



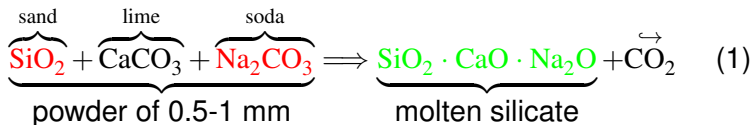
Velké Karlovice, 23 May 2019

Coupled Numerical Modelling of Redox Reactions and Glass Melt Fining Processes

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1. Glass fining principle



- ▶ 200 kg de CO₂/T of glass:
 - ▶ 25 Nm³ of CO₂/m³ of glass, or **140 m³ de CO₂/m³ of glass at T = 1400°C.**
- ▶ The small solubility of CO₂ ⇒ bubble formation: **10⁸ bulles/m³.**

1. Glass fining principle

- ▶ According to Hadamard and Rybczynski¹, the rising velocity is

$$V_T = \frac{\rho g a^2(t)}{3\mu(T)}. \quad (2)$$

- ▶ How to remove the bubble from the glass bath?
 - ▶ **Increase T** to decrease $\mu(T)$;
 - ▶ **Enhance a** .
- ▶ To increase the bubble size, “**fining**” agents are added:
 - ▶ Sulfate: Na_2SO_4 ;
 - ▶ Transition metals: $\text{As}^{5+}/\text{As}^{3+}$, $\text{Sb}^{5+}/\text{Sb}^{3+}$, etc.
- ▶ ↗ T promote the reduced state \Rightarrow “**fining gases**” release O_2 et SO_2 .

¹J. Hadamard: Mouvement permanent lent d'une sphère liquide et visqueuse dans un liquide visqueux, in: C. R. Acad. Sci. Paris 152 (1911), pp. 1735–1738; W. Rybczynski: Über die fortschreitende bewegun einer flussingen kugel in einem zaben medium, in: Bull. de l'Acad. des Sci. de Cracovie, série A 1 (1911), pp. 40–46.

1. Glass fining principle

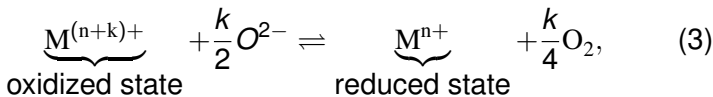
2. Oxidation-reduction of glass former liquids
 - 2.1 Thermodynamic model

3. Mass transfer between the two phases
 - 3.1 Unique Bubble
 - 3.2 Bubble population

4. Synthesis

2. Oxidation-reduction of glass former liquids

2.1 Thermodynamic model



- ▶ The entropy production is²:

$$d_i S = \frac{\mathcal{A}}{T} d\zeta, \quad \mathcal{A} = \mu_{\text{M}^{(n+k)+}} + \frac{k}{2} \mu_{\text{O}^{2-}} - \mu_{\text{M}^{n+}} - \frac{k}{4} \mu_{\text{O}_2}. \quad (4)$$

- ▶ The thermodynamic equilibrium $\Rightarrow \mathcal{A} = 0$:

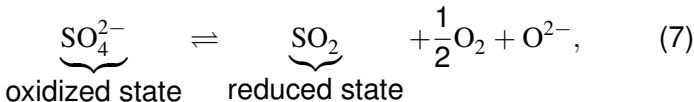
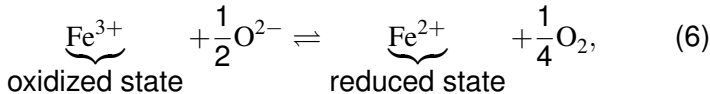
$$K_M = \frac{a_{\text{M}^{n+}} a_{\text{O}_2}^{k/4}}{a_{\text{M}^{(n+k)+}} a_{\text{O}^{2-}}^{k/2}}, \quad K'_M = \frac{C_{\text{M}^{n+}} P_{\text{O}_2}^{k/4}}{C_{\text{M}^{(n+k)+}}}. \quad (5)$$

²D. Kondepudi/I. Prigogine: Modern Thermodynamics: From Heat Engines to Dissipative Structures, 2nd, New York 2015.

