

# Oxygen mass transfer at liquid-metal–vapour interfaces under a low total pressure

P. CASTELLO, E. RICCI, A. PASSERONE

*Istituto di Chimica Fisica Applicata dei Materiali del C.N.R., Via De Marini 6, 16149, Genova, Italy*

P. COSTA

*Istituto di Scienza e Tecnologie Chimiche – Facoltà di Ingegneria dell'Università di Genova – Via all'Opera Pia 15/a, 16145, Genova, Italy*

The problem of oxygen exchange at the interface between a gas and a liquid metal is treated for systems under a "vacuum" (Knudsen regime, pressures lower than 1 Pa), where, due to the large mean free path of gas molecules in a vacuum, transport processes in the gas phase have no influence on the total interphase mass exchange, which is controlled by interface phenomena and by oxygen partition equilibrium inside the liquid. Owing to the double contribution of molecular  $O_2$  and volatile oxides to the oxygen flux from the surface, non-equilibrium steady-state conditions can be established, in which no variations in the composition of the two phases occur with time, as the result of opposite oxygen exchanges. The total oxygen and metal evaporation rates are evaluated as a function of the overall thermodynamic driving forces, and an account of the transport kinetics is given by using appropriate coefficients. A *steady-state saturation degree*  $s_r$ , is defined which relates the oxygen activity in the liquid metal to the  $O_2$  pressure imposed and to the vapour pressures of volatile oxides. When metals able to form volatile oxides are considered, pressures of molecular  $O_2$  higher than those defined under equilibrium conditions have to be imposed in the experimental set-up in order to obtain a certain saturation degree, as a consequence of the condensation of the oxide vapours on the reactor walls. *Effective oxidation parameters* are determined, which define the conditions leading the liquid to a definite steady-state composition under a "vacuum" when it is out of equilibrium. The effective value of the oxygen pressure which corresponds to the complete oxygen saturation of the metal,  $P_{O_2,s}^E$ , is evaluated at different temperatures for the systems Si–O and Al–O. The results are represented as curves of  $\lg P_{O_2,s}^E$  against  $T$ , which separate different *oxidation regimes*; these results agree well with the experimental data found in the literature.

## Nomenclature

$a_\eta$	activity of the component $\eta$ in the liquid phase.
$k_\eta$	partial-transport coefficients for the mass transfer of the component $\eta$ ( $\text{mol s g}^{-1} \text{cm}^{-1}$ ).
$K_\eta$	global-transport coefficients for the mass transfer of the component $\eta$ ( $\text{mol s g}^{-1} \text{cm}^{-1}$ ).
$M_\eta$	molecular weight of the species $\eta$ ( $\text{g mol}^{-1}$ ).
$N_M^{\text{tot}}$	global metal flux between the gas and the condensed phase ( $\text{mol cm}^{-2} \text{s}^{-1}$ ).
$N_{O_2}^{\text{tot}}$	global oxygen flux between the gas and the condensed phase ( $\text{mol cm}^{-2} \text{s}^{-1}$ ).
$P_j$	partial pressure of the $j^{\text{th}}$ oxide (Pa).
$P_M$	vapour pressure of the pure metal (Pa).
$P_{O_2}$	partial pressure of molecular $O_2$ (Pa).
$P_{\text{tot}}$	total pressure (Pa).
$P_M^E$	effective metal-vapour pressure (Pa).
$P_{O_2}^E$	effective oxidation pressure (Pa).
$R^E$	effective evaporation ratio.
$s$	actual value of the bulk-saturation degree.

$s_r$	value of the bulk-saturation degree in steady-state (regime) conditions.
$T$	temperature in the system, far from the container wall (K).
$T_w$	temperature of the container wall (K).
$x_\eta$	molar fraction of the component $\eta$ in the liquid phase.
$\alpha_\eta$	condensation coefficient of the species $\eta$ ( $\text{cm}^{-3/2}$ ).

## Subscripts

l	a quantity evaluated for a liquid below the saturation point.
liq	quantity in the bulk liquid.
s	a quantity evaluated in conditions where the liquid metal is saturated with oxygen.
I	a quantity in the interfacial liquid layer.

## 1. Introduction

The presence of reactive gases in the working atmosphere can significantly affect the surface properties of

liquids through adsorption and/or surface reactions. Oxygen, which shows a strong surface activity towards a large number of metallic systems [1], is the most important of these contaminants in liquid metal and alloy systems. Since the presence of this gas can never be completely avoided, basic investigations on high-temperature capillarity are generally performed under controlled atmospheres, such as helium, ultra high vacuums and buffer mixtures [2, 3, 4].

For this reason, it seems extremely useful to provide theoretical models which enable the prediction with reasonable accuracy, of the degree of contamination of a surface, in order to relate the physical properties which are observed to real surface-composition data. To achieve such a result it is necessary to consider the interplay of all the possible means of mass transport, adsorption, solution and reaction phenomena in the liquid-gas system, defining which one of these factors mainly controls the oxygen mass transfer at the liquid-gas interface, as a function of the boundary conditions.

A kinetic-fluidodynamic model of oxygen exchanges between the gas phase and the condensed phase at different  $O_2$  partial pressures under inert atmospheres (He flowing with an inlet pressure of the order of 0.1 MPa) has been presented in a previous work [5].

In that case, diffusion was the main mass-transport mechanism in the gas phase, and reactions between metal vapours and oxygen can occur. If the ratio between the reaction and the diffusion rates is favourable, specific *reaction regimes* can be established in which the oxygen consumption takes place in the gaseous layers far from the liquid surface. In this case, a steady state is established in which  $O_2$  does not contaminate the liquid surface.

The aim of the present paper is to provide an approach to the problem of oxygen mass transfer under pressures lower than 1 Pa, that is in conditions of the Knudsen-diffusion regime, which can be regarded as a vacuum. In these conditions, when metals able to form volatile oxides are considered [6, 7, 8, 9], condensation of the oxide vapours on the reactor walls can enhance the rate of oxide vaporization. The oxygen content of unsaturated liquid metals can be decreased by purification via suboxides [10, 11]; the removal of oxide vapours from the reactor is expected to raise the effectiveness of the process [12].

Deoxidation at high temperature under very low total pressures is a technique which is largely used in industrial metal refining; some aspects of this methodology are reconsidered here, with particular regard to surface contamination in high temperature capillarity measurements.

## 2. The model system

Consider a liquid metal drop placed at the centre of a closed chamber, whose farthest wall is at a distance  $L$  from the liquid-metal surface. The following conditions apply.

1. The temperature, near the drop, is maintained at a constant value,  $T$ , which is higher than that for the chamber walls,  $T_w$ .

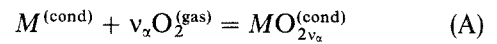
2. If a total pressure  $P_{tot}$  of less than 1 Pa, at least, is maintained inside the chamber, Hertz-Knudsen conditions of a thermomolecular regime are assured for the mass-transport phenomena in the gas phase [12].

3. The activity coefficient of the liquid metal is assumed to be unity.

4. Small amounts of dissolved oxygen are assumed not to affect significantly the vapour pressure of the pure metal,  $P_M$  which is assumed to depend only on the temperature,  $T$ .

5. The residual partial pressure of oxygen in the atmosphere,  $P_{O_2,g}$ , is considered to be constant, assuming that its value is continuously restored by microleaks through the vacuum seals.

6. A molar fraction  $x_{O,l} \leq x_{O,s}$  of oxygen is dissolved into the metal, where  $x_{O,s}$  indicates the limit of solubility [13]. Above this limit, the formation reaction of the *first stable oxide* in the condensed phase, given by



is shifted to the right. The term *first oxide* denotes the oxide with the minimum oxygen content which is thermodynamically stable under the conditions imposed.

