mixture of these states. If two fluorine atoms interact so as to form and evaporate as F₂, the \( E \) represents half of the energy to cause this. If the evaporation occurs as single fluorine atoms, then it is just the energy of evaporation of a single fluorine atom from the clean molybdenum surface.

8 P. Kiskin, Phys. Rev. 120, 405 (1965).

Work Function in the System Thorium–Rhenium

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(Received 26 August 1963)

THE purpose of this communication is to compare some experimental results reported recently by Anderson et al., with similar theoretical predictions presented by Gyftopoulos and Levine.

Anderson et al. give experimental results on the work function of and the desorption rate from a thorium surface partially or fully covered by thorium. One of their conclusions is that their experimental measurements are in disagreement with the theoretical results published by Gyftopoulos and Levine. Unfortunately, Anderson et al. have been misled to this conclusion by misquoting Ref. 2 and by failing to verify it through use of the formalism therein.

To see this clearly, consider the theoretical formula for the variation of the work function of any metallic surface covered by any monatomic metallic vapor:

\[
\frac{\phi_m - \phi_a(\theta)}{\phi_m - \phi_f} = 1 - G(\theta) \left[ 1 - \frac{0.76 \times 10^{-4} \sigma \beta \cos \beta}{(1 + 1/4 \epsilon_0 q R^2)(1 + 0.75 \sigma \beta \cos \beta/4 \epsilon_0)} \right],
\]

where all the terms have been defined in Ref. 2.

For the adsorption system Th–Re, tabulated physical constants necessary for the calculation are:
- covalent radius of Re: \( r_m = 1.28 \times 10^{-10} \text{m} \)
- covalent radius of Th: \( r_f = 1.65 \times 10^{-10} \text{m} \)
- sum of covalent radii: \( R = 2.93 \times 10^{-10} \text{m} \)
- polarizability of Th: \( \alpha = 8.2 \times 10^{-20} \text{F·m} \).

For the particular reproducible specimens, of Re immersed in Th, investigated by Anderson et al., the following constants were reported:
- work function of bare surface: \( \phi_m = 4.85 \text{ eV} \)
- work function at one monolayer: \( \phi_f = 3.33 \text{ eV} \)
- adsorbate density at one monolayer: \( \sigma_f = 7.95 \times 10^{15} \text{m}^{-2} \)
- adsorbate density at maximum electron emission: \( \sigma_a = 4.2 \times 10^{15} \text{m}^{-2} \)

The point of maximum emission where \( \theta_m = 4.2/7.95 = 0.53, \sigma \beta \theta_m = 4.2 \times 10^{15}, G(\theta_m) = 0.46, \) Eq. (2) yields:

\[
\phi_f = 3.1 \text{ eV}.
\]

This is to be compared with the experimental value 3.15 eV.

In conclusion, the theory advanced in Ref. 2 is in agreement with the results of Anderson et al., at least as far as the numbers quoted in Ref. 1 are concerned.

Regarding thermal desorption, a completely theoretical derivation of desorption energies of composite surfaces for both atoms and ions, without adjustable parameters, is given in an article by Levine and Gyftopoulos that is to be published.

3 This value is calculated with a Richardson constant \( A = 75 \).
4 See Ref. 2, p. 71. Anderson et al. guess this density to be equal to \( 15.3 \times 10^{15} \text{m}^{-2} \).
5 See Ref. 2, Eq. (12), p. 70.
6 J. D. Levine and E. P. Gyftopoulos, J. Surface Sci. (to be published).

High-Frequency Oscillations in a Thermal Plasma

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(Received 3 September 1963)

LOW-FREQUENCY ion oscillations are frequently observed in thermal plasma devices, such as power converter plasma diodes, and are associated with drift of the plasma electrons. Birdsal and Bridges have suggested that an instability of the drifting electrons should give rise to high-frequency oscillations with period near the electron transit time across the device, and that such oscillations decrease the average electron current and density. Relaxation of the resultant charge imbalance would produce a cycle of the ion oscillation.

Oscillations of this type have been observed in a thermal cesium plasma. The apparatus is a cesium-vapor diode utilizing a 1.27-cm (4-in.) diam electron-bombardment-heated tungsten button, opposed by a moveable cold plate, operating in an axial magnetic field.

