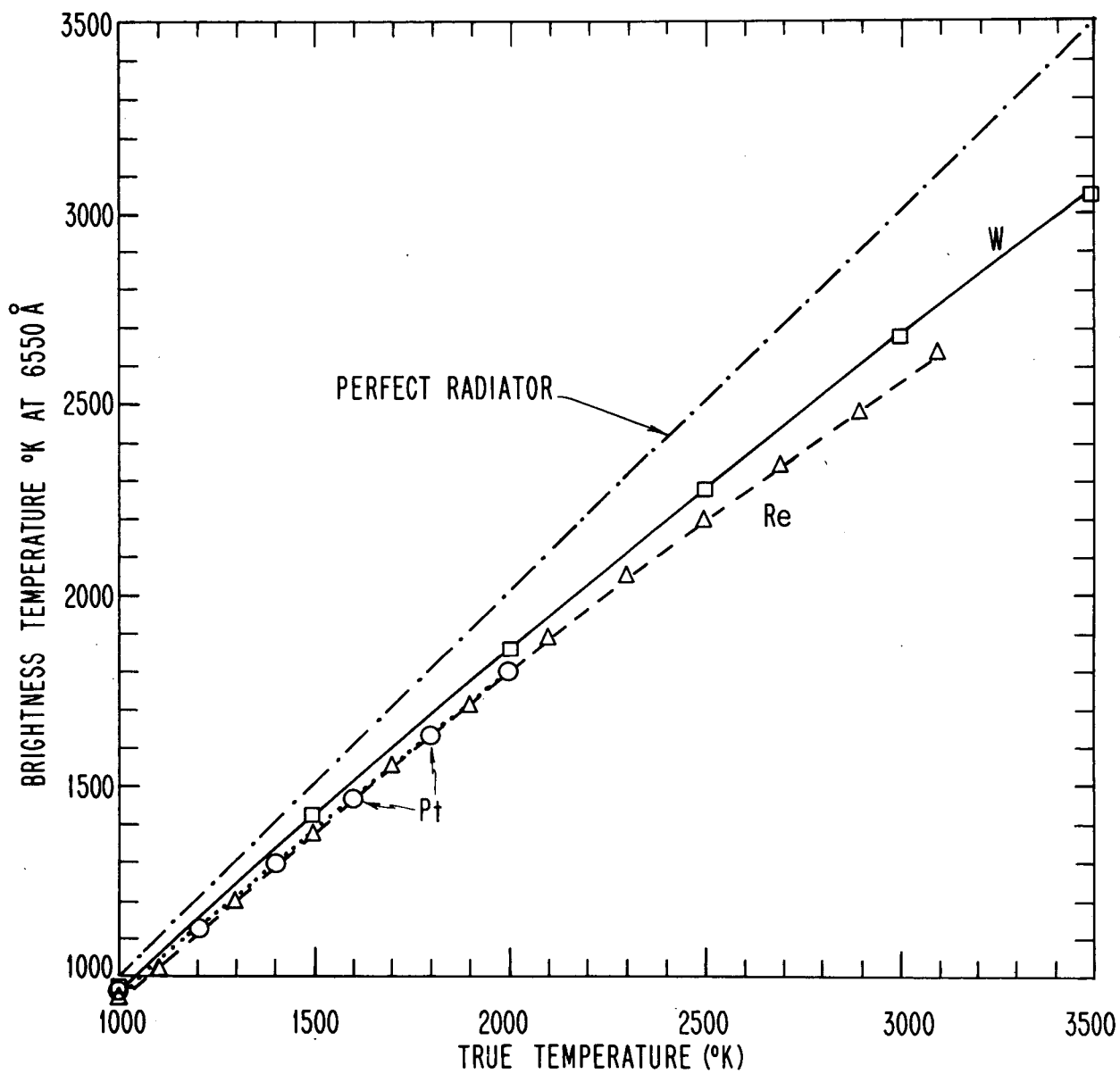
The true filament temperatures are determined by reference to tabulated properties of tungsten. The diameter of the W calibrating filament is determined by weighing (after the completion of the experiment) and its true temperature is then known as a function of heating current from the Jones-Langmuir tables for tungsten (JON 27). The brightness temperature of the calibrating filament is matched to the brightness temperatures of the well-aged surface ionization filaments for various values of heating current by viewing the crossed filaments through the red filters of a Micro Optical Pyrometer made by the Pyrometer Instrument Co., Bergenfield, N. J. The effective wavelength of

these filters is $\pm 3\%$ of the standard 6550 A over the entire temperature range covered (BOL 64). Since both the calibrating filament and the filaments to be calibrated are inside the same vacuum envelope, the errors due to absorption of radiation by the quartz window cancel out. The proper emissivity corrections are made with the aid of the curves shown in Fig. 2, and the final true temperature calibrations are calculated as shown in Fig. 3.

