Diffusion in Temperature Gradients

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Background

- Strong temperature gradients are often technically important in energy applications, i.e. they may occur in heat exchangers, superheater tubes etc.
- Often composites or joints between dissimilar materials, e.g. Stainless steels/high strength steels

Content

- Background- importance of temperature gradients
- Coupling effects and irreversible thermodynamics treatment
- Thermal migration in pure metal and the Kirkendall effect
- Implementation in DICTRA
- Thermomigration of carbon in steel

General approach for isothermal diffusion

Flux :

$$J = -L\frac{\partial \mu}{\partial x} = -L\frac{\partial \mu}{\partial c}\frac{\partial c}{\partial x} = -D\frac{\partial c}{\partial x}$$

$$D = L\frac{\partial \mu}{\partial c}$$

Kinetic parameters from model.

Darken's thermodynamic factor, e.g. from Calphad analysis.

Base models on a vacancy mechanism!

Carbon diffusion in T - gradient?

$$J_C = -\frac{u_C}{V_s} y_{Va} M_{CVa} \nabla \mu_C \qquad \mu_C(T, u_C) \qquad u_C = \frac{x_C}{\sum_{j \in S} x_j}$$

$$= -\frac{u_C}{V_s} y_{Va} M_{CVa} \left(\frac{\partial \mu_C}{\partial u_C} \nabla u_C + \frac{\partial \mu_C}{\partial T} \nabla T \right) \quad ??$$

Cannot be used as $\frac{\partial \mu_C}{\partial T} = -S_C$ depends on the reference state!

Coupling effects

Flux / Force	Heat	Electric	diffusion
Temperature gradient	Fourier	Seebeck	Soret Thermo-migration
Voltage	Peltier	Ohm	Electro migration
Chemical potential gradient	Dufour	Volta (galvanic cell)	Fick

Irreversible thermodynamics treatment

$$J_k = -\sum \frac{L_{kj}}{T} \nabla \mu_j - \frac{L_{kT}}{T^2} \nabla T$$

$$J_Q = -\sum \frac{L_{Tj}}{T} \nabla \mu_j - \frac{L_{TT}}{T^2} \nabla T$$

Onsager reciprocity laws:

$$L_{kj} = L_{jk}$$

$$L_{Tj} = L_{jT}$$

Heat of transport Q_j^*:

$$J_k = -\sum \frac{L_{kj}}{T} \nabla \mu_j - \frac{L_{kT}}{T^2} \nabla T = -\sum \frac{L_{kj}}{T} \left(\nabla \mu_j + \frac{Q_j^*}{T^2} \nabla T \right)$$

i.e. $L_{kT} = \sum L_{kj} Q_j^*$

In lattice fixed frame of reference vacancy mechansim yields

$$L_{kk} = \frac{u_k y_{Va}}{V_s} M_{kVa}$$

$L_{kj} = 0$ when $i \neq j$

When no off-diagonal coefficients:

$$Q_j^* = \left(\frac{\partial J_Q}{\partial J_j} \right)_{\nabla T = 0}$$

Thermal migration – a Kirkendall effect or a cross effect?

- Pure component A in lattice-fixed frame:

$$J_A = -\frac{u_A y_{Va}}{V_s} M_{AVa} \frac{Q_A^*}{T^2} \nabla T$$

Kirkendall (marker) velocity :

$$v_K = -\sum V_S J_k$$

Transform to number-fixed frame

$$\sum_{i=1}^{n} a_i J_i = 0$$

$$L_{kT} = \frac{u_k y_{Va}}{V_s} M_{kVa} Q_k^*$$

$$L_{kT}'/T^2 = \sum_{i=1}^{n} (\delta_{ki} - u_k a_i) \frac{u_i}{V_s} y_{Va} M_{iVa} Q_i^* / T$$

