Remarks on the Thermodynamic Conditions for the Oxide Scale Formation on Metals

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ABSTRACT

Basing on a thermodynamic description the authors discuss the reasons for different equilibrium pressures of oxidant on the interface between a metal and a solid scale and between a metal and gaseous oxidation products. Numerous oxide systems are analyzed in terms of free enthalpy of cohesion (atomization) of the oxidation product and free enthalpy of cohesion of metal and dissociation of oxidant. It is shown that, the higher the energy gain resulting from the formation of an oxide, the lower is the dissociation pressure compared to the free enthalpy of cohesion of the metal and of the molecule of oxidant.

Keywords: Pressure of metal oxidation, cohesion energy of the oxides

1. INTRODUCTION

The theory of corrosion is able to explain the mechanisms of formation of complex multiphase scales on metals and alloys and to describe the transport processes in these scales, often responsible of the overall rate of the degradation processes /1-5/. An important question concerns the magnitude of the minimum oxidant pressure required to form scales on different metals. This depends on the standard free enthalpy of metal oxidation. However, the reasons for different values of ΔG° or the correlation between ΔG° and the properties of metals or their location in the periodic table are not discussed.

In the present paper some problems connected with the conditions of metals oxidation and formation of scales (in equilibrium with metal) are discussed. With reference to thermodynamic description of metal/scale systems we give an explanation of the observed differences in oxidant pressure on the metal/scale interface.

2. EQUILIBRIUM PRESSURE OF OXIDANT AT THE METAL/OXIDE INTERFACE IN RELATION TO BOND ENERGY

Depending on metal type, oxidation leads to the formation of a compound having a general formula M_nX_m according to the following equation:

$$2n/mM + X_2 = 2/mM_nX_m \qquad \Delta H_1 = 2/m\, \Delta_f H^\circ \quad (1)$$

where M denotes metal, X – oxidant. In order to define conditions necessary for the formation of a solid scale on metal we should consider the metal/oxidation product equilibrium. Thus, for the reaction (1) the equilibrium constant (K_1) equals inverse oxidant activity (a_{X_2}):

$$K_1 = a_{X_2}^{-1} \quad (2)$$

The equilibrium constant is the following function of temperature:

$$-\Delta G^{o}_{f}(T)/RT = \ln K_1 = -\ln a_{X_2} = -\ln(p_{X_2}/p^{o}(1\,\text{atm})) \qquad (3)$$

The oxidant activity is generally expressed in terms of pressure. For the majority of oxides and sulfides the temperature dependence of the free enthalpy of formation ΔG^{o} is a linear function /6/ described as follows:

$$\Delta G^{o} = \Delta H_{0} - \overline{\Delta S}\, T \qquad (4)$$

where $\overline{\Delta S}$ includes the reaction entropy and a combination of temperature dependent terms.

For illustration, Fig.1 presents the temperature dependence of $(2/m\Delta_{f}G^{o})$ for a number of metal/oxide systems, which are linear functions obeying Eq.(4). Thermodynamic data have been taken from refs /6-8/. Phase diagrams of this type were first proposed by Richardson and Jaffes /9/. The fact that the straight lines are approximately parallel (except that for K/K_2O) indicates that the $\overline{\Delta S}$ value for different reactions is practically the same and almost insensitive to temperature. In turn, this is understandable because metal and its oxidation product are condensed and their formation entropies referred to the same amount of oxidant differ only to a small degree. The observed differences are related to different M/X ratios and arrangements of atoms in the crystal lattice (crystallographic structure).

As can be seen, in agreement with Eq. (3), the more negative the free enthalpy of formation of a compound $(\Delta_{f}G^{o})$, the lower the equilibrium pressure in the M/M_nX_m system. In Eq. (4) there is a term ΔH_{o}, which might be interpreted as the hypothetical formation enthalpy of an oxide in a reaction involving two oxygen atoms (like in Eq. (1)) at a temperature of 0 K. The ΔH_{o} is negative, and the more negative its value, the lower the equilibrium pressure. So, by comparing the values of ΔH_{o} for oxide formation on different metals, we can predict which of the metals oxidizes at a lower oxidant pressure. Since ΔH_{o} is not much different from the oxide formation enthalpy at a standard temperature of 298 K in many earlier works, the standard oxide formation enthalpy was used as a criterion for the sequence of oxidation with the increasing pressure of oxidant /10/. In the above discussion ΔH_{o} and the standard enthalpy reaction (1) (ΔH^{o}_{1}) are related to the reaction involving two oxidant atoms (X_2), so that the standard formation enthalpy should be multiplied by the corresponding coefficient $(2/m\Delta_{f}H^{o})$. As shown by Eq. (4), the criterion of the 'reaction heat' (ΔH_{o}) referring to the 'stability of a compound' or more precisely to the possibility of its formation at a given temperature is correct when the $\overline{\Delta S}$ parameter of the reactions under consideration (at a given temperature) is approximately constant or depends very little on temperature.