B. Preparation for Runs

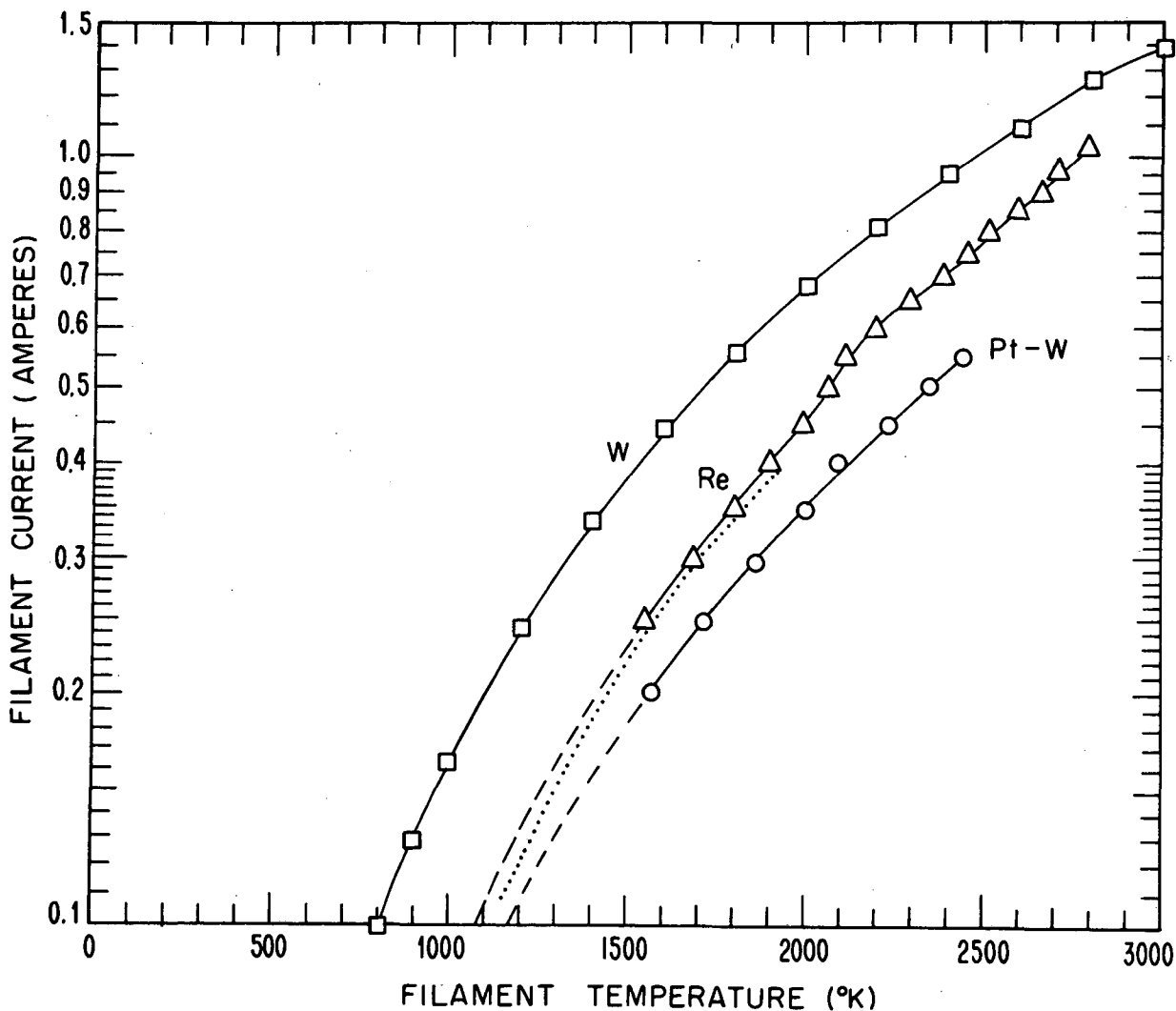
At the start of a run, the oven is loaded with the beam material and placed in the apparatus. The Rb is obtained sealed in glass vials and assayed for low impurity content from the American Potash and Chemical Company. The Na is from the United Mineral and Chemical Company, sealed in glass vials and free from oil. By measurements with a mass-filter detector (WIL 64b) this Na was shown after the first few minutes of heating to produce a beam with negligible contamination by other alkali metals, a frequent major source of error in Na surface ionization measurements (ZAN 59). The NaI is reagent grade from Baker and Adamson, and the LiI is anhydrous C.P. from A. D. Mackay. The NaI and LiI were also assayed with the massfilter detector and the content of other alkali metals was negligible.

Before surface ionization measurements can be made, the filaments must be aged for several hours in a good vacuum at a high temperature to clean them. The filaments are biased positive with respect to ground to drive off positive ions. The bias used for aging and for surface ionization measurements is 30 volts, chosen to be in the plateau region above the voltage necessary to drive the ions off the filaments and to suppress electron emission, but below the voltage where secondary



MUB-4803

Fig. 2. Emissivity corrections for tungsten, rhenium and platinum (HAN 58, SIM 55, FAR 39). The emissivity of the 92% platinum - 8% tungsten alloy is assumed to be the same as that of pure platinum.



MUB-4804

Fig. 3. True temperature versus heating current for 0.003 inch diameter filaments of tungsten, rhenium and 92% platinum - 8% tungsten alloy. For other diameter filaments, multiply current by

$$\left(\frac{\text{diameter in inches}}{0.003} \right)^{3/2}$$

The dotted line is the Pt-W calibration of Roberts (ROB 59).

electrons are emitted from ion bombardment of the collector.

