

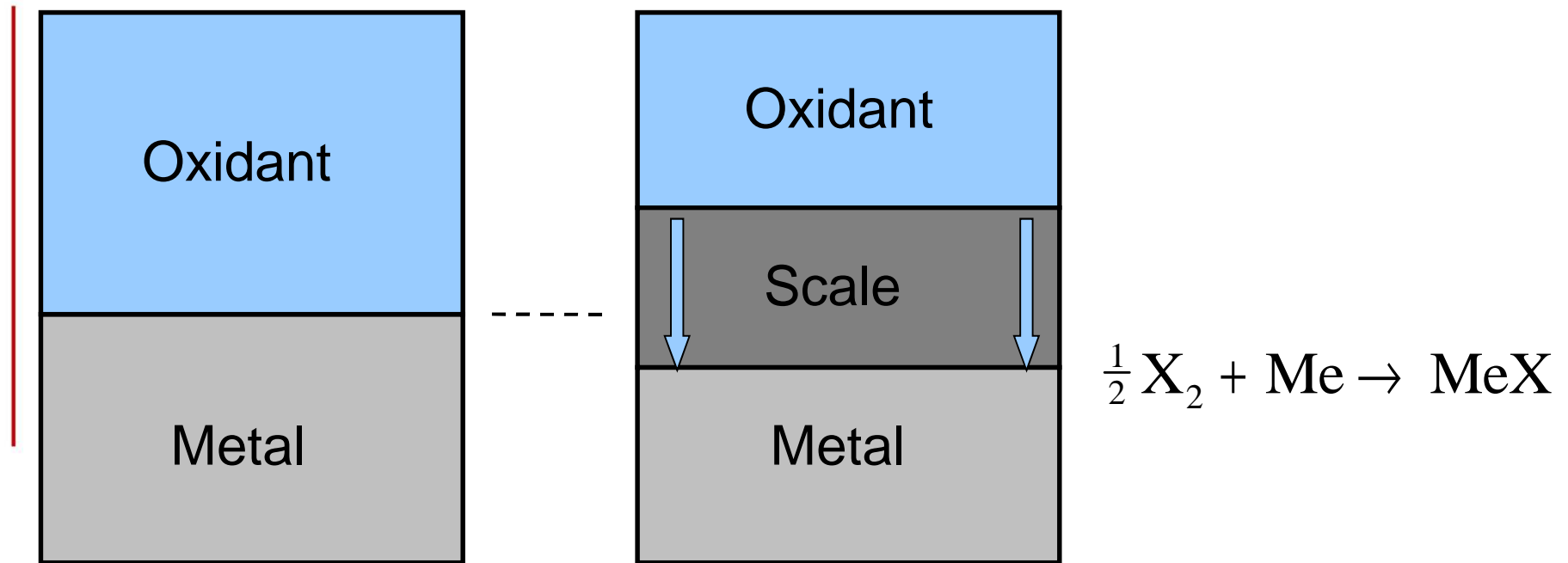
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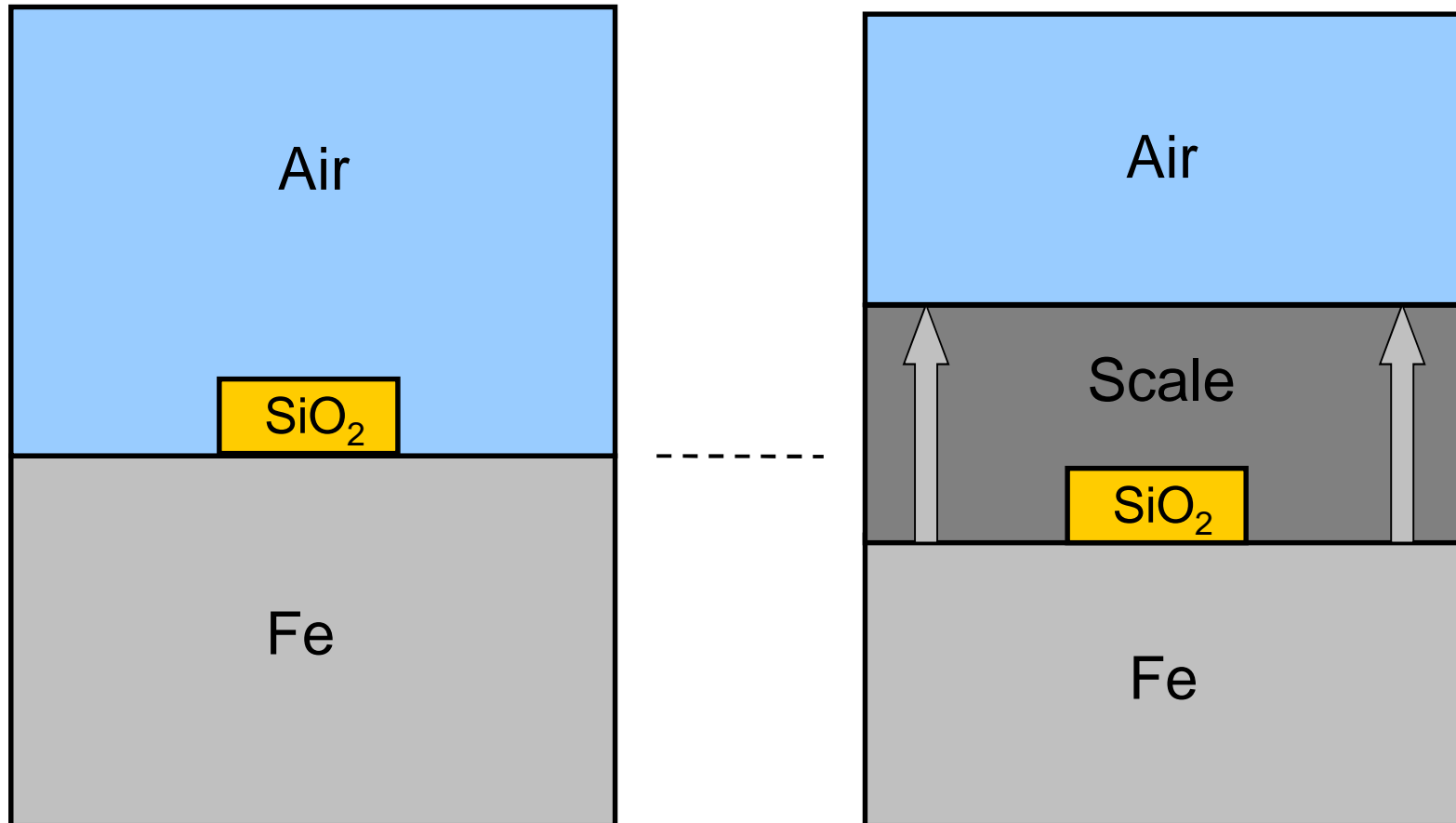
WAGNER'S THEORY OF METAL OXIDATION