On analyzing the properties of metals and various phase diagrams, e.g. metal-oxide (see Fig. 1), it is difficult to find a rule that might explain why some metals oxidize at very low pressures while others do so at much higher pressures of an oxidant. The differences are remarkable though. For calcium, as for other alkaline earth metals, the equilibrium pressures (activities) are similar and extremely low, e.g., about

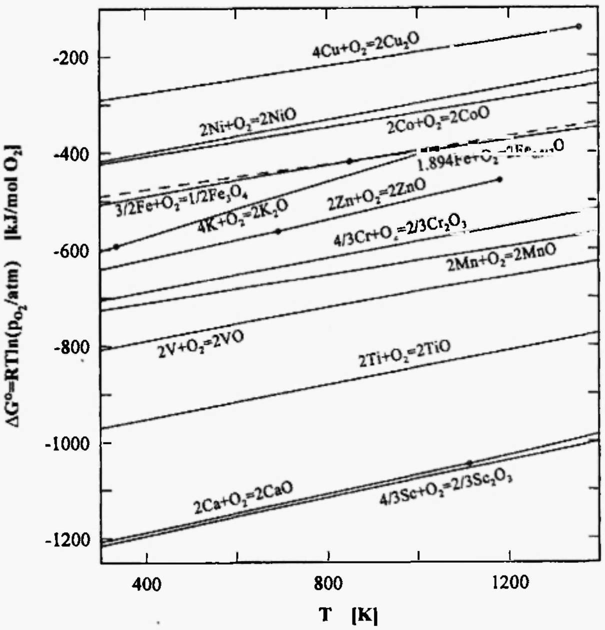

Fig. 1: Temperature dependence of standard free enthalpy of formation $(2/m\,\Delta_{f}G^{o})$ for the oxides of metals belonging to the fourth period /6-8/.

10^{-50} atm at 1000 K, while for 3d transition metals they are much higher and vary in a wide range (10^{-30} – 10^{4} atm). Fig. 1 shows that the sequence of straight lines is practically consistent with the location of the elements in the periodic table, even though some irregularities can be found, e.g. K/K_2O (different slope). Also the equilibrium line for Ca/CaO is situated over the line for Sc/Sc_2O_3 and similarly the Mn/MnO line lies over the line for Cr/Cr_2O_3, while the Zn/ZnO line lies much below the line for Cu/Cu_2O. So, a question arises why the standard free enthalpies of reaction (1), $(\Delta_f G^0)$, for different metal/oxide systems, differ so much?

Let us consider the formation of a solid scale on metal as a sequence of the following processes: sublimation of the metal ($M_{(g)}$), dissociation of the oxidant into atoms $X_{(g)}$, reaction of oxidant and metal atoms to form oxide molecules in the gas phase and finally condensation of these molecules to form oxide crystals:

$$2n/mM_{(cry)} = 2n/mM_{(g)} \qquad \Delta H_5^0 = 2n/m\Delta H^0_{subM} = 2n/mE_{M-M} \tag{5}$$

$$X_2 = 2\,X_{(g)} \qquad \Delta H_6^0 = \Delta H^0_{disX_2} = E_{X-X} \tag{6}$$

$$2n/m\,M_{(g)} + 2X_{(g)} = 2/m\,M_nX_{m\,(g)} \qquad \Delta H_7^0 = -2/m\Delta H^0_{bond} = -2/mE_{bond} \tag{7}$$

$$2/m\,M_nX_{m\,(g)} = 2/m\,M_nX_{m\,(cry)} \qquad \Delta H_8^0 = 2/m\Delta H^0_{cond\,M_nX_m} = -2/m\Delta H^0_{sub\,M_nX_m} \tag{8}$$

The above equilibria can be analyzed in terms of thermodynamic functions. Let's first consider the values of thermodynamic functions at 0 K (at 0 K the system is isoentropic). The standard free enthalpies of reactions (1), (5) – (8) are equal to a combination of the standard enthalpy of the reaction (1) $(\Delta G_1^0 = \Delta H_1^0)$, with the metal sublimation enthalpy $(2n/m\Delta H^0_{sub\,M})$, which determines the energy of metallic bond (cohesion or atomization energy), the oxidant molecule dissociation enthalpy $(\Delta H^0_{dis\,X_2})$, which determines the bond energy of the X_2 molecule $(-E_{X-X})$. The enthalpy of reaction (7) determines the bond energy of the gas molecule M_nX_m $(-2/m\,E_{bond})$ and the enthalpy of reaction (8) is the heat evolved by the condensation of the metal oxide vapor M_nX_m $(\Delta H^0_{cond\,M_nX_m})$, and is equal to the negative of the sublimation enthalpy $(-\Delta H^0_{sub\,M_nX_m})$. (The superscript "0" is related to the values of thermodynamic functions at the temperature of 0 K).

Summing up reactions (7) and (8) is equivalent to the formation of crystal lattice from the metal and oxidant atoms in the gas phase according to the reaction:

$$2n/mM_{(g)} + 2X_{(g)} = 2/m\,M_nX_{m\,(cry)} \qquad \Delta H_9^0 = -2/m\Delta H^0_{coh\,M_nX_m} = -2/m\,E_{coh\,M_nX_m} \tag{9}$$

The negative enthalpy of that process is equal to the crystal atomization enthalpy, i.e. the cohesion energy (bond energy) of the crystal $(-2/m\,E_{coh})$.

