Positive and Negative Ion Sublimation from Transition Metal Surfaces: A Review of Some Recent Results

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Singly charged, positive and negative, atomic ions have been observed to sublime freely from $4d$ and $5d$ transition metal surfaces in the 1800 to 2600 K temperature range. The rates of sublimation were found to be about equal to those which would be observed under conditions of thermal equilibrium. Ion sublimation energies were obtained from the temperature dependence of these sublimation rates. The energies were found to be consistent with currently accepted values for the atom sublimation energy, electron work function, and first ionization potentials of the elements investigated.

The electron affinities of these metal atoms were determined from an isothermal measurement of the ratio of positive to negative ion sublimation rates. The results were compared with some recent theoretical estimates of this quantity for those $3d$ transition metals whose valence electron configurations are analogous to the $4d$ and $5d$ elements considered here.

Key words: Mass spectrometry; positive and negative ions; sublimation; transition metals.

An atomically clean metal surface may be characterized by the energies associated with the sublimation processes:

(1) $e_s \rightarrow e_g$; ϕ, the electron work function

(2) $M_s \rightarrow M_g$; l_0, the atom sublimation energy

(3) $M_s - e_s \rightarrow M_g^+$; l_+, the positive ion sublimation energy

(4) $M_s + e_s \rightarrow M_g^-$; l_-, the negative ion sublimation energy.
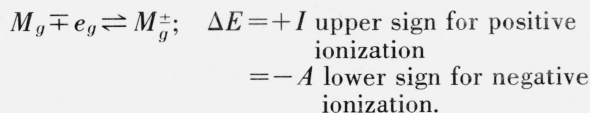
At temperatures less than about $\frac{2}{3}$ of the melting point, the energies associated with these processes may be strongly influenced by the geometric arrangement of the surface atoms. The observed difference in work function between different crystalline faces is an example of such anisotropic behavior. At high temperatures the geometric structure and symmetry characteristics of the surface become less important as a result of rapid surface migration and large sublimation rates. In fact, in the neighborhood of the melting point the surface can be thought of as a two-dimensional liquid whose properties tend to be uniform in contrast to the considerable anisotropy exhibited at lower temperatures.

Process (3) has been observed for a number of refractory transition metals [1–8, 10].[1] Early attempts at a reliable measurement of l_+ were limited by primi-

tive vacuum conditions and the presence of easily ionized alkali atom impurities. Process (4) can be observed when $A(M)$, the electron affinity of M, is positive (M_g^- is stable). It has been reported for graphite, tungsten, rhenium, molybdenum, and tantalum [7, 8, 9, 10].

1. A Generalized Saha-Langmuir Equation

Consider the thermodynamic equilibrium existing inside of an isothermal metal enclosure. In addition to blackbody photons, the stable gaseous species are electrons e_g, metal atoms M_g, singly charged positive ions M_g^+, and singly charged negative ions M_g^- when the electron affinity of the atom is positive. If the number density of charged particles is sufficiently small so that space-charge effects may be neglected, then the partial pressures (p_x) are governed by the following equilibria:

$$M_g \mp e_g \rightleftharpoons M_g^{\pm}; \quad \Delta E = +I \text{ upper sign for positive ionization}$$
$$= -A \text{ lower sign for negative ionization.}$$

The quantity ΔE is the energy (or free-energy) change for these ionization processes at absolute zero. The equilibrium constants are given by

$$(p_{\pm}/p_0)(p_e)^{\pm 1} = (Q_{\pm}/Q_0)(Q_e)^{\pm 1} \exp(-\Delta E/kT). \quad (1)$$

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

The Q's are the molar partition functions for these gaseous species which are assumed to be in thermal equilibrium with the walls of the enclosure. The partial pressure of electrons (p_e) is given by the well-known Richardson equation:

$$p_e = Q_e \exp\left(-\phi/kT\right) \qquad (2)$$

The electronic work function ϕ is defined as the free-energy change at 0 K for electron sublimation. Substituting eq (2) into (1) yields the result that

$$(p_\pm/p_0) = (Q_\pm/Q_0) \exp\left[(-\Delta E \pm \phi)/kT\right]. \qquad (3)$$