With the diode short circuited and the button temperature such that an excess of ions is available, smooth ion oscillations are observed as diode current fluctuations with frequency depending only on the button-to-plate spacing. In addition, an L-C circuit and detector picks up a signal with frequency 500 to 1000 times
higher occurring in bursts once each cycle of the lower frequency fluctuation. Figure 1, prepared from oscilloscope photographs, shows the waveform of the low-frequency fluctuations and the envelope of the high-frequency bursts. (The small pips of alternating sign occurring in the detector output are the low-frequency current fluctuations, differentiated by the coupling coil).

Table I lists the observed low and high frequencies as a function of diode spacing.

The high-frequency bursts always occur in conjunction with the low-frequency fluctuations. The detailed shape of the high-frequency envelope may vary somewhat as conditions are changed, but the bursts occur slightly before or at the onset of each low-frequency current pulse. The higher frequency is 500 to 1000 times the lower; this ratio being near the square root of the ion-electron mass ratio.

Table I, Oscillation frequency and burst frequency as a function of diode spacing.

<table>
<thead>
<tr>
<th>Diode spacing (cm)</th>
<th>Oscillation frequency (ke/sec)</th>
<th>Burst frequency (ke/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.56</td>
<td>100</td>
<td>86</td>
</tr>
<tr>
<td>0.73</td>
<td>72</td>
<td>65</td>
</tr>
<tr>
<td>0.89</td>
<td>56</td>
<td>60</td>
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<tr>
<td>0.96</td>
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<td>1.25</td>
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<tr>
<td>1.45</td>
<td>34</td>
<td>34</td>
</tr>
<tr>
<td>1.50</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>


Erratum: A Complete E, P, V, T, S Thermodynamic Description of Metals Based on the P, u Mirror-Image Approximation

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In a recent paper we concluded that the mirror image (about $P_H$, $V_H$) of the Hugoniot must approach the isentropic expansion curve that passes through the shocked state $P_H$, $V_H$ as $P_H \to 0$. While this conclusion is valid, the proof given in the second half of the Appendix for the general fluid is incorrect for it is based on the erroneous statement that "any isentrope in the $P,u$ plane can be generated from any other isentrope by a translation in the $u$-direction." (This statement is true only for the trivial case where the initial thermodynamic states of the isentropes are identical.) The previous proof may be redone in the following way. Consider the Hugoniot and isentrope passing through the initial state $P_0, V_0, S_0, H_0 = 0$, and the expansion isentrope from the shocked state $P_H, V_H, S_H, H_H > 0$, with $dP/du > 0$ on all three curves. Then,

\[ u(P_H, S_H) = \int_{P_0}^{P_H} \left( \frac{dP}{d_u} \right) s_u \]

and

\[ Q = \left[ \frac{Q}{u(P_0, S_0)} - u(P_0, S_0) \right] u(P_0, S_0) \]

for a thermodynamic fluid with $\left( \frac{\partial P}{\partial u} \right)_{S} > 0$, i.e., with $\partial V/\partial P S < 0$. Thus, for such a fluid (e.g., a $\gamma$-law gas), $Q > 1$, which implies that the isentropes cannot be generated by a translation in the $u$ direction. But

\[ u(P_H, S_H) - u(P_H, S_0) \alpha (P_H - P_0) \]

and $\alpha > 1$, which means that

\[ u(P_0, S_0) \]

from which it follows that $u(P_0, S_0) / u_H > 0$ as $P_H \to P_0$, since

\[ u(P_0, S_0) / u_H < \left[ \frac{Q}{u(P_0, S_0)} - u(P_0, S_0) \right] u_{\alpha}(P_H - P_0)^2. \]

If we now consider the mirror images of all three curves (the initial state is now $P_n, T_n, S_n, 2H_H$, and $dP/du < 0$, we find

\[ R = \left[ 2H_H - u(P_n, S_n) \right] / u_H \to 0 \] as \( P_H \to P_0 \)

here, $u(P_n, S_n)$ is on the mirror-image curve.

Another proof is based on the elegant analysis of Walsh and Christian, who derived the maximum and minimum values for $u(P_n, S_n) - u(P_0, S_0)$ under the assumption that $\partial E/\partial u = \partial P_0$ = constant. Both these values [see their Eqs. (15) and (22)] approach 1 as $P_H \to P_0$, implying that $R \to 0$, too.