The cohesion energy referred to one molecule M_nX_m is a sum of the bond energy of the gaseous molecule and its condensation enthalpy (taken with a negative sign):

$$E_{coh\,M_nX_m} = E_{bond\,M_nX_m} + (-\Delta H^0_{cond\,M_nX_m}) \tag{10}$$

Following Hess's law, the sum of enthalpies of reactions (5)-(9) yields the enthalpy of reaction (1):

$$\Delta H_1^0 = 2/m\Delta_f H^0 = 2n/m\Delta H^0_{sub\,M} + \Delta H^0_{dis\,X_2} - 2/m\Delta H^0_{bond\,M_nX_m} + 2/m\Delta H^0_{cond\,M_nX_m} \tag{11a}$$

or

$$\Delta H_1^0 = 2/m\Delta_f H^0 = -(2/m\,E_{cohM_nX_m} - 2n/m\,E_{M-M} - E_{X-X}) = RT\ln(p_{X_2}/p^0) \tag{11b}$$

It can be seen that the magnitude of ΔH_1^0 depends on the cohesion energy of the oxide, the bond energy of the metal and the dissociation energy of the oxidant.

In order to assess the influence of each term of equation (11) on the value of ΔH_1^0, in Fig.2, we have collected the enthalpies of the processes (1), (5)-(9) for metals belonging to the fourth period. The comparison involves the standard formation enthalpies for oxides

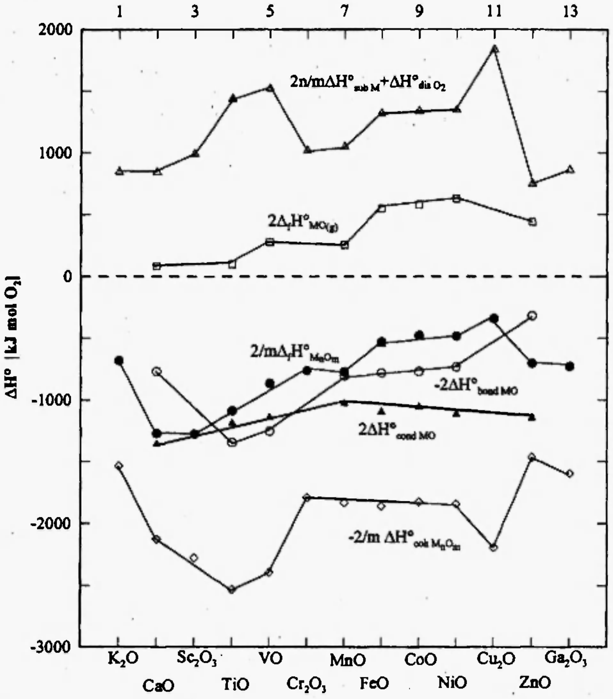

Fig. 2: Standard formation enthalpies (at 298 K) for the oxides /6,8/ of metals from the fourth period ($2/m\Delta_f H^o$) (points ●), enthalpies of metals sublimation /7/ and oxygen dissociation /7/ ($2n/m\Delta H^o_{sub\,MO}+\Delta H^o_{disO_2}$) (points ▲), enthalpy of cohesion of solid oxide ($-2/m\Delta H^o_{coh\,M_nO_m}$) (points ◇), calculated from Eq. (11b), enthalpies of bonds in gaseous molecules /11/ ($-2\Delta H^o_{bond\,MO}$) (points O), enthalpies of condensation of MO ($\Delta H^o_{cond\,MO}$) (points Δ), calculated from Eq. (11a).

($2/m\Delta_f H^o$), the terms associated with the metal sublimation and the oxidant dissociation ($2n/m\Delta H^o_{sub\,M}+\Delta H^o_{disO_2}$), the cohesion energies of the solid oxide ($-2/m\Delta H^o_{coh\,M_nO_m}$), which have been calculated from equation (11a) on the basis of bond energies of diatomic molecules MO ($2\Delta H^o_{cond\,MO}$) /11,12/. To avoid problematic recalculations of each enthalpy into the value at 0 K, we have used the standard data at 298 K /6-8,11,12/, which differ only slightly from those at 0 K.

As shown in Fig.2, the endothermic component ($2/m\Delta H^o_{sub\,M}+\Delta H^o_{disO_2}$) (the curve situated in the uppermost part of the plot) attains quite high values and owing to significant cohesion energies of oxides ($-2/m\Delta H^o_{coh\,M_nO_m}$) (the curve in the lowest part of the plot) the formation enthalpies ($2/m\Delta_f H^o_{M_nO_m}$) take relatively big negative values. Among the oxides presented one that draws attention is Cu_2O because it has almost the highest cohesion energy. This results from the metal/oxygen ratio, which is two times higher than for other oxides. The plot also contains data on the bond energy of gaseous diatomic molecules ($-2\Delta H^o_{bond\,MO}$) /11/, which appear approximately twice smaller than the cohesion energies of the corresponding solid oxides. Fig. 2 shows the values obtained by subtraction of bond energy ($2\Delta H^o_{sub\,M}+\Delta H^o_{disO_2}$) of molecules MO (points □) from the term $2\Delta H^o_{bond\,MO}$. These values determine the formation enthalpies of gaseous molecules ($2\Delta_f H^o_{MO\,(g)}$). In all cases the values obtained are positive and range from 10 to 500 kJ, so that the heat effect associated with the formation of a gaseous molecule cannot compensate for the endothermic effect. The formation enthalpy of oxides takes relatively high negative values only due to the significant condensation enthalpy ($2\Delta H^o_{cond\,MO}$).