The flux (j) of particles evaporating from (or condensing upon) the walls of the enclosure is given by

$$j = \alpha p / (2\pi mkT)^{1/2} \qquad (4)$$

where α is the evaporation (or condensation) coefficient and p is the equilibrium vapor pressure. Since the masses (m) of the atomic ions and atoms are very nearly equal and, *assuming* that the *evaporation coefficients* for *ions* and *atoms* are also *equal*, the ratio of sublimation rates obtained from eqs (3) and (4) is

$$j_\pm/j_0 = (Q_\pm/Q_0) \exp\left[(-\Delta E \pm \phi)/kT\right]. \qquad (5)$$

For the atomic and ionic species under consideration, the ratio of molar partition functions is equal to the ratio of electronic partition functions:

$$(Q_\pm/Q_0) = (\omega_\pm/\omega_0),$$

since the translational factors cancel because of the equality of the particle masses. When Russel-Saunders spin-orbit coupling is obeyed, the electronic partition function can be written as

$$\omega = \sum_n g_n \exp\left(-\epsilon_n/kT\right) \qquad (6)$$

where $\epsilon_0 = 0$ and $g_n = 2J_n + 1$. The quantity g_n is the statistical weight of the level of energy ϵ_n, and J_n the inner quantum number of the electronic state n. The summation need only be carried out for those states which are significantly populated at the temperature T. Under the condition of thermal equilibrium on the metal surface, eq (5) yields a result for the sublimation ratio of singly charged positive ions to neutral atoms which may be recognized as the familiar Saha-Langmuir equation [11]; namely,

$$j_+/j_0 = (\omega_+/\omega_0) \exp\left[(\phi-I)/kT\right]. \qquad (7)$$

Similarly, when negative self-surface ionization is considered, eq (5) yields the ratio of subliming negative ions to atoms:

$$j_-/j_0 = (\omega_-/\omega_0) \exp\left[(A-\phi)/kT\right]. \qquad (8)$$

The ratio of positive to negative self-surface ionization, obtained from eqs (7) and (8), is

$$j_+/j_- = (\omega_+/\omega_-) \exp\left[(2\phi-I-A)/kT\right]. \qquad (9)$$

The atomic properties I and A can be shown to be related to the sublimation energies ϕ, l_0, l_+, and l_- from a consideration of the cycles given in figure 1; namely, that

$$\phi - I = l_0 - l_+, \qquad (10)$$

$$A - \phi = l_0 - l_-, \qquad (11)$$

and

$$2\phi - I - A = l_- - l_+ = l_0 + \phi - A - l_+. \qquad (12)$$

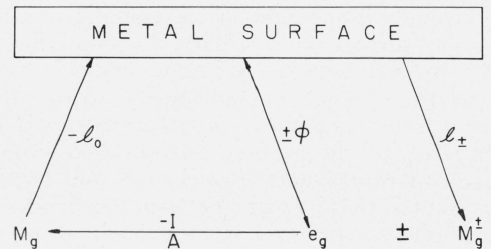The equilibrium vapor pressure of metal atoms (p_0) is given by

$$p_0 = \exp\left[(\Delta S/k) - (l_0/kT)\right], \qquad (13)$$

where ΔS and l_0 are the atom sublimation entropy and energy at some temperature T. Substituting eq (13) into (3), one obtains for the sublimation pressure of positive and negative ions:

$$p_\pm\left[\frac{Q_0}{Q_\pm} \exp\left(\frac{-\Delta S}{k}\right)\right] = \exp\left(\frac{-\Delta E \pm \phi - l_0}{kT}\right). \qquad (14)$$