When  $x_{O,l} = x_{O,s}$  that is, when the metal and the oxide exist at the same time in the condensed phase, the atmospheric composition is fixed at constant  $T$  for a system at equilibrium, and it can be calculated if the chemical equilibria conditions in the metal-oxygen system are known. In particular, the vapour pressures  $P_{j,s}$  of the species containing oxygen (suboxides) resulting from thermal decomposition of the oxide depend exclusively on  $T$ . Because of the remarkable complexity of oxide vaporization phenomena [6, 7, 14, 15], the evaluation of the equilibrium partial pressures of suboxides requires specific considerations; these are presented in the Appendix.

## 3. Interphase mass transfer

Consider the following chemical equilibria conditions in the model system, for  $x_{O,l} \leq x_{O,s}$ ,

$$M^{(cond)} = M^{(gas)} \quad (B)$$

$$O_2^{(gas)} = 2O^{(liq)} \quad (C)$$

$$M^{(gas)} + \nu_j O_2^{(gas)} = MO_{2\nu_j}^{(gas)} \quad (D)$$

Assuming the fugacity coefficients of gases to be equal to unity, the following equations can be written

$$P_{M,l} = P_M \quad (1)$$

$$P_{O_2,l} a_{O,l}^{-2} = P_{O_2,s} a_{O,s}^{-2} \quad (2)$$

$$P_{M,l} P_{O_2,l}^{\nu_j} P_{j,l}^{-1} = P_{M,s} P_{O_2,s}^{\nu_j} P_{j,s}^{-1} \quad (3)$$

Where  $a_{O,l}$  is the oxygen activity in the liquid metal. The quantities marked with a subscript  $l$  in Equation 3 indicate the equilibrium vapour pressures of a metal with an oxygen activity  $a_{O,l}$ .

If the *saturation degree*,  $s$ , of the bulk liquid with respect to dissolved oxygen is defined as

$$s = \frac{a_{O,l}}{a_{O,s}} \quad (4)$$

then according to Equation 2, the oxygen partial pressure in equilibrium with a molar fraction of dissolved oxygen  $x_{O_2,l}$  can be expressed as the product of the quantity  $s$  by the saturation pressure,  $P_{O_2,s}$ , that is,

$$P_{O_2,l} = s^2 P_{O_2,s} \quad (5)$$

Substituting Equations 5 and 1 in Equation 3 an analogous relationship for the  $j^{\text{th}}$  oxide partial pressure can be obtained

$$P_{j,l} = s^{2\nu_j} P_{j,s} \quad (6)$$

The mass transfer between the gas and the condensed phase can be formalized through the evaluation of the global fluxes of oxygen and metal to and from the surface.

Using Equations 5 and 6, the rates of evaporation of oxygen and metal vapours per unit surface can be expressed by means of the overall thermodynamic driving force, that is by the difference between the equilibrium partial pressure and actual pressure, which will be indicated by the subscript g. These rates are given, respectively, by

$$N_{O_2}^{\text{tot}} = K_{O_2}(s^2 P_{O_2,s} - P_{O_2,g}) + \sum_j \nu_j K_j (s^{2\nu_j} P_{j,s} - P_{j,g}) \quad (7)$$

$$N_M^{\text{tot}} = K_M(P_M - P_{M,g}) + \sum_j K_j (s^{2\nu_j} P_{j,s} - P_{j,g}) \quad (8)$$

The quantities  $K_{O_2}$ ,  $K_M$ ,  $K_j$ , are global kinetic coefficients for the mass transfer, whose evaluation requires a separate discussion that will be treated in Section 5.

As can be seen from Equations 7 and 8, there are two different kinds of contributions to both the total fluxes: one given by "free" molecular  $O_2$  and metal atoms, and the other is given by the  $j$  species, where oxygen and metal are linked together as oxides.

At equilibrium all the pressure gradients disappear, and the net fluxes are equal to zero. Equations 7 and 8 show that steady-state conditions for the system can also be attained *out of the equilibrium* between the gas and the condensed phase; in this case no variations of the composition of the two phases are to be expected, as a consequence of the balance of the not-null opposite contributions to the oxygen and metal transfer to and from the liquid.

A steady-state condition is attained, by definition, when the saturation degree of the liquid remains constant under unchanging boundary conditions; that is, when the following relationship is verified

$$\frac{N_{O_2}^{\text{tot}}}{N_M^{\text{tot}}} = \frac{a_{O,l}}{a_{M,l}} \quad (9)$$

where  $a_{M,l}$  is the liquid-metal activity.

If the *oxygen transfer* is considered, remembering that oxygen generally has a very low solubility in liquid metals [13], an approximate formulation of the steady-state conditions, under the model-system assumptions, can be obtained

$$N_{O_2}^{\text{tot}} \approx 0 \quad (10)$$

This is a reasonable approximation provided that

the following condition is verified

$$\frac{P_M}{\sum_j P_{j,s}} \ll 1/a_{O,l}$$

as will generally occur when it is expected that volatile oxides will form.

When the condition expressed by Equation 10 is reached, the saturation degree of the liquid assumes a *steady-state value* under definite conditions of  $P_{O_2,g}$ ,  $P_{j,g}$  and  $T$ .

A *steady-state saturation degree*,  $s_r$ , can be derived from Equations 7 and 10; it is defined by the following equation which is solvable by an iterative procedure,

$$s_r = \left( \frac{P_{O_2,g} + \sum_j \nu_j (K_j/K_{O_2}) P_{j,g}}{P_{O_2,s} + \sum_j \nu_j (K_j/K_{O_2}) P_{j,s} s_r^{2(\nu_j-1)}} \right)^{1/2} \quad (11)$$

As expected, when the saturation values  $P_{O_2,s}(T)$ ,  $P_{j,s}(T)$  are imposed (oxygen saturation, with the system in monovariant equilibrium)  $s_r$  becomes equal to unity.

#### 4. Mass-transfer coefficients

Concentration gradients inside the system are created when the concentration of dissolved oxygen is different from the equilibrium value with respect to the gas phase. The related overall thermodynamic driving forces (Equation 7) can be split into a number of factors; each of which is referred to the mass transfer through a single region of the system. For oxygen they correspond to the following steps.

(a) *Mass transfer inside the liquid phase.* This mass transfer is from the bulk liquid, with an activity  $a_{O,l} = s a_{O,s}$  to the liquid close to the interface ( $a_{O,l} = s_1 a_{O,s}$ ). By arbitrarily choosing to express the relative driving force in terms of the equilibrium partial pressures, the oxygen flux can be written as

$$N_{O_2}^{\text{liq}} = k_{O,\text{liq}} P_{O_2,s} (s^2 - s_1^2) \quad (12)$$

where  $k_{O,\text{liq}}$  is a function of the oxygen diffusivity in the liquid, of the liquid phase geometry, of the degree of turbulence and of the saturation itself. So Equation 12 is little more than pure formalism, but it will be useful below to make the global coefficients explicit.

(b) *Liquid-interface mass transfer.* This mass transfer is from the layer at saturation ( $s_1$ ) to the interface (whose saturation degree can be indicated as  $s'_1$ ).  $s'_1$  can be defined as the ratio between the actual surface oxygen adsorption  $\Gamma(x_{O,l})$  and the maximum value of  $\Gamma$ , corresponding to the saturation of all the available surface sites [16]. Assuming that *local* equilibrium conditions exist between the surface and the interfacial liquid layer, the oxygen partial pressure corresponding to  $s'_1$  is also related to  $s_1$  by Sievert's law [1]; that is

$$P_{O_2,l_s} = s_1^2 P_{O_2,s} \quad (13)$$

(c) *Interface-gas mass transfer.* This mass transfer is from the layer at saturation ( $s_1$ ) to the gas just overhanging the liquid surface (at a partial pressure of  $P_{O_2,l}$ ). Expressing, as usual, the condensation flux in terms of the number of collisions corresponding to the

partial pressure  $P_{O_2,l}$  and assuming that the evaporation flux is equal to the condensation flux corresponding to  $P_{O_2,l_{eq}}$ , the driving force for the net oxygen flux is

$$P_{O_2,l_{eq}} - P_{O_2,l} = s_1^2 P_{O_2,s_1} - P_{O_2,l} \quad (14)$$

(d) *Mass transfer inside the gas phase.* This mass transfer is from the layer at  $P_{O_2,l}$  to the gas phase at a partial pressure of  $P_{O_2,g}$ .