<http://home.agh.edu.pl/~grzesik>

Schematic illustration of scale formation according to Tamann (1920)



Schematic illustration of the classic Pfeil experiment (1929)



Literature on Wagner's theory

1. C. Wagner, Z. phys. Chem., 21, 25 (1933)
2. C. Wagner, Z. phys. Chem., 32, 447 (1936)
3. C. Wagner, Atom Movements ASM, Cleveland, 1951



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Publications of other authors describing Wagner's theory

1. F. Gesmundo, Solid State Phenomena, 21&22, 57 (1992)
2. T. Norby, „Wagner-type theory for oxidation of metals with co-transport of hydrogen ions”, 196th Electrochemical Society Meeting, Honolulu, Hawaii, October 1999
3. P. Kofstad, „High Temperature Corrosion”, Elsevier Applied Science Publishers Ltd., London-New York, 1988
4. P. Kofstad, „High-Temperature Oxidation of Metals”, John Wiley & Sons, Inc, New York-London-Sydney, 1978
5. A.S. Khanna, „Introduction to High Temperature Oxidation and Corrosion”, ASM International, Materials Park, 2002
6. S. Mrowec, „An Introduction to the Theory of Metal Oxidation”, National Bureau of Standards and the National Science Foundation, Washington, D.C., 1982

Wagner's theory of metal oxidation: assumptions

1. The scale growing on the metal surface is compact in its entirety.
2. Diffusion of reagents in the scale takes place in the form of ions and electrons through point defects in the crystalline lattice of the reaction product.
3. The scale formation process is determined by diffusion, the rate of which is lower than that of chemical reactions at the interface.
4. Electronic and ionic defects in the crystalline lattice of the scale travel due to ambipolar diffusion.
5. Diffusion of reagents in the scale proceeds under the influence of a lattice defect gradient caused by the oxidant chemical potential gradient.
6. Point defect concentrations are established at the scale interfaces, thank to which the oxidation process proceeds according to the parabolic rate law.
7. There is a state close to thermodynamic equilibrium at the scale interfaces.