Using eq (4) and collecting terms, the dependence of the rates of positive- and negative-ion sublimation upon temperature is given by

$$j_+\left[T^{1/2}\left(\frac{\omega_0}{\omega_+}\right)\exp\left(-\frac{\Delta S}{k}\right)\right]$$

$$= \frac{\alpha_+}{(2\pi mk)^{1/2}}\exp\left(\frac{\phi-I-l_0}{kT}\right) \qquad (15a)$$

PSI: $\quad l_+ + \phi - I - l_0 = 0$

NSI: $\quad l_- - \phi + A - l_0 = 0$

FIGURE 1. *Thermal cycles for positive and negative self-surface ionization.*

and

$$j_- \left[T^{1/2} \left(\frac{\omega_0}{\omega_-} \right) \exp \left(-\frac{\Delta S}{k} \right) \right]$$

$$= \frac{\alpha_-}{(2\pi mk)^{1/2}} \exp \left(\frac{A - \phi - l_0}{kT} \right), \qquad (15b)$$

where from eqs (10) and (11) it is seen that $\phi - I - l_0 = -l_+$ and $A - \phi - l_0 = -l_-$. The l's are sublimation energies at some mean temperature T in the middle of an experimental temperature range, and, like ϕ, I, and A, remain virtually unchanged from their values at absolute zero.

2. Apparatus

The apparatus used in these studies consisted of a direction-focusing mass spectrometer. The surface ionization source of the mass analyzer was designed to facilitate the collection of negative ions, which evaporate in observable quantities only at surface temperatures at which electron emission is intense. A cylindrical modification of a Pierce lens [12] was used to collect the charged particles evaporating from the experimental surfaces. When the apparatus was biased for the detection of negative charges, the large electron flux focused by the lens was deflected by a small magnetic field and collected on a molybdenum plate. Because of space limitations in the ion source, the lens design was limited to the efficient collection of only about 2 mA of electron emission. At surface temperatures in excess of that which yields this value of the saturation electron current, a negative space charge begins to accumulate and the collection efficiency for negative ions decreases. This problem is not encountered in the case of positive ion sublimation so that meaningful measurements at a constant ion collection efficiency can be made at higher surface temperatures and larger positive ion currents.

Both the positive and negative ions were accelerated by the components of the Pierce lens to an energy of 4 kV prior to their traversal through the entrance slit of the 15-cm radius, 60° sector, magnetic analyzer. The first dynode of a 16-stage Cu-Be electron multiplier detector was maintained at ground potential, so that both positive and negative mass analyzed ions were collected with 4 kV of energy. The multiplier was operated with 190 V between stages so that the sixteenth dynode was at +3040 V for both positive- and negative-ion detection. The output pulses were 20 to 30 ns. wide and were amplified with a voltage gain of 5000. The resultant pulse-height distribution was found to be about the same for both positive and negative ions. Thus, the secondary electron yields for 4 kV positive and negative ions impacting on the first dynode surface do not appear to exhibit any significant charge discrimination. This is of particular importance for the determination of the ratio of positive to negative ion sublimation rates. The amplified pulses were then processed to give uniform 1-V, 50-ns pulses which actuated a counter with a 10-MHz bandpass. The background count for

this instrument was usually less than 10 pulses/minute with the magnetic analyzer detuned and the experimental surface temperature well below 1800 K.

3. Experimental Results

The temperature dependence of the rates of sublimation of singly charged positive and negative ions of tungsten, rhenium, molybdenum, and tantalum are shown in figures 2, 3, and 4. Figure 5 gives the results of some measurements of the rate of positive ion sublimation from a niobium surface. The quantity $j_\pm$ (corrected) is the experimental ion count corrected for the slightly temperature dependent factor

$$[T^{1/2}(\omega_0/\omega_\pm) \exp (-\Delta S/k)]$$

given on the lefthand side of eqs (15a) and (15b). The values obtained for this factor were normalized in the middle of each experimental temperature range. The values for ΔS were obtained from the compilation of Stull and Sinke [13]. The ω_0 and ω_+ were calculated from eq (6) using Moore's energy level compilation [14]. For the negative ion electronic partition function ω_-, only one bound state was assumed with a J_0 value equal to that of the ground state of the atom with the next highest atomic number. This assumption appears to be reasonable since virtually all of the negative ions which have been observed so far exhibit this property [15]. The evaporation coefficients $(\alpha_\pm)$ were assumed to be temperature independent with values of unity.

