

in an atmosphere of hydrogen to obviate oxidation. A block was cut from the center of a large cylinder thus obtained.

The impure sample, analyzed, after the experiments, gave Fe_2O_3 , Al_2O_3 , 0.07%, SiO_2 , 0.04%. The results obtained are given below.

PURE COPPER TOTAL IMPURITIES 0.019%			IMPURE COPPER TOTAL IMPURITIES 0.11%	
	a^2			a^2
1083	0.308 \pm 0.0017		1083	0.301
1093	0.308	0.0017	1097	0.299
1146	0.304	0.0017	1110	0.315 (?)
1210	0.305	0.0017	1160	0.292
1271	0.304	0.0017	1195	0.290
1318	0.297	0.0017	1220	0.287
			1335	0.275

The probable error of a^2 for the case of pure copper calculated by the method of least squares is 0.0017. Note that the effect of impurities becomes more pronounced as the temperature rises.

The results are plotted in figure 5.

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² See Desains, *Ann. chim. phys.* (3) 51, 417 (1857).

THE RELATION BETWEEN TEMPERATURE AND WORK FUNCTION IN THERMIONIC EMISSION

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In a recent article in these PROCEEDINGS² it was shown that some sorts of ionization accompanying chemical action not only followed the Richardson equation, but possessed such other properties in common with thermionic emission as to suggest that they might be looked upon as special cases of the latter.

Under the conditions in which ions were formed at a surface only when chemical action was taking place, distinct relationship was shown to exist between the difference in temperature of emission of the positive and negative ions (∂T) and the difference in their work functions (∂b) as determined by the usual treatment of an equation of the Richardson form.

It is the purpose of the present paper to show that an interdependence also exists between the difference in temperature (∂T) and the difference in work function (∂b) for the positive and negative thermionic currents from a given surface in the presence of various gases.

The apparatus used was similar to that described before except that a mica shield was so placed as to prevent the diffusion of air between the electrodes. The inner electrode was a thin-walled aluminum cylinder closed at one end and cooled by a current of dry air blown down the center.

A saturation current could not be obtained since the experiments were conducted at atmospheric pressure. The difference of potential between the electrodes was maintained at 225 volts. The temperature T in table 1 is arbitrarily taken as that at which the current was 1×10^{-15} amps. per sq. cm.

In table 1 are listed the data obtained from the thermionic emission from gold in the presence of various gases.

GAS	CHARGE ON ION	T (ABSOLUTE)	∂T	B ($\times 10^4$)	∂B
Ethyl alcohol	+	674		2.33	
	-	705	31	2.7	0.37
Hydrogen	+	660		3.41	
	-	697	37	3.8	0.39
Oxygen	+	704		3.23	
	-	790	86	4.04	0.81
Carbon dioxide	+	722		3.35	
	-	803	81	4.2	0.85
Propyl alcohol	+	635		1.84	
	-	726	91	2.64	0.80
Helium	+	715		3.16	
	-	757	42	4.15	0.99
Butyl alcohol	+	642		2.51	
	-	753	111	3.6	1.09
Nitrogen	+	707		2.88	
	-	817	110	4.02	1.14

The data is clearly indicative of a dependence of ∂T on ∂b ; where the difference in the amount of work necessary to remove a negative ion over that required to remove a positive ion is small the difference in temperature is likewise small, and vice versa. Helium offers the widest variation of any of the gases. Unfortunately, the supply of helium was limited and contaminated with traces of air so the data cannot be considered highly reliable. However, it is possible that, since helium is mon-atomic, the condition is somewhat different from the other cases.

This same interdependence between temperature and work function is shown by another series of experiments in which a changing electrode surface was used while the gas was maintained the same. A film of oxide was allowed to build up slowly on outer electrodes made of iron, copper and brass. While the surface was being oxidized consecutive determinations were made of first the positive and then the negative emission. Representative data are given in table 2.

ELECTRODE MATERIAL	GAS	TABLE 2		B ($\times 10^4$)	∂b
		CHARGE ON ION	T (ABSOLUTE)		
Iron	Oxygen	+	757	3.41	
		-	812	65	4.61
Iron oxide	Oxygen	+	796	3.8	
		-	797	1	3.86
Iron oxide (heavy)	Oxygen	+	793	3.92	
		-	789	4	3.64
Brass	Oxygen	+	764	3.23	
		-	810	54	5.31
Brass (oxidized)	Oxygen	+	785	3.30	
		-	760	25	3.14
Iron	Hydrogen	+	717	3.88	
		-	742	25	4.37
Iron oxide	Hydrogen	+	717	3.38	
		-	650	67	3.14
Iron oxide	Ethyl alcohol	+	733	5.3	
		-	708	25	3.7

While it is never possible to duplicate exactly surface conditions the nature and order of magnitude of the data given in the above table are always characteristic of such experiments.

The data representing various stages in the oxidation of the iron surface show clearly that the accumulation of oxide on the surface is accompanied by an increase in b and T for the positive ions which is concomitant with a corresponding decrease for the negative ions. When the work done in removing an ion is the same for both the positive and the negative the temperature is likewise the same.

