Coupled heat and mass transfer during nonisothermal absorption by falling droplets

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Applications:
1. two-phase absorber design and analysis
2. chemical engineering
3. refrigeration engineering and air-conditioning
Applications

Examples of industrial operations where thermal effects of absorption are important:

1. absorption of ammonia into water
2. water vapor absorption by aqueous solutions of LiBr, LiCl and potassium formate (HCOOK)
3. absorption of carbon dioxide and hydrogen sulfide into amine solutions
4. absorption of friendly refrigerants such as R32, R134a and R124 by dimethyl acetamide
5. absorption of trifluoroethanol and hexafluoroisopropanol by solvents from the group of organic heterocycles
6. chlorinating of organic liquids
7. absorption of $SO_2$ and HCl into water and aqueous solutions
Process is characterized by:
D - coefficient of diffusion in a liquid phase
a - coefficient of thermal diffusivity
\(\lambda\) - thermal conductivity
L - heat of absorption
\(X_s\) - gas solubility

Fig. 1 Dependence of Henry constant from temperature
fundamentals

Linear approximation of absorbate:

\[ x_s = d \cdot T_s + b \]

Fig. 2 Equilibrium state of aqueous solution of LiBr in water
Table 1. Values of $D$, $\alpha$, $X_s$, $L$, $Le$, $K$ and $d$ for absorption of different gases in water at normal temperature and pressure

<table>
<thead>
<tr>
<th>Gas</th>
<th>$D \times 10^9$ [m$^2 \cdot$ s$^{-1}$]</th>
<th>$\alpha$</th>
<th>$X_s$</th>
<th>$L$ [kJ/kg]</th>
<th>$Le$</th>
<th>$K$</th>
<th>$d$ [K$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>1.98</td>
<td>0.88</td>
<td>$1.69 \cdot 10^{-3}$</td>
<td>418</td>
<td>$1.37 \cdot 10^{-2}$</td>
<td>-120</td>
<td>$-8.24 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>1.61</td>
<td>2.58</td>
<td>$3.85 \cdot 10^{-3}$</td>
<td>627</td>
<td>$10^{-2}$</td>
<td>-42</td>
<td>$-1.57 \cdot 10^{-4}$</td>
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<tr>
<td>Cl$_2$</td>
<td>1.44</td>
<td>2.3</td>
<td>$7.29 \cdot 10^{-3}$</td>
<td>334</td>
<td>$8.7 \cdot 10^{-3}$</td>
<td>-33</td>
<td>$-3.72 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>1.7</td>
<td>39.4</td>
<td>0.1015</td>
<td>1254</td>
<td>$1.05 \cdot 10^{-2}$</td>
<td>-0.58</td>
<td>$-5.75 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>1.7</td>
<td>702</td>
<td>0.3468</td>
<td>2090</td>
<td>$1.13 \cdot 10^{-2}$</td>
<td>-0.336</td>
<td>$-5.97 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>HCl</td>
<td>3.1</td>
<td>442</td>
<td>0.4189</td>
<td>450</td>
<td>$1.88 \cdot 10^{-2}$</td>
<td>-1.433</td>
<td>$-1.55 \cdot 10^{-3}$</td>
</tr>
</tbody>
</table>
fundamentals

Fig. 3 Regimes of two-phase flow
state of the art

Film flow:

Bubbly flow:
state of the art

Slug flow

Droplets
## state of the art

### Table 2

<table>
<thead>
<tr>
<th>Authors</th>
<th>Hydrodynamic solution</th>
<th>Diapason of Re numbers</th>
<th>Method of solution</th>
<th>System</th>
</tr>
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<tbody>
<tr>
<td>Nakoryakov, Grigoreva</td>
<td>-</td>
<td>-</td>
<td>Analytical</td>
<td>Water vapor-LiBr</td>
</tr>
<tr>
<td>(1977)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Lu et al. (1998)</td>
<td>Hadamard-Rybczinski</td>
<td>Re &lt; 1</td>
<td>Numerical</td>
<td>Water vapor-LiBr</td>
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<td></td>
<td>(1911)</td>
<td></td>
<td></td>
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<td>Morioka et al. (1992)</td>
<td>Hamielec, Johnson</td>
<td>Re ≤ 80</td>
<td>Numerical</td>
<td>Water vapor-LiBr</td>
</tr>
<tr>
<td></td>
<td>(1962)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Advantages of spray absorbers:
1. higher contact surfaces per unit volume and higher rates of mass transfer in spray absorbers in comparison with conventional falling film absorbers
2. intensification of the HMT process and miniaturization of equipment

Fig. 4 Schematic view of a spray absorber
fundamentals

Fig. 5 Terminal velocity and aspect ratio of water drops falling in air at 20 °C and 1 bar
fundamentals

Fig. 6 Streamlines and vorticity contours inside a water drop falling in air at Re = 100
fundamentals

Fig. 7 Velocity of circulations inside water droplets falling in air with terminal velocity

drops oscillate
Fundamentals

Fig. 8 Shape of water drops falling in air
state of the art  Nakoryakov (1977)


Stagnant droplet. Thin concentration and temperature boundary layers approximation