2. Oxidation-reduction of glass former liquids

2.1 Thermodynamic model

- For several reactions:



$$d_i S = \frac{1}{T} (\mathcal{A}_{\text{Fe}} d\zeta_{\text{Fe}} + \mathcal{A}_{\text{S}} d\zeta_{\text{S}}). \quad (8)$$

- The thermodynamic equilibrium:

$$\begin{aligned} \mathcal{A}_{\text{Fe}} = 0, \quad K_{\text{Fe}} &= \frac{C_{\text{Fe}^{2+}} P_{\text{O}_2}^{1/4}}{C_{\text{Fe}^{3+}}} \\ \mathcal{A}_{\text{S}} = 0, \quad K_{\text{S}} &= \frac{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}}{C_{\text{SO}_4^{2-}}}. \end{aligned} \quad (9)$$

2. Oxidation-reduction of glass former liquids

2.1 Thermodynamic model

- ▶ The phase rule of Gibbs: $f = C - R - \varphi + 2$.
 - ▶ R chemical reactions to satisfy;
 - ▶ C chemical equilibrium to satisfy between each phases:

$$\mu_{\text{O}_2}(\text{glass}) = \mu_{\text{O}_2}(\text{gas}) \Rightarrow C_{\text{O}_2} = \underbrace{\mathcal{L}_{\text{O}_2}}_{\text{Henry coefficient}} P_{\text{O}_2}, \quad (10)$$

$$\mathcal{L}_{\text{O}_2} = A_{\text{O}_2}^{(s)} e^{B_{\text{O}_2}^{(s)}/T}. \quad (11)$$

2. Oxidation-reduction of glass former liquids

2.1 Thermodynamic model

- R reactions of oxidation-reduction:

$$\sum_{i=1}^{N_l} \nu'_{ri} A_i + \sum_{j=1}^{N_g} \beta'_{rj} G_j \rightleftharpoons \sum_{i=1}^{N_l} \nu''_{ri} A_i + \sum_{j=1}^{N_g} \beta''_{rj} G_j, \quad r \in [1; R]. \quad (12)$$

- A_i : ionic species $i \in [1; N_l]$; G_j : gas species $j \in [1; N_g]$

$$\frac{A_r}{\mathcal{R}T} = -\frac{\Delta G_r}{\mathcal{R}T} - \ln \prod_{i=1}^{N_l} C_{A_i}^{\nu'_{ri}} \prod_{j=1}^{N_g} C_{G_j}^{\beta'_{rj}}, \quad (13)$$

$$\nu_{ri} = \nu''_{ri} - \nu'_{ri}, \forall i \in [1; N_l], \quad \beta_{rj} = \beta''_{rj} - \beta'_{rj}, \forall j \in [1; N_g]. \quad (14)$$

- Phase equilibrium gives:

$$\alpha_j G_j(g) \rightleftharpoons G_j(f), \forall j \in [1; N_g] \quad (15)$$

$$C_{G_j} = \mathcal{L}_{G_j} P_{G_j}^{\alpha_j}, \quad \mathcal{L}_{G_j} = A_{G_j}^{(s)} e^{B_{G_j}^{(s)}/T}. \quad (16)$$

2. Oxidation-reduction of glass former liquids

2.1 Thermodynamic model

- ▶ **Thermodynamic equilibrium between the liquid and the atmospheric phase at P_{atm} .**
 - ▶ K_r : obtained by chemical equilibrium³, or by electrochemistry⁴.
 - ▶ \mathcal{L}_{G_j} : obtained by computation (physically dissolved), by equilibrium and chemical analysis (chemically dissolved)⁵.

³M.-H. Chopinet/D. Lizarazu/C. Rocanière: L'importance des phénomènes d'oxydo-réduction dans le verre, in: C. R. Chim. 5.12 (2002), pp. 939–949.