General equation expressing the flux of component “i”:

$$j_i = c_i B_i f_i$$

j_i – flux of component “i”

B_i – mobility of component “i”

f_i – driving force of component “i”

$$f_i = \frac{d\eta_i}{dx} = - \frac{1}{N_a} \left(\frac{d\mu_i}{dx} + z_i F \frac{d\phi}{dx} \right)$$

η_i – electrochemical potential of component “i”

μ_i – chemical potential of component “i”

N_a – Avogadro’s number

F – Faraday’s constant, C/mol

ϕ – electrical potential

z_i – valence of component “i”

$$j_i = -c_i B_i \frac{1}{N_a} \left(\frac{d\mu_i}{dx} + z_i F \frac{d\phi}{dx} \right)$$

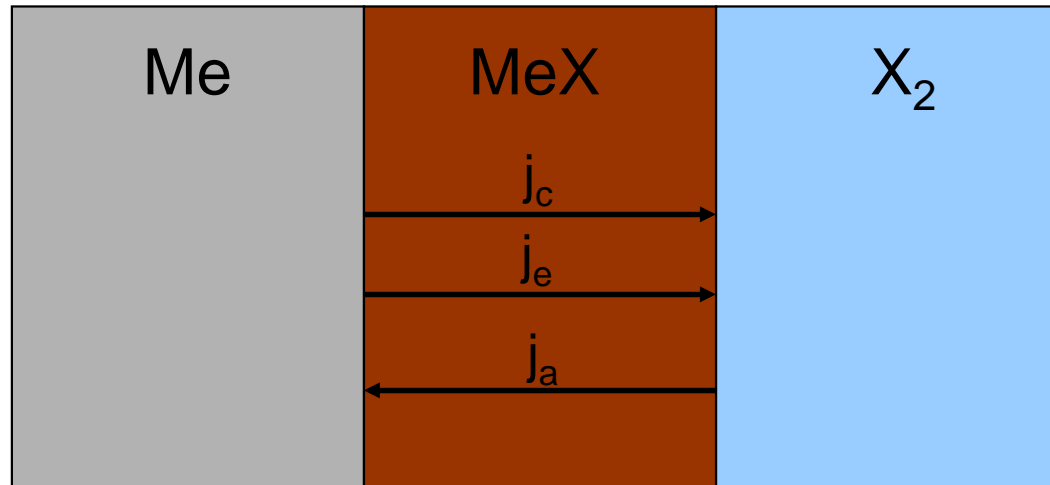
Nernst-Einstein equation:

$$B_i = \frac{D_i}{kT}$$

D_i – diffusion coefficient of component “ i ”

Taking the equation above into account, the flux of component “ i ” can be expressed as:

$$j_i = -c_i \frac{D_i}{RT} \left(\frac{d\mu_i}{dx} + z_i F \frac{d\phi}{dx} \right)$$



$$j_c = -c_c \frac{D_c}{RT} \left(\frac{d\mu_c}{dx} + z_c F \frac{d\phi}{dx} \right)$$

$$j_a = -c_a \frac{D_a}{RT} \left(\frac{d\mu_a}{dx} + z_a F \frac{d\phi}{dx} \right)$$

$$j_e = -c_e \frac{D_e}{RT} \left(\frac{d\mu_e}{dx} + z_e F \frac{d\phi}{dx} \right)$$

$z_e = -1$, therefore:

$$j_e = -c_e \frac{D_e}{RT} \left(\frac{d\mu_e}{dx} - F \frac{d\phi}{dx} \right)$$

Because the migration of point defects in the scale takes place due to ambipolar diffusion, the electroneutrality condition must be fulfilled:

$$z_c j_c + z_a j_a - j_e = 0$$

By inserting the fluxes into the equation above, the electrical potential gradient can be determined:

$$\frac{d\phi}{dx} = \frac{1}{F} \cdot \frac{-c_c D_c z_c \frac{d\mu_c}{dx} - c_a D_a z_a \frac{d\mu_a}{dx} + c_e D_e \frac{d\mu_e}{dx}}{z_c^2 c_c D_c + z_a^2 c_a D_a + c_e D_e}$$