Application to Fe-M-C

$$\sum_{i=1}^{n} a_i J_i = J_{Fe} + J_M = 0$$

$$M_i = y_{Va} M_{iVa}$$

$$L_{FeT}'/T^2 = \frac{1}{V_s}\left((1-u_{Fe})u_{Fe}M_{Fe}Q_{Fe}^* - u_{Fe}u_M M_M Q_M^*\right)/T$$

$$L_{MT}'/T^2 = \frac{1}{V_s}\left(-u_M u_{Fe} M_{Fe} Q_{Fe}^* + (1-u_M)u_M M_M Q_M^*\right)/T = -L_{FeT}'/T^2$$

$$L_{CT}'/T^2 = \frac{u_C}{V_s}\left(-u_{Fe}M_{Fe}Q_{Fe}^* - u_M M_M Q_M^* + y_{Va}M_{CVa}Q_C^*\right)/T$$

$$L_{CT}'/T^2 \cong \frac{u_C}{V_s} y_{Va} M_{CVa} Q_C^* / T$$

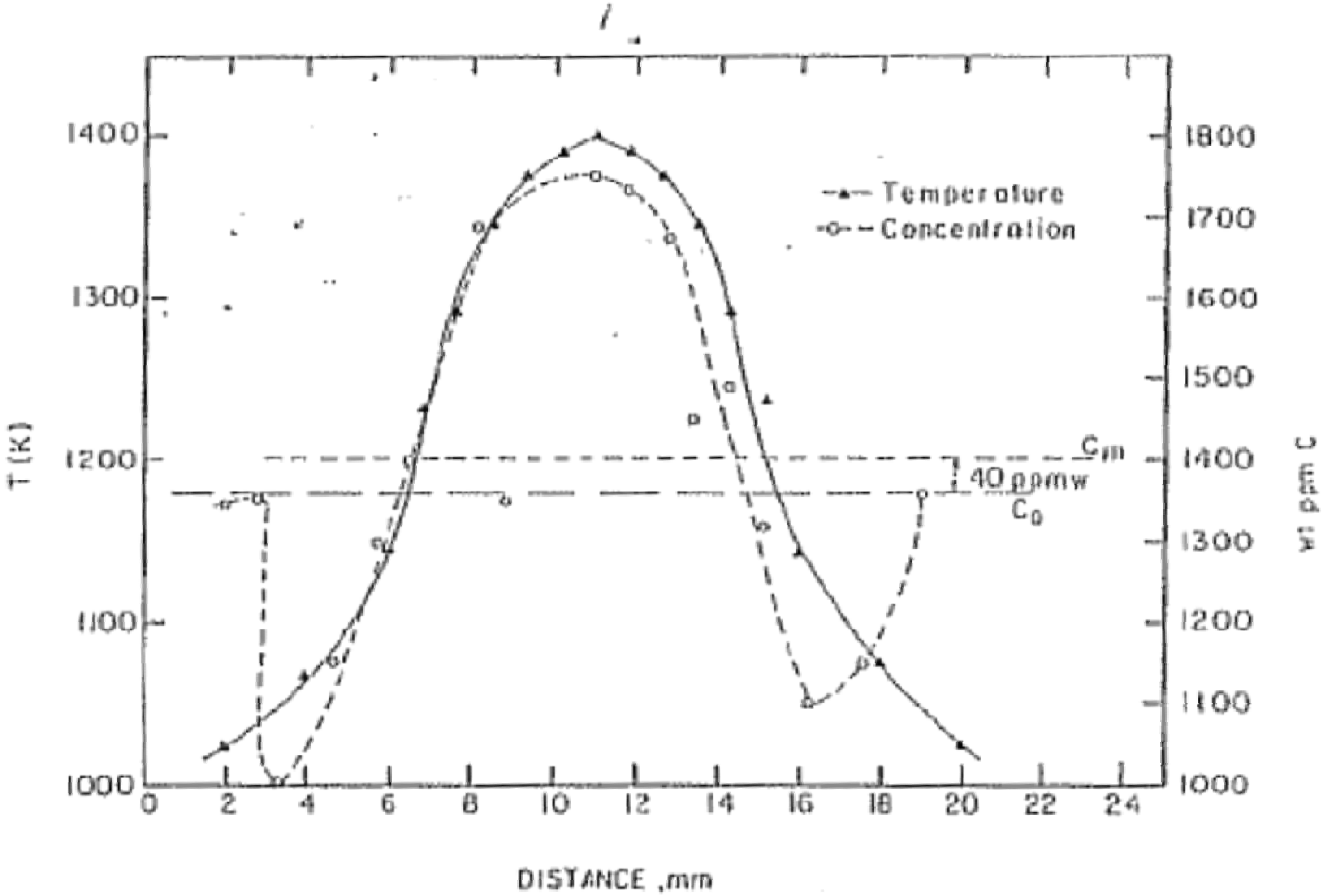
Implementation in DICTRA

- Temperature field i.e. $T(x,t)$, given as input, i.e. heat flow equation not solved.
- The partial differential equations with the extra term solved with the Galerkin method.