Table 1 gives a summary of the sublimation energies, obtained in this laboratory, for the positive ions of a number of transition metals [5, 7, 8, 10] of rows 4 and 5 of the periodic table. The agreement between the l_+ calculated from eq (10) and the experimental values
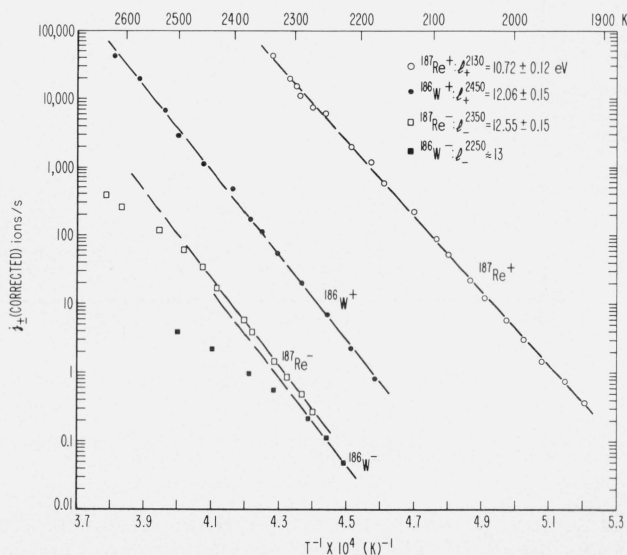

FIGURE 2. *Positive and negative self-surface ionization of tungsten and rhenium.*

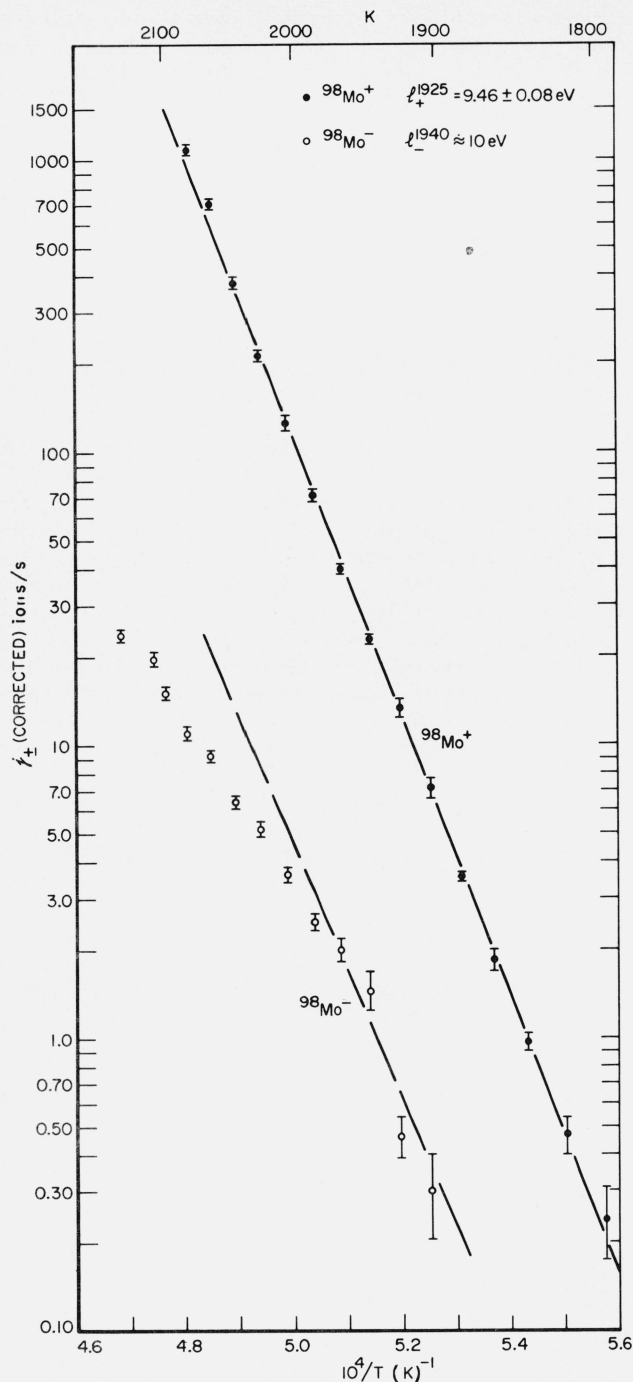The uncertainties in the sublimation energies are the standard errors in the slopes of the lines.