In conditions of very low total pressure the mean free path,  $l$ , of the molecules can be assumed to be much greater than the characteristic dimensions of the gas phase,  $L$ . As a consequence, no significant pressure gradients can be established in the gaseous environment, and it can be assumed that

$$P_{O_2,l} \approx P_{O_2,g} \quad (15)$$

Thus, under the conditions considered, the transport phenomena in the gas phase are not a controlling stage for the oxygen exchange.

Similar considerations apply to oxides, taking into account that the contribution of oxygen "bonded" to the liquid-phase mass transfer in stages a and b can be neglected, with reference to the extremely low solubility of condensed oxides in liquid metals. On the other hand, the total oxygen flux at the interface must take into account the contribution from the evaporation of oxides.

For stage c, the oxide  $j$  is subject to the driving force

$$P_{j,l_{eq}} - P_{j,l} = s_1^{2\nu_j} P_{j,s} - P_{j,l} \quad (16)$$

while for the step d it can be assumed that

$$P_{j,l} \approx P_{j,g} \quad (17)$$

Thus, the total oxygen flux at the interface, (expressed in  $\text{mol cm}^{-2} \text{s}^{-1}$ ), can be written as:

$$N_{O_2}^I = k_{O_2,l}(s_1^2 P_{O_2,s} - P_{O_2,l}) + \sum_j \nu_j k_{j,l}(s_1^{2\nu_j} P_{j,s} - P_{j,l}) \quad (18)$$

where  $k_{O_2,l}$  and  $k_{j,l}$  are the coefficients of the Hertz–Langmuir–Knudsen equation for the evaporation from a surface under a vacuum [12]. For an evaporating element or a compound  $\eta$ , such a coefficient is given by

$$k_{\eta,l} = \alpha_\eta \left( \frac{1}{2\pi RT M_\eta} \right)^{1/2} \quad (19)$$

where  $\alpha_\eta$  is the condensation coefficient of the evaporating species  $\eta$  and  $M_\eta$  is the molecular weight of  $\eta$ , expressed in  $\text{g mol}^{-1}$ .

Equation 18 can be simplified when, in addition to high vacuum, the presence of a wall, cold and/or infinitely extended with respect to the liquid metal sample, is imposed at a distance  $d \ll l$  from the interface. In such conditions, a quantitative condensation of the metal and oxide vapours can be invoked, so that the following further conditions can be assumed

$$P_{j,g} \ll s_1^{2\nu_j} P_{j,s} \quad (20a)$$

$$P_{M,g} \ll P_{M,s} \quad (20b)$$

## 5. Evaluation of the global kinetic coefficients

The global kinetic coefficients,  $K$ , can be expressed in an explicit form by using the relationships derived from the separate evaluation of the oxygen flux. Combining Equations 12 and 18 under the conditions expressed by Equations 15, 17, 20a and 20b, the following expressions of the saturation degree,  $s_1$ , and of the total oxygen flux can be obtained

$$s_1^2 = \frac{k_{O_2,l_{iq}} s^2 P_{O_2,s} + k_{O_2,l} P_{O_2,g}}{k_{O_2,l_{iq}} P_{O_2,s} + k_{O_2,l} P_{O_2,s} + \sum_j \nu_j k_{j,l} P_{j,s} s_1^{2(\nu_j-1)}} \quad (21)$$

$$N_{O_2}^{\text{tot}} = k_{O_2,l_{iq}} P_{O_2,s}$$

$$\times \frac{s^2 [k_{O_2,l} P_{O_2,s} + \sum_j \nu_j k_{j,l} P_{j,s} s_1^{2(\nu_j-1)}] - k_{O_2,l} P_{O_2,g}}{k_{O_2,l_{iq}} P_{O_2,s} + k_{O_2,l} P_{O_2,s} + \sum_j \nu_j k_{j,l} P_{j,s} s_1^{2(\nu_j-1)}} \quad (22)$$

If Equations 22 and 27 are compared under the conditions of Equation 20a, the following relationship between the kinetic coefficients is obtained

$$\frac{K_j}{K_{O_2}} = \frac{k_{j,l}}{k_{O_2,l}} \left( \frac{s_1}{s} \right)^{2(\nu_j-1)} \quad (23)$$

Remembering that  $K_{O_2}$  and  $K_j$  are the *global* kinetic coefficients for the oxygen mass transfer, this expression shows that, in vacuum conditions and in the presence of a sink which removes the oxide vapours, the oxygen exchange between the liquid metal and the gas is controlled by:

- (a) the evaporation of oxygen and oxides and condensation at the gas–liquid interface (the factor  $k_{j,l}/k_{O_2,l}$ ),
- (b) the oxygen partition equilibrium between the surface and the bulk (the factor  $s_1/s$ ).

No factors for the mass transfer in the gas phase are contained in Equation 23 because of the fact that transport and/or the reaction phenomena in the gas phase are not controlling stages for the process.

Finally, remembering the definition in Equation 19, the explicit form of the ratio between the global kinetic coefficients can be given by

$$\frac{K_j}{K_{O_2}} = \frac{\alpha_j}{\alpha_{O_2}} (m + \nu_j)^{-1/2} \left( \frac{s_1}{s} \right)^{2(\nu_j-1)} \quad (24)$$

where

$$m = M_M/M_{O_2}.$$

## 6. Evaluation of the oxygen content under steady-state conditions

On the basis of Equation 24, the steady-state saturation degree,  $s_r$  (see Equation 11), can also be made explicit. A further considerable simplification can be introduced by assuming that condensation on the reactor walls *quantitatively removes* the oxide vapours from the working atmosphere, so that

$$P_{j,g} \approx P_{M,g} \approx 0$$

This is likely to happen in the following two cases:

- (i) when the temperature of the chamber wall is considerably lower than that of the sample (as a conse-

quence, the vapour pressure of the elements and the compounds condensed on the cold wall can be neglected);

(ii) when the whole chamber is *at the same temperature*, but the surface of the reactor wall is much larger than the sample surface (in this case, the oxide flux coming from the sample cannot completely coat the chamber walls in a time which is comparable with the experiment times; as a consequence, vapour-pressure gradients exist between oxide-covered and clean portions of the walls, so that the probability of recondensation on the clean sections is extremely high).

When at least one of these conditions is verified, the saturation degree,  $s_r$ , can be expressed as

$$s_r = \left( \frac{P_{O_2,g}}{P_{O_2,s} + \sum_j v_j \frac{\alpha_j}{\alpha_{O_2}} (m + v_j)^{-1/2} P_{j,s} s_r^{2(v_j-1)} \left[ \left( \frac{s_l}{s} \right)^{2(v_j-1)} \right]_{s_r}} \right)^{1/2} \quad (25)$$

Equation 25 relates the bulk oxygen activity to  $P_{O_2,g}$  at a definite value of  $T$ , which is the result generally achieved through the Sievert's law, that is

$$s^{\text{Siev}} = \left( \frac{P_{O_2,g}}{P_{O_2,s}} \right)^{1/2}$$

As can be seen, the Sievert's theory neglects the contribution of significantly volatile oxygen compounds; this is absolutely probable when a constant oxygen pressure is imposed and gaseous suboxides are not removed from the environment. In this case, the condition  $P_{j,g} = s^{2v_j} P_{j,s}$  holds true and the oxide-vapours gradient in Equation 7 is equal to zero. In contrast, when any kind of quantitative or semi-quantitative removal of suboxides takes place (condensation, pumping), being in several cases  $P_{j,s}$  much higher than  $P_{O_2,s}$  [6, 7], the system can reach a non-equilibrium steady state in which

$$s_r \ll \left( \frac{P_{O_2,g}}{P_{O_2,s}} \right)^{1/2}$$

*The saturation degree of the bulk liquid can be much lower than that expected in gas-liquid equilibrium conditions.*

For Equation 25 to be effectively applicable to real systems, two problems remain to be solved.