The Rb, Na and NaI measurements were made with one set of filaments and the LiI run was made with another set. The first set of filaments was aged for 25 hours before the NaI run, with W at 2350°K, Re at 2100° and Pt-W at 2050°K. Then, before the Na run, the detector was washed with reagent grade CH₃OH to remove old beam material and the filaments were re-aged for 9 hours at the same temperatures. The filaments were again aged before the Rb run at the same temperatures, the W filament for 8 hours and the Re and Pt-W filaments for 2 hours.

The second set of filaments, used for the LiI measurements, was aged for 7 hours, with W at 2100°K, Re at 2000°K and Pt-W at 2000°K. The Re was then re-aged as given in Fig. 7.

The oven is slowly brought up to operating temperature over a period of several hours to remove any volatile impurities. The final oven temperature is chosen to give a beam flux of about 10^{12} molecules $\text{sec}^{-1} \text{cm}^{-2}$ at the detector. With the oven on and the liquid nitrogen in the trap the operating pressure is 1 to 3×10^{-7} torr (mm of Hg).

C. Data Normalization

All the data are corrected for drifts in beam intensity during the run by using the signal on the W filament at 2350°K which is recorded every few minutes.

The Rb data are normalized in terms of fraction ionized by reference to the theoretical predictions of the Saha-Langmuir equation for W and Re and to the experimental data of Datz and Taylor for Pt-W (DAT 56a). This normalization automatically corrects for the few percent error due to slight deviations from the nominal filament diameters and for slight variations in ion collection efficiency with filament position.

Using these corrections for the actual filaments used, the data for Na on W, Re, and Pt-W are expressed relative to each other. The absolute fraction ionized is then calculated by normalizing to the data for Na on W of Datz and Taylor (DAT 56a). Similarly, the corrections from the Rb run are used to express the data for NaI on W, Re, and Pt-W relative to one another and the absolute fraction ionized is calculated by normalizing to the data of Johnson and Phipps for NaI on W (JOH 39).

The LiI data are taken on a different set of filaments and so the above corrections for detector geometry cannot be made. Therefore there is an uncertainty of several percent in the relative fraction ionized values for the various filaments. There is also an uncertainty of perhaps $\pm 75^\circ\text{K}$ in the temperature calibrations which are made for wire from the same spool, but not for the identical piece of wire used. The tentative normalization in terms of fraction ionized is discussed in the next section.

IV. EXPERIMENTAL RESULTS AND INTERPRETATION

A. Theory

If atoms remain on a hot surface long enough to reach equilibrium and then evaporate, we expect from statistical mechanics that the ratio of atoms evaporating as singly charged positive ions to atoms evaporating as neutrals is given by the partition function, called the Saha-Langmuir equation

$$\alpha = \frac{n_+}{n_n} = \frac{\omega_+}{\omega_n} \exp\left(-\frac{\Delta}{kT}\right) \quad (1)$$

where n_+ is the number of atoms evaporating as singly charged positive ions per second, n_n is the number of atoms evaporating as neutral atoms

per second, ω_+ is the degeneracy of the ions, ω_n is the degeneracy of the neutrals and Δ is the energy difference between the state of ion plus surface and the state of neutral plus surface. This energy difference is

$$\Delta = I - \bar{\Phi} \quad (2)$$

where I is the first ionization potential of the atom (the energy lost in taking an electron away from the atom) and $\bar{\Phi}$ is the work function of the surface (the energy gained in supplying an electron to the surface).

The fraction ionized or the ratio of ions produced to atoms reaching the surface is then given by

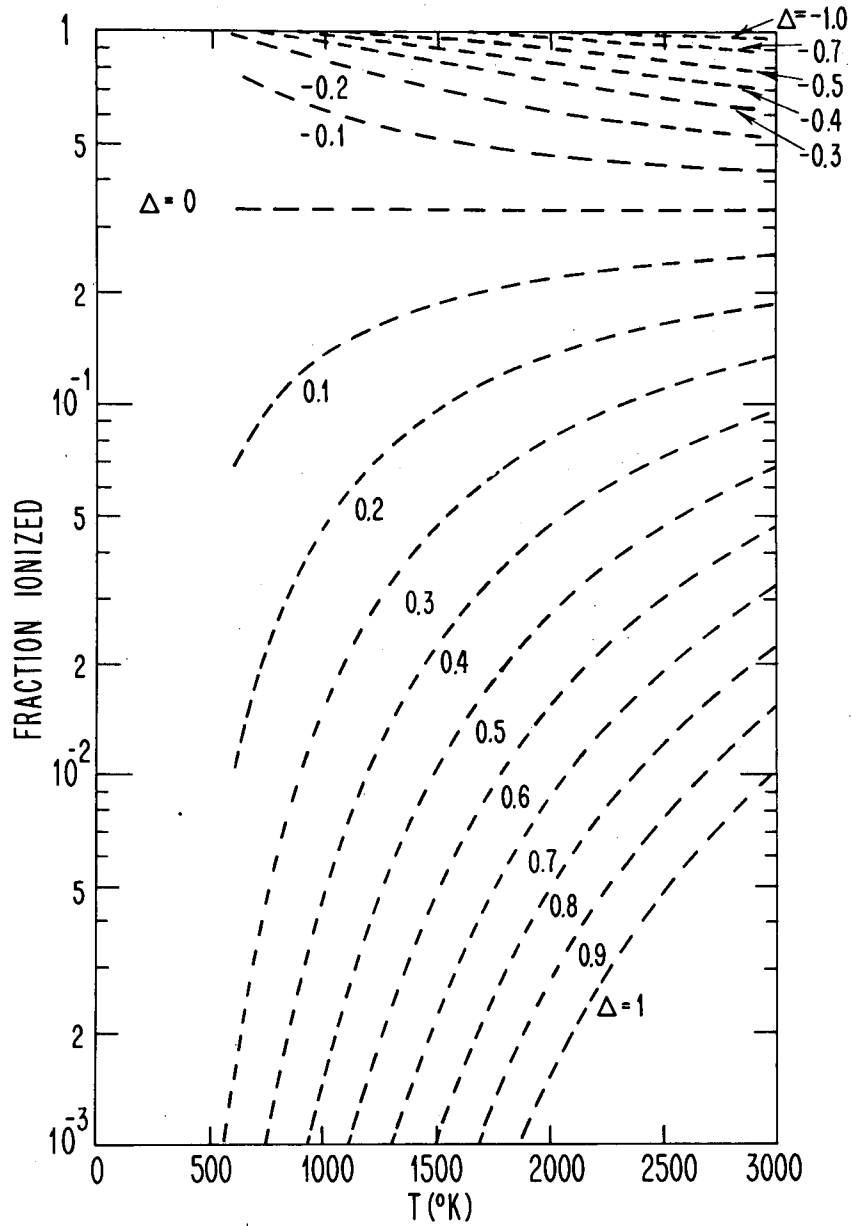
$$\beta = \frac{n_+}{n_+ + n_n} = \frac{\alpha}{\alpha + 1} = \left[1 + \frac{\omega_n}{\omega_+} \exp\left(\frac{\Delta}{kT}\right) \right]^{-1} \quad (3)$$