By analyzing different systems we can see that the low value of $\Delta_f H^o$ for CaO, in spite of small bond energy of the CaO molecule, results from a relatively high condensation enthalpy of CaO and low sublimation enthalpy of Ca. In turn TiO and VO exhibit the highest cohesion energies and, despite significant sublimation enthalpy of both metals, these oxides have high (negative) formation enthalpies $\Delta_f H^o$. In the case of chromium and manganese for the formation of chromium oxide ($Cr_{2/3}O$) smaller amount of metal is necessary compared to MnO and due to this the cohesion energy of 2/3 Cr_2O_3 is smaller than the cohesion energy of 2 MnO. Even if chromium has the sublimation energy ($\Delta H^o_{sub\,Cr}=397.75$ kJ/mol) much higher than manganese ($\Delta H^o_{sub\,Mn}=280.93$ kJ/mol) its smaller metal/oxygen ratio is the reason why the absolute value of $\Delta_f H^o$ for MnO is bigger (more negative) than that for 2/3 $\Delta_f H^o$ for Cr_2O_3. In the case of Cu_2O, despite the large cohesion energy and the small sublimation energy of copper ($\Delta H^o_{sub\,Cu}$ = 337.45 kJ/mol), $\Delta_f H^o$ is the highest (the least negative) due to the necessity of reacting two copper atoms (674.9 kJ). In turn the relatively small value of $\Delta_f H^o$ for ZnO, in spite of low bond energy of ZnO molecule, results from its high condensation enthalpy and the low sublimation enthalpy of zinc.

Fig. 3 presents the same dependences for metals from the fifth and sixth period. The term associated with the sublimation of metals and the dissociation of oxygen has similar values as for 3d-metals (Fig. 2), although the sublimation enthalpies of these metals are high. This is due to the formation of MO_2 type compounds in which the content of metal is twice smaller. Despite the more loosely-packed structure compared to the MO oxides the cohesion energies of Yb_2O_3, ZrO_2, HfO_2, WO_2, and MoO_2 are fairly high and therefore their formation enthalpies ($\Delta_f H^o$) have large negative values. Oxides from group VIII (4d, 5d) exhibit small cohesion energies. As the sublimation enthalpies of metals are high, the formation energies of the oxides assume small negative values or no solid products are formed. It follows from the above analysis that the formation enthalpies of oxides and thereby the equilibrium pressures at the metal/oxide interface (at 0 K) are complex functions of the bond energy of the oxide and depend strongly on the cohesion energy of the metal and of the oxide dissociation.

At higher temperatures the maximum energies needed for bond cleavage in metal, dissociation of oxidant, atomization of the compound etc. are equal to standard free enthalpies ΔG^o_I of reactions (1), (5)-(9) and therefore by analogy with the preceding considerations we obtain the following equation:

$$\Delta G^o_I = -(2/m\Delta G^o_{coh\,M_nX_m} - 2n/m\Delta G^o_{sub\,M} - \Delta G^o_{dis\,X_2}) \quad (12)$$

Figure 4 shows the temperature dependence of the standard free enthalpies of sublimation of the 3d transition metals and of oxygen dissociation ($2n/m\Delta G^o_{sub\,M} + \Delta G^o_{disO_2}$), while Fig. 5 shows the temperature dependence of the standard free enthalpy of reaction (9) ($-2/m\Delta G^o_{coh\,M_nO_m}$) /6,7/. As can be seen, the temperature dependences of the free enthalpies of sublimation of metals are practically linear and most of the lines are parallel one to another (in agreement with

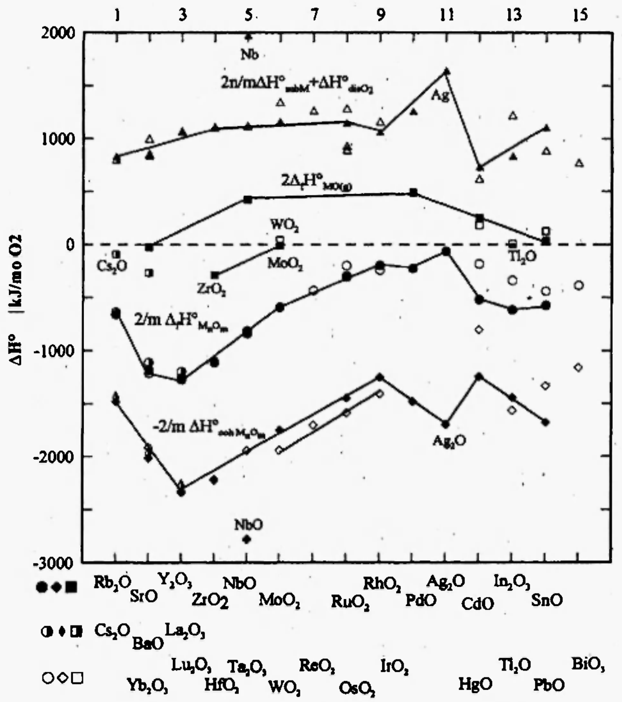

Fig. 3: Standard formation enthalpies (at 298 K) of metal oxides /6-8/ ($2/m\Delta_f H^o$) (points ●, O), enthalpies of metal sublimation /7/ and oxygen dissociation /7/ ($2n/m\Delta H^o_{sub\,MO} + \Delta H^o_{disO_2}$) (points ▲, Δ), enthalpies of cohesion of solid oxides ($-2/m\Delta H^o_{coh\,M_nO_m}$) (points ◆,◇), calculated from Eq. (11b), enthalpies of formation of gaseous molecules /7/ MO_2 ($\Delta_f H^o_{MO_2(g)}$) and MO /7/ ($2\Delta_f H^o_{MO(g)}$) (points ■, □). Points (◇, ◐, ◧) mark values related to Cs, Cs_2O, Ba, BaO, La, La_2O_3. Full markers refer to metals from the fifth period and their oxides, empty markers – to metals from the sixth period and their oxides.