1. The condensation coefficients  $\alpha_j$ ,  $\alpha_{O_2}$  of the evaporating species should be known. As a first approximation, their ratio can be considered to be equal to unity if the efficiency of the evaporating process is assumed to have about the same value for both species.

2. An evaluation of the  $s_l/s$  ratio has to be made.

To achieve this second result, a deeper study of the oxygen mass transfer in the liquid phase is needed. Such a study, leading to a definition of the transport coefficient  $k_{O,liq}$ , would make the quantity  $s_l$  valuable in definite conditions of  $P_{O_2,g}$  and  $T$  according to Equation 21, and it would consequently make all the factors in Equation 25 completely defined.

## 7. Effective oxidation parameters

Vacuum conditions, with the additional effect of vapour condensation, can determine a significant lowering of the degree of contamination of oxygen-unsaturated liquids with respect to normal gas-liquid equilibrium conditions, as shown in Equation 25.

Thus, the following basic question can now be addressed: how can clean samples be obtained? That is, in which conditions of residual  $P_{O_2}$  and  $T$  does  $s$  reach its maximum value  $m$ ? In order to give an answer, slightly different formalism has to be introduced.

If Equation 10 is written in its explicit form, it follows that a steady-state condition with respect to

the oxygen exchange is reached when the  $O_2$  residual pressure is

$$P_{O_2}^E = P_{O_2,l} + \sum_j \frac{K_j}{K_{O_2}} v_j P_{j,l} \quad (26)$$

$P_{O_2}^E$  can be regarded as the *effective oxidation pressure*, it is the  $O_2$  pressure which maintains a sample with an oxygen activity of  $a_{O,l}$  in a steady state. The summation is related to the existence of significantly volatile metal-oxygen compounds. It takes into account the loss of oxygen linked as oxides by considering that this loss has to be balanced only by an additional counterflux of pure  $O_2$ , because the condensation of vapours on the reactor wall virtually eliminates the oxides from the gas phase.

The value of  $P_{O_2}^E$  depends on the saturation degree of the liquid. This dependence can be made explicit through Equations 5, 6 and 24; that is

$$P_{O_2}^E(s) = s^2 P_{O_2,s} + \sum_j v_j \frac{\alpha_j}{\alpha_{O_2}} (m + v_j)^{-1/2} \times \left( \frac{s_l}{s} \right)^{2(v_j-1)} P_{j,s} s^{2v_j} \quad (27)$$

According to this equation, the saturation degree of a system can be controlled through the  $O_2$  pressure conditions. Starting from a liquid metal with a saturation degree of  $s_{in}$ , in a steady state under a residual  $O_2$  pressure,  $P_{O_2}^E(s_{in})$ , an increase or a decrease of the oxygen content can be obtained respectively, by increasing or lowering  $P_{O_2}$ . In particular, the oxygen content of the molten metal could be *lowered* by imposing, at a particular value of  $T$ , an oxygen pressure  $P_{O_2,g} = P_{O_2}^E(s_{fin}) < P_{O_2}^E(s_{in})$ .

Nevertheless, the effective feasibility of such a process depends *not only* on the volatility of the oxygen and the oxides but also of that of the metal.

If the vapour pressure of the metal is much greater than that of the oxides, the oxygen loss from the liquid can be smaller than that of metal: as a consequence, oxygen impurities *concentrate* in the liquid phase.

A feasibility study on the vacuum refining of metal–oxygen solutions has been proposed by L. Brewer and G. Roseblatt [10]. On the basis of thermodynamic considerations, they introduced a parameter  $R$ , defined as the ratio between the oxygen molar fractions in the gas and in the liquid phase. A refining effect, in equilibrium conditions between the gas and the liquid, can be expected for  $R > 10$ . However, the Brewer and Roseblatt estimation of vacuum-refining feasibility can be upgraded by also taking into account specific kinetic arguments and by referring to the ratios between the global fluxes coming from the surface and the activities of the elements in the liquid phase.

An *effective evaporation ratio*,  $R^E$ , can thus be defined by

$$R^E = \frac{N_{O_2}^{\text{tot}} a_{M,l}}{N_M^{\text{tot}} a_{O,l}} \quad (28)$$

Reading Equation 28 on the basis of Equation 9, a vacuum refining of a liquid metal with an oxygen activity of  $a_{O,l}$  is possible if  $R^E \gg 1$ . In order to refer to measurable quantities, the ratio between two effective pressures can be considered instead of that between the fluxes. For this purpose, an *effective metal vapour pressure*,  $P_M^E$ , which is analogous to  $P_{O_2}^E$  can be defined as the pressure which is able to counterbalance the total metal evaporation under the conditions given by Equation 20a and b making the global metal flux equal to zero, that is

$$P_M^E = P_M + \sum_j \frac{K_j}{K_M} s^{2\nu_j} P_{j,s} \quad (29)$$

Following the same criteria as has already been used for oxygen mass transfer, it can be demonstrated that the global metal mass transfer is controlled only by the interface–gas phenomena and that the following relationship exists

$$\frac{K_j}{K_M} = \frac{k_{j,l}}{k_{M,l}} \quad (30)$$

Thus, the following expression for  $P_M^E$  can be found, by using Equation 19,

$$P_M^E(s) = P_M + \sum_j \frac{\alpha_j}{\alpha_M} \left( \frac{m}{m + \nu_j} \right)^{1/2} s^{2\nu_j} P_{j,s} \quad (31)$$

By the definition of both of the effective pressures, the effective evaporation ratio,  $R^E$ , can now be written as

$$R^E = \frac{P_{O_2}^E K_{O_2} a_{M,l}}{P_M^E K_M a_{O,l}} \quad (32)$$

and finally, remembering Equations 24 and 30, it can be rewritten as

$$R^E = \frac{P_{O_2}^E}{P_M^E} \frac{\alpha_{O_2}}{\alpha_M} m^{1/2} \left( \frac{s_1}{s} \right)^{-2(\nu_j-1)} \frac{a_{M,l}}{a_{O,l}} \quad (33)$$

When the fundamental condition  $R^E \gg 1$  is verified, the refining of a liquid with an oxygen activity  $a_{O,l}$ , can be obtained in the following two different ways.

1. By lowering the  $O_2$  residual pressure in the system at a constant  $T$ ; this condition is often not attain-

able experimentally, due to the extremely low values  $P_{O_2}$  would have to reach for certain metal oxides.

2. By modifying the temperature conditions [17, 18, 19], making the oxide volatility increase. This requires an estimation of the derivatives of vapour pressure with respect to  $T$  for both the oxides and the metal, in order to be sure that their ratio does not become unfavourable as the temperature increases.