In Fig. 4 the fraction ionized, β , is graphed versus temperature, as a function of Δ , for alkali metal atoms for which $\omega_n/\omega_+ = 2$.

It has been found in the cases measured that to a first approximation the Saha-Langmuir equation is obeyed by atoms impinging on metal surfaces which are hot enough and clean enough to avoid chemical contamination (WER 58, ZAN 59, SCH 63).

The values of Δ for the alkali metals are given in Table I, using the following values of the work function $\bar{\Phi}$: W = 4.58 ev (WER 58), Re = 5.17 ev (WER 58), Pt-W = 5.30 ev (the average of many determinations given in the literature for Pt quoted in SCH 63). $\bar{\Phi}$ for Pt is given widely different values in the literature, probably because its low melting point makes cleaning the surface very difficult.

The ionization efficiency as a function of temperature can thus be estimated for any of the alkali metals by the use of Fig. 4 and Table I.



MUB-4805

Fig. 4. Fraction ionized versus temperature for the alkali metals from the Saha-Langmuir equation. $\Delta = I - \Phi$ in ev.

Table I

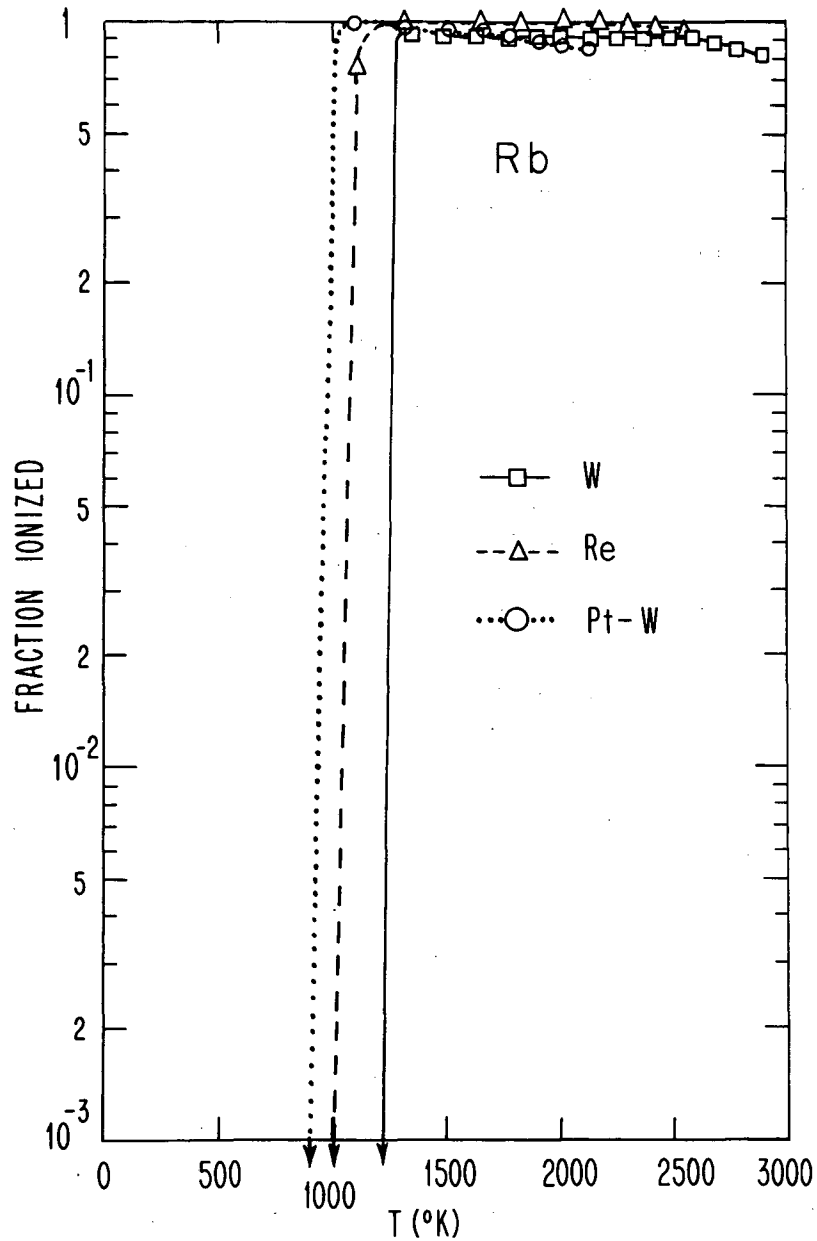
 Δ for the Alkali Metals (ev)