FIGURE 3. *Positive and negative self-surface ionization of molybdenum.*

The error bars represent the range of values obtained in at least ten determinations. The uncertainty in the sublimation energy is the standard error in the slope.

is seen to be within the estimated uncertainties. The quantities l_0, I, and ϕ for these metals were obtained from recent compilations [10, 13, 14, 16]. The intercepts of all of the experimental lines given in figures 2 to 5, divided by the subliming surface areas, fall within a factor of three of a value 5×10^{28} cm^{-2} sec^{-1}. This is
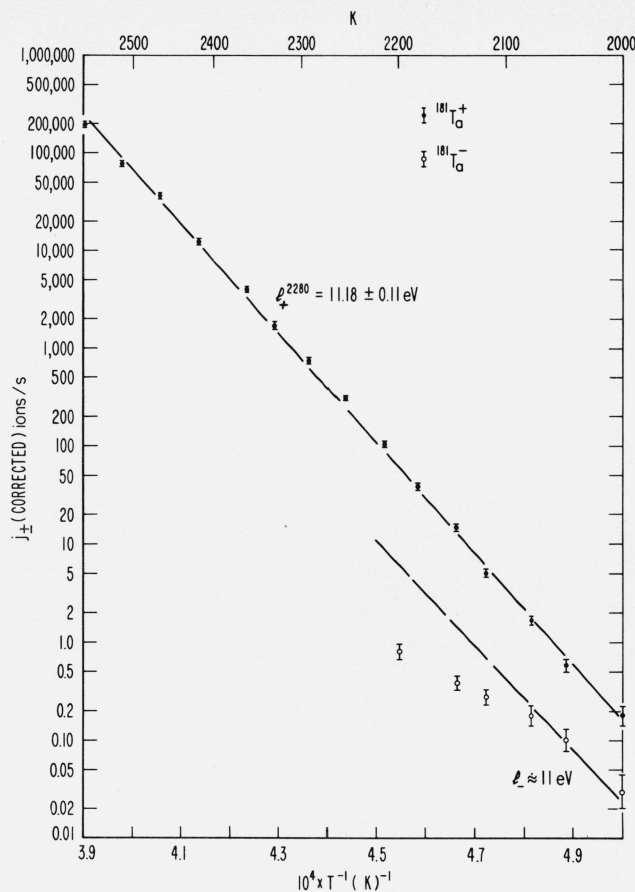
FIGURE 4. *Positive and negative ion sublimation from a tantalum surface.*

The error bars represent the range of values obtained in at least ten determinations. The uncertainty in the sublimation energy is the standard error in the slope.

consistent with a maximum limiting sublimation rate of one monolayer ($\sim 10^{15}$ cm^{-2}) per lattice vibration time ($\sim 10^{-14}$ s). It can therefore be concluded that a relatively large fraction of the evaporating ions was focused by the Pierce lens into the mass analyzer and ultimately detected by the electron multiplier. This result, together with the demonstrated validity of the thermal cycle eq (10), supports the conclusion that the observed free sublimation rates are approximately equal to those which would be observed in a closed