$$\frac{\partial u_k}{\partial t} = -\nabla \cdot \left(-\sum_{i=1}^{n} D_{ki}^{n}{}' \frac{1}{V_S} \nabla u_i - \frac{L_{kT}{}'}{T^2} \nabla T \right)$$

Thermomigration of carbon in steel

Okafor et al. 1982



Carbon flux in T - gradient:

$$J_C = -\frac{u_C}{V_s} y_{Va} M_{CVa} \left(\frac{\partial \mu_C}{\partial x} + \frac{Q_C^*}{T} \frac{\partial T}{\partial x} \right)$$

$$= -\frac{D_C}{V_s} \left(\frac{\partial u_C}{\partial x} + \frac{Q_C^*}{T} \frac{1}{\partial \mu_C / \partial u_C} \frac{\partial T}{\partial x} \right)$$

Stationary $t \rightarrow \infty$ $J_C = 0$ everywhere

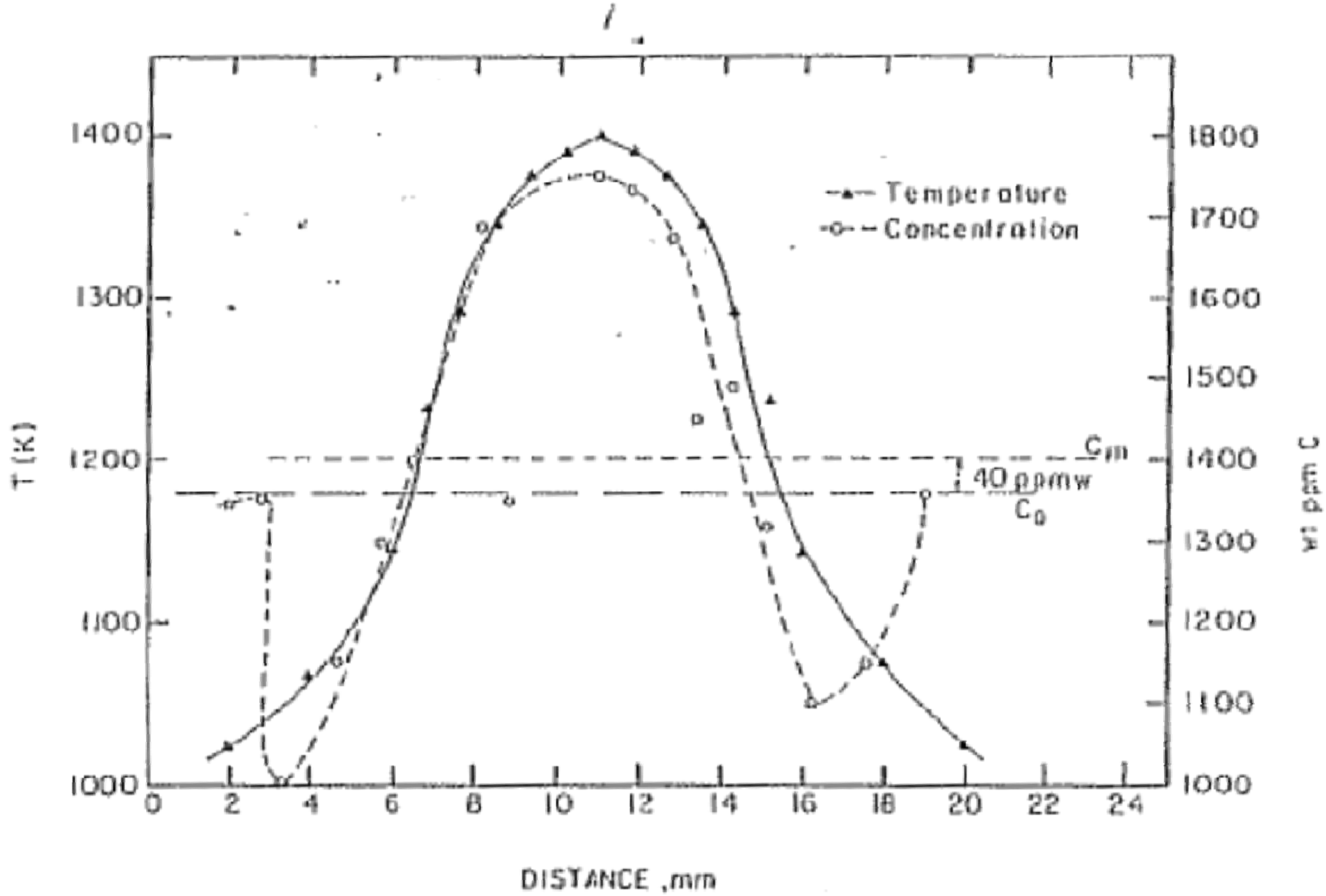
$$Q_C^* = -\frac{\partial u_C}{\partial \ln T} \frac{\partial \mu_C}{\partial u_C}$$

