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(3) Dissociation of SrO by temperature alone, the Sr atoms and O₂ molecules (or O atoms) leaving the filament and subsequently recombining on the surface on which they are deposited may represent as much as 0.4 of the total SrO leaving the filament. This conclusion is based on thermochemical data; if the band spectrum value of 5.2 eV for *D*₀ be accepted, the fraction is not over 0.002.

(4) The latent heat of evaporation λ_0 , at 0°K is 126.0 kcal with a probable error of about 0.8 kcal.

If processes (6) and (7) occur at the maximum rate thermodynamically possible, the value of λ_0 should be increased to 126.6 kcal. This increase does not seem probable because it contradicts available data from the band spectrum.

(5) The radioactive tracer method is convenient, sensitive, and accurate but must be employed with caution.

Advice from Conyers Herring during this work is gratefully acknowledged.

II. The Reduction of SrO by Tungsten in Vacuum

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(Received July 24, 1950)

It is shown that in the temperature range 1150–1550°K, SrO is reduced by tungsten in vacuum. Both the rate of the reaction and its equilibrium constant can be calculated, giving values in substantial agreement with the experiments, which were performed under conditions such that both could be measured. The use of radioactive isotopes simplified the experimental work.

INTRODUCTION

THE performance of oxide cathodes is generally believed to depend on small quantities of excess Ba or Sr metal in the oxide lattice. Of the various methods postulated for producing this Ba or Sr, chemical reduction of the oxide by the support metal is qualitatively the best established experimentally. However, almost no quantitative work has been published on either the equilibrium or kinetics of such processes, probably because the serious difficulties, inherent in making any quantitative measurements on chemical reactions between solid phases,¹ might be accentuated in these reactions.

It has been shown² that the reaction between MgO and tungsten can be studied experimentally by a technique that is simple in principle and which yields simultaneously both the equilibrium constant and the rate of the reaction. The observed values were, within experimental precision, just those computed from thermodynamics and kinetic theory. White³ has computed the free energies of several such reactions.

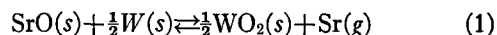
The present work indicates that the reaction between SrO and W can be studied quantitatively in the temperature range 1150–1550°K and the behavior is only slightly more complex than that of the MgO–W reaction.²

PRINCIPLE OF THE EXPERIMENTAL METHOD

Because the principle of the experimental method was not adequately discussed in the previous report²

and because the writers hope to investigate other reactions by the same method, the principle is presented here in some detail.

Consider an evacuated glass bulb as in Fig. 2 in the preceding paper, "The vaporization of SrO" (hereinafter referred to as I), containing a W filament coated with SrO which is heated to a temperature determined pyrometrically. A reaction capable of producing Sr metal will result either in simple oxidation of the tungsten as in



or in the formation of a complex salt as in



Among the components of (1) and (2) the Sr alone will be present only in the gaseous phase in the experimental temperature range 1150–1550°K and its pressure is therefore⁴ the equilibrium constant. The published vapor pressures of SrO and W are so low that they will clearly be present in the solid phase and evidence to be presented shows the same to be true of WO₂ and SrWO₃.

The kinetic criterion,⁵ is usually employed to detect equilibrium. For this example, the temperature of the

⁴ See for example E. Fermi, *Thermodynamics* (Prentice-Hall Inc., New York, 1937).

⁵ H. Hunt, *Physical Chemistry* (Thomas Y. Crowell Company, New York, 1947), states that chemical equilibrium may be considered from the three viewpoints: "Thermodynamically, a reaction is at equilibrium when the free energy change is zero. Statistically it is at equilibrium when the mathematical probability has reached a maximum value for the system. Kinetically it is at equilibrium when the forward and reverse absolute rates are equal."

¹ C. N. Hinshelwood, *Kinetics of Chemical Change* (Oxford University Press, London, 1940), see especially page 252.

² G. E. Moore, *J. Chem. Phys.* **9**, 427 (1941).

³ A. H. White, *J. Appl. Phys.* **20**, 856 (1949).

TABLE I. Experimental measurements—reaction between W and SrO.

Tube no.	T°K	Age—hr.	Total Sr micrograms	LogM'	ΔT°
Group 1a. Hydrogen evolution—SrO coat only					
928	1364	40.0	405	-5.441	62
1222	1452	2.4	1029	-3.815	22
927	1495	1.7	1108	-3.633	2
930	1520	0.67	995	-3.276	22
r.m.s. deviation					35
Group 1b. Hydrogen evolution—SrO + W powder in coat					
1588	1228	151.0	0.26	-6.209	6
1585	1475	2.0	1907	-3.469	42
1586	1475	2.0	350	-4.203	46
1221	1515	1.0	437	-3.807	39
r.m.s. deviation					37

filament would be controlled by heating the bulb in an oven. The thermodynamic system would comprise everything inside the bulb and the steady-state pressure of Sr would be determined at a series of temperatures. The forward reaction produces Sr atoms, labelled group (a), which stream outward from the filament. In the reverse reaction, incoming Sr atoms labelled group (b) again form SrO. The flux of atoms in these two groups would be equal at equilibrium. Measurement of the low equilibrium pressures would be difficult and the maintenance of a chemically inert bulb at high temperatures is not feasible.

