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The oxidation of metals in relation to the periodic classification

H. E. N. STONE
Physics Department, Imperial College, London, UK

The majority of the solid elements from lithium to bismuth have been oxidation-tested in air in the range 0 to 1400°C. Heating was carried out for a constant time of 4 h at each test temperature. From the results the temperature corresponding to a weight change of 1 mg/cm^2/4 h was determined by interpolation for each element; this temperature has been plotted on charts with atomic number as abscissa. A provisional classification of the elements is subsequently proposed which is based principally on the temperature/atomic number plots.

1. Introduction

Studies of the oxidation and scaling of metals are legion, but although the similarity of certain groups of metals in this respect is well recognized, comparatively little appears to be known of their behaviour when considered in their totality. Part at least of the reason for this state of affairs lies probably in the difficulty of finding an acceptable criterion for comparison. In the present work, the approach is empirical. Oxidation tests, using the weight-change method, have been carried out in air for a fixed time at each of successively higher temperatures for most of the solid elements up to and including bismuth. From these data, curves of weight change against temperature were drawn, from which it was possible to extract a temperature (T_p) for a constant degree of weight change for each element. The degree of weight change selected for the parameter T_p was 1 mg/cm^2/4 h, a value which had the merit of encompassing the maximum number of elements within the scope of this survey. Plots of T_p versus atomic number form the basic conclusions of the paper. A provisional classification of the elements is subsequently proposed, which is based principally on the T_p plots. It is appreciated that many details of experimental technique and interpretation are controversial, and some relevant notes are included in the Appendix*.

2. Experimental

The raw materials were in most cases the purest commercially available. The metals Be, Mg, Al, Ru, Rh, Pd, W, Ir, Pt and Bi were Johnson Matthey's "Specpure" grade (purity approx. 99.995%). Rare Earth Products Ltd were the source for Sc, La, Gd, Er, and Dy (approx. 99.8% purity), boron was from Electronic Space Products Inc, Los Angeles (99.8%), and carbon from Ringsdorffwerke Gmbh. Osmium was available as an alloy containing 0.1% Fe. The remainder, with the exception of red phosphorus, sulphur, indium and mercury (Hopkin and Williams laboratory reagent grade), were from Koch-Light Laboratories Ltd. Of these, Li, Na, K, Ca, Sr, Ba, Ti, V, Y, Zr, Nb, Ce, Nd, Pr, Yb, Hf, and Ta were approximately of 99.9% purity, the remainder approximately 99.999% purity. Purities quoted are as given by the suppliers, and apparently refer throughout to metallic impurities. The metals Al, Sc, Ti, V, Fe, Co, Ni, Cu, Zr, Nb, Mo, Ag, Hf, Ta, W, Pt, and Au were in wrought form, chromium and manganese were in the form of electrodeposited flakes, and the remainder, apart from obvious exceptions such as boron and carbon, appeared to be in the as-cast state. Samples were tested as-received, except that it was necessary first to consolidate Ru, Rh, Pd, Er, Hf, Re and Ir (available in sponge form) by argon-arc melting, and also sulphur was pre-melted into block form. Samples were cleaned and degreased where necessary, but no special surface treatments were given. Samples of high surface/weight ratio were selected or cut as far as possible, and in all cases an estimate of surface area was made by direct mensuration. Surface

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*Text references to the Appendix are given by superscript letters.

areas were in the range 0.2 to 4 cm^2, typically about 1 cm^2; sample weights were between 0.04 and 6 g. Single samples of each element were tested, except for a few repeats where there was any doubt about the experimental manipulation; for example, a repeat iron gave a temperature intercept 15° C below the first, and this is thought to be a fair indication of the reproducibility.

Samples were tested in static air in a tube furnace (hot zone 8 in. long) heated by silicon carbide elements; the work tube was $2\frac{1}{4}$ in. in internal diameter, closed at one end only. The rate of heating was such that a temperature of, for example, 800°C was reached in about 2 h and the time for cooling halfway from that temperature to ambient was 1 h. For a T_p determination the sample, in most instances placed on a boat of sintered alumina, was first heated from cold to 200°C, held at the latter temperature for 4 h, and furnace cooled. After re-weighing, the sample was replaced in the furnace and the procedure repeated at 400, 600° C, etc. as necessary until the temperature corresponding to a weight change of 1 $mg/cm^2/4$ h could be interpolated from the results. In a few instances, intermediate temperatures of test, also room temperature and the ice point, were used. Low melting point metals such as zinc were weighed and heated in sintered alumina crucibles 9 mm in diameter; the elements Li, Na, K, Be, Hg, As and Se were manipulated throughout in individual test-tubes, of glass 13 mm in diameter for Li, Na, K and Hg, and of clear silica 6 mm bore for Be, As and Se, in each case with one end open to the atmosphere.