The chemical potential of the metal and oxidant is associated by Gibbs-Duhem's equation (for an isothermal-isobaric process):

$$N_{\text{Me}} d\mu_{\text{Me}} + N_{\text{X}} d\mu_{\text{X}} = 0$$

N_{Me} and N_{X} – denote molar fractions of the metal and oxidant, respectively

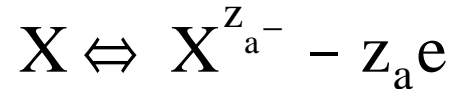
For compounds exhibiting minor deviation from stoichiometry, the ratio of the metal and oxidant molar fractions is inversely proportional to their valences:

$$\frac{N_{\text{X}}}{N_{\text{Me}}} = \frac{z_{\text{c}}}{|z_{\text{a}}|}$$

Thus, the Gibbs-Duhem equation assumes the following form:

$$d\mu_{\text{Me}} = - \frac{N_{\text{X}}}{N_{\text{Me}}} d\mu_{\text{X}} = - \frac{z_{\text{c}}}{|z_{\text{a}}|} d\mu_{\text{X}}$$

Ionization reactions of the metal and oxidant:



In thermodynamic equilibrium conditions:

$$\mu_{\text{Me}} = \mu_c + z_c \mu_e$$

$$\mu_{\text{X}} = \mu_a - |z_a| \mu_e$$

After inserting the correlations above, cation and anion fluxes can be expressed by the following equations:

$$j_c = -c_c \frac{D_c}{RT} \cdot \frac{c_e D_e}{z_c^2 c_c D_c + z_a^2 c_a D_a + c_e D_e} \frac{d\mu_{\text{Me}}}{dx}$$

$$j_a = -c_a \frac{D_a}{RT} \cdot \frac{c_e D_e}{z_c^2 c_c D_c + z_a^2 c_a D_a + c_e D_e} \frac{d\mu_{\text{X}}}{dx}$$

If electron mobility is significantly higher than ionic defect mobility, i.e. $D_a \ll D_e \gg D_c$, then:

$$j_c = -c_c \frac{D_c}{RT} \frac{d\mu_{Me}}{dx}$$

$$j_a = -c_a \frac{D_a}{RT} \frac{d\mu_X}{dx}$$

Scale growth, dX , is the result of reactions at both interfaces:

$$dX = dX_c - dX_a$$

Increase in scale thickness as a function of time at both its interfaces is described by Stefan's condition, which assumes the following form:

$$\frac{dX_a}{dt} = \frac{j'_a}{c'_X(\text{Me}_a X_b)}$$

$$\frac{dX_c}{dt} = \frac{j''_c}{c''_{\text{Me}}(\text{Me}_a X_b)}$$

Therefore:

$$\frac{dX}{dt} = \frac{j''_c}{c''_{\text{Me}}(\text{Me}_a X_b)} - \frac{j'_a}{c'_X(\text{Me}_a X_b)}$$

After inserting the expression describing the fluxes into the previous equation, scale thickness increase can be expressed as:

$$\frac{dX}{dt} = - \frac{c_c D_c}{c''_{Me} (Me_a X_b)} \frac{1}{RT} \frac{d\mu_{Me}}{dx} - \frac{c_a D_a}{c'_X (Me_a X_b)} \frac{1}{RT} \frac{|z_a|}{z_c} \frac{d\mu_{Me}}{dx}$$

$$\frac{dX}{dt} = - \frac{1}{RT} \left(\frac{c_c D_c}{c''_{Me} (Me_a X_b)} + \frac{c_a D_a}{c'_X (Me_a X_b)} \frac{|z_a|}{z_c} \right) \frac{d\mu_{Me}}{dx}$$

Taking into account that:

$$c_d D_d = c_i D_i^*$$

D_i^* - self-diffusion coefficient of component "i"

Meanwhile:

$$\frac{dX}{dt} = - \frac{1}{RT} \left(D_{Me}^* + \frac{|z_a|}{z_c} D_X^* \right) \frac{d\mu_{Me}}{dx}$$

Because the correlation between self-diffusion coefficients of a given substance and its chemical potential gradient is unknown, the average value must be calculated:

$$\frac{dX}{dt} = - \frac{1}{RTX} \int_{\mu'_{Me}}^{\mu''_{Me}} \left(D_{Me}^* + \frac{|z_a|}{z_c} D_X^* \right) d\mu_{Me}$$