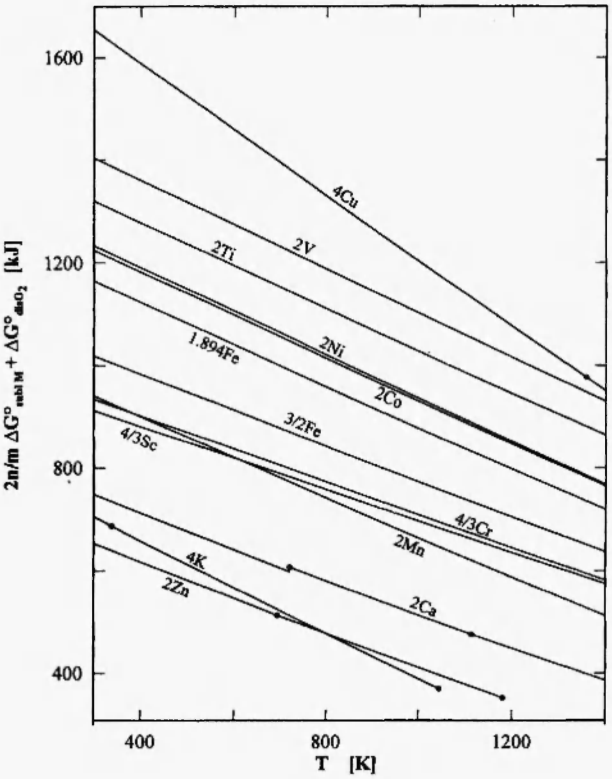

Fig. 4: Temperature dependence of standard free enthalpies of metal sublimation /7/ and oxygen dissociation ($2n/m\Delta G^{o}_{\mathrm{sub\,MO}} + \Delta G^{o}_{\mathrm{disO_2}}$).

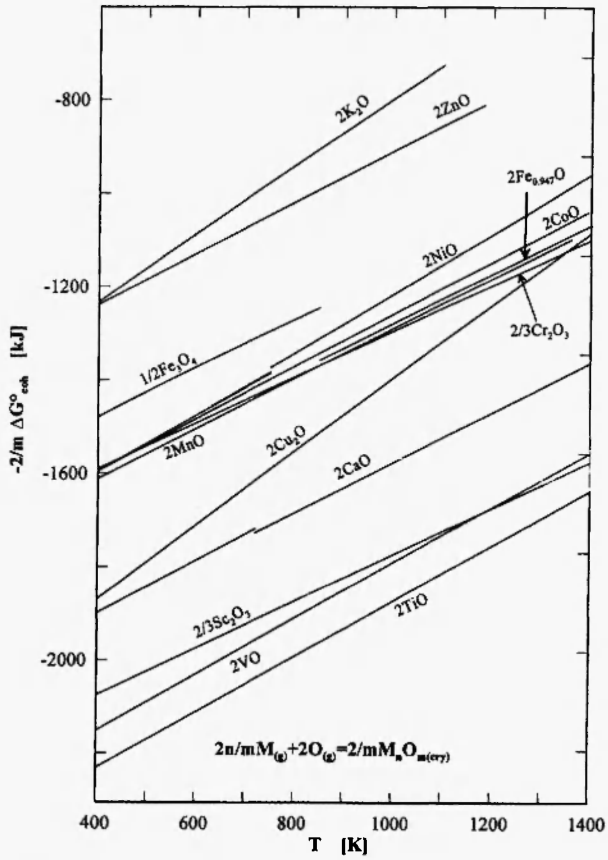

Fig. 5: Temperature dependence of the standard free enthalpy of cohesion for oxides of metals of the fourth period ($2/m\Delta H^{o}_{\mathrm{coh\,M_nO_m}}$) calculated from Eq.(12).