## 8. The generalization of the solid–gas–interface reactions for oxygen-saturated system

When the condensed phase is completely saturated with oxygen, the saturation degree,  $s$  is equal to unity Equation 4, as a consequence  $s_l/s = 1$ . In this case, the effective value of the residual oxygen pressure that must be imposed over the condensed phase in order to saturate it, can be derived from Equation 27 which simplifies to

$$P_{O_2,s}^E = P_{O_2,s} + \sum_j \nu_j \frac{\alpha_j}{\alpha_{O_2}} (m + \nu_j)^{-1/2} P_{j,s} \quad (34)$$

This equation defines the effective saturation pressure for oxygen  $P_{O_2,s}^E$ , and it applies for the oxidation of liquid and solid metals under vacuum conditions and in the presence of a cold wall (to remove oxide vapours).

When  $P_{O_2,g} > P_{O_2,s}^E$  is imposed, a thermodynamically stable oxide layer, which thickens with time, is expected to form on the surface. This can be defined as the *surface oxidation regime*. In contrast if  $P_{O_2,g} < P_{O_2,s}^E$ , the following phenomena are expected.

1. A *liquid metal* dissolves oxygen in proportion to the pressure imposed, according to Equation 25.

2. A *solid metal* which is able to form volatile suboxides enters a regime of *active corrosion*, the surface reacts with oxygen, forming compounds that evaporate rapidly, determining the consumption of the sample. This behaviour has been observed by different researchers [8, 9] on solid silicon.

Both these phenomena can be regarded as an *oxide regime removal*.

## 9. Applications and discussion

Although the uncertainty in  $s_1$  has still to be solved, data supporting the present theory when restricted to saturated systems ( $s = 1$ ) can be found in the literature. This seems to confirm the validity of the approach taken here, and it encourages further study.

Equation 34 can be used to define the  $P_{O_2}$  and  $T$  conditions for a transition between the two aforementioned regimes, under a vacuum, with complete removal of the oxide vapours; as a first approximation, the ratio between the condensation coefficients  $\alpha_j$  and  $\alpha_{O_2}$  can be considered as being equal to unity.

The values of  $P_{O_2,s}(T)$  and  $P_{j,s}(T)$  can be evaluated from thermochemical data [20], by taking into account the reactions describing the vaporization processes and imposing for each value of  $T$  the condition

of three-phase monovariant equilibrium. Owing to the contribution of the suboxides to the total oxygen loss,  $P_{O_2, \text{sat}}^E$  can be several orders of magnitude larger than the corresponding saturation value under conditions of equilibrium between the gas and the condensed phase, as shown, for example, in Table I for the systems Si-O and Al-O.

In the case of the Si-O system, the following equilibria have to be considered [7]

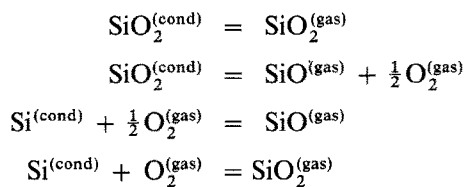


TABLE I A comparison of the oxygen equilibrium saturation pressure,  $P_{O_2, s}$ , and the oxygen effective pressure,  $P_{O_2, s}^E$ , for condensed Si and Al

$T(\text{K})$	Si-O system		Al-O system	
	$P_{O_2, s}(\text{MPa})$	$P_{O_2, s}^E(\text{MPa})$	$P_{O_2, s}(\text{MPa})$	$P_{O_2, s}^E(\text{MPa})$
700	$3.5 \times 10^{-60}$	$3.2 \times 10^{-19}$	$2.5 \times 10^{-72}$	$1.4 \times 10^{-22}$
800	$1.1 \times 10^{-51}$	$6.4 \times 10^{-16}$	$4.8 \times 10^{-62}$	$8.1 \times 10^{-19}$
900	$4.0 \times 10^{-45}$	$2.2 \times 10^{-13}$	$4.8 \times 10^{-54}$	$6.9 \times 10^{-16}$
933 <sup>a</sup>	—	—	$8.6 \times 10^{-53}$	$4.3 \times 10^{-15}$
1000	$7.1 \times 10^{-40}$	$2.4 \times 10^{-11}$	$1.3 \times 10^{-48}$	$1.8 \times 10^{-13}$
1100	$1.4 \times 10^{-35}$	$1.1 \times 10^{-9}$	$2.6 \times 10^{-43}$	$1.2 \times 10^{-11}$
1200	$5.3 \times 10^{-32}$	$2.6 \times 10^{-8}$	$6.7 \times 10^{-39}$	$5.0 \times 10^{-10}$
1300	$5.5 \times 10^{-29}$	$3.8 \times 10^{-7}$	$3.6 \times 10^{-35}$	$7.2 \times 10^{-9}$
1400	$2.1 \times 10^{-26}$	$3.6 \times 10^{-6}$	$5.6 \times 10^{-32}$	$8.8 \times 10^{-8}$
1500	$3.7 \times 10^{-24}$	$2.6 \times 10^{-5}$	$3.3 \times 10^{-29}$	$8.4 \times 10^{-7}$
1600	$3.4 \times 10^{-22}$	$1.5 \times 10^{-4}$	$8.6 \times 10^{-27}$	$4.9 \times 10^{-6}$
1685 <sup>b</sup>	$1.0 \times 10^{-20}$	$3.5 \times 10^{-4}$	—	—
1700	$1.9 \times 10^{-20}$	$4.4 \times 10^{-4}$	$1.2 \times 10^{-24}$	$2.5 \times 10^{-5}$
1800	$7.8 \times 10^{-19}$	$1.5 \times 10^{-3}$	$9.2 \times 10^{-23}$	$1.1 \times 10^{-4}$

<sup>a</sup>The melting point of aluminium.

<sup>b</sup>The melting point of silicon.

By considering SiO to be the predominant oxide in the gas phase and by applying Equation 34, the effective oxygen saturation pressure in the silicon-oxygen system can be evaluated. The result of these calculations is presented in Fig. 1 in which a curve on a plane  $\log P_{O_2}-T$  defines the transition between the surface oxidation and the oxide removal regimes for oxygen-saturated condensed silicon from 273 to 2000 K, under Knudsen conditions. Studies of this kind of transition, limited to the oxidation of solid silicon, have been made by Gelain *et al.* [21], who experimentally determined the transition temperature between passivation and active corrosion under different constant-oxygen residual pressures. They also presented a very accurate theoretical treatment, with specific reference to the oxidation of solid silicon, obtaining an almost-perfect fit to the experimental data.

The treatment presented here is more general, but when the boundary conditions of Gelain *et al.* are imposed, results which are quite similar to those of Gelain *et al.* were obtained as a particular case. Indeed, the part of the curve in Fig. 1 for solid silicon (below 1685 K) agrees very well with the experimental data of Gelain *et al.* (represented by the squares). This seems to confirm that the approximations made for the condensation coefficients,  $\alpha$ , do not very significantly affect the final result.