3. Results

Results are presented in Figs. 1-5 for elements from lithium to sulphur, potassium to selenium, strontium to tellurium, barium to ytterbium, and hafnium to bismuth rsepectively. In these figures, the unbroken line with circles represents the variation of T_p with atomic number $(Z)^{(a-e)}$. The unbroken line with no legend characters represents the variation of metal melting point (T_m^{metal}) with Z. The dashed line connects points, each of which represents the melting point of an oxide of the appropriate element (data from [1-4]); where the oxide is not the normal valency compound, the melting point of the appropriate monoxide has been used, except in the cases of V, Mn, and Mo (VO_2, Mn_3O_4 and MoO_2). At the ends of the second short and first long periods some melting points have been omitted for clarity, in view of the proximity of T_p to the melting points of elements and oxides. Fig. 6 gives, by way of illustration, the actual curves from which T_p was derived for elements from Ca to Ga inclusive$^{(f,g)}$.

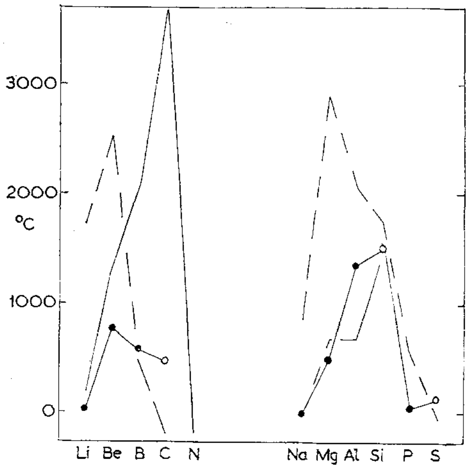

Figure 1 T_p versus atomic number, for elements of the short periods.
(Full line without points = melting points of elements, dashed line without points = melting points of oxides, full circles = weight increase of 1 $mg/cm^2/4$ h, open circles = weight loss of 1 $mg/cm^2/4$ h.

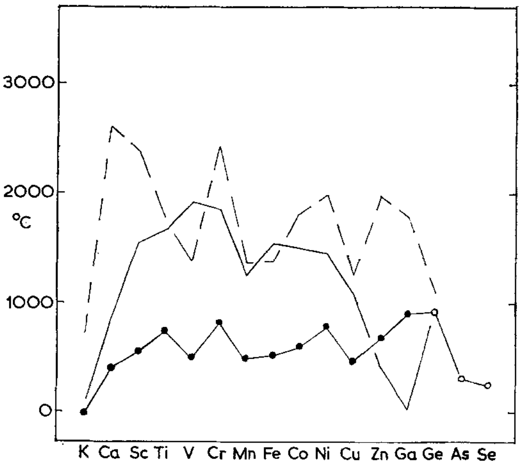

Figure 2 As Fig. 1, for elements of the first long period.

4. Discussion

A principal feature to be noted in Figs. 1-5 is the preeminence of palladium (Fig. 3) and platinum (Fig. 5) in oxidation resistance. Also notable are high values of T_p for aluminium and silicon (Fig. 1). The remainder of the elements have lower values of T_p. Such are the obvious

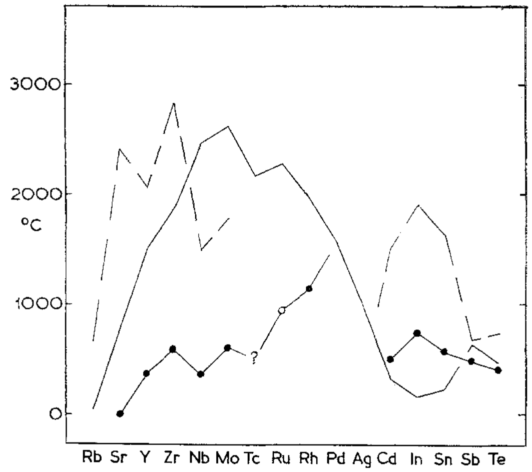

Figure 3 As Fig. 1, for elements of the second long period.