⁴C. Rüssel: Iron oxide-doped alkali-lime-silica glasses, in: Glastechn. Ber 66 (1993), pp. 68–74.

⁵F. W. Krämer: Solubility of gases in glass melts, in: Properties of glass-forming melts, 2005, chap. 13, pp. 405–482.

2. Oxidation-reduction of glass former liquids

2.1 Thermodynamic model

- ▶ Glass with sulfate and low iron concentration. At 1280°C:

$$\mathcal{R}_{\text{Fe}} = \frac{C_{\text{Fe}^{2+}}}{C_{\text{Fe}}} = 0.186, \quad (17)$$

$$C_{\text{SO}_3^{2-}} = 0.49 \text{ wt } \%. \quad (18)$$

- ▶ K_r taken from the two references⁶.
- ▶ \mathcal{L}_{G_j} taken from the paper of Beerkens.

⁶Chopinnet/Lizarazu/Rocanière: L'importance des phénomènes d'oxydo-réduction dans le verre (see n. 3); R. G. C. Beerkens: Analysis of advanced and fast fining processes for glass melts, in: *Advances in Fusion and Processing of Glass III*, New York 2003, pp. 3–24.

2. Oxidation-reduction of glass former liquids

2.1 Thermodynamic model

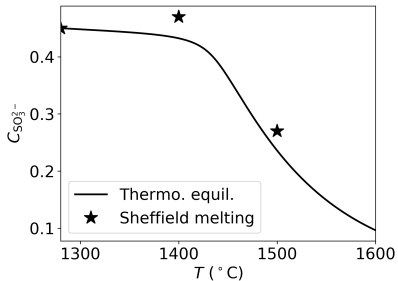


Figure 1: $\text{C}_{\text{SO}_3^{2-}}$ (% masse) vs. T .

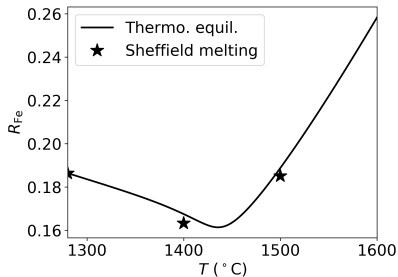
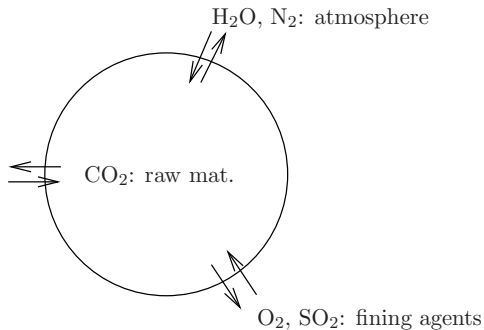


Figure 2: \mathcal{R}_{Fe} vs. T .

3. Mass transfer between the two phases

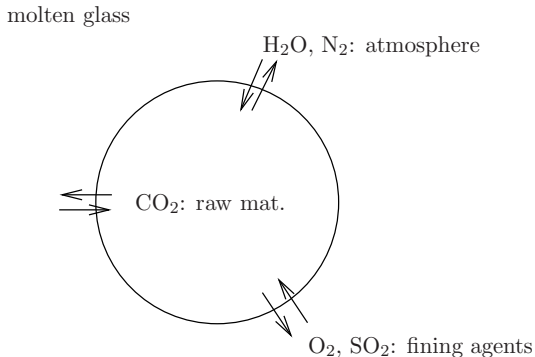
3.1 Unique Bubble

molten glass



3. Mass transfer between the two phases

3.1 Unique Bubble



Mass transfer with multicomponent bubbles.

3. Mass transfer between the two phases

3.1 Unique Bubble

- ▶ The bubble volume changes due to the mass gradient between the bubble and the liquid.