However, if the reflection of Sr atoms is negligible at phase boundaries and if the equilibrium pressures were so low that the mean free path of Sr atoms was larger than the bulb radius, atoms of groups (a) and (b) could not interact. The two groups would be independent and one might expect Sr atoms to be produced at a rate depending only on temperature, regardless of whether any Sr atoms strike the filament. Experimental technique would be convenient, because only the filament need be heated, the thermodynamic system consisting only of the filament itself instead of the entire interior of the bulb. The number of (b) atoms could be reduced essentially to zero by operating the bulb at ambient temperature, at which substantially no Sr could evaporate from the glass surface. Because the filament diameter is small compared with the bulb diameter, any Sr atoms reflected from the bulb would strike the cool glass many times before returning to the filament. Therefore, almost no atoms of group (b) would be produced by reflection at the bulb unless the reflection coefficient is extremely high; negligible reflection is indicated by the sharp shadows of the filament supports observed in the experimental films of Sr metal deposited on the glass.

When atoms of group (b) can be neglected, the Sr leaving the filament per unit time can be measured and expressed as a pressure, by operating the filament at a controlled temperature for a known length of time and converting the mass of Sr observed on the bulb into pressure by Eq. 1 (1). The outward flux of Sr atoms at

TABLE II. Experimental measurements—reaction between W and SrO.

Group 2a. Radioactive SrCO ₃ coat applied—no W powder					
125	1200	140.5	21	-6.662	3
124	1242	70.0	57	-5.931	16
129	1299	24.0	74	-5.354	11
126	1300	43.0	98	-5.487	2
127	1300	24.0	36	-5.668	19
128	1300	42.0	49	-5.775	29
r.m.s. deviation					16
Group 2b. Radioactive SrCO ₃ coat applied with W powder					
132	1217	74.0	48	-6.033	32
131	1350	22.5	108	-5.132	18
135	1357	22.5	159	-4.996	12
133	1395	2.0	45	-4.496	2
134	1395	2.0	27	-4.713	21
137	1430	1.0	98	-3.851	41
136	1434	1.3	80	-4.057	12
r.m.s. deviation					23

the filament surface corresponds to the pressure in the system. The cool glass surface completely removes gaseous Sr, so that the reaction will proceed as rapidly either: (1) as atoms of group (a) can leave the filament at the equilibrium pressure, or (2) as allowed by constraints of the system, such as diffusion of reactants and reaction products through solid phases. (1) is the maximum possible rate and requires that there be no reflection at phase boundaries.

It is clear that the measurement of m gives the rate of the reaction. The equilibrium pressure of Sr can be predicted from published thermodynamic data, as indicated below; because this computed pressure is equal to the observed value, it is believed that the measurements also give the equilibrium pressure of the reaction. This belief is supported by the fact that the observed values of m seem independent of large changes

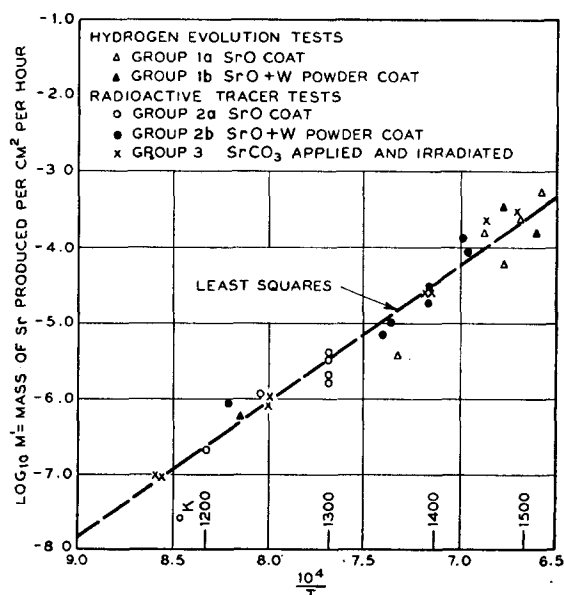


Fig. 1. Experimental measurements of the rate of production of Sr atoms by chemical reaction between SrO and W.

in the interfacial area between SrO and W, keeping the apparent surface constant.

Such considerations have previously been applied to purely physical reactions such as the vaporization of metals, but have not yet been established for the gaseous product of chemical reactions between solids.