	Li	Na	K	Rb	Cs	0
W	+0.81	+0.56	-0.24	-0.40	-0.71	4.58
Re	+0.22	-0.03	-0.83	-0.99	-1.30	5.17
Pt-W	+0.09	-0.16	-0.96	-1.12	-1.43	5.30
I	5.39	5.14	4.34	4.18	3.87	

The difficulty in surface ionization of Li and Na, for which Δ is highly positive, is apparent from Fig. 4. Not only is the fraction ionized low, but any contamination of the surface which may alter the effective work function by a fraction of an electron volt will greatly affect the fraction ionized. Crossed molecular beam experiments with Na and Li beams have therefore been very difficult to perform.

B. Rb

The surface ionization data for Rb are shown in Fig. 5. The data were taken only to calibrate the detector, and as the ionization is nearly total over the temperature range the curves are not particularly interesting. Since we have normalized the curves to the fractional ionization expected from the Saha-Langmuir equation for W and Re, and to the experimental data of Datz and Taylor for Pt-W, only the variations of the slopes can provide new information. The slope of the Re curve is as expected from the Saha-Langmuir equation, but the W curve shows a small unexplained deviation from it. The slope of the Pt-W



MUB-4806

Fig. 5. Surface ionization of rubidium on tungsten, rhenium and 92% platinum - 8% tungsten filaments. The fraction ionized for tungsten and rhenium is normalized to the predictions of the Saha-Langmuir equation and for platinum-tungsten to the data of Datz and Taylor (DAT 56a).

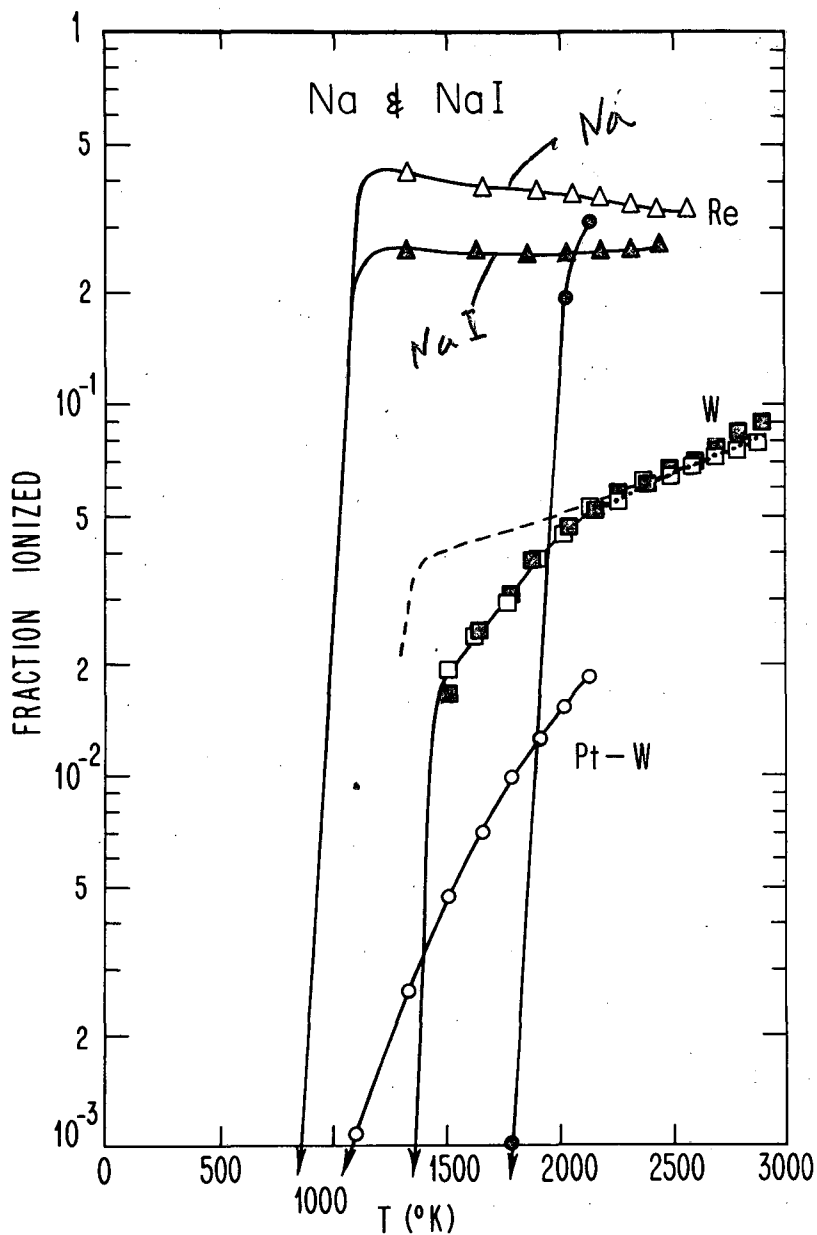
curve corresponds to $\Delta = -0.45$, approximately that found by Datz and Taylor (DAT 56a), instead of $\Delta = -1.12$ expected from Table I. Thus it appears as if the effective work function of the Pt-W is lowered. Touw and Trischka (TOU 63) found that if the surface of Pt-W is contaminated with hydrocarbons the effective work function as measured by the electron emission is lowered and that in this state of lowered work function the Pt-W does not detect alkali halides. Conversely, if the surface is oxygenated, the electron work function is raised and the Pt-W detects alkali halides. We have in later experiments found similar behavior in this laboratory, treating the Pt-W filament at 2000°K for several minutes with a pressure of 4×10^{-4} torr of methane or conversely of air (WIL 64a). Thus, perhaps the untreated Pt-W filaments used by Datz and Taylor and by us in the experiments described in this report were somewhat contaminated with hydrocarbons.