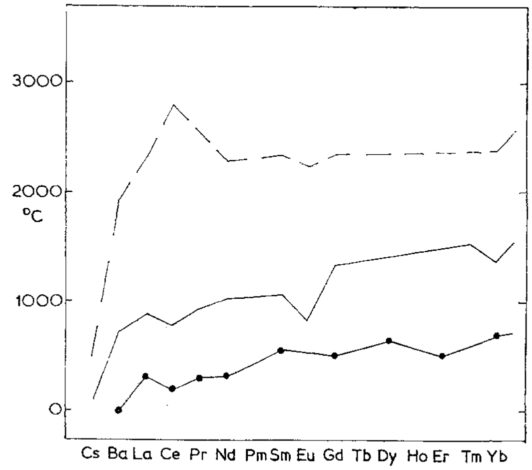

Figure 4 As Fig. 1, for elements of the third long period (Ba-Yb).

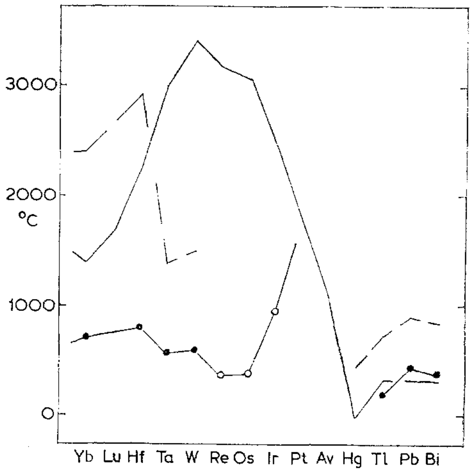

Figure 5 As Fig. 1, for elements of the third long period (Hf-Bi).

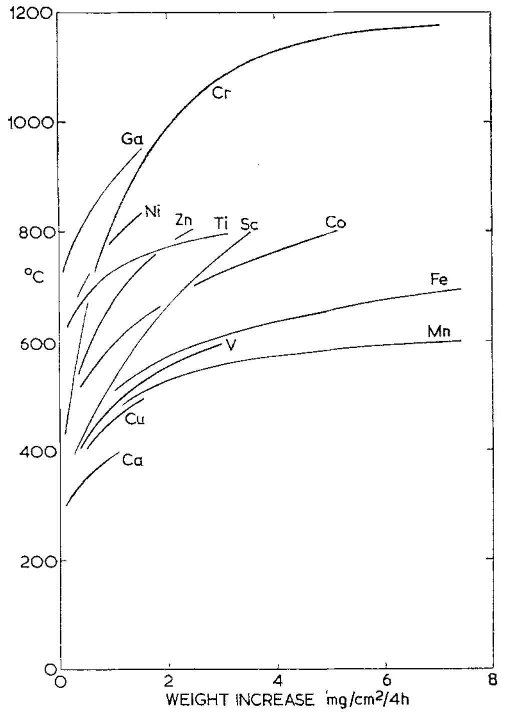

Figure 6 Weight increase versus temperature (constant time), for elements of the first long period.

conclusions; to continue further and attempt to classify the elements, we may proceed as follows, using an argument on the following lines(h). An oxide layer on a metal substrate may to a certain degree be considered as a separate entity, in other words it will behave similarly to a discrete mass of the same oxide. Now Anderson [5, 6], Gregg [7] and Glasson [8], following Tammann, have shown that in the phenomenology of inorganic solids a significant point is reached at about 0.5 T_m(i) (where T_m is the melting point in degrees Kelvin); namely, above 0.5 T_m, lattice diffusion is dominant, but below about 0.5 T_m lattice diffusion is dormant, and only surface diffusion reactions operate markedly. Gregg and Glasson find that 0.5 T_m corresponds to changes in the sintering and agglomeration characteristics of oxide masses during calcination processes. In a general way, therefore, and without attempting to specify the actual mechanism in the present context of metallic oxidation, it is possible that a significant change in the phenomenology of