EXPERIMENTAL

(A) Measurement and Control of Temperature

This was treated as in I. To darken the surface of the SrO and thus increase the spectral emissivity, tungsten powder was added in many filaments. Particle size analysis indicated that this powder also increased the interfacial area between tungsten and SrO by a factor of three. The probable error in determining the true temperature of a darkened filament is believed to be about 5°C; for the coats without the tungsten powder, this is approximately 10°C.

Control of temperature during runs is more difficult than its determination at individual test points. Operation at either constant current or constant voltage will not assure constant temperature. Two effects are responsible: (1) spectral and total emissivities vary as a result of chemical reaction and (2) resistivity varies during the reaction, probably because reaction products penetrate the tungsten filament. These changes were frequently large during aging periods required to produce sufficient Sr for accurate analysis. The scatter

TABLE III. Experimental measurements—reaction between W and SrO.

SrCO ₃ applied to filament and then irradiated					
201	—	0	0.24		
209	—	0	1.7		
211	1166	360	10.4	−7.018	3
202	1168	362	10.3	−7.023	1
207	1250	93.5	30.4	−5.965	4
210	1250	93.5	23.2	−6.082	5
212	1395	22.5	183	−4.566	5
206	1400	22.5	181	−4.571	11
204	1454	2.0	140	−3.633	43
203	1490	2.0	176	−3.532	19
r.m.s. deviation					17

in the results for the first tubes tested amounted to about 35°C expressed as an r.m.s. deviation from the curve best fitting the experimental data. Improved temperature control was primarily responsible for decreasing this in subsequent groups. This involved frequent pyrometer and reflectometer observation of a filament during aging, which was laborious. In order to make pyrometer measurements only at the necessary intervals, the radiation from the experimental filament was monitored photoelectrically. The emission in a photo-cell which viewed the filament was calibrated as a function of filament temperature. If while aging the experimental tube, the photo-emission changed by more than the equivalent of 10°, new pyrometer and reflectometer measurements were made. This method did not correct for increased transmission loss caused by deposit of metallic Sr on the bulb, but experience indicated when this correction became appreciable, and only slight scatter was caused by the latter action.

(B) Measurement of the Total Mass of Sr

Both the hydrogen evolution and the radioactive isotope methods described in I were used in this work. However, in contrast to I, the total bulb deposit, μ , measured in II was essentially the same by either method, indicating that the deposit was substantially all Sr metal.

(C) Tube Design and Exhaust

The structures of Figs. I-1 and I-2 were used and the exhaust was as described previously.

(D) Preparation of Filaments

The filament supports (or cores) were either G. E. 8111 0.010-in. wire, or ribbons rolled to 0.040 in. \times 0.0005 in. from G. E. 218 "non-sag" wire. The former was analyzed spectrochemically indicating a purity greater than 99.99 percent. The coat was SrCO₃ of high purity and about 5 mg was applied per cm² of filament area. The filaments were all coated either by Diggory's "eyelet" method or coated with non-radioactive SrCO₃ and the coated filament then treated in the pile. Both methods are described in I. No radioactive impurities were detected in either treatment.

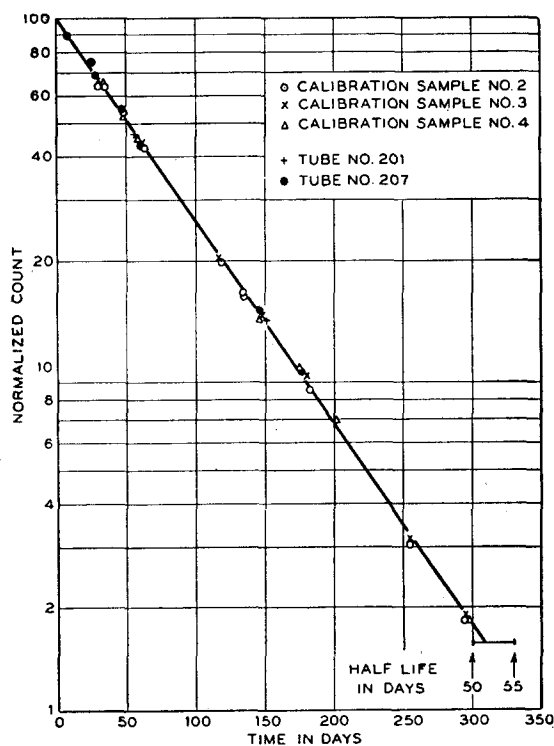


FIG. 2. Decay of radioactivity in Sr metal produced in chemical reaction. Rate of decay indicates no W in volatile reaction product.

TABLE IV. Computed rates of reaction.