For ideal solution:

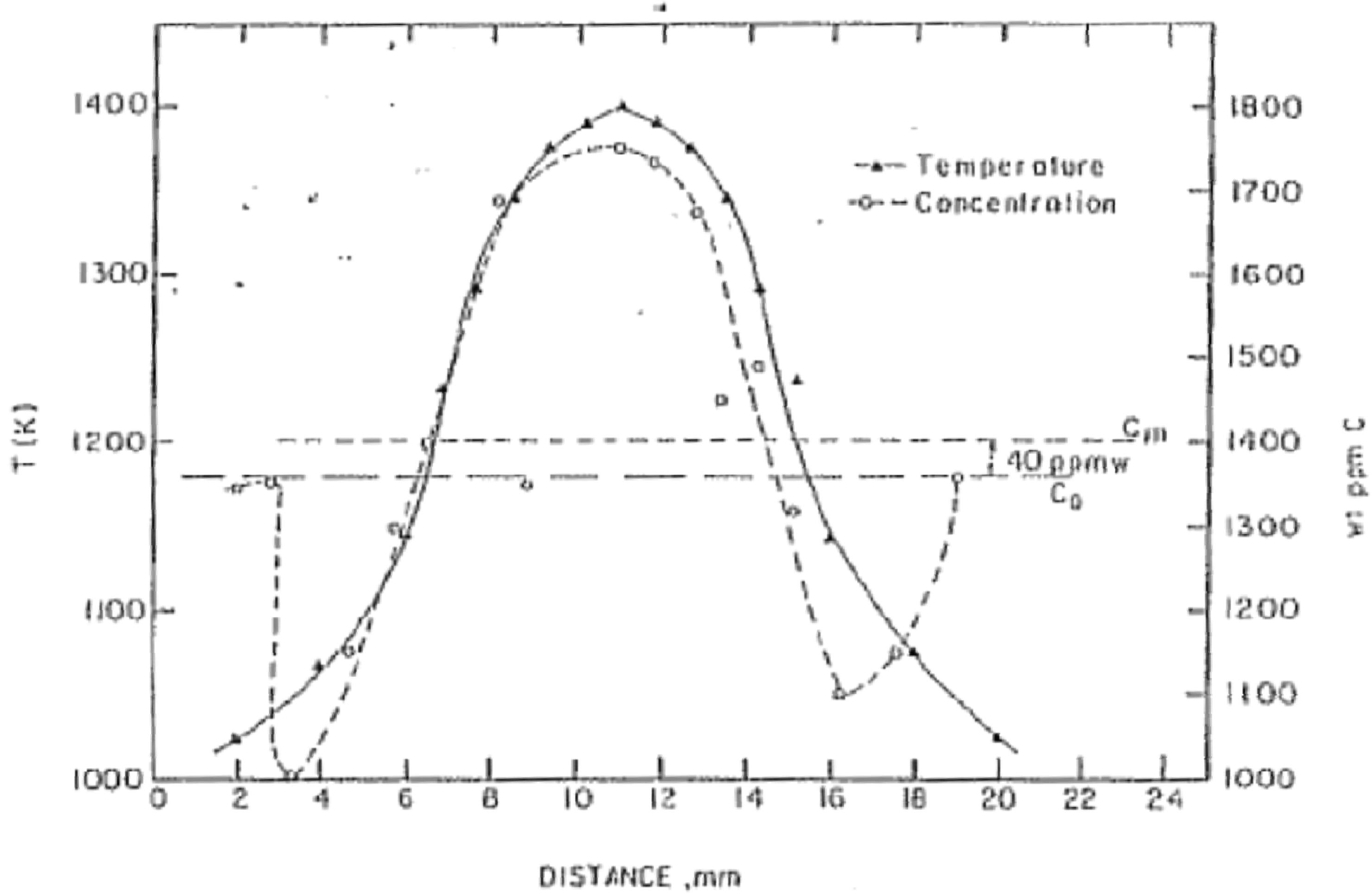
$$\frac{\partial \mu_C}{\partial u_C} = RT / u_C \Rightarrow Q_C^* = R \frac{\partial \ln u_C}{\partial (1/T)}$$