C. Na and NaI

The comparison of the Na and NaI curves shown in Fig. 6 demonstrates that differential detection may be used to distinguish between Na and NaI. At temperatures between 1400°K and 1800°K the Pt-W filament detects Na at least an order of magnitude more efficiently than NaI, while W and Re detect both with comparable efficiency over a wide temperature range.

The correspondence between the Na and NaI curves for both W and Re suggests a model in which the alkali halide dissociates on the surface and the fraction ionized is then determined mainly by the interaction of the atom with the metal surface, just as if the atom itself had been deposited by the molecular beam.

The curves for Na and NaI on W corresponds to $\Delta = 0.43$ instead of 0.56 given in Table I. The W thus acts in these cases as if the



MUB-4807

Fig. 6. Surface ionization of Na (open symbols) and NaI (solid symbols) on tungsten, rhenium and 92% platinum - 8% tungsten. The absolute fraction ionized is given by normalizing the Na data to the data of Datz and Taylor for Na on W (dotted curve) (DAT 56a) and by normalizing the NaI data to the data of Johnson and Phipps for the NaI on W (dashed curve) (JOH 39).

effective work function were higher than the usual value. This deviation is expected (ZAN 59) due to the polycrystalline nature of the W filament. A variety of crystal faces of different work functions are exposed on the filament surface. For instance the [111] direction has a work function of 4.49 ev and the [110] direction has a work function of 5.41 ev (REY 63). Those faces of higher work function contribute the dominant part of the ions for atoms with high ionization potential and give therefore a higher effective work function.

The Na on Re curve is close to that expected from the tabulated value of $\Delta = -0.03$, and the NaI on Re curve appears as if in this case the effective work function were about a tenth of an electron volt higher.

The Na on Pt-W curve corresponds to a value of $\Delta = +0.60$ instead of the value of -0.16 from Table I, i.e., the apparent work function is lower than the nominal value. This apparent low work function for Na on Pt-W has been consistently observed in this laboratory during the course of crossed molecular beam studies of chemical reactions. This behavior we have observed contrasts strongly to that observed by Datz and Taylor, who found that Na was detected on Pt-W with unusually high efficiency compared to the rest of the alkali metals, in fact higher than K on Pt-W (DAT 56a). This discrepancy is another example of the lack of consistency often found in surface ionization experiments with platinum, due probably to the difficulty in obtaining a clean surface.

D. Li and LiI

As is shown in Fig. 6, the surface ionization of Na and NaI on W is almost identical. A similar correspondence between the ionization of potassium and the potassium halides on W was found by Datz and Taylor

(DAT 56a, DAT 56b). In Fig. 7 we have presented the data of Datz and Taylor for Li on W and Pt-W and have normalized our data for Li on W, Re, and Pt-W to them by assuming that LiI also surface ionizes similarly to Li on W.

On the basis of this assumption or any other reasonable assumption, we see that differential detection may also be used with the Li and LiI system, with a Pt-W temperature in the range of 1700°K to 2100°K.

The Δ for W is 0.65 instead of the tabulated 0.81, which as with Na may be explained in terms of a "patchy" polycrystalline surface of differing work functions leading to a higher effective work function.