(1) Tempera- ture °K	(2) ΔG for (3)	(3) G for SrO cal./mole	(4) G for $\frac{1}{2}O_2$	(5) G for Sr	(6) ΔG for (8)	(7) $\log_{10} p_1$ for	(8) $\log_{10} M'$ (2)	(9) $\log_{10} M'$ (2)	(10) $\log_{10} M'$ method 2 for (2)
1000	-46,250	-155,540	-23,992	-14,644	71,550	-12.74	-14.07	-10.04	-9.96
1100	-44,150	-158,520	-26,899	-16,975	72,390	-10.51	-11.90	-8.22	-8.17
1200	-42,050	-161,350	-29,846	-19,377	71,080	-8.69	-10.07	-6.69	-6.57
1300	-39,975	-164,430	-32,839	-21,829	70,790	-7.09	-8.48	-5.40	-5.26
1400	-37,850	-167,615	-35,858	-24,377	70,530	-5.75	-7.15	-4.27	-4.15
1500	-35,750	-170,900	-38,939	-27,027	70,180	-4.56	-5.98	-3.30	-3.32
1600	-33,650	-174,270	-42,002	-29,627	69,995	-3.58	-5.01	-2.48	-2.51

M' = grams of Sr leaving each cm² of filament surface per hour.

p_1 = outward pressure of Sr gas at filament surface in dynes per cm².

G expressed in calories per mole, elements and SrO in standard states.

RESULTS

Results are given in Tables I to III and Fig. 3. Table I gives data on tubes tested by the hydrogen evolution method; the first four filaments were coated with SrCO₃ only, and the second four were coated with a mixture of tungsten powder and SrCO₃. Table II gives data for the first set in which radioactive tracers were used. The first six were coated with SrCO₃ only and the second seven with SrCO₃ and tungsten powder. In all tubes of Table II, the SrCO₃ was irradiated before application to the filament. Table III gives data on ten tubes containing filaments which had been coated with SrCO₃ and the coated filament then irradiated. None of these 10 contained tungsten powder.

Tubes 201 and 209, Table III, served as "blanks"; that is, after assembly, the thimble was never lifted above the filament until the outer bulb was removed. Any radioactivity on the outer bulb would then result from Sr atoms which had been transferred mechanically during assembly or in other stages of preparation. The amount produced by the reaction should be much greater than the amount in such a blank if the former is to be determined with precision. The examples show that this condition was fulfilled.

The results are plotted in Fig. 1 in which the ordinates are $\log_{10} M'$, the mass in grams of Sr produced per hour per cm² of apparent surface. Abscissas are expressed in reciprocal temperatures. Theoretical computations and the experimental data are both sensibly straight lines in these coordinates, although exact linearity would not be expected. The dashed line shows a least square fit of the experimental data. The perpendicular distance from the point to the line was minimized although it is recognized that inaccuracy in temperature determination is probably considerably more serious than uncertainty in the mass of Sr produced. The line fits the equation

$$\log_{10} M' = -\frac{1.810 \times 10^4}{T} + 8.460. \quad (5)$$

Comparison with Fig. 3 of I shows that the amount of Sr produced from a SrO coat on tungsten is con-

siderably more than 100-fold greater than the total Sr (SrO+Sr) from a similar coat on platinum.

The deviation in *temperature* of each point from the line is listed under ΔT° . The r.m.s. value of the deviation for each group is also listed. The r.m.s. deviation of all the points from the least square line is 24.9°K.

The mean *magnitude* of the deviation from the least square curve was 19°. There was no significant difference between the filaments with tungsten powder and those without. The mean deviations of the two groups from the least square line were of the order of 0.25°—an insignificant amount—but were in the opposite direction from that expected if the rate of reaction per unit apparent surface were limited by the interfacial area between W and SrO. Similarly, there was no correlation, either in magnitude or direction, between the deviation and the total amount of Sr produced by a filament.

Radioactive Decay

Decay for several samples of Sr89 in SrCO₃ produced by the irradiation of filaments previously coated with non-radioactive material is shown in Fig. 2. Three different calibration samples are compared with two experimentally produced deposits on glass bulbs. The calibration samples were used both to determine the absolute amounts of Sr in the experimental deposits and to judge their purity. Figure 2 illustrates only the latter use. In order to plot the data for all samples on a single curve, the activity from each was normalized by designating the initial count 100 percent and expressing all subsequent counts as a percentage. This was used as ordinate and the time in days after the first count as abscissas. If radioactive tungsten (or impurities from the W) represented some of the count initially attributed to Sr, the curves for the experimental samples would deviate from those of the calibration samples.