The problem of the transition between the surface oxidation and the oxide removal regimes under Knudsen conditions has also been approached by Laurent *et al.* [19], in an attempt to explain their observations on the wetting behaviour of liquid Al on alumina. They supposed that the oxygen fluxes to and from the oxidized surface originated from the vaporization of a compact oxide layer, and they calculated these fluxes at different temperatures, then they drew a limit curve on the  $\log P_{O_2}-T$  plane separating an *oxide-layer thickening zone* from an *erosion zone*. They have also

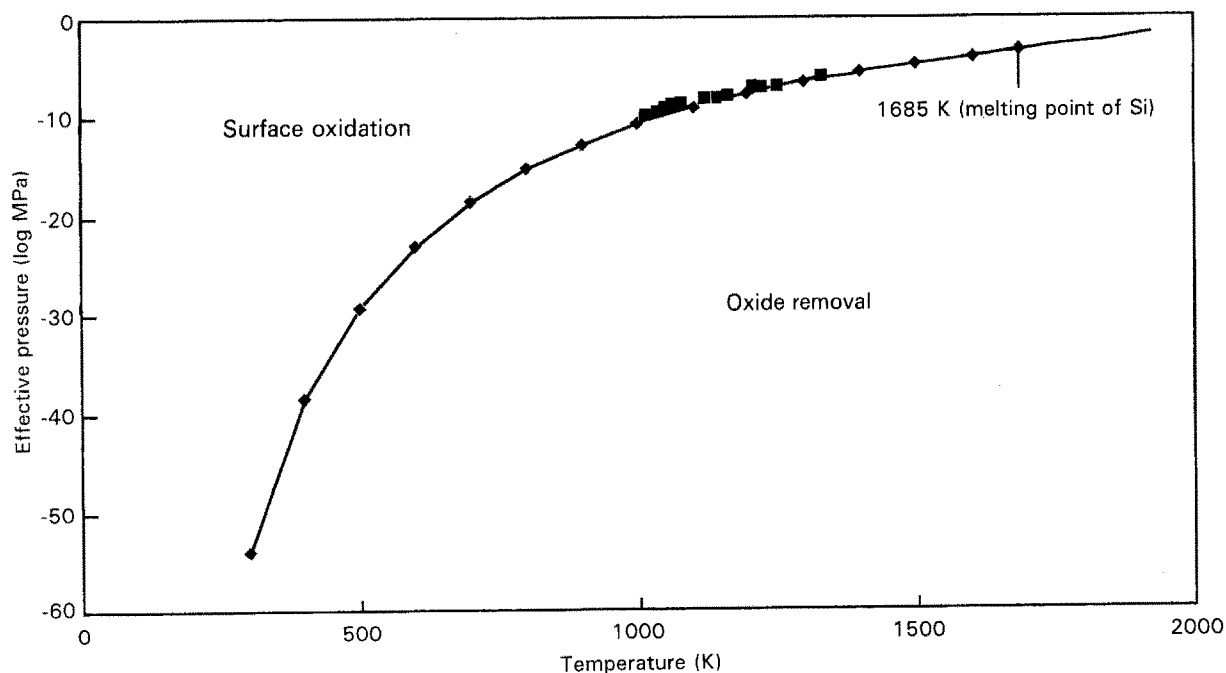
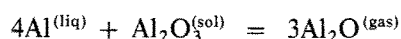


Figure 1 The effective oxygen saturation pressure plotted against  $T$  for condensed Si, under a "vacuum": (■) data from [21], and (◆) values of the effective saturation pressure.

calculated the time (in seconds) needed for an oxide monolayer to disappear when the system is under oxide removal regime conditions. Nevertheless, when using this model for a best choice of experiment timing, they observed that the order of magnitude of the calculated deoxidation time was much higher than the experimental observations. They supposed, as an explanation according to the model of an oxidized aluminium surface proposed by Pask [17], that structural faults or cracks filled with liquid Al coming from the bulk are present in the oxide layer. As a consequence, they thought that the following reaction takes place



resulting in a three-phase monovariant equilibrium which imposes the equilibrium vapour pressures for the molecular oxygen, for the metal and for the oxides. These conditions are the same as those given by the model presented here for  $s = 1$ ; that is they are those of Equation 34.

Following the same procedure for silicon, the transition curve between the surface oxidation and the oxide removal regime was obtained for condensed Al, (shown in Fig. 2). The curve is shifted towards higher residual-pressure values with respect to that presented by V. Laurent *et al.*, this is because the suboxide vapour pressures (that is, their contribution to the oxygen loss) are maximized in conditions of three-phase equilibrium [6, 7]. This is in better agreement with the observed time of deoxidation, which is smaller than that predicted by Laurent's model.

Although capillarity measurements, being the surface properties most strongly affected by the degree of surface cleanliness, can give indirect information on the surface-oxidation kinetics, the most immediate way of investigating these phenomena is offered by

surface spectroscopy (AES). Unfortunately, this kind of data for liquid metals, due to experimental difficulties, is currently lacking except for a very few systems.

Surface analyses on liquid Al have been performed by Goumiri and Joud [22], who investigated the oxidation kinetics of both liquid and solid aluminium surfaces which had previously been cleaned by ion sputtering under conditions of

$$P_{\text{O}_2} \approx 10^{-18} \text{ MPa}, \quad T = 293 \text{ K}$$

for *solid* Al, and of

$$P_{\text{O}_2} \approx 10^{-17} \text{ MPa}, \quad T = 973 \text{ K}$$

for *liquid* Al. The results of their experiments are represented in Fig. 2 by the squares.

The points for the solid sample lies in the surface oxidation regime zone of the diagram. In contrast liquid Al is not expected to be coated under the experimental conditions imposed. These theoretical expectation agree very well with the experimental observations. A rapid oxidation of solid surfaces which had previously been sputtered has, in fact, been reported by Goumiri and Joud. In contrast, no sign of contamination was observed during the experiments on liquid aluminium.

## 10. Conclusions

An approach to the problem of the oxygen exchange at the interface between a gas and a liquid metal for systems under a "vacuum" (Knudsen regime, pressures lower than 1 Pa) has been given. This implements a treatment, previously presented in [5], for systems under total pressures of the order of 0.1 MPa, in which gas-phase diffusion plays a fundamental role. Under a vacuum, transport processes in the gas phase have no control over the total interphase mass exchange, because of the large mean free path of the

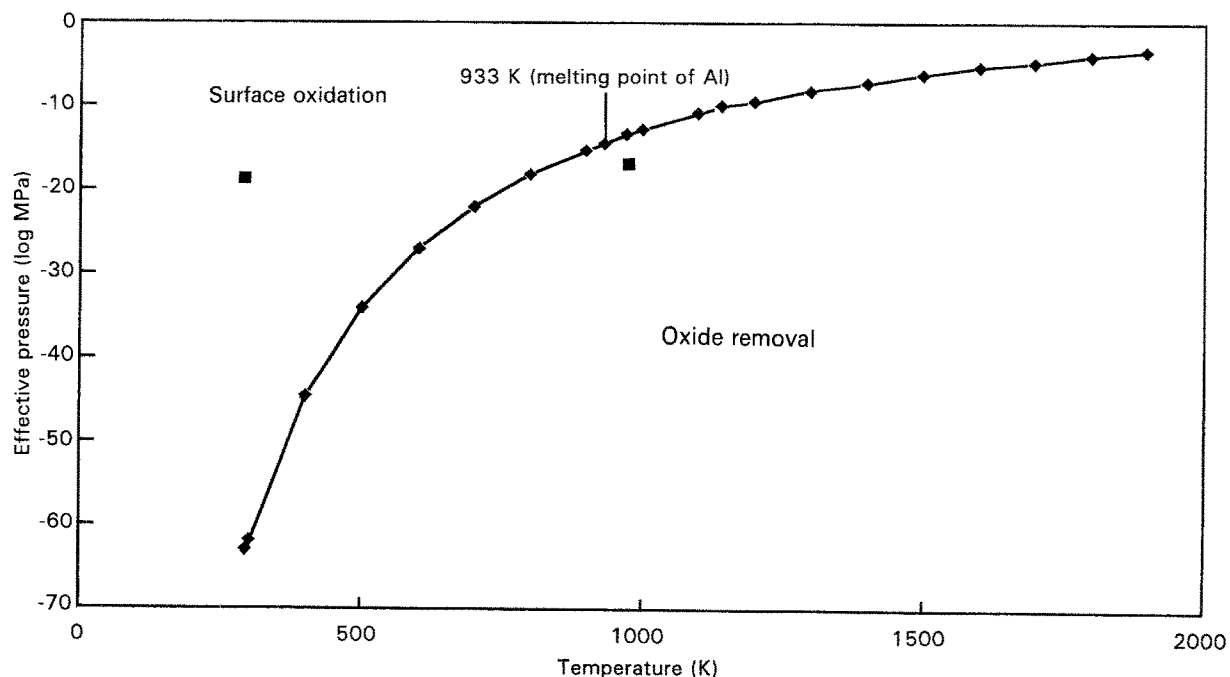


Figure 2 The effective oxygen saturation pressure plotted against  $T$  for condensed Al, under a "vacuum": (■) data from [22], and (◆) values of the effective saturation pressure.



molecules under very-low pressure conditions. Moreover, when metals which are able to form volatile oxides are considered, condensation of the oxide vapours on the reactor walls must be taken into account. The removal of oxide vapours from above the metal surface can significantly displace the oxidation equilibrium by enhancing the rate of oxide vaporization; this effect can be exploited, in some cases, to deoxidize and/or purify a liquid metal.