Eq. (4)). The different slopes for some metals, like Cr, Sc, K, originate from different values of the coefficient (2n/m), which for the remaining metals is equal to 2. The free enthalpies of cohesion of the oxides discussed (Fig. 5) have a slightly stronger dependence on temperature compared to the sublimation of metals and a similar decrease of the absolute values ($-\Delta G^{o}_{\mathrm{coh}}$) with increasing temperature. Summing up the above functions yields the dependence of the standard free enthalpies of reaction (1) ($2/m\Delta_f G^{o}$) on temperature, which is given in Fig.1 for the systems discussed. Thus, the value of $\Delta_f G^{o}$ at different temperatures is related to that of $\Delta G^{o}_{\mathrm{coh}}$ for the oxides and to the free enthalpies of sublimation of metals and oxygen dissociation. By analyzing the data shown in Figs. 1, 4 and 5 we can explain the location of the curves describing the states of equilibrium and consequently the values of the equilibrium pressures at higher temperatures. The non-typical shape of the equilibrium line for the K/K_2O system can be accounted for by a stronger dependence of the standard free enthalpy of sublimation of potassium ($4\Delta G^{o}_{\mathrm{sub\,K}}$) and the free enthalpy of cohesion of K_2O ($2\Delta G^{o}_{\mathrm{coh}}$) on temperature, compared to other systems. The relative location of the curves is associated with the value and kind of temperature dependence of ΔG^{o} for the metals and corresponding oxides. As already mentioned, the relatively low equilibrium pressure for the Zn/ZnO system results mainly from a small value of $\Delta G^{o}_{\mathrm{sub\,Zn}}$. Similarly, the relative location of the equilibrium curves for the Mn/MnO and Cr/Cr_2O_3 systems is due to a significant difference in the standard free enthalpies of sublimation of Mn and Cr ($2\Delta G^{o}_{\mathrm{sub\,Mn}}$ and

$4/3\Delta G^{\circ}_{\mathrm{subCr}}$) and to a small difference in the values of standard free enthalpies of cohesion of both oxides. Other systems can be analyzed in the same way.

To sum up the above considerations, it can be stated that in cases when solid oxides are formed on metals the standard free enthalpies of oxide formation must be negative (see Fig. 1) because in open systems at atmospheric pressure (1 atm) the maximum equilibrium pressure is 1 atm and $\Delta G^{\circ}_{\mathrm{I}} = 0$. Thus, at temperatures higher than that corresponding to $\Delta G^{\circ}_{\mathrm{I}} = 0$ no solid scale forms on metals (in closed systems the values of equilibrium pressures can exceed 1 atm and ($\Delta G^{\circ}_{\mathrm{I}} > 0$). Thus the necessary condition for the formation of a solid oxide on a metal surface (at the pressure of 1 atm) resulting from Eq. (12) is:

$$-2/m\Delta G^{\circ}_{\mathrm{bond\,M_nX_m}} - 2/m\Delta G^{\circ}_{\mathrm{sub\,M_nX_m}} + 2m/n\Delta G^{\circ}_{\mathrm{subM}} + \Delta G^{\circ}_{\mathrm{dis\,X_2}} \leq 0 \qquad (13)$$

or

$$-2/m\Delta G^{\circ}_{\mathrm{coh\,M_nX_m}} + 2m/n\Delta G^{\circ}_{\mathrm{subM}} + \Delta G^{\circ}_{\mathrm{dis\,X_2}} < 0 \qquad (13a)$$

which shows that the standard free enthalpy of metal sublimation and oxidant dissociation cannot be greater than the standard free enthalpy of cohesion of the oxide.

The next conclusion resulting from Eq. (12) is that the larger (more negative) the difference between the free enthalpy of cohesion of the oxide and the free enthalpies of metal sublimation and oxidant dissociation, the lower will be the equilibrium pressure necessary for the formation of the solid oxidation product, or, in other words, the greater the energy gain associated with the formation of a solid scale compared to the atomization energy of metal and oxidant molecule (sublimation of metal and oxidant dissociation).

3. EQUILIBRIUM BETWEEN THE METALS AND THE GASEOUS OXIDATION PRODUCTS.

As already mentioned, there are many metals which oxidize to produce solid scales with a high oxidation number. Below the equilibrium pressure these metals coexist with gaseous oxide molecules where the metal ions have lower oxidation numbers. For illustration this situation is observed in the systems: Cr-O, Zr-O, Mo-O, W-O. What determines the pressure of oxide vapors over the metal and the rate of metal consumption?

Let us consider a simple equilibrium of a metal M with a gaseous molecule MX:

$$\mathrm{M_{(cry)}} + 1/2\mathrm{X_2} = \mathrm{MX_{(g)}} \qquad \Delta_{\mathrm{f}}H^{\circ}_{\mathrm{MX\,(g)}} \qquad (14)$$

The equilibrium constant in this case is:

$$-\Delta_{\mathrm{f}}G^{\circ}_{14}/RT = \ln K_{14} = \ln (p_{\mathrm{MX}}/p^{1/2}_{\mathrm{X_2}}) \qquad (15)$$

The equilibrium pressure of the oxide vapors (at a given temperature), or more exactly the $p_{\mathrm{MX}}/p^{1/2}_{\mathrm{X_2}}$ ratio, depends on the value of $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{MX\,(g)}}$. As in the previous paragraph, let us consider the equilibrium processes (9)-(11) at 0 K. As in Eq.(16), the formation enthalpy of $\mathrm{MX_{(g)}}$ (at 0 K) can be expressed as a difference between the bond energy in the gaseous molecule and the bond energies in metal and oxidant:

$$\Delta_{\mathrm{f}}H^{\circ}_{14} = -(E_{\mathrm{bond\,MX}} - E_{\mathrm{coh\,M}} - 1/2\,E_{\mathrm{X-X}}) \qquad (16)$$