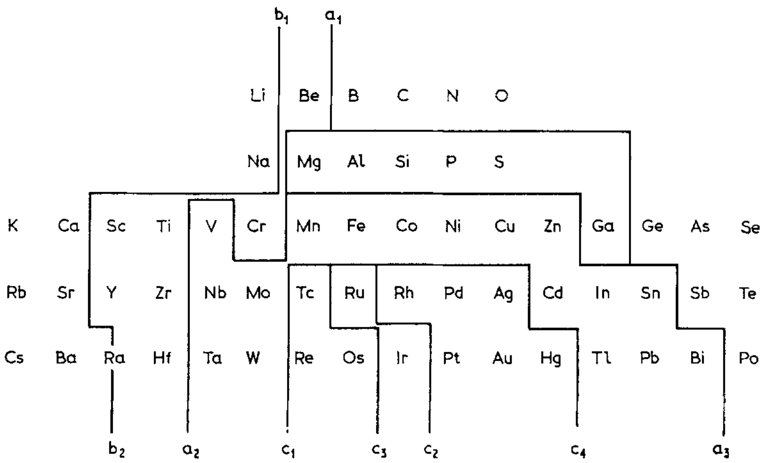

Figure 7 The Periodic Classification.

a_1a_2 boundary between elements for which $T_p \sim 0.5\ T_m^{metal}$ (to the left) and $T_p \sim 0.5\ T_m^{oxide}$ (to the right of the boundary).

a_1a_3 boundary between above groups of elements taken together, and the remainder of the elements (the latter to the right).

$a_1a_2a_3$ closed area with Mg, Al, Si, S, P, Ga; suggested zone where $T_p \sim 0.5\ T_b^{element}$.

b_1b_2 boundary between elements which oxidize completely at room temperature (to the left of the line), and other elements.

c_1c_2 line enclosing transition metals with volatile oxides (oxides of Ru and Ir relatively unstable).

c_1c_3 line enclosing transition metals with volatile oxides (oxide relatively stable).

c_2c_4 line enclosing the noble elements.

N.B. "Ra" signifies rare earth elements.

oxidation may occur at temperatures related directly to the melting point of an oxidation product. In particular, we may consider (Figs. 1-5) whether or not T_p approximates to 0.5 T_m^{oxide} in view of the fact that T_p itself approximates to what may well be a significant point, that is, the "turnover" of the delta *w* versus *T* curve (Fig. 6). If one considers Figs. 1-5 with such considerations in mind, it appears that T_p approximates to 0.5 T_m^{oxide} for oxides of Ta, W and Tl, Pb, Bi in the third long period (Fig. 5), and Nb, Mo and Cd, In, Sn in the second long period (Fig. 3). In the first long period (Fig. 2) there is a general tendency for T_p for elements from titanium to zinc inclusive to approximate to 0.5 T_m^{oxide}, the correspondence being closest with titanium, vanadium, nickel and zinc. In the short periods, T_p does not appear to approximate to 0.5 T_m^{oxide}. Elements for which T_p is conceivably $\sim$0.5 T_m^{oxide}, then, are limited to the long periods and to a band of the periodic table from and including group VA to zinc, tin, bismuth. A corollary of this tentative classification is that the elements Ru, Rh, Pd, Ag and Re, Os, Ir, Pt, Au, Hg form a distinctive enclave (c_1c_4 in Fig. 7). These elements range from rhenium, which oxidizes at relatively low T_p by loss of acidic oxide Re_2O_7, to the noble metals such as silver; these elements would not, *prima facie*, be expected to be classified with those for which T_p approximates to 0.5 T_m^{oxide}.

The elements of groups IIA to IVA inclusive show quite a different variation of T_p and it is proposed that a relation of the form $T_p \sim 0.5\ T_m^{metal}$ exists as may be noted (Figs. 1-5) from the graphs of T_p compared with the melting points of the appropriate elements. The alkali metals may be included in this group. Certainly the rare earth elements show a $T_p \sim 0.5\ T_m^{metal}$ relation (Fig. 4). The apparent change from $T_p \sim 0.5\ T_m^{oxide}$ to $T_p \sim 0.5\ T_m^{metal}$ as one moves from group VA to group IVA is an interesting problem(j). (The suggested boundary marking this change is shown as a_1-a_2 in Fig. 7.) The change may be perhaps consistent with an extension of the argument given above; some data of Stone [9-11] suggest that in composites of oxides of the same metal, the effective Tammann temperature (0.5 T_m) is that of the oxide which forms the preponderant phase. Extending that argument to the present case, we may speculate that in the oxidation of metals of groups IA to IVA the metal substrate functions as the preponderant phase which impresses its oxidation/temperature characteristic on the oxidation behaviour of the composite.