TABLE 1. *Positive ion sublimation energies*

Ion	T	[a]$l_{+(obs.)}$	[b]$(l_0 + I - \phi)$
	(K)	(eV)	(eV)
^{93}Nb$^+$	2100	10.4	$7.5 + 6.8 - 3.9 = 10.5$
^{98}Mo$^+$	1925	9.5	$6.7 + 7.1 - 4.3 = 9.5$
^{181}Ta$^+$	2280	11.2	$7.9 + 7.9 - 4.1 = 11.7$
^{186}W$^+$	2450	12.1	$8.9 + 8.0 - 4.5 = 12.4$
^{187}Re$^+$	2130	10.7	$7.8 + 7.9 - 5.0 = 10.7$

[a] Typical standard errors in the least square determination of l_+ are between 0.1 and 0.2 eV.

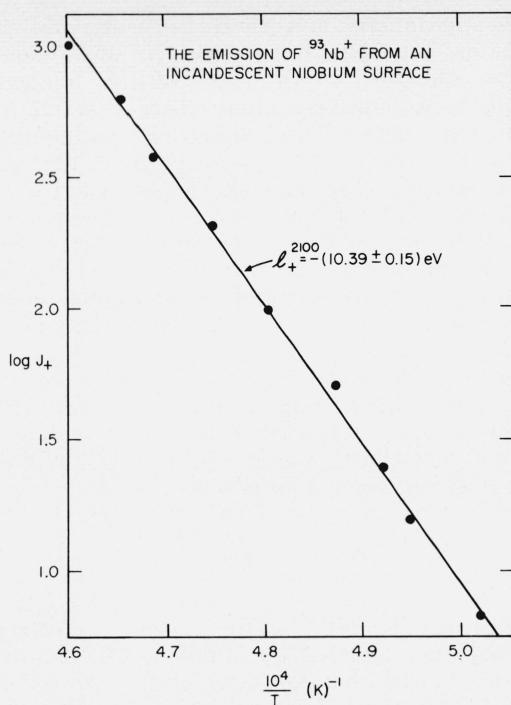[b] Uncertainties in l_0, I and ϕ are each about 0.1 eV.

FIGURE 5. *The sublimation of* $^{93}Nb^+$ *from a heated niobium surface.*

The uncertainty in the sublimation energy is the standard error in the slope of the line.

THE EMISSION OF $^{93}Nb^+$ FROM AN INCANDESCENT NIOBIUM SURFACE

$l_+^{2100} = (10.39 \pm 0.15)$ eV

TABLE 2. *Isothermal positive to negative ion ratios obtained for the self-surface ionization of molybdenum, tantalium, tungsten, and rhenium.*

The errors given for j_+ and j_- are average deviations from an arithmetic mean of at least six successive ion counts.

Ion	T	j_+	j_-	$kT \ln [\omega_- j_+/\omega_+ j_-]$
	(K)	*(ions/sec)*	*(ions/sec)*	*(eV)*
^{98}Mo	1903	7.4 ± 0.4	0.30 ± 0.12	0.53 ± 0.07
	1924	13.3 ± 0.6	0.45 ± 0.08	0.56 ± 0.03
	1945	22.3 ± 0.5	1.40 ± 0.20	0.46 ± 0.02
	1965	37.5 ± 0.4	1.87 ± 0.13	0.51 ± 0.01
	1985	66.8 ± 1.5	2.30 ± 0.15	0.58 ± 0.01
				0.53 ± 0.03 eV
^{181}Ta	2000	0.18 ± 0.04	0.03 ± 0.01	-0.04 ± 0.08
	2047	0.58 ± 0.10	0.10 ± 0.03	-0.06 ± 0.06
	2077	1.67 ± 0.13	0.18 ± 0.05	$+0.02 \pm 0.06$
				-0.03 ± 0.07 eV
^{186}W	2225	3.0 ± 0.2	0.07 ± 0.03	0.76 ± 0.08
	2250	6.6 ± 0.2	0.18 ± 0.03	0.74 ± 0.04
	2280	12.6 ± 0.2	0.30 ± 0.06	0.77 ± 0.04
				0.76 ± 0.05 eV
^{187}Re	2272	$7,210 \pm 40$	0.32 ± 0.05	2.01 ± 0.03
	2290	$11,020 \pm 60$	0.49 ± 0.04	2.02 ± 0.02
	2314	$18,650 \pm 100$	0.84 ± 0.08	2.04 ± 0.02
	2333	$30,730 \pm 120$	1.40 ± 0.15	2.06 ± 0.02
				2.03 ± 0.02 eV