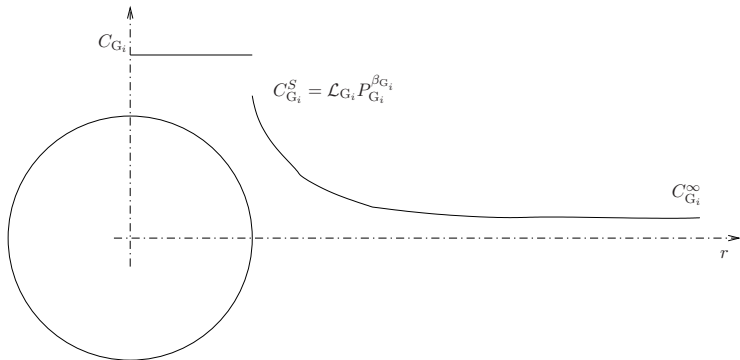


Figure 3: C_i vs. r .

3. Mass transfer between the two phases

3.1 Unique Bubble

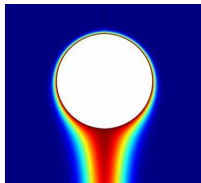


Figure 4: C_{O_2} around a rising bubble.

- ▶ For a rising bubble, C_{G_i} changes over a thin boundary layer, δ :

$$J_{G_i} = \frac{D_{G_i} (C_{G_i}^{\infty} - C_{G_i}^S)}{\delta} = \frac{2a}{\delta} \frac{D_{G_i}}{2a} (C_{G_i}^{\infty} - C_{G_i}^S). \quad (19)$$

- ▶ The **Sherwood** number is roughly defined:

$$\mathbf{Sh}_{G_i} = \frac{2a}{\delta}, \quad Sh_{G_i} = f(Pe_{G_i}), \quad \text{with } \mathbf{Pe}_{G_i} = \frac{2aV_T}{D_{G_i}}. \quad (20)$$

3. Mass transfer between the two phases

3.1 Unique Bubble

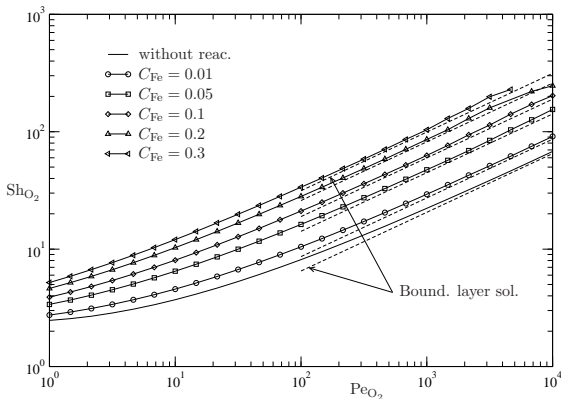


Figure 5: Sh_{O_2} vs. Pe_{O_2} for several C_{Fe} at $T = 1400^\circ C^7$.

⁷F. Pigeonneau: Mass transfer of rising bubble in molten glass with instantaneous oxidation-reduction reaction, in: *Chem. Eng. Sci.* 64 (2009), pp. 3120–3129.

3. Mass transfer between the two phases

3.1 Unique Bubble

- H₂O, N₂; CO₂ ; O₂ and SO₂.

$$\frac{dn_{G_i}}{dt} = 2\pi a \text{Sh}_{G_i} \mathcal{D}_{G_i} (C_{G_i}^{\infty} - \mathcal{L}_{G_i} P_{G_i}^{\beta_{G_i}}), \quad (21)$$

$$\frac{3\mathcal{R}T \sum_{i=1}^{N_g} n_{G_i}}{4\pi a^3} = P_0 + \rho g(H - z) + \frac{2\sigma}{a}, \quad (22)$$