If it is assumed that the scale formation process proceeds according to the parabolic rate law, then:

$$k'_p = \frac{1}{RT} \int_{\mu''_{Me}}^{\mu'_{Me}} \left(D_{Me}^* + \frac{|z_a|}{z_c} D_X^* \right) d\mu_{Me}$$

From the Gibbs-Duhem equation and the correlation between chemical potential and oxidant pressure, the following equation can be derived:

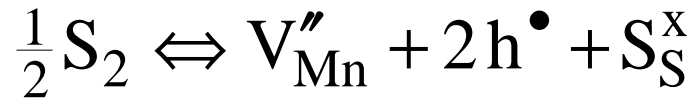
$$d\mu_{\text{Me}} = - \frac{z_c}{|z_a|} d\mu_{\text{X}} = - \frac{1}{2} \frac{z_c}{|z_a|} RT d \ln p_{\text{X}_2}$$

The parabolic oxidation rate constant is thus:

$$k'_p = \frac{1}{2} \int_{p'_{\text{X}_2}}^{p''_{\text{X}_2}} \left(\frac{z_c}{|z_a|} D_{\text{Me}}^* + D_{\text{X}}^* \right) d \ln p_{\text{X}_2}$$

Application of Wagner's metal oxidation theory

Example I: $Mn_{1-y}S$



$$K = [V''_{Mn}] \cdot [h^\bullet]^2 \cdot p_{S_2}^{-1/2}$$

$$2[V''_{Mn}] = [h^\bullet]$$

$$[V''_{Mn}] = 0.63 \cdot K^{1/3} \cdot p_{S_2}^{1/6}$$

$$k'_p = \frac{1}{2} \int_{p'_{X_2}}^{p''_{X_2}} \left(\frac{z_c}{|z_a|} D_{Me}^* + D_X^* \right) d \ln p_{X_2}$$

$$k'_p = \frac{1}{2} \int_{p'_{X_2}}^{p''_{X_2}} D_{Me}^* d \ln p_{X_2}$$

$$D_{Me}^* = D_{Me} \cdot [V''_{Mn}] = 0.63 \cdot K^{1/3} \cdot D_{Me} \cdot p_{S_2}^{1/6}$$

$$k'_p = \frac{1}{2} \cdot 0.63 \cdot K^{1/3} \cdot D_{Me} \cdot \int_{p'_{S_2}}^{p''_{S_2}} p_{S_2}^{1/6} d \ln p_{S_2}$$

$$k'_p = 3 \cdot 0.63 \cdot K^{1/3} \cdot D_{Me} \cdot p_{S_2}^{1/6} = 3D_{Me}^*$$

$$k'_p = (1 + |p|) \cdot D_{Me}^* = [\text{def}] \cdot \tilde{D}$$



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Application of Wagner's metal oxidation theory

Example II: calculating the self-diffusion coefficient (Fueki-Wagner method)

$$k'_p = \frac{1}{2} \int_{p'_{X_2}}^{p''_{X_2}} \left(\frac{z_c}{|z_a|} D_{Me}^* + D_X^* \right) d \ln p_{X_2}$$

$$k'_p = \frac{1}{2} \int_{p'_{X_2}}^{p''_{X_2}} D_{Me}^* d \ln p_{X_2}$$

$$\left. \frac{d k'_p}{d \ln p_{X_2}} \right|_{p''_{X_2}} = \frac{1}{2} D_{Me}^*$$

$$D_{Me}^* = 2 \cdot \left. \frac{d k'_p}{d \ln p_{X_2}} \right|_{p''_{X_2}}$$

Application of Wagner's metal oxidation theory

Example II: calculating the self-diffusion coefficient (Fueki-Wagner method), cont.
nickel oxidation

Fueki-Wagner:

$$D_{\text{Ni}}^* = 1,1 \cdot 10^{-3} \cdot \exp\left(-\frac{50300}{RT}\right)$$

Lindner:

$$D_{\text{Ni}(t)}^* = 1,7 \cdot 10^{-2} \cdot \exp\left(-\frac{56000}{RT}\right)$$

Moore:

$$D_{\text{Ni}(t)}^* = 3,9 \cdot 10^{-4} \cdot \exp\left(-\frac{44200}{RT}\right)$$

Note: the results above were obtained for the same oxygen pressure value

THE END