Okafor et al. 1982

$$Q_C^* = -12\,300\ J\ mol^{-1}$$



Stationary conditions $\frac{\partial u_C}{\partial x} \propto \frac{\partial T}{\partial x}$?



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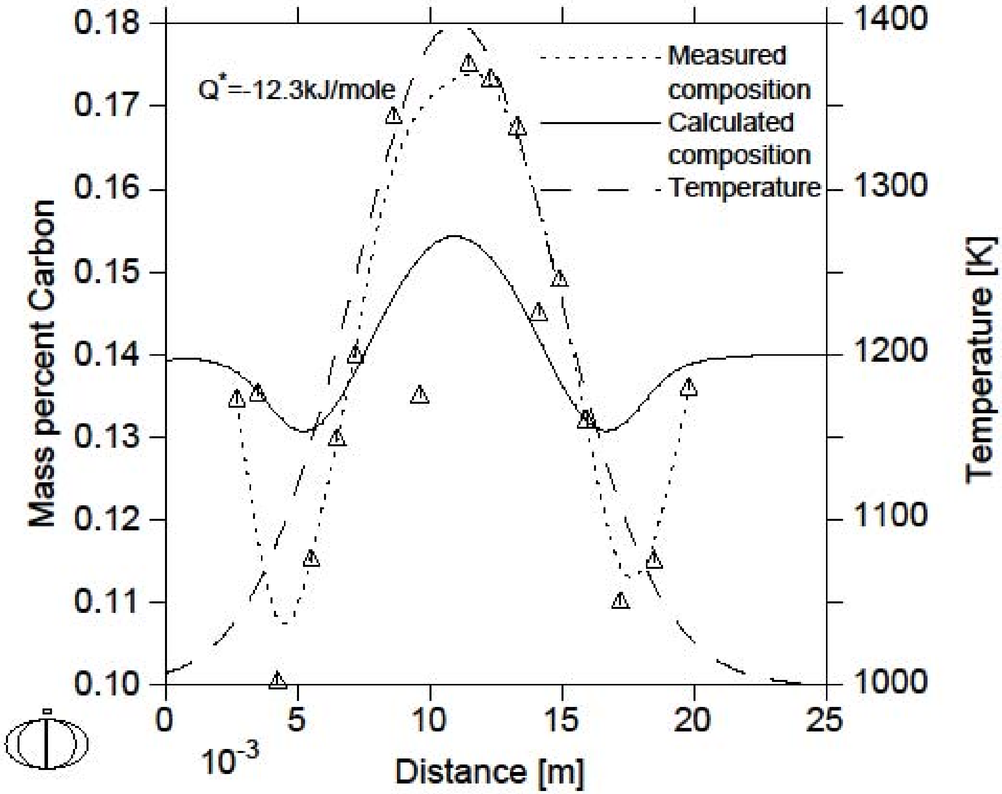