$$\frac{dz}{dt} = \frac{ga^2}{3\nu}. \quad (23)$$

3. Mass transfer between the two phases

3.1 Unique Bubble

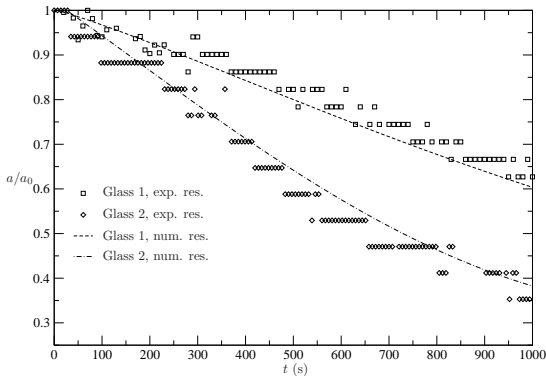


Figure 6: a/a_0 vs. t for 2 glasses with different iron contents at $T = 1400^\circ\text{C}$ ⁹.

⁸F. Pigeonneau/D. Martin/O. Mario: Shrinkage of oxygen bubble rising in a molten glass, in: *Chem. Eng. Sci.* 65 (2010), pp. 3158–3168.

⁹Ibid.

3. Mass transfer between the two phases

3.1 Unique Bubble

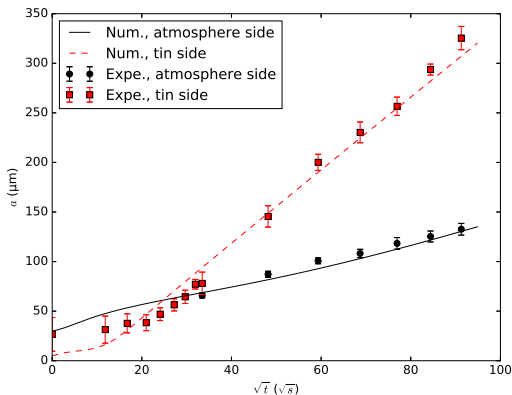


Figure 7: a (μm) vs. \sqrt{t} ($\sqrt{\text{s}}$) for a float glass¹⁰.

¹⁰D. Boloré/F. Pigeonneau: Spatial distribution of nucleated bubbles in molten glasses undergoing coalescence and growth, in: *J. Am. Ceram. Soc.* 101.5 (2018), pp. 1892–1905.

3. Mass transfer between the two phases

3.2 Bubble population

- ▶ A unique bubble exchanges $\sim 10^{-8}$ mol/s.
- ▶ During the glass melting, $N_b \sim 10^8$ bulles/m³.

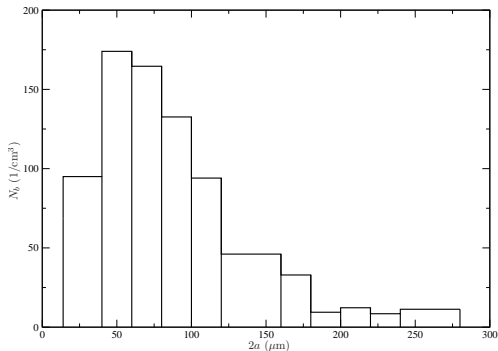
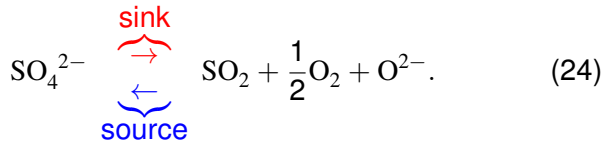


Figure 8: N_b vs. $2a$ in a molten glass ($T = 1300^\circ\text{C}$).

3. Mass transfer between the two phases

3.2 Bubble population

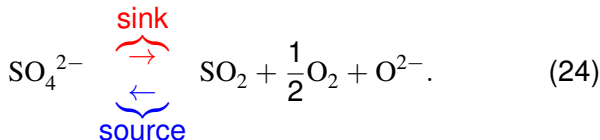
- ▶ The **consumption** (release) of a bubble population is a **sink** (source) of gas:



3. Mass transfer between the two phases

3.2 Bubble population

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The mass transfer between the bubble population and the liquid is crucial to the chemical equilibrium after the melting.