system in thermal equilibrium with vaporization coefficients ($\alpha_\pm$) not very different from unity.

The ratio of positive to negative self-surface ionization could be reliably measured only over a rather limited temperature range. This is seen in figures 2 to 4, where the lowest temperature was determined by the smallest negative ion sublimation rate detectable with the present apparatus (5 to 20 ions/minute). The upper temperature was limited by an electron emission which was sufficient to saturate the Pierce lens. This resulted in a negative space charge buildup with a consequent lowering of the negative ion collection efficiency. It is seen that this limiting temperature was about 2100 K for the low work function metals, tantalum and molybdenum, while the higher work functions of tungsten and rhenium allowed efficient negative ion collection up to temperatures of 2300 and 2500 K, respectively.

The results obtained for these positive to negative ion ratios are given in table 2. The quantities j_+ and j_- are the actual ion count rates observed at each of the experimental temperatures. The partition function ratios (ω_-/ω_+) were calculated in the manner described above. The quantity $kT \ln [(\omega_-/\omega_+)(j_+/j_-)]$, given in the last column, is equal to $(2\phi - I - A)$ or $(\phi + l_0 - l_+ - A)$ according to eqs (9) and (12). Solving (9), (10), (11), and (12) for A, the electron affinity, yields

$$A = \phi + l_0 - l_- = \phi + l_0 - l_+ - kT \ln \left[\frac{\omega_- j_+}{\omega_+ j_-} \right]. \quad (16)$$

Table 3 gives the electron affinities for the four transition metals. They were calculated using eq (16). A reliable value for l_- could be obtained from eq (15b) only in the case of rhenium, as shown in figure 2. Consequently, it was possible to make two independent estimates of its electron affinity. It is seen that, despite the small absolute value of $A(\text{Re})$, the agreement between the two estimates is good and considerable confidence in the stability of Re^- is gained.

TABLE 3. *The electron affinities of Mo, Ta, W, and Re as calculated from eq (16).*

	$\phi + l_0 - l_+ - kT \ln [\omega_- j_+/\omega_+ j_-]$	$(\phi + l_0 - l_-)$
	eV	*(eV)*
$A(\text{Mo})$:	$4.3 + 6.7 - 9.5 - 0.5 = 1.0$	....
$A(\text{Ta})$:	$4.1 + 7.9 - 11.2 + 0.03 = 0.8$	....
$A(\text{W})$:	$4.5 + 8.9 - 12.1 - 0.8 = 0.5$	....
$A(\text{Re})$:	$5.0 + 7.8 - 10.7 - 2.0 = 0.1$	$5.0 + 7.8 - 12.6 = 0.2$

4. Conclusions

It has been shown that at temperatures in excess of about 1800 K the sublimation of singly charged, positive and negative ions from refractory metal surfaces are in accordance with the thermal cycle eqs (10) and (11). The measured quantities l_+, l_-, and A are consistent with the currently accepted values for

l_0, ϕ, and I. Under the high-temperature conditions of these measurements, no evidence for surface anisotropy was observed.

