

Letters to the Editor

THERMODYNAMIC CONTRIBUTION OF ACTIVE PARTICLES TO THE ENERGY BALANCE OF METALLURGICAL REACTIONS¹⁾

ТЕРМОДИНАМИЧЕСКИЙ ВКЛАД ОТ АКТИВНЫХ ЧАСТИЦ В ЭНЕРГЕТИЧЕСКИЙ БАЛАНС РЕАКЦИЙ В МЕТАЛЛУРГИИ

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The investigation (by the Born-Haber cycle) of the reaction heat arising when FeO is formed by oxygen in the atomic and the ionic state shows that active particles substantially increase the combination heat and the probability of this reaction taking place at the plasma/metal interface.

An investigation of conditions in the thermal boundary layer and in the plasma sheath, based upon the Poisson relation as expressed by the Maxwell-Boltzmann equations, indicates that, given an oxygen plasma in a state of thermodynamic equilibrium at a temperature of 10,000 K and an initial positive ion and electron density of $1.59 \times 10^{22} \text{ m}^{-3}$ [1], only some 10^{21} m^{-3} of ions will participate in the reaction with the metal surface [2]. The rest of the reacting system will be made up of atoms and molecules with high levels of vibrational energy and with a density of the order of 10^{22} m^{-3} of heavy particles. As the total number of particles in an oxygen plasma at $1 \times 10^4 \text{ K}$ is known to be $1.735 \times 10^{22} \text{ m}^{-3}$, the proportion of heavy particles is large enough for them to exert a substantial influence on the thermodynamics of any chemical reactions proceeding in the system.

The contribution of active particles to metallurgical processes will here be analysed on a concrete example, the surface oxidation of iron in the presence of atomic oxygen.

The formation of FeO assumes a close bond between one atom of oxygen and one atom of iron. The bond between Fe^{2+} cations and O^{2-} anions is predominantly ionic in nature [3]. Irrespective of the type of crystallographic lattice and the kind of bonding forces in question, the quantities of energy involved in the formation of FeO can always be investigated by means of the Born-Haber thermodynamic cycle and the relevant experimental data [4, 5].

The Born-Haber cycle is a thermodynamic cycle which reveals the interdependences between the ionization potentials, the electron affinities, the lattice energies, the heat of evaporation, and the heat of dissociation of the elements that combine to form a compound. This cycle can be exploited to assess how a change in any of those quantities will alter the reaction heat arising in the formation of that compound.

A born-Haber cycle for the formation of FeO must take into account the following thermochemical reactions:

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$$\text{Fe}_{(s)} = \text{Fe}_{(a)} \quad \Delta H_{\text{sub}}(\text{Fe}_{(s)}) = 398.6 \text{ kJ mol}^{-1} \quad (1)$$

$$\text{Fe}_{(a)} = \text{Fe}_{(g)}^{2+} + 2e^- \quad I_{\text{Fe}^{2+}} = 2323.25 \text{ kJ mol}^{-1} \quad (2)$$

$$\frac{1}{2}\text{O}_{2(g)} = \text{O}_{(a)} \quad \frac{1}{2}\Delta H_{\text{dis}}(\text{O}_{2(g)}) = 247.0 \text{ kJ mol}^{-1} \quad (3)$$

$$\text{O}_{(a)} + 2e^- = \text{O}^{2-} \quad E_{\text{O}^{2-},(a)} = -648.95 \text{ kJ mol}^{-1} \quad (4)$$

$$\text{Fe}_{(g)}^{2+} + \text{O}_{(a)}^{2-} = \text{FeO}_{(s)} \quad U_{\text{lattice}} = ? \quad (5)$$

$$\text{FeO}_{(s)} + \frac{1}{2}\text{O}_{2(g)} = \text{FeO}_{(s)} \quad \Delta H_{\text{comb}}(\text{FeO}_{(s)}) = -264.6 \text{ kJ mol}^{-1} \quad (6)$$

The resultant change, expressed by equation (6), can be ascertained by successive analyses of the reactions described by the preceding five equations, as indicated by the scheme in Fig. 1.

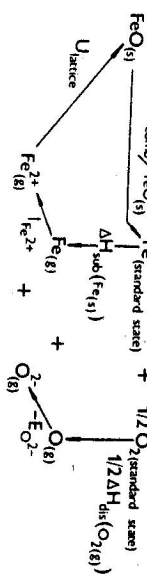


Fig. 1.

Given requisite data, a Born-Haber cycle can be utilized for calculating the reaction heat ΔH_{comb} . Because of its general validity, this cycle can also be applied for determining the magnitude of $\Delta H_{\text{comb}}(\text{FeO}_{(s)})$ in cases when the reaction involves active particles of oxygen, i.e. atomic and ionic oxygen particles.

The lattice energy of $\text{FeO}_{(s)}$ can be established with the aid of the Born-Haber cycle from equation (7):

$$\begin{aligned} U_{\text{lattice}}(\text{FeO}_{(s)}) &= -[-\Delta H_{\text{comb}}(\text{FeO}_{(s)}) + \Delta H_{\text{sub}}(\text{Fe}_{(s)}) + \\ &+ \frac{1}{2}\Delta H_{\text{dis}}(\text{O}_{2(g)}) + I_{\text{Fe}^{2+}} - E_{\text{O}^{2-}}] = \\ &= -[264.6 + 398.6 + 247.0 + 2323.25 + 648.95] = \\ &= -3882.2 \text{ kJ mol}^{-1}. \end{aligned} \quad (7)$$