Figure 6 shows the enthalpies of metal sublimation and oxygen dissociation ($\Delta H^{\circ}_{\mathrm{sub\,M}} + 1/2\Delta H^{\circ}_{\mathrm{dis\,O_2}}$), bond energy of the diatomic molecules ($-\Delta H^{\circ}_{\mathrm{bond\,MO}}$) and the enthalpy of reaction (14) ($\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{MO_{(g)}}}$) /7/ for a number of metals and gaseous MO oxides. The sum of bond energies in the metal and in the oxidant molecule has large positive values, which significantly overcome the bond energies of the diatomic molecules of the corresponding oxides ($\Delta H^{\circ}_{\mathrm{bond\,MO}}$). As a result, the formation enthalpies of oxides ($\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{MO_{(g)}}}$) are positive. By analyzing different metals and their oxides, the following rule emerges: When the cohesion energy of the metal is high, the bond energy in a gaseous oxide molecule is also relatively high. Due to the existing differences, the standard enthalpies of reaction (14) for the systems discussed fall

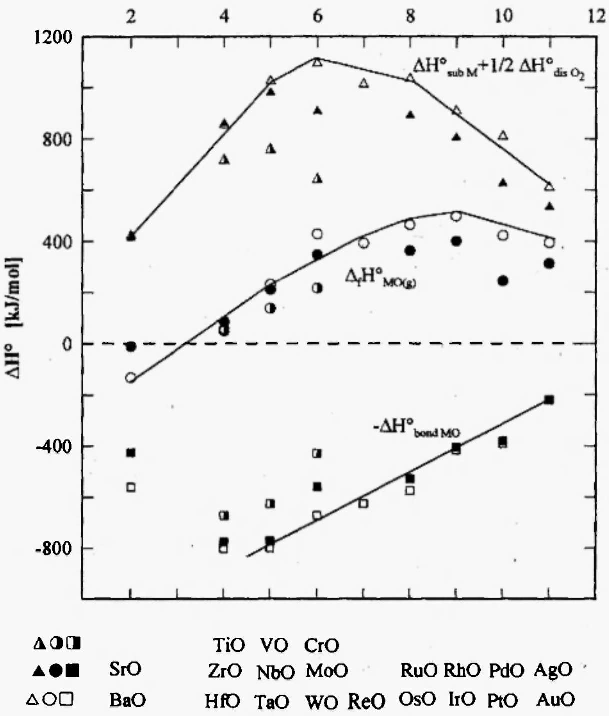

Fig. 6: Standard enthalpies of formation of gaseous molecules for a number of metal oxides /7/ MO ($\Delta_f H^o$) (points ◐, ●, O), enthalpies of metal sublimation and oxygen dissociation /7/ ($2n/m\Delta H^o_{sub\,MO} + \Delta H^o_{dis\,O_2}$) (points Δ, ▲, Δ), enthalpies of bonds /11/ in gaseous molecules ($-2\Delta H^o_{bond\,MO}$) (points ◨, ■, □). Points (◐, ◭, □) refer to metals from the fourth period, full markers – metals from the fifth period and empty ones – metals from the sixth period.

in the range 10-600 kJ (except for SrO and BaO). As follows from Figs. 2 and 6, the differences in bond energies between gas molecules MO in equilibrium with the metal and the solid oxides are small. This indicates that strong repulsive interactions between the metal ions inhibit the condensation of oxide vapors. Such a behavior is probably related to the electronic configurations of metal ions and to the energy of electrostatic interactions.

As already mentioned, the equilibrium pressure of metal oxide vapors at elevated temperatures depends on the standard free enthalpies of formation of gas molecules (Eq.14) which in turn depend on the ΔG^o of the processes (5)-(7). Thus, for the MO molecules we obtain the following relation:

$$\Delta_f G^o_{14} = -(\Delta G^o_{bond\,MO} - \Delta G^o_{sub\,M} - 1/2\Delta G^o_{disO_2}) = RT\ln(p_{MO}/p^{1/2}_{O_2}) \qquad (17)$$

Fig.7 presents the temperature dependence of the free enthalpies of formation for a number of oxides ($\Delta_f G^o$), as well as those of metal sublimation and oxygen dissociation ($\Delta H^o_{sub\,M} + 1/2\Delta H^o_{dis\,O_2}$) and