The majority of the elements of the long periods have been tentatively classified, and it remains to consider the behaviour of those of the short periods. In the first short period (Fig. 1), T_p for beryllium is $\sim 0.5\ T_m^{\text{metal}}$, boron oxidizes by formation of adherent liquid oxide, and carbon by formation of very volatile oxides; the behaviour of boron and carbon is therefore distinctive and unlikely to have analogy with metallic oxidation. However, the second short period includes two elements, clearly metallic, namely magnesium and aluminium, which do not appear to follow either a $T_p \sim 0.5\ T_m^{\text{oxide}}$ or $T_p \sim 0.5\ T_m^{\text{metal}}$ regime. A clue to a method of classifying magnesium and aluminium may be noted by turning to Fig. 8, in which the element *boiling* points are compared with T_p for elements from sodium to sulphur; a tendency may be seen for elements of this period to conform to a relation $T_p \sim 0.5\ T_b^{\text{element}}$ (where T_b is the boiling point of the element at standard pressure) No explanation can be advanced for this relation; its present justification is that it characterizes a group of elements which are otherwise difficult to classify. As a corollary it is suggested that T_p for gallium $\sim 0.5\ T_b^{\text{element}}$, and this classification of gallium with aluminium is consistent with the similar oxidation behaviour of these two metals. The possible "0.5 T_b^{element}" elements are included in the closed area between lines a_1, a_2 and a_3 in Fig. 7. Consideration of the sole remaining elements Ge, As, Se, Sb, Te is somewhat outside the scope of this survey; in so far as one can generalize, they appear to have a parameter such that T_p equals $\sim 1 \times T_m^{\text{oxide}}$ or $\sim 1 \times T_m^{\text{metal}}$, presumably because the restricted coordination in these elements (cf. metals) is not conducive to solid state diffusion and conformity with Tammann's rule.

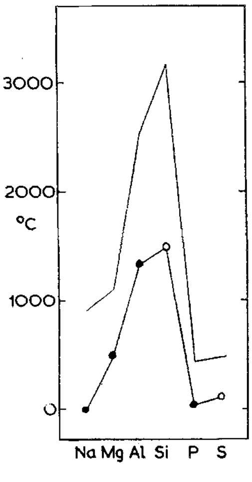

Figure 8 T_p versus atomic number, for elements of the second short period.
(Full line without experimental points = boiling points of elements; circles represent values of T_p.)

As a general corollary, a study of the melting point data of elements and oxides (Figs. 1-5) without reference to the T_p points provides some interesting coincidences. These are of two categories. Firstly, in groups IA to VA the crossover of the T_m^{metal} and T_m^{oxide} curves occurs between groups IVA and VA. Secondly, where $0.5\ T_m^{\text{oxide}}$ is greater than $1.0\ T_m^{\text{metal}}$, that metal is found to require a protective atmosphere to prevent complete oxidation at room temperature (cf. Pilling and Bedworth [12]); the correspondence is particularly notable with the rare earth metals (Fig. 4), where the dividing line comes in the middle of the series, but with europium classed amongst the more reactive metals of lower atomic number, and samarium a stable metal, as is found practically.

A final word remains to be said regarding chromium. In relation to the classification by T_p ratio, chromium has been placed with metals for which $T_p \sim 0.5\ T_m^{\text{metal}}$ (Fig. 7). However, the actual temperature/weight change curve (Fig. 6) is somewhat unusual because unlike the curves for other metals, final flattening of the curve does not occur until well above T_p (i.e. $\sim 1180°$C). Now $0.5\ T_m^{\text{oxide}(Cr_2O_3)}$ is $\sim 1050°$C and $0.5\ T_b^{\text{element}(Cr)}$ is $\sim 1180°$C; consequently it is suggested that there exist strong tendencies to "0.5 T_m^{oxide}" and "0.5 T_b^{metal}" behaviour in this metal. It is also known that volatilization of chromium trioxide plays a part in the high-temperature oxidation of chromium, and this is consistent with the occurrence of volatile acid oxides on or near the line Cr-Tc-Os in the periodic table. This classification as "0.5 T_m^{metal}", but with reservations, is the counterpart to the complex oxidation behaviour of chromium, involving oxide formation, spalling and evaporation, and in certain instances metal evaporation.