Study the coupling between the oxidation-reduction and the fining process

3. Mass transfer between the two phases

3.2 Bubble population

- ▶ **Spatially homogeneous medium** \Rightarrow only t is considered.
- ▶ **Medium** = liquid + N_{cl} bubble classes, $N_{b,k}$ ($k = 1, N_{cl}$).
- ▶ R chemical reactions are involved:

$$\sum_{i=1}^{N_l} \nu'_{ri} A_i + \sum_{j=1}^{N_{ga}} \beta'_{rj} G_j \rightleftharpoons \sum_{i=1}^{N_l} \nu''_{ri} A_i + \sum_{j=1}^{N_{ga}} \beta''_{rj} G_j, \quad (25)$$

$$\frac{dC_{A_i}}{dt} = \sum_{r=1}^R \nu_{ri} \dot{\zeta}_r, \quad \text{pour } i = 1 \text{ à } N_l, \quad (26)$$

$$\frac{dC_{G_j}}{dt} = \sum_{r=1}^R \beta_{rj} \dot{\zeta}_r + S_{b,G_j}, \quad \text{pour } j = 1 \text{ à } N_g. \quad (27)$$

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3. Mass transfer between the two phases

3.2 Bubble population

$$\frac{dn_{G_j}}{dt} = 2\pi a \text{Sh}_{G_j} \mathcal{D}_{G_j} \left(C_{G_j} - \mathcal{L}_{G_j} P_{G_j}^{\alpha_{G_j}} \right). \quad (28)$$

- ▶ For the bubble class k of density $N_{b,k}$, the gas consumption is

$$N_{b,k} \frac{dn_{G_j}}{dt} = 2\pi a_k \text{Sh}_{G_j,k} \mathcal{D}_{G_j} \left(C_{G_j} - \mathcal{L}_{G_j} P_{G_j}^{\alpha_{G_j}} \right) N_{b,k}. \quad (29)$$

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- ▶ So, S_{b,G_j} is equal to:

$$S_{b,G_j} = -2\pi \mathcal{D}_{G_j} \sum_{k=1}^{N_{cl}} a_k \text{Sh}_{G_j,k} \left(C_{G_j} - \mathcal{L}_{G_j} P_{G_j,k}^{\alpha_{G_j}} \right) N_{b,k}. \quad (30)$$

3. Mass transfer between the two phases

3.2 Bubble population

- ▶ $\dot{\zeta}_r$ is determined assuming instantaneous reactions.
- ▶ $\forall t$, the chemical equilibrium is verified and the consumption or the production of gas defines the chemical state.

$$\sum_{i=1}^{N_l} \frac{\nu_{ri}}{C_{A_i}} \frac{dC_{A_i}}{dt} + \sum_{j=1}^{N_{ga}} \frac{\beta_{rj}}{C_{G_j}} \frac{dC_{G_j}}{dt} = \frac{1}{K_r} \frac{dK_r}{dt}, \quad (31)$$

$$\sum_{k=1}^R M_{rk} \dot{\zeta}_k = \frac{d \ln K_r}{dT} \frac{dT}{dt} - \sum_{j=1}^{N_g} \frac{\beta_{rj}}{C_{G_j}} S_{b,G_j}, \quad r \in [1; R] \quad (32)$$

$$M_{rk} = \sum_{i=1}^{N_l} \frac{\nu_{ri} \nu_{ki}}{C_{A_i}} + \sum_{j=1}^{N_g} \frac{\beta_{rj} \beta_{kj}}{C_{G_j}}. \quad (33)$$

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3. Mass transfer between the two phases

3.2 Bubble population

- ▶ Glass: $T = 1200^{\circ}\text{C}$ ($\mathcal{R}_{\text{Fe}} = 0.2$, $C_{\text{Fe}} = 0.1\%$ m et $C_{\text{SO}_3} = 0.35\%$ m) with 5 bubble classes¹¹:

Class, k	1	2	3	4	5
$N_{b,k}$ (m^{-3})	$2.2 \cdot 10^7$	$1.2 \cdot 10^8$	$1.2 \cdot 10^8$	$5.7 \cdot 10^7$	$1.4 \cdot 10^7$
a_k (m)	$4.9 \cdot 10^{-5}$	$9.4 \cdot 10^{-5}$	$1.5 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$3.3 \cdot 10^{-4}$

Table 1: Volume densities and initial radii of the 5 bubble classes.