Specifically, after irradiation, the tungsten has 73.2 days half-life activity of 7 millicuries per gram (W185), while the Sr in the coat has a 55-day half-life activity of only 0.11 millicurie per gram. Thus the activity per microgram for tungsten is about 64 times greater than for Sr when removed from the pile. To process the tubes

requires several weeks, so because of its longer half-life, a microgram of tungsten on the bulb would give at least 2 orders of magnitude higher count than a microgram of Sr. The decay curves thus give a critical test for accumulation of W, or any compound containing W, on the bulbs. The agreement in half-life in the decay curves for calibration samples and bulb deposits therefore shows that the bulb deposit must be much less than one percent tungsten; the experiment is accordingly believed to measure only Sr (or SrO). This is supported by spectrochemical tests in which no W was found on the bulb in tests which would detect 0.5 microgram.

The curve is terminated at an ordinate of 1/64 (or 0.0156) representing 6 half-lives. The abscissas should then represent 6 times the half-life of the Sr isotope. The half-life determined in this way is between 51.5 and 52.0 days. Numerous tests on several samples consistently give half-lives of 51 to 53 days for Sr 89, while the most recent AEC Bulletins give 55 days, although earlier bulletins give 53 days. A small systematic error of unknown origin may therefore exist in the present measurements, although recent correspondence with AEC indicates that the 51- to 53-day figure may be reliable.

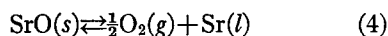
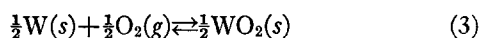
DISCUSSION

It was shown above that the rate at which Sr metal atoms leave a tungsten filament can be measured by two methods. However, the chemical reaction producing these Sr atoms was not identified. In this section, the rate of Sr production is discussed from a thermodynamic point of view, and a choice is made between reactions (1) and (2). It is shown that the observed rate is greater than could be justified thermodynamically if (1) occurs but is essentially that to be expected from (2). This conclusion is supported by chemical and x-ray data. In the computations, the assumed reaction [either (1) or (2)] is first resolved into simpler reactions whose sum is equivalent to that investigated, but each of which is more readily discussed than their sum.

Reaction (1)

WO₂ is the lowest recognized oxide of W; calculations indicate that the maximum rate of Sr production according to (1) would be as great as in any process forming a higher oxide; the rate would be almost identical if WO₃ were produced.

Reaction (1) is resolved into the components



The free energy changes in (3) and (5) are obtained from equilibrium data; in (4) the change is computed by determining a free energy G for each substance with

reference to the elements at 0°K. Reactions (3), (4), and (5) will be discussed in turn.

Component Reaction (3)

ΔG for (3) can be computed from the equilibrium pressure of O₂ by the equation⁴

$$\Delta G = (RT/2) \ln P_{O_2} \quad (6)$$

using the relations for P_{O_2} given by Wohler⁶ or by Chaudron⁷ and Van Liempt.⁸ These authors combined their own measurements of equilibria in the W-H₂O system with dissociation equilibria of H₂O. The data of Wohler are preferred because they were obtained more recently, although the difference is not significant for the precision now practical in the present experiment. Values of ΔG in (3) computed from Wohler's data are listed in the second column of Table IV.

Component Reaction (4)

An absolute value for the free energy of each constituent was computed from specific heats. In I, the free

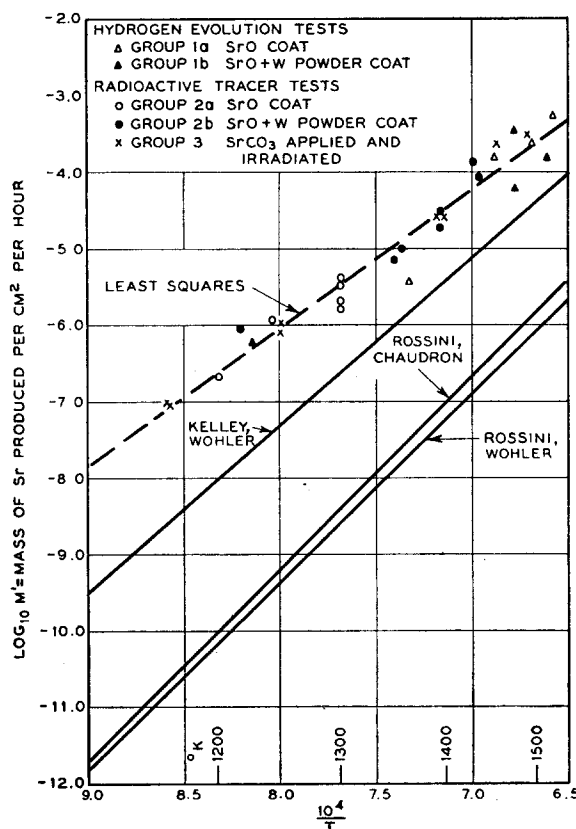


FIG. 3. Comparison of observed rate of Sr production with computed rates, assuming reaction I.

⁶ Wohler, Shibata, and Kunst, *Zeits. Electrochemie* **38**, 808 (1932); temperature 973–1323°K.