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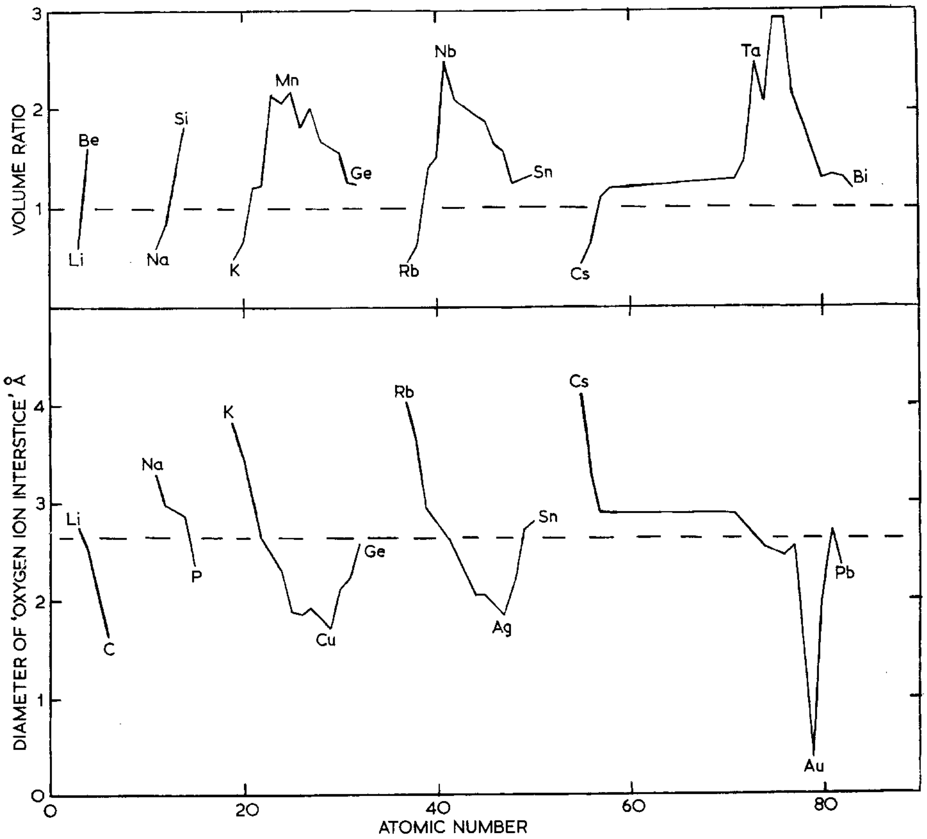

Figure 9 (Appendix)
Diameter of hypothetical hole for oxygen versus atomic number (dashed line represents the diameter of the oxygen ion), also:

$$\text{volume ratio}\left(\frac{\text{volume of oxide formed}}{\text{volume of metal consumed}}\right)\text{versus atomic}$$

number.

Appendix

(a) Weight changes (and therefore values of T_p), are calculated throughout on the basis of original surface areas. For oxidation in the liquid state, this procedure would be a good approximation in the case of aluminium and gallium, which liquify inside tenaceous oxide skins of about the same shape as the solid specimen. For Zn, Cd, In, Sn, Pb, Bi, T_p calculated on the cross-sectional area of the crucible was 160, 120, 150, 70, 20, 20° C respectively less than those given in Figs. 1-5. All data given refer to quiescent conditions and are therefore not necessarily applicable to practical melting.

(b) Ten values of T_p in Figs. 1-5 are recorded as weight losses (open circles). Conversion to a calculated weight gain basis would show little difference at low atomic number (e.g. carbon), but greater discrepancy at high Z (e.g. Re).