For the reaction with atomic oxygen, $\Delta H_{\text{comb}}(\text{FeO}_{(s)})$ can be determined by a relation derived from equation (7):

$$\begin{aligned} \Delta H_{\text{comb}}(\text{Fe}^{++}\text{O}) &= U_{\text{lattice}}(\text{FeO}_{(s)}) + \Delta H_{\text{sub}}(\text{Fe}_{(s)}) + I_{\text{Fe}^{2+}} - E_{\text{O}^{2-}(a)} = \\ &= -3882.2 + 398.6 + 2323.25 + 648.95 = -511.4 \text{ kJ mol}^{-1}. \end{aligned}$$

The Born-Haber cycle for the reaction of atomic oxygen with iron can be presented in the form shown in Fig. 2. Comparison of this scheme with Fig. 1 shows the impact of plasma technology: as some

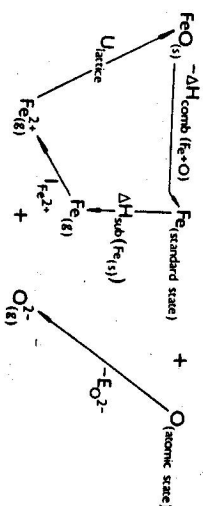


Fig. 2.

of the oxygen is present in the atomic state, there is no need to expend the energy otherwise needed for dislocation of the corresponding amount of molecular oxygen in the field of force of the metal. Consequently, the reaction heat ΔH_{comb} associated with the formation of FeO is augmented by this dissociation energy, which is $247.0 \text{ kJ mol}^{-1}$. That represents a roughly 93% increase in enthalpy as against the same reaction proceeding under standard conditions.

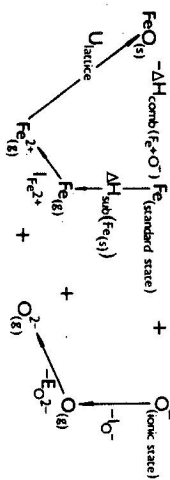


Fig. 3.

The Born-Haber cycle can be similarly employed for examining the thermodynamic contribution of the reaction between Fe and negative oxygen ions O^- . With reference to the scheme in Fig. 3,

$$\begin{aligned} \Delta H_{\text{comb}}(\text{Fe}^{++}\text{O}^-) &= U_{\text{lattice}}(\text{FeO}_{(s)}) + \Delta H_{\text{sub}}(\text{Fe}_{(s)}) + I_{\text{Fe}^{2+}} - I_{\text{O}^-} - \\ &- E_{\text{O}^{2-}} = -3882.2 + 398.6 + 2323.25 - 141.6 + 648.95 = -653.0 \text{ kJ mol}^{-1}. \end{aligned}$$

The thermodynamic contribution of the reaction between Fe and positive oxygen ions O^+ , as indicated in Fig. 4, is evident from the following expression:

$$\begin{aligned} \Delta H_{\text{comb}}(\text{Fe}^{++}\text{O}^+) &= U_{\text{lattice}}(\text{FeO}_{(s)}) + \Delta H_{\text{sub}}(\text{Fe}_{(s)}) + I_{\text{Fe}^{2+}} - I_{\text{O}^+} - \\ &- E_{\text{O}^{2-}} = -3882.2 + 398.6 + 2323.25 - 1313.83 + 648.95 = -1825.23 \text{ kJ mol}^{-1}. \end{aligned}$$

The enthalpy value is at least to some extent indicative of the degree of probability that the chemical reaction will proceed as described. In general, this probability is expressed as

$$\Delta G = \Delta H - T\Delta S, \quad (8)$$

where ΔG is the change in free enthalpy, ΔH — the change in enthalpy, and ΔS — the change in entropy.

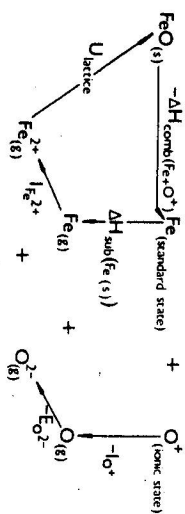


Fig. 4.

The processes considered as probable are those for which this relation yields a negative value of ΔG . In most reactions proceeding at or close to laboratory temperature, the term $T\Delta S$ is small compared with ΔH . Therefore, at the constant temperature and pressure levels usual in laboratory work, the reactions likely to occur in an enclosed system (i.e. a system incapable of any exchange of energy with its environment) are exothermic reactions, as these generally display negative ΔG values. Endothermic reactions, which normally exhibit positive ΔG values, are in general improbable under such conditions.

If we now apply this to the formation of FeO in systems devoid of any thermal equilibrium, where the product temperature is lower than the melting point of the iron oxide, and the reaction at the interface between the plasma and the cooler metal takes place in the presence of active oxygen particles, it becomes clear that the extra heat ΔH defined by equation (8) increases the probability of the reaction taking place as intended.

At high temperatures of the starting materials and of the products which are typical for plasma processes in homogeneous systems, the magnitude of the term $T\Delta S$ increases sharply, and therefore the positive or negative character of ΔG depends upon that of ΔS . In general, ΔS is positive for processes in which large particle agglomerations decompose into smaller ones, which implies that for the $\text{Fe} + \frac{1}{2}\text{O}_2 \rightarrow \text{FeO}$ reaction, ΔS will be negative. This reaction is likely to proceed less completely at extremely high than at more moderate temperatures.

This last conclusion can be extrapolated further: it seems likely that at extremely high temperatures, complex molecules will be rare, and there will probably be no chemical reactions combining atoms or simple molecules into larger and more complex molecules.

The preceding analysis suggests that the FeO-forming reaction will most likely proceed at high concentrations of active particles in the plasma and at relatively low temperatures of the reacting metal.

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