Equations governing mass and heat transport:

\[
\frac{\partial x}{\partial t} = D \left( \frac{\partial^2 x}{\partial r^2} + \frac{2}{r} \frac{\partial x}{\partial r} \right) \tag{1}
\]

\[
\frac{\partial T}{\partial t} = a \left( \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) \tag{2}
\]

with initial and boundary conditions

\[ x=x_0, \ T=T_0 \text{ at } t = 0 \text{ and in the bulk of a droplet } \tag{3} \]
Conditions at the droplet surface

\[ x(t, R) = dT(t, R) + b \quad \lambda \frac{dT}{dr} \bigg|_{r=R} = \rho LD \frac{dx}{dr} \bigg|_{r=R} \quad (4) \]

Analytical solution:

\[ \text{Sh} = \frac{q_c R}{\rho D (dT_0 + b - x_0)} = \frac{Lu}{\sqrt{\pi Fo}} \left( \frac{1}{\sqrt{Lu} - \sqrt{\pi Fo}} - \frac{K}{1 - \sqrt{\pi Fo}} \right) \quad (5) \]

where \( Fo = Dt / R^2 \), \( K = \frac{d \cdot L}{c_p} \), \( Le = D / a \), \( dT_0 + b - x_0 \)

\[ x_0' = dT_0 + b - \text{equilibrium concentration, corresponding to initial temperature} \]
\[ T_0' = (x_0 - b) / d - \text{equilibrium temperature, corresponding to initial concentration} \]

Effect of heat release during absorption on the rate of mass transfer:

L → increase of \( T_s \) → decrease of \( x_s \) → reduces a driving force of mass transfer and mass flux during absorption
2. Lu et al. (1998)

Equations governing mass and heat transport:

\[
\frac{\partial x}{\partial t} + v_r \frac{\partial x}{\partial r} + \frac{v_\theta}{r} \cdot \frac{\partial x}{\partial \theta} = D \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial x}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial x}{\partial \theta} \right) \right\} \tag{6}
\]

\[
\frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} + \frac{v_\theta}{r} \frac{\partial T}{\partial \theta} = a \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial T}{\partial \theta} \right) \right\} \tag{7}
\]

Hadamard-Rybczinski (1911) solution:

\[
\psi_i = \frac{U r^2 \sin^2 \theta}{4(1 + k)} \left(1 - \frac{r^2}{R^2}\right) \tag{8}
\]

where \(k\) - viscosity ratio in dispersed and continuous phases, \(i = 1,2\)
state of the art  Lu et al. (1998)

Boundary conditions:

Linear absorbate approximation, all heat of absorption is dissipated in a droplet. Symmetry of temperature and concentration fields:

at $\theta = 0$ and $\theta = \pi$  \[ \frac{\partial T}{\partial \theta} = \frac{\partial x}{\partial \theta} = 0 \]  

(9)

Condition of zero heat and mass fluxes in a center of a droplet:

at $r = 0$  \[ \frac{\partial T}{\partial r} = \frac{\partial x}{\partial r} = 0 \]  

(10)
state of the art  Lu et al. (1998)

Fig. 9  Concentration profile development with time inside a droplet.
System LiBr - water vapor
state of the art  Lu et al. (1998)

Fig. 10  Concentration profile along the $\theta$ for $\text{Pe} = 0$ and $\text{Pe} = 5000$

$\tau = 0.03$

$W$

$A$: $\text{Pe}=0$; $B$: $\text{Pe}=100$; $C$: $\text{Pe}=5000$

$r = 0.2$
$r = 0.8$
state of the art  Lu et al. (1998)

Fig. 11  Influence of thermal effect and internal circulation on absorption rate
Hamielec and Johnson (1962) (Re ≤ 80)

\[ \psi_i = (A_1r^2 + A_2r^4)\sin^2 \theta + (A_3r^2 + A_4r^4)\sin^2 \theta \cdot \cos \theta \]  \hspace{1cm} (11)

where \( A_i \) are functions of viscosity ratio in dispersed and continuous phases.

Boundary conditions:
Linear absorbate approximation, all heat of absorption is dissipated in a droplet.
Symmetry of temperature and concentration fields
Morioka (1992) do not use condition of zero mass flux in a center of a droplet.

Fig. 12 Steady-state velocity vectors inside a droplet for Re = 1 and Re = 10
state of the art  Morioka et al. (1992)

**Fig. 13** Profiles of temperature and concentration, isotherms and lines of constant concentration. $\text{Re} = 1$ and $t/\text{Re} = 300$
**Fig. 14** Profiles of temperature and concentration, isotherms and lines of constant concentration. $Re = 10$ and $t/Re = 100$
state of the art  Morioka et al. (1992)

Fig. 15 Profiles of temperature and concentration, isotherms and lines of constant concentration. Re = 10 and t/Re = 200
state of the art  Morioka et al. (1992)

Fig. 16 Profiles of temperature and concentration, isotherms and lines of constant concentration. Re = 10 and t/Re = 300
state of the art  Morioka et al. (1992)

**Fig. 17** Local absorption rate of absorbate
Fig. 18 Dependence of average temperature of a droplet vs. time

state of the art  Morioka et al. (1992)
Venegas et al. (2004)


\[ \psi_i = (B_1 r^2 + B_2 r^3 + B_3 r^4) \sin^2 \theta + (B_4 r^2 + B_5 r^3 + B_6 r^4) \sin^2 \theta \cdot \cos \theta \]  \