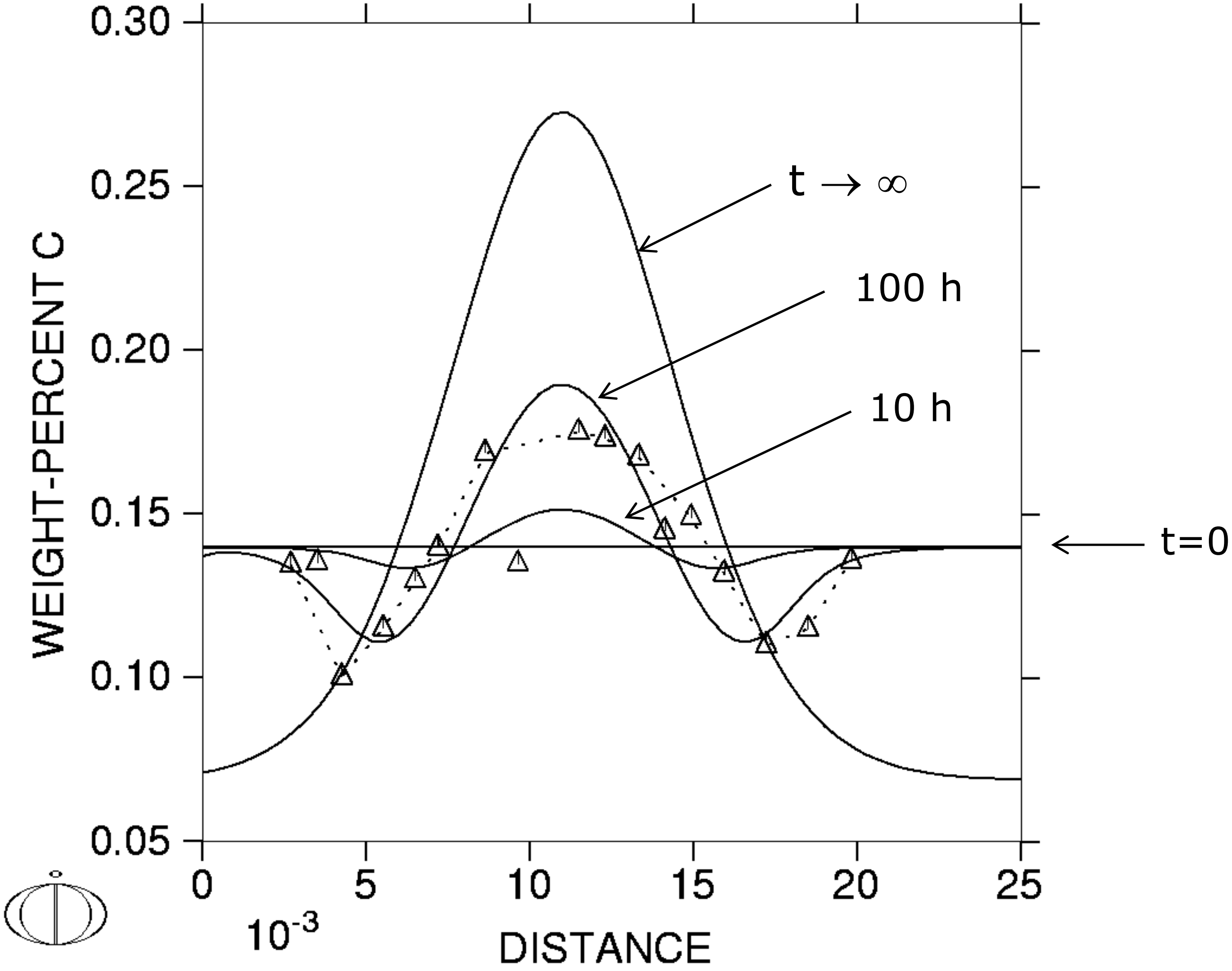
Q*=-12.3kJ/mole
Measured composition
Calculated composition
Temperature
Mass percent Carbon
Temperature [K]
Distance [m]
10^-3
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
1400
1300
1200
1100
1000
0
5
10
15
20
25

Höglund and Ågren 2009

$$Q_C^* = -44\,000\ J\ mol^{-1}$$

Δ: exp, Okafor et al 1982

A 200 K T-difference has about the same effect as carbon concentration differece of 1 at%.



Steady state was not established during the experiments by Okafor et al.!