⁷ G. Chaudron, *Comptes Rendus* **170**, 1056 (1920); temperature 873–1373°K.

⁸ J. A. M. Van Liempt, *Zeits. f. Anorg. Chemie* **120**, 267 (1922) and **126**, 183 (1923).

energy was referred to solid SrO at 0°K; this is satisfactory for the purely physical process of evaporation, but the basis for chemical reactions must be the elements at some reference temperature. Computation of G for SrO thus requires a value for ΔH , the heat of reaction (4). Three critically discussed values, all at 298.1°K, are available:

130,160 calories by Kelley⁹ in 1935.

140,800 calories by Bichowsky and Rossini¹⁰ in 1936.

141,100 calories by Rossini¹¹ in 1950.

The last is preferred although computations were carried out for each of the others. The disagreement in this quantity introduces much the most important uncertainty in the calculations. Because tabulated values of entropy are always referred to 0°K, this is used as a reference temperature. The free energy of SrO can then be computed for any temperature from specific heats^{12,13} and the appropriate value for the heat of reaction. Column 3 of Table IV gives the values of G for SrO, using Rossini's value for ΔH .

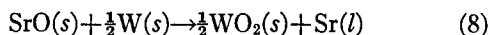
For $\frac{1}{2}\text{O}_2$, values of G were computed from the specific heat data of Johnston and Walker.¹⁴ Values are given in column 4 of Table IV.

Although no specific heats have been published for solid or liquid Sr, values can be estimated with what is probably sufficient accuracy for these experiments. A Debye temperature of 150°K was first estimated using methods¹⁵ which give values in agreement with experiment for both Mg and Ca (as well as other metals). The specific heat curve, C_p , can then be computed. Between 100°K and 1044°K, the melting point, the equation

$$C_p = 6.25 + 0.00120T - 8120/T^2 \quad (7)$$

was assumed in analogy with experimental values for Ca. The heat of fusion was taken as 2190 cal. and C_p of the liquid as 7.5. Values of G computed for Sr metal in this way are given in column 5 of Table IV.

By subtracting column 3 from the sum of columns 4 and 5, ΔG° is given for reaction (4) proceeding toward the right. Adding this result to that in column 2 gives column 6 which is ΔG° for the reaction



which is the sum of (3) and (4). Because these are positive, it has sometimes been concluded^{16,17} that such reactions cannot occur, for example that W cannot

reduce SrO to give Sr. However, the data in column 6 show *only* that W cannot reduce SrO to give Sr *in its standard state* in the temperature range 1000–1600°K. Throughout the temperature range the standard state of Sr is liquid in equilibrium with its vapor. But the free energy decrease in the purely physical reaction (5) can be made as great as desired by isothermal vaporization of the liquid at a sufficiently low pressure. The change in free energy for the isothermal expansion of the vapor considered as a perfect gas is⁴

$$\Delta G = RT \ln(p_1/p_2), \quad (9)$$

where p_2 is the pressure of Sr vapor in equilibrium with its solid or liquid phase. Because of this physical equilibrium, the free energy change in vaporizing any amount of the liquid at p_2 is zero. By then allowing the gas to expand from p_2 to a pressure p_1 such that by (9) the physical reaction (5) represents a loss of free energy just equal to the gain for (8), one obtains the equilibrium pressure p_1 for reaction (1). Computed values of p_1 in dynes are given in column 7 of Table IV using Dushman's¹⁸ values for p_2 . These values of p_1 were converted to mass M' of Sr in grams per cm² of filament surface per hour using Eq. I (1), and are shown in column 8 of Table IV. The values are plotted as full lines on Fig. 3 and compared with the observed points and the least square curve. It is seen that the measured values are several orders of magnitude *higher* than those computed for the combination of either the Wohler or the Chaudron data with the Rossini value for the heat of formation of SrO. The observed values are about one order of magnitude higher than those computed if Wohler's data are combined with Kelley's improbably low choice for ΔH in (4). Because the equilibrium pressure is the greatest that could exist over the reacting substances, the fact that the observed values are higher shows that reaction (1) cannot be occurring.

This conclusion is supported by observation. Experimentally significant quantities of W were observed on the bulbs of the tubes used in the W–MgO experiments,² suggesting that the reaction product containing W, presumably WO₂, possessed¹⁹ an appreciable vapor pressure. Both spectrochemical and radioactive tests, (Fig. 2) of bulb deposits in the W–SrO reaction at the same temperature as in the MgO experiment showed no observable W. The vapor pressure of the reaction product containing W must therefore be much lower than that of WO₂.

Reaction (2)

Because the oxides of tungsten are acidic and SrO is strongly basic, chemical combination would be expected at high temperatures. Almost nothing has been published regarding such compounds. Only SrWO₄ has

¹⁸ S. Dushman, *Scientific Foundations of Vacuum Technique* (John Wiley and Sons, Inc., New York, 1949).