A detailed review of atomic negative ions has been given recently by Smirnov [17]. He summarized both the experimental and theoretical electron affinity estimates that have been made for the elements of rows, 2, 3, and 4 and columns 1 and 6 of the periodic table. The experimental results given here are the first determinations of the electron affinities of the transition elements in rows 5 and 6. The method described should be applicable to all of those refractory metals whose atoms can form stable negative ions.

Clementi [18] has made a set of Hartree-Fock calculations for the 4th-row transition elements. From these calculations he was able to make correlation energy corrections to the 4th-row negative ion energies and hence obtained estimates of the electron affinities. Table 4 shows a comparison between these theoretical estimates and the self-surface ionization values determined in this laboratory for the 5th- and 6th-row transition metals. The value for niobium was estimated on the basis of approximate negative ion yields. Because of its low work function [5] (~ 3.9 eV), copious electron emission made it impossible to obtain accurate positive to negative ion ratios with the present instrument. Molybdenum and chromium as well as tantalum and vanadium have analogous valence elec-

tron configurations and there is remarkably good agreement between the theoretical and measured electron affinities. In the case of the manganese-rhenium pair, however, where there is a full s and half-filled d shell in their ground-state configurations, there is disagreement. Clementi predicts that such a valence electron structure should *not* yield a stable negative ion. In fact, his calculation gives a value of -1.1 eV for $A(\text{Mn})$. The negative self-surface ionization of rhenium has shown however, that the $5d^5 6s^2$ structure is indeed capable of producing a stable rhenium negative ion with a binding energy of about 0.15 eV.

A number of years ago, Gordy and Thomas [19] found that a linear relationship exists between the electronegativity and work function of metals. This empirical fact can be understood in terms of eqs (10) and (11), since elimination of l_0 yields

$$\phi = \frac{I+A}{2} + \frac{l_- - l_+}{2}. \qquad (17)$$

The quantity $(I+A)/2$ is the absolute electronegativity (X_m) first defined by Mulliken [20]. Gordy and Thomas showed that for most of the metals in the periodic table the following relation was obeyed:

$$\phi = 2.3 X_p + 0.34, \qquad (18)$$

where the quantity X_p is the electronegativity given by Pauling [21]. Skinner and Pritchard [22] have shown that $X_m = 3.1\, X_p$ so that (18) may be written in terms of X_m as follows:

$$\phi = 0.74\, X_m + 0.34. \qquad (19)$$

Comparing this result with eq (17) shows that, while the linear dependence of ϕ on X_m is predicted, the empirically determined coefficient is not quite unity as required by eq (17). However, detailed examination of the Gordy-Thomas correlation shows that a 25 percent increase in the coefficient of X_m would not do much of an injustice to the data which they used. In any case, the results of the present work strongly suggests the general applicability of eq (17) rather than its empirical counterpart, eq (19). It should be pointed out that the "constant" term in eq (19) is really given by $(l_- - l_+)/2$, which from eq (16) is seen to be equal to $kT/2 \ln [\omega_-/j_+/\omega_+ j_-]$. As shown in table 2 this quantity depends upon the metal to which it is applied. Consequently, the empirical validity of eq (19) can only be considered approximate at best.

TABLE 4. *Electron affinities*

(Comparison with theoretical estimates)

		V	Cr	Mn
E. Clementi: Phys. Rev. **135**, A980 (1964). (correlation energy estimates)	4th row valence electron configuration	$3d^3 4s^2$	$3d^5 4s$	$3d^5 4s^2$
	A(eV)	0.94 ± 0.25	0.98 ± 0.35	-1.07 ± 0.20
This work: (self-surface ionization)		Nb	Mo	Tc
	5th row valence electron configuration	$4d^4 5s$	$4d^5 5s$	$4d^5 5s^2$
	A(eV)	~ 1.0 (est.)	1.0 ± 0.2	....
		Ta	W	Re
	6th row valence electron configuration	$5d^3 6s^2$	$5d^4 6s^2$	$5d^5 6s^2$
	A(eV)	0.8 ± 0.3	0.5 ± 0.3	0.15 ± 0.10

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