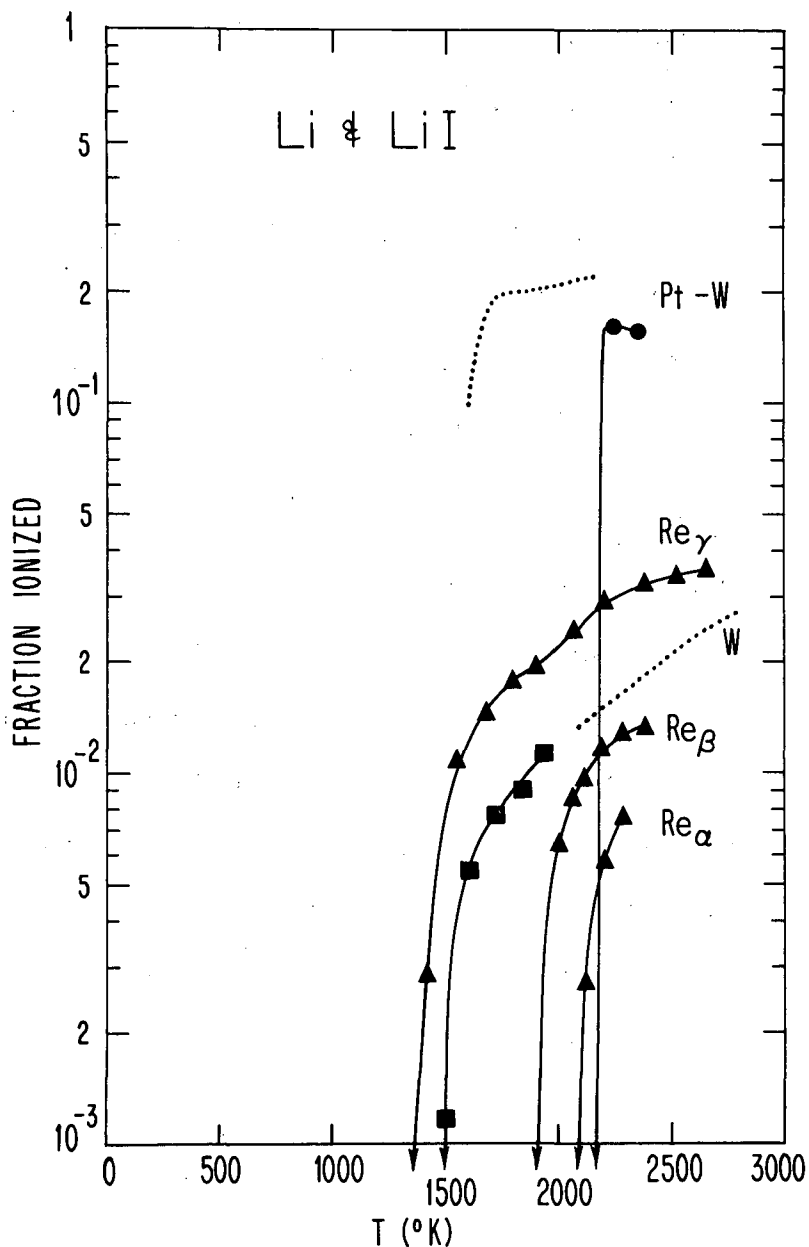
E. Contamination

The variation of the curves for Re as a function of aging temperature illustrates the great difficulty and the great importance of obtaining clean surfaces or at least reproducibly dirty surfaces especially when working with substances which ionize with difficulty.

Similar variations in surface ionization properties with aging have been observed in other systems, including Na and NaI on Re. In fact, one can differentially distinguish between Na and NaI by using first a Re filament that has not yet been cleaning by prolonged aging and which ionizes only the Na and then aging the filament quickly at a high temperature, whereupon it ionizes both Na and NaI.

Thus it seems likely that the property of differential detection may be due to contamination of the surface. Contamination is particularly severe with Pt-W, in part because it cannot be aged as hot as W and Re.

An interesting test of this hypothesis would be to try the controlled contamination technique of Touw and Trischka (TOU 63) with W



MUB-4808

Fig. 7. Surface ionization of Li (dotted curves) from Datz and Taylor (DAT 56a) and our data for LiI (solid symbols) on tungsten, rhenium and 92% platinum - 8% tungsten. The absolute fraction ionized for LiI is merely plausible on the basis of the Li data.

Re_α : Aged 7 hours at 2000°K.

Re_β : Aged in addition for several minutes at 2450°K.

Re_γ : Aged in addition for several minutes at 2750°K.

and Re filaments to see if they could be made, like Pt-W, to reversibly change from a state in which the alkali halides are ionized to one in which such ionization does not occur.

The surface ionization of LiI and NaI was also checked with a mass spectrometer behind the Re and Pt-W filaments (WIL 64b). Only the alkali metal ions and no alkali halide ions were observed, confirming earlier measurements (TOU 40, ION 48).

V. CONCLUSIONS

Differential surface ionization has been shown to distinguish between Na and NaI and between Li and LiI. It is likely that differential surface ionization can generally distinguish between the alkali metals and their corresponding halides and that the inefficient ionization of alkali halides on Pt-W is due to surface contamination. Properly aged Re has considerably higher ionization efficiency than W for Na, NaI and LiI, and therefore can be used to advantage in place of W.

Acknowledgments

The authors wish to thank David Ham who helped set up the Test Stand and who performed a number of important preliminary experiments. This work was done under the auspices of the United States Atomic Energy Commission. Fellowship support from the National Science Foundation is gratefully acknowledged by K. R. W.