The same correlation between ∂b and ∂T that was observed with the gold surface is to be noted in the emission from iron in the presence of hydrogen and of oxygen.

The emissions from iron oxide in hydrogen and in ethyl alcohol show a marked similarity in that the work necessary to remove the positive ion is abnormally high. When the alcohol vapor was mixed with an excess of oxygen to prevent a reduction of the oxide, the values of T and b obtained were those of the oxygen and not of the alcohol. It is most probable, therefore, that the small positive current obtained from alcohol or hydrogen alone on the oxide comes from the iron which has been reduced and not from the oxide. Similar results were obtained for the oxides of copper, lead and brass, but not for aluminum. Aluminum oxide, which failed to show any appreciable tendency to hold back the positive ions, is alone, of the oxides used, not capable of being reduced by hydrogen.

Without any recourse to theory or to the nature of the ions emitted, the observed interdependence between temperature and work function should serve as another method for determining contact potentials. The values of either ∂b or ∂T measure the difference in work necessary to remove

an ion of one sign over the other from an emitter in various gases, and should, therefore, be a direct measure of the change in contact difference of potential occasioned by changing the nature of the gas.

For purposes of simplicity these phenomena, characterized by an analogous behavior of the positive and negative emission currents and a definite interdependence between temperature and work function, can best be interpreted by the assumption that the gas molecules upon approaching sufficiently close to the surface are dissociated by the combined surface forces into positive and negative ions. These surface forces, dissociating molecules into ions and holding the ions thus formed to the surface, may be considered as composed of two specific forces, an electrostatic image force, and an intrinsic force. The electrostatic image force, given by $e^2/4d^2$ where e is the charge on the ion and d the distance from the surface, is appreciable to about 10^{-4} cm. from the surface, and is non-selective in character, i.e., it is the same for the positive as for the negative ion. The intrinsic force, on the other hand, is selective in character in that it allows a more ready escape of ions of one sign than of the other. For pure metal surfaces such as gold, copper and iron it will be noted that the positive ions always escape at a lower temperature than do the negative, while for the highly oxidized iron surface the conditions are just reversed. The nature of this intrinsic force, as given by its selective behavior, is that of one possessing the properties of a resultant electrical field effective to a few molecular diameters out from the surface. Such a field would be positive for iron or gold, but negative for the iron oxide.

These combined forces holding ions to the surface are opposed by the kinetic energy of agitation, so that when the temperature rises to a sufficiently high point ions will begin to escape from the surface because of their kinetic energy, and will thus come under the influence of the external applied field.

This picture accounts at once for the interdependence between temperature and work function. Just to the extent that an ion of one sign is held more tightly to the surface than is an ion of the other, to that extent is a higher temperature required for its removal, hence the existing relationship between ∂b and ∂T .

An interesting fact brought to light by this research is that it is possible to alter the nature of the surface so as to cause the intrinsic field to change sign, as is illustrated by the gradual change in b and T accompanying the accumulation of oxide on the iron surface. This change in the intrinsic field is doubtless due to the presence of the negative oxygen ions in the oxide, which, with increasing concentration on the surface, gradually neutralize the positive intrinsic field of the pure metal, and finally, upon high oxidation, actually establish a negative field.

If this mode of interpretation is correct it ought to be possible to make

direct determinations of the contact potential which must change sign as ∂T and ∂b , as observed above, pass through zero. Further experiments are in progress to test the foregoing viewpoint.

The writer's best thanks are due Professor R. A. Millikan for his interest and advice.

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² These PROCEEDINGS, 12, 560, 1926.

ON THE SPECTRUM OF ARGON IN THE EXTREME ULTRA-VIOLET

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The spectrum of Argon has recently been made the subject of several investigations which have led to the discovery of its structure. The key to success lay in finding the two strong resonance lines in the extreme ultra-violet.¹ From these as a starting point, and from ingenious experiments on the absorption of excited Argon, Meissner² was enabled to arrange the conspicuous group of red lines. The writer sorted out the principal series, and a list of other terms³ and Meissner independently obtained the prin-

TABLE 1
LINES APPEARING IN THE ARGON SPECTRUM WHOSE INTENSITIES DO NOT VARY
PROPORTIONATELY WITH THE TWO RESONANCE LINES

INT.	λ	MEISSNER'S ASSIGNMENT
7	894.32	$1p_0 - 3d_5$
8	879.95	$1p_0 - 2s_4$
8	876.06	$1p_0 - 3d_2$
7	869.76	$1p_0 - 2s_2$
6	866.80	$1p_0 - 3s'_1$
6	842.80	$1p_0 - 4d_5$
4	834.98	$1p_0 - 3s_4$
6	834.38	$1p_0 - 4d_2$
4	826.37	$1p_0 - 4s'_1$
4	825.33	$1p_0 - 3s_2$
2+	820.11	$1p_0 - 5d_5$
1?	816.40	
3+	816.22	$1p_0 - 5d_2$
0+	809.90	$1p_0 - 6d_5$
0+	806.65	
2+	806.44	
1+	801.22	
0+	799.21	
1	797.57	