¹⁹ T. Millner and J. Neugebauer, *Nature* **163**, 601 (1949).

⁹ K. K. Kelley, Bureau of Mines Bulletin 384, p. 37.

¹⁰ F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

¹¹ F. D. Rossini, private communication dated April 28, 1950.

¹² C. T. Anderson, *J. Am. Chem. Soc.* **57**, 429 (1935).

¹³ J. J. Lander, submitted to *J. Am. Chem. Soc.*

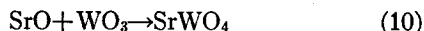
¹⁴ H. L. Johnston and M. K. Walker, *J. Am. Chem. Soc.* **57**, 682 (1935).

¹⁵ N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford University Press, London, 1936).

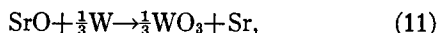
¹⁶ H. J. T. Ellingham, *J. Soc. Chem. Industry* (May, 1944).

¹⁷ C. W. Dannatt and H. J. T. Ellingham, *Disc. Faraday Soc.*, No. 4 (1948).

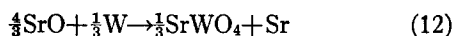
been previously identified²⁰ and the only thermochemical datum found¹⁰ was its heat of formation from which the heat of the exothermic reaction



was computed to be 56,400 calories.* No specific heat data are available. If Kopp's law be assumed²¹ for SrWO_4 , the free energy decrease in a reaction like (2) in which SrWO_4 was produced will be 56,400 calories greater per mole of W consumed than if WO_3 were the end product. Thus by adding $\frac{1}{3}$ of (10) to



one obtains



and by virtue of tungstate formation, reaction (12) would be driven to the right by about 18.8 kg cal. more free energy per atomic weight of Sr produced than (11), thus predicting a greater rate of Sr production. But there is no experimental evidence that SrWO_4 is formed. Although the tungstite, SrWO_3 , seems more probable, no tungstites are mentioned in the literature. However, K. H. Storks at these Laboratories, observed a small amount of crystalline SrWO_3 in x-ray examination of some of these filaments. At about the same time Eisenstein²² identified BaWO_3 (also not previously known) at the interface of nickel-tungsten alloy filaments coated with BaO . He also tentatively identified SrWO_3 at the interface of similar filaments coated with SrO . Because of this evidence, it is believed that the reaction occurring in the present work is (2).

In the absence of thermochemical data on SrWO_3 , it is assumed that reaction (2) is driven toward the right by 18.8 kg cal. more free energy per atomic weight of Sr produced than (1), just as is the case with (12) relative to (11). This assumption is equivalent to taking the heat of a reaction in which WO_2 combines with SrO to be two-thirds as great as that in which WO_3 reacts with the same basic oxide. Although this is not a safe generalization, some compounds behave as postulated, and the heat and free energy of formation of WO_2 are two-thirds those of WO_3 . Therefore, 18.8 kg cal. is added to the standard free energy change for reaction (1) in Table IV to give corresponding values for reaction (2). From these, the corresponding rates of reaction (2) are listed in column 9. The expected rate is plotted in Fig. 4, together with the experimental points and their least square curve, from Fig. 1. The mean square deviation of the points from the computed line (using Rossini's estimate) is 28°; from the least square fit of the experi-

mental points, this deviation is 25°. Thus the experimental points agree nearly as well with the theoretical curve as with the best experimental fit.

Because of this agreement²³ and because the rate of reaction was not influenced by the addition of sufficient W powder to triple the interfacial area for the same surface area, it is believed that the measurements give the equilibrium pressure of Sr over reaction (2). This pressure is then given by

$$\log_{10} P_{\text{atm}} = 2.286 + 0.5 \log T - (1.810 \times 10^4 / T).$$

Discussion of Assumptions

The magnitude of error in computing the free energy of Sr can hardly be as large as the uncertainty in the published values for the heat of formation of SrO , and will therefore not introduce any significant uncertainty into the computed rate of reaction (1) or (2). Nevertheless, the use of an estimated Debye temperature may arouse misgivings, so that the free energy of Sr vapor was estimated by another method previously used by White³ for a different reaction. This requires the heat of vaporization of solid Sr at 298.1°K, and White assumed that this was equal to the value determined in the high temperature range by vapor pressure measurement.