REFERENCES

- BOL 64 P. V. Bollerman, Pyrometer Instrument Co., private communication.
- COP 35 M. J. Copley and T. E. Phillips, *J. Chem. Phys.*, 3, 594 (1935).
- DAT 56a S. Datz and E. H. Taylor, *J. Chem. Phys.* 25, 389 (1956).
- DAT 56b S. Datz and E. H. Taylor, *J. Chem. Phys.* 25, 395 (1956).
- DAT 64 S. Datz and R. E. Minturn, *J. Chem. Phys.* 41, 1153 (1964).
- FAR 39 A. Farkas and H. W. Melville, Experimental Methods in Gas Reactions (Macmillan and Company, London, 1939), p. 112.
- HAN 58 Handbook of Chemistry and Physics, C. D. Hodgman, editor, Fortieth Edition (Chemical Rubber Publishing Company, Cleveland, 1958), p. 2955. (Data from Roeser and Wensel, National Bureau of Standards).
- HEN 37 J. O. Hendricks, T. E. Phipps, and M. J. Copley, *J. Chem. Phys.* 5, 868 (1937).
- HER 61a D. Herschbach, "Chemical Reactions in Crossed Molecular Beams", *The Vortex* 22, 348 (1961).
- HER 61b D. R. Herschbach, G. H. Kwei, and J. A. Norris, *J. Chem. Phys.* 34, 1842 (1961).
- HER 62 D. R. Herschbach, *Discussions Faraday Soc.* 33, 149 (1962).
- HER 64 R. R. Herm, R. Gordon and D. R. Herschbach, *J. Chem. Phys.*, in press.
- ION 48 N. I. Ionov, *Zh. Eksperim. i Teor. Fiz.* 18, 174 (1948).
- IVE 23 H. E. Ives, *Phys. Rev.* 21, 385 (1923).
- JOH 39 A. A. Johnson and T. E. Phipps, *J. Chem. Phys.* 7, 1039 (1939).
- JON 27 H. A. Jones and I. Langmuir, *Gen. Elec. Rev.* 30, 310 (1927).
- KIN 23 K. H. Kingdon and I. Langmuir, *Phys. Rev.* 21, 380 (1923).
- KIN 61a J. L. Kinsey, G. H. Kwei, and D. R. Herschbach, *Bull. Am. Phys. Soc.* 6, 152 (1961).
- KIN 61b J. L. Kinsey, private communication.

- KWE 60 G. H. Kwei, J. A. Norris, and D. R. Herschbach, Bull. Am. Phys. Soc. 5, 503 (1960).
- KWE 61 G. H. Kwei, J. A. Norris, J. L. Kinsey, and D. R. Herschbach, 2nd International Conference on the Physics of Electronic and Atomic Collisions (W. A. Benjamin, Inc., New York, 1961), p. 98.
- KWE 64 G. H. Kwei, Ph.D. Thesis, University of California, Berkeley, 1964.
- NOR 61 J. A. Norris, G. H. Kwei, J. L. Kinsey, and D. R. Herschbach, Bull. Am. Phys. Soc. 6, 339 (1961).
- NOR 63 J. A. Norris, "Chemical Reactions in Crossed Molecular Beams", (Ph.D. Thesis) University of California Radiation Laboratory Report, UCRL-10848, June 27, 1963.
- REY 63 F. L. Reynolds, J. Chem. Phys. 39, 1107 (1963).
- ROB 59 R. W. Roberts, "The Scattering of a Potassium Atomic Beam by a Crossed Beam of Bromine Molecules", Ph.D. Thesis, Brown University, July 1959.
- ROD 32 W. H. Rodebush and W. F. Henry, Phys. Rev. 39, 386 (1932).
- SCH 63 W. Schroen, Z. Physik 176, 237 (1963). The value of $\bar{\Phi}$ used for Pt-W is the value Schroen gives as an average of many determinations given in the literature for Pt.
- SIM 55 C. T. Sims, C. M. Craighead and R. I. Jaffee, J. Metals 7, 168 (1955).
- STA 38 S. V. Starodubtsev, Dissertation, Leningrad, 1938.
- STA 48 S. V. Starodubtsev, Tr. Fiz.-Tekhn. Inst. Akad. Nauk Uz. SSR I, 5 (1948).
- TOU 40 B. Toubes and G. K. Rollefson, J. Chem. Phys. 8, 495 (1940).
- TOU 63 T. R. Touw and J. W. Trischka, J. Appl. Phys. 34, 3635 (1963).
- WER 58 J. R. Werning, "Thermal Ionization at Hot Metal Surfaces", (Ph.D. Thesis) University of California Radiation Laboratory Report UCRL-8455, September 1958.
- WIL 62 K. R. Wilson and D. R. Herschbach, Bull. Am. Phys. Soc. 7, 497 (1962).
- WIL 64a K. R. Wilson, G. H. Kwei, J. A. Norris, R. R. Herm, J. H. Bireley, and D. R. Herschbach, J. Chem. Phys. 41, 1154 (1964).

- WIL 64b K. R. Wilson, "Apparatus for Molecular Beam Studies of Chemical Dynamics", University of California Radiation Laboratory Report UCRL-11605, August 15, 1964.
- WIL 64d K. R. Wilson, "Molecular Beam Studies of Chemical Dynamics", Ph.D. Thesis, University of California, Berkeley, November, 1964.
- WIL 64e K. R. Wilson and D. R. Herschbach, to be published.
- ZAN 59 E. Ya. Zandberg and N. I. Ionov, Usp. Fiz. Nauk 67, 581 (1959).
- ZIM 44 Bruno H. Zimm and Joseph E. Mayer, J. Chem. Phys. 12, 362 (1944).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