- ▶ Only SO_2 and O_2 are considered.
- ▶ Initially, the bubbles are only composed by O_2 .
 1. $dT/dt = 10$ K/min ;
 2. $dT/dt = 1$ K/min.

¹¹O. Stahlavsky et al.: The bubble effect on the redox state of glass, in: VIII International Seminar on Mathematical Modelling and Advanced Numerical Methods in Furnaces Design and Operation, Velké Karlovice 2005.

3. Mass transfer between the two phases

3.2 Bubble population

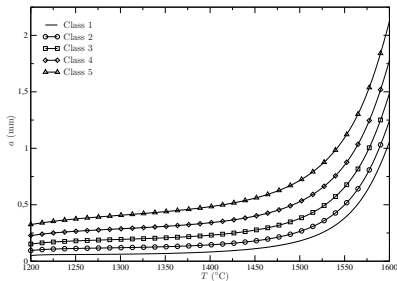


Figure 9: a (mm) vs. T ($^{\circ}\text{C}$) for the 5 classes at $\frac{dT}{dt} = 10$ K/min.

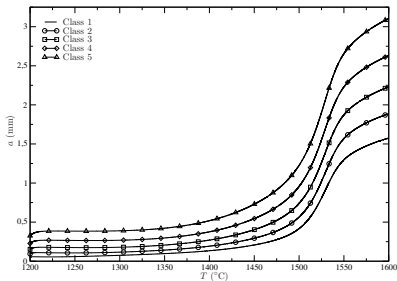


Figure 10: a (mm) vs. T ($^{\circ}\text{C}$) for the 5 classes at $\frac{dT}{dt} = 1$ K/min.

3. Mass transfer between the two phases

3.2 Bubble population

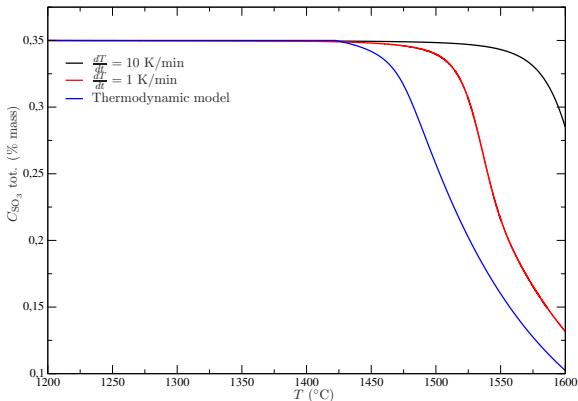


Figure 11: C_{SO_3} total (% masse) vs. T ($^\circ\text{C}$).

3. Mass transfer between the two phases

3.2 Bubble population

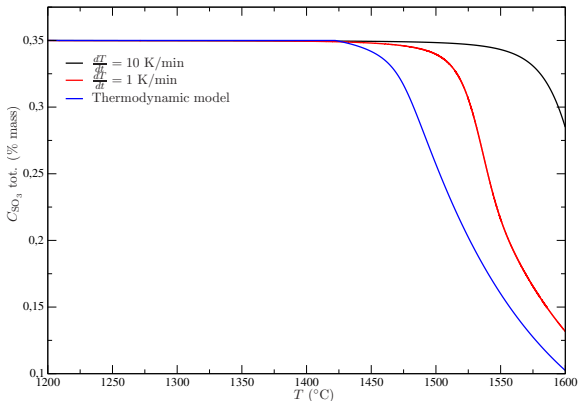


Figure 11: C_{SO_3} total (% masse) vs. T ($^{\circ}\text{C}$).