(c) Rhodium first gained weight with rising temperature, but lost weight above 1000° C; the experimental point is an extrapolation.Palladium and platinum were tested to 1500° C without showing changes in weight. Silver and gold were tested to near their melting points without change in weight; mercury neither gains nor loses measurable weight in 4 h at room temperature. Dark or coloured scales form in profusion on metals of the first long period; elsewhere they occur only at the ends of the periods (Cd, In, Tl, Pb, Bi), with possible exceptions in Li, Ru, Pr, Nd, Re, Os (dark) and Be, Al, Ga (grey).

(d) The elements Y, Zr, Nb, Mo were subjected to repeat determinations with cylinder oxygen in place of the air atmosphere, other conditions remaining the same. The results gave T_p values of 400, 610, 440, 550° C respectively (c.f. 380, 590, 370, 600° C respectively in air).

(e) The temperature interval from which T_p was interpolated, namely, 200° C, is such that the determinations were necessarily somewhat crude, but not, it is considered, inadmissably so considering the compass of the whole investigation.

(f) It will be noted from Fig. 6 that the use of other degrees of oxidation to represent T_p would not in general, affect the order of merit of the elements, nor indeed would it necessarily change the absolute magnitude of the temperature intercept out of all recognition. For example, if one takes intercepts at the value 0.4 mg/cm^2/4 h [13], the difference between the temperature for this change and the temperature for T_p (1 mg/cm^2/4 h) is in most cases in the range 30 to 100°C, typically 50°C. The value chosen (1 mg/cm^2/4 h) had the incidental advantage that gross spalling, and hence mechanical loss from specimens due to intermittent heating, was avoided.

(g) Linear relationships of approximately equal slope were noted for most elements when the *logarithm* of the weight increase was plotted (not illustrated) against temperature of test. Linear relations were also apparent when the same quantity was plotted against the reciprocal of the absolute temperature.

(h) The abscissa in Figs. 1-5 inclusive has been drawn at a level of 0 K to facilitate this discussion.

(i) It is not suggested that the ratio is exactly 0.5 T_m; the relation is simply a good empirical rule.

(j) This change does not appear to coincide with the Pilling/Bedworth [12] division between oxide products smaller or greater in volume than the metal from which the products are derived. But a naive calculation based on a model of the metal/oxygen interface at the start of the oxidation process offers quite good agreement. We may consider a model of a first oxidation layer on an idealized metal surface and for the purpose of the argument a simple cubic array of metal atoms will initially be assumed to lie in the surface plane. Calculation of the diameter of the central interstice "formed" during transformation of the metal atoms to ions (six-fold co-ordination basis) has been made, with results indicated in Fig. 9, and shows that the point at which the change from $T_p \sim 0.5\ T_m^{\text{metal}}$ to $T_p \sim 0.5\ T_m^{\text{oxide}}$ occurs coincides approximately with the point at which an oxygen ion may just fill this interstice between the metal ions.

References

1. O. KUBASCHEWSKI and B. E. HOPKINS, "Oxidation of Metals and Alloys" (Butterworths, London, 1962).
2. O. KUBASCHEWSKI and E. L. EVANS, "Metallurgical Thermochemistry" (Pergamon Press, London 1958).
3. "Phase Diagrams for Ceramists" (American Ceramic Society, Columbus, Ohio, 1964).
4. R. E. HONIG and D. A. KRAMER, *R.C.A. Review* **30** (1969) no. 2.
5. J. S. ANDERSON, *Disc. Faraday Soc.* **4** (1948) 230.
6. D. J. M. BEVAN, J. S. SHELTON, and J. S. ANDERSON, *J. Chem. Soc.* (1948) 1729.
7. S. J. GREGG, *J. Chem. Soc.* (1953) 3940.
8. D. R. GLASSON, *J. Applied Chem.* **17** (1967) 91.
9. H. E. N. STONE, *Mat. Sci. Eng.* **5** (1969/70) 44.
10. H. E. N. STONE and B. L. DANIELL, *JISI* **207** (1969) 237.
11. H. E. N. STONE and N. A. LOCKINGTON, *Mat. Sci. Eng.* **2** (1967) 107.
12. N. B. PILLING and R. E. BEDWORTH, *J. Inst. Met.* **29** (1923) 529.
13. H. H. UHLIG, ed., "Corrosion Handbook" (John Wiley & Sons, New York, 1948) p. 644.

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