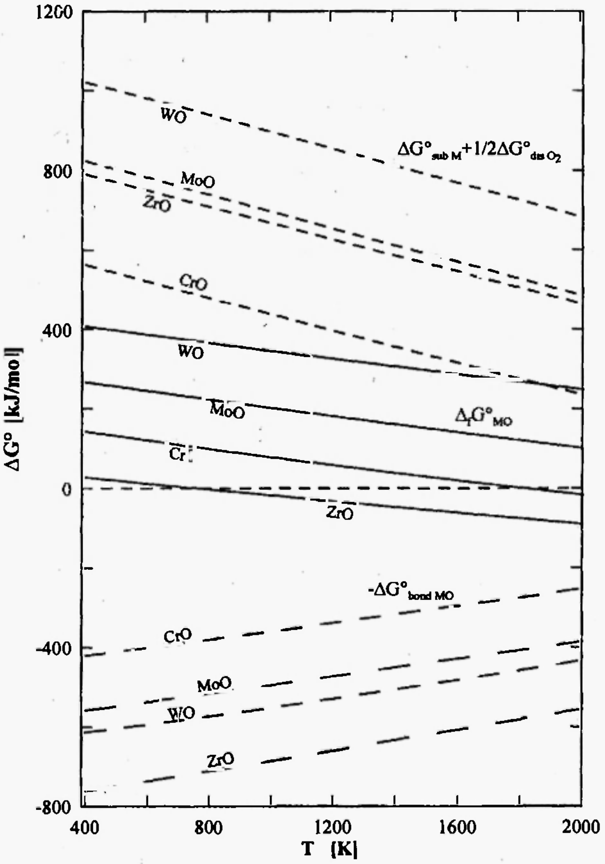

Fig. 7: Temperature dependence of standard free enthalpy /7/ of formation of gaseous molecules MO ($\Delta_f G^o$), standard free enthalpy of bond /7/ in gaseous molecules ($-\Delta G^o_{bond\ MO}$) and standard free enthalpy of metal sublimation /7/ and oxygen dissociation /7/ ($\Delta G^o_{sub\,M} + 1/2\,\Delta G^o_{disO_2}$).

standard free bond energies ($-\Delta G^{\mathrm{o}}_{\mathrm{bond\ MO_{(g)}}}$) for the MO molecules in the gas phase. As can be seen, the plots obtained are practically linear and parallel to each other. The majority of $\Delta_{\mathrm{f}}G^{\mathrm{o}}$ values are positive except for ZrO and CrO at high temperatures. For positive $\Delta_{\mathrm{f}}G^{o}$ values the logarithm of the ratio of oxide to oxygen pressure is smaller than 1 so $p_{\mathrm{MO}} < p_{\mathrm{O_2}}^{1/2}$. The ratio equals 1 when $\Delta_{\mathrm{f}}G^{\mathrm{o}} = 0$ and it is > 1 when $\Delta_{\mathrm{f}}G^{\mathrm{o}} < 0$. It follows from Eq. (15) that the higher the equilibrium pressure of oxygen, the higher is the pressure of oxide vapor. The smaller the $\Delta_{\mathrm{f}}G^{o}$ (positive), the higher is the pressure of oxide vapor, which increases further when $\Delta_{\mathrm{f}}G^{\mathrm{o}}$ becomes negative at sufficiently high temperatures (MO vapor pressure exceeds $p_{\mathrm{O_2}}^{1/2}$). Oxidation of metal in the flowing gas will proceed faster when the equilibrium pressure of the oxide (p_{MO}) and the oxidant pressure in the atmosphere are higher.

The occurrence of oxygen and oxide molecules MO enables the formation of higher oxidation products, such as MO_2 or MO_3. When the respective equilibria are attained it is possible to determine the vapor pressures of the oxide molecules MO_x. The formation of a solid oxide, e.g. MO_2, on a metal at oxidant pressure exceeding the equilibrium oxygen pressure changes the kinetics of metal oxidation (reaction rate controlled by diffusion). However, the outer surface of the scale is always in contact with the MO_x vapors. The solid scale may grow slowly but the metal consumption may be significant because of the high pressure of MO_x molecules in the atmosphere. This situation is observed in the case of molybdenum or chromium /2,13/.

As shown in Fig. 2, for most systems in which solid oxides are formed, the standard formation enthalpies of gaseous oxides MO have large positive values of about 250 kJ/mol. At elevated temperatures they become lower by 20 - 30%. Therefore at low equilibrium pressures of oxidant at the M/MO_{cry} interface, e.g. of the order of 10^{-10} atm or less, the oxide vapor pressures will also be very low (at 1000 K less than 10^{-25} atm) and as a consequence they will not affect the oxidation rate.

4. CONCLUSIONS

The analysis carried out in this work can be summarized as follows:

- When a solid scale forms on a metal the equilibrium pressure at the metal/oxide interface (which must be exceeded for the metal to react with oxygen) depends on the bond energies of the oxide, the metal and the oxidant molecule.
- To assess the magnitude of the interactions between the atoms the standard free enthalpy of cohesion for the phases in equilibrium and the free enthalpy of the oxidant dissociation can be used.
- The larger the energy gain related to the formation of a solid oxide, the lower will be the oxidant pressure at the interface, compared to the free enthalpies of bonds in the metal and the oxidant molecule.
- The analysis of a number of metal/oxide systems indicates that, despite quite regular changes of the cohesion energy of metals, the cohesion energies of oxides are diverse and therefore the standard free energies of oxide formation do not reflect the location of metals in the periodic table, since the latter results from the difference in bond energies of the phases in equilibrium.
- The condensation enthalpies calculated from the thermodynamic data are mostly higher than the bond energies of gaseous molecules and decide about the formation of solid scales and the magnitude of the oxidant pressure which is sufficient to oxidize a given metal.
- The analysis of systems in which a metal coexists with gaseous oxidation products shows that the smaller is the difference between the standard free enthalpy of bond ($-\Delta G^{\mathrm{o}}_{\mathrm{bond\ MO}}$) in a gaseous molecule and the free enthalpies of metal sublimation and oxygen dissociation, the bigger is the ratio of pressures of oxide vapors and oxidant ($p_{\mathrm{MX}}/p_{\mathrm{X_2}}^{1/2}$). When the oxygen pressure increases the same happens to the oxide vapor pressure and this accelerates the oxidation of metal.
- Small differences in the bond energy of metal oxide

molecules indicate that lack of formation of MO-type oxides on a number of metals is caused by strong repulsive interactions between the metal ions in these oxides.

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