Owing to the double contribution of molecular  $O_2$  and volatile oxides to the oxygen flux from the surface, non-equilibrium steady-state conditions can be established, in which no variations of composition of the two phases occurs with time, as a result of opposite not-null oxygen exchanges. The problem can be approached by evaluating the total oxygen and metal evaporation rates as a function of the overall thermodynamic driving forces. By splitting these forces into separate factors, referred to single regions of the system, and giving an account of the transport kinetics by using appropriate coefficients, a *steady-state saturation degree*,  $s_r$ , is defined.  $s_r$  expresses the oxygen activity in the liquid metal in non-equilibrium steady-state conditions, as a function of the residual oxygen pressure in the working atmosphere and of the vapour pressures of volatile oxides, which depend on the temperature  $T$ .

From the evaluation of the total fluxes to and from the surface, definitions of *effective oxidation parameters* can also be derived; despite their formal thermodynamic appearance (as an *effective oxidation pressure*,  $P_{O_2}^E$ , or as an *effective metal-vapour pressure*,  $P_M^E$ ), they contain coefficients that also account for the kinetics. They define the oxygen residual pressure and the temperature conditions that lead the liquid to a definite steady-state composition under a "vacuum" when not in thermodynamic equilibrium.

The coefficients contained in the expressions of the effective parameters were completely defined in the particular case in which the oxygen content of the metal was equal (or nearly equal) to the limit of solubility.

The effective value of the saturation oxygen pressure,  $P_{O_2,s}^E$  was evaluated at different temperatures for the systems Si-O and Al-O. The results were several orders of magnitude higher than the corresponding equilibrium values, and they agree well with experimental data found in the literature.

Curves of  $\log P_{O_2,s}^E$  against  $T$ , separating different oxidation regimes, were drawn; they can be regarded as being analogous to the usual stability diagrams given by  $\log P_{O_2,s}$  versus  $T$  [23], but they are referred to systems out of equilibrium, and upgraded with kinetic arguments.

Thus, an accurate control tool for determining the degree of oxygen-contamination of liquid metals under a vacuum is available; this would be useful in capillarity measurements, in order to relate the observed surface properties to the actual liquid composition.

However, further studies are required to find a general definition of the coefficients appearing in the expressions of the effective parameters; the oxygen

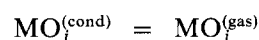
mass transfer inside the liquid phase needs, in particular, to be examined further, in order to make a correlation of  $P_{O_2}^E$  with the liquid saturation degrees,  $s$ , explicit for the entire range of liquid compositions.

## Acknowledgements

This work was supported by the Progetto Finalizzato "Special materials for advanced technologies" of the Italian National Research Council (CNR).

## Appendix Vaporization of an oxide in equilibrium with a condensed metal

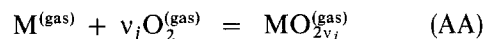
As a rule, oxide vaporization cannot be reduced to a simple equilibrium such as



In several equilibria involving oxygen, more than one oxide and frequently suboxide polymers as well [24], generally coexist. As a consequence, metal-oxygen compounds are present with a stoichiometry which is different from that of the most stable condensed oxide, and they often predominate in the gas phase.

As an example, when monovariant equilibrium conditions between Al(liq),  $Al_2O_3$  and gas are established in the Al-O system, the main constituents of the atmosphere are Al(gas) and  $Al_2O$ (gas) [7].

In general,  $j$ -oxides (with  $j = 1, 2, 3, 4 \dots$ ), whose formation can be formally described as



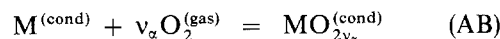
can be present in the gas phase.

When the condensed phase is saturated with oxygen, and equilibrium conditions are attained with the gas, the equilibrium constant can be written as

$$K_p^{react, AA} = \exp\left(\frac{-\Delta G_{react, AA}^0}{RT}\right) = \frac{P_{j,s}}{P_{O_2,s}^{v_j} P_M} \quad (A1)$$

$\Delta G_{react, AA}^0$  can be calculated from thermochemical data [20].

The quantity  $P_{O_2,s}$  in Equation A1 must also verify the analogous equation written for the oxidation of the condensed phase



Thus

$$K_p^{react, AB} = \exp\left(\frac{-\Delta G_{react, AB}^0}{RT}\right) = \left(P_{O_2,s}^{v_\alpha}\right)^{-1} \quad (A2)$$

Upon substitution of the calculated value of  $\Delta G_{react, AB}^0$  in Equation A2,  $P_{O_2,s}(T)$  can be determined.

According to the conditions of the model, the vapour pressure of the metal is assumed to depend only on the temperature, and it can be consequently calculated from thermochemical data. Inserting the estimated values of  $P_{O_2,s}$  and  $P_M$  into Equation A1 allows the value of  $P_{j,s}$  to be obtained. Thus, the equilibrium pressures of the elements and the compounds predominating in the gas phase above a liquid metal coexisting with its most stable oxide in condi-

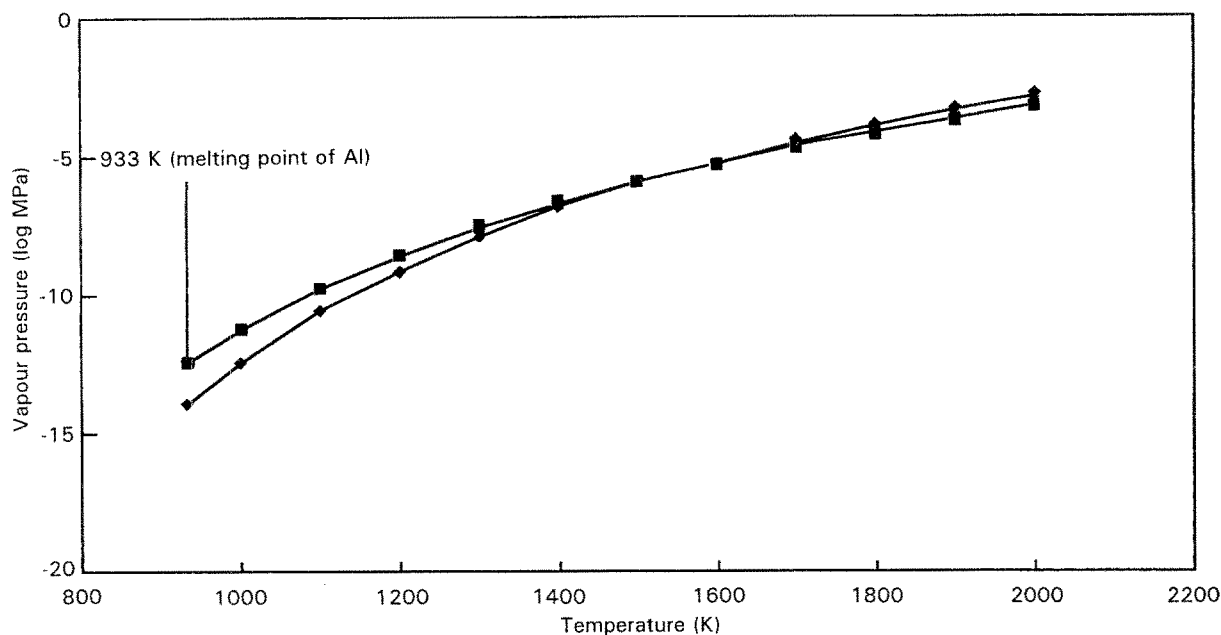


Figure A1 The vapour pressures of the predominant gaseous species in the system Al-O plotted against  $T$  in monovariant equilibrium conditions: (■)  $P_{Al^+}$  and (♦)  $P_{Al_2O_3}$ .