The liquid is oversaturated in sulfate at high heating rate.

3. Mass transfer between the two phases

3.2 Bubble population

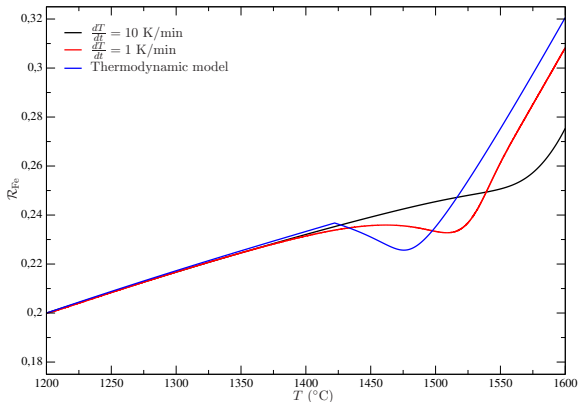


Figure 12: \mathcal{R}_{Fe} vs. T ($^{\circ}\text{C}$).

3. Mass transfer between the two phases

3.2 Bubble population

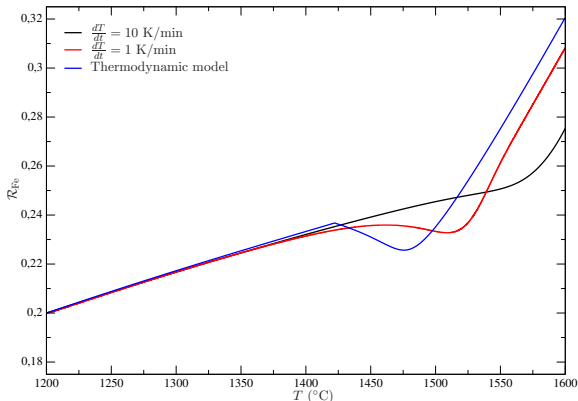


Figure 12: \mathcal{R}_{Fe} vs. T ($^{\circ}\text{C}$).

The liquid is more oxidized at high heating rate.

3. Mass transfer between the two phases

3.2 Bubble population

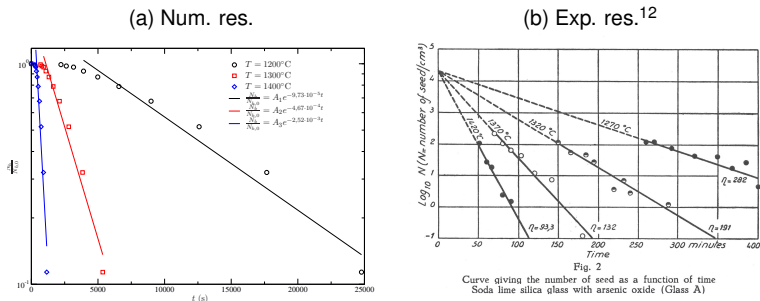


Figure 13: $\frac{N_b}{N_{b,0}}$ vs. t (s).

$$N(t) = N_0 e^{-\alpha t}, \quad (34)$$

- ▶ At $T = 1300^\circ\text{C}$, $\alpha = 4.67 \cdot 10^{-4} \text{ s}^{-1}$.
- ▶ Bastick found at $T = 1320^\circ\text{C}$, $\alpha = 5 \cdot 10^{-4} \text{ s}^{-1}$.

¹²R. E. Bastick: Laboratory experiments on the refining of glass, in: Symposium sur l'affinage du verre, Paris 1956, pp. 127–138.

4. Synthesis

- ▶ The thermodynamic model allows us to easily describe the liquid/gas interactions.
- ▶ The kinetic model is based on the instantaneous oxidation-reduction reactions.
- ▶ The bubble growth rates change strongly with the gas consumption.
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