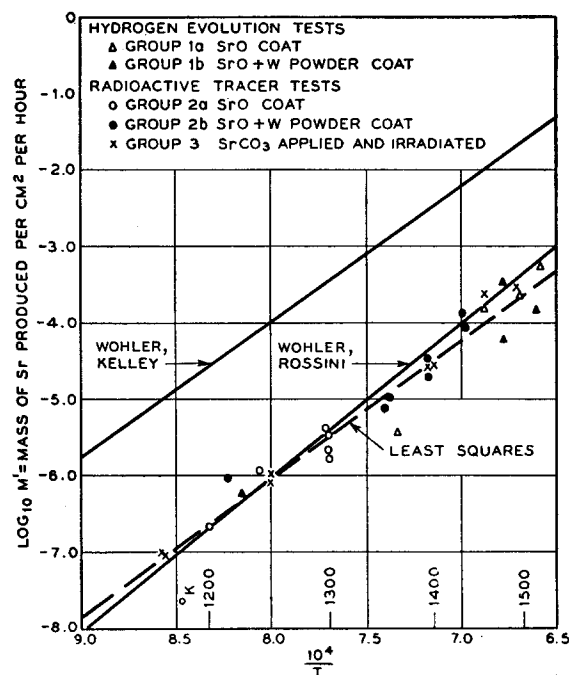


FIG. 4. Comparison of observed rate of Sr production with computed rates, assuming reaction II.

²⁰ J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans, Green and Company, New York, 1931), Vol. XI.

* The heat of corresponding reaction in which MgO replaces SrO is only 3300 cal. exothermic.¹⁰ This much smaller value probably explains why no complex compound formation was observed in the MgO experiment.

²¹ H. S. Taylor, *A Treatise on Physical Chemistry* (D. Van Nostrand Company, New York, 1931).

²² Quarterly Progress Report, December 15, 1948, Nr 074 081.

²³ W. F. Giaque, *J. Am. Chem. Soc.* **71**, 3192 (1949) has indicated that in some reactions between solid phases and with a gaseous reaction product, the experimental state of aggregation of the solids should be considered before identifying observed equilibria with those computed from thermodynamic data on the macroscopic properties of the solids. Such effects are not judged important here, because no effect was observed when tungsten powder was used and because SrO seems invariably to occur in very minute crystals.

This is equivalent to assuming that the specific heats of solid and vapor are equal from 298.1°K to 1000°K, which is certainly not correct but which is convenient for many calculations whose end accuracy will not be significantly influenced by the error in this assumption. Values of $\log M'$ expected from reaction (2) computing the free energy of Sr in this way are listed in column 10 of Table IV and may be compared with those in column 9.

Reflection at Phase Boundaries and Diffusion through Phases

Because this comparison of theory with experiment depends on a low reflection for Sr atoms crossing phase boundaries, the experiments are believed evidence for a reflection coefficient below 50 percent.

The fact that the rate of reaction seems unaffected by any diffusion processes occurring could not have been foretold by any method known to the writers. However, it seems to be true for a number of similar reactions on which study is not yet complete. But diffusion processes almost surely limit the rate of reaction when the cathode alloy contains a small percentage of some metal which reacts vigorously with the oxide as in the systems generally employed for commercial oxide coated cathodes.

Consideration of Equilibrium

Although one might question equilibrium constants measured in chemical reactions which are proceeding in only one direction at the maximum possible rate, there are parallels in purely physical reactions. Langmuir²⁴ studied the process of evaporation: i.e., tungsten atoms from a solid tungsten surface. He assumed that the number of atoms leaving the tungsten filament was independent of whether any were returning. The vapor

pressures so determined were equal to those determined by the Knudsen method and technique was far easier, especially for refractory metals. Langmuir and Kingdon²⁵ verified the Saha equation by applying similar considerations to the ionization of Cs atoms on tungsten filaments. As a third example, the work of Mayer²⁶ and his students on electron affinities requires that the rate of formation and departure of negative halogen ions on a filament be determined by the number of incident halogen molecules and a true equilibrium between ions of groups (a) and (b) is not necessary.

CONCLUSIONS

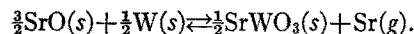
(1) Tungsten filaments coated with SrO produce Sr metal in the temperature range 1150–1550°K at a rate M' in grams per cm² per hour given by

$$\log_{10} M' = -\frac{1.810 \times 10^4}{T} + 8.460.$$

(2) This rate is believed to correspond to the *equilibrium pressure* of Sr metal vapor in reaction (2) which is thus given by

$$\log_{10} P_{\text{atm}} = 2.286 + 0.5 \log T - \frac{1.810 \times 10^4}{T}.$$

(3) The reaction occurring is



(4) The reflection coefficient for Sr atoms in crossing phase boundaries is less than 0.5.

The writers appreciate suggestions by A. H. White and assistance in computation by Mrs. G. V. Smith, throughout this work.

²⁵ I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. **107A**, 61 (1925).

²⁶ See for example P. P. Sutton, J. Chem. Phys. **3**, 20 (1935).

²⁴ I. Langmuir, Phys. Rev. **2**, 329 (1913).