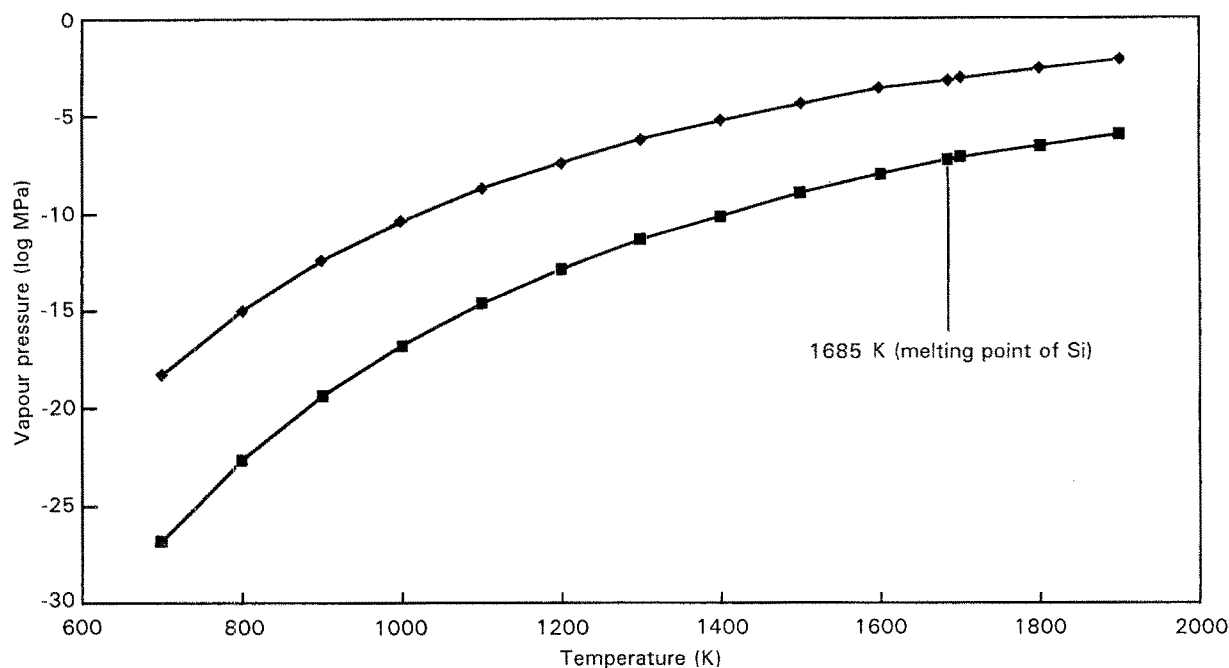


Figure A2 The vapour pressures of the predominant gaseous species in the system Si-O plotted against  $T$  in monovariant equilibrium conditions: (■)  $P_{Si^+}$  and (♦)  $P_{SiO_2}$ .

tions of monovariance can be easily and rapidly evaluated. As a first approximation it is not necessary to consider the group of related equilibria which effectively originate from the vapours.

If necessary, the values of  $P_{j,s}$  can be more accurately calculated by taking into account all the gas-solid reactions which are actually responsible for the formation of each  $j^{\text{th}}$ -oxide, and the relevant equations for  $K_p$  can be solved under monovariant metal-solid-oxide-gas equilibrium conditions.

The results of such calculations for the systems Al-O and Si-O are given in Figs A1 and A2; the data

agree very well with those in the literature [6, 7].  $Al_2O$  and SiO are the only significant gaseous oxides in the system Al-O and Si-O respectively, when monovariant equilibrium conditions are imposed.

## References

1. C. H. P. LUPIS "Chemical Thermodynamics of Materials" (Elsevier Publishers, Amsterdam, Holland, 1983).
2. J. F. PADDAY In "Surface & Colloid Science" Ed. E. Matijevic (Wiley Intersc., New York, 1969).
3. JU. V. NAIDICH, in "Progress in Surface and Membrane Science", Vol. 14, Eds. D. A. Cadenhead and J. F. Danielli (Academic Press, New York, 1981).

4. E. RICCI and A. PASSERONE, *Mater. Sci. Eng.* **A161** (1993), 31.
5. E. RICCI, A. PASSERONE, P. CASTELLO and P. COSTA, *J. Mater. Sci.* **29** (1994) 1833.
6. H. H. KELLOGG, *Trans. Met. Soc. AIME*, **263** (1966), 602.
7. D. BERUTO, L. BARCO and G. BELLERI, *Ceramurgia International* **1** (1975), 87.
8. C. WAGNER, *J. Appl. Phys.* **29** (1958), 1295.
9. E. A. GULBRANSEN, K. F. ANDREW and F. A. BRASSART, *J. Electrochem. Soc.* **113** (1966), 834.
10. L. BREWER and G. M. ROSEMBLATT, *Trans. Met. Soc. AIME* **224** (1962), 1268.
11. O. WINKLER and R. BAKISH, "Vacuum Metallurgy" (Elsevier Publishers, Amsterdam, 1971).
12. R. OHNO in "Liquid Metals—Chemistry and Physics", Chap. 2, Ed. S. Z. Beer (Marcel Dekker Inc., New York, 1972).
13. S. OTSUKA and Z. KOZUKA, *Trans. Jpn. Inst. Met.* **22** (1981), 558.
14. R. H. LAMOREAUX, D. L. HILDEBRAND and L. BREWER, *High Temp. Sci.* **20** (1985), 37.
15. R. J. ACKERMANN and R. J. THORN, in "Progress in Ceramic Science", Vol. 1, Chap. 2, Ed. J. E. Burke (Pergamon Press, New York, 1961).
16. E. RICCI, A. PASSERONE and J. C. JOUD, *Surface Sci.* **206** (1988), 533.
17. J. J. BRENNAN and J. A. PASK, *J. Am. Cer. Soc.* **51** (1968), 569.
18. L. COUDURIER, J. ADORIAN, D. PIQUE and N. EUSTATHOPOULOS, *Rev. Int. Hautes Temp. Refract.* **21** (1984), 81.
19. V. LAURENT, D. CHATAIN, C. CHATILLON and N. EUSTATHOPOULOS, *Acta Met* **36** (1988), 1797.
20. O. KNACKE, O. KUBASCHEWSKI and K. HESSELMANN, "Thermo-chemical Properties of Inorganic Substances" Second Edition (Springer Verlag, Verlag Stahleisen m. b. H Dusseldorf, 1991).
21. C. GELAIN, A. CASSUTO and P. LE GOFF, *Oxidation of Metals* **3** (1971), 139.
22. L. GOUMIRI and J. C. JOUD, *Acta Met.* **30** (1982), 1397.
23. Y. AUSTIN CHANG and KER-CHANG HSIEH "Phase Diagrams of Ternary Copper-Oxygen-Metal Systems" (ASM International, Metals Park, Ohio, 1989).
24. R. COLIN, J. DROWART and G. VERHAGEN, *Trans. Faraday Soc.* **61**, n. 511 Part 7 (1965), 1364.

*Received 31 January 1994  
and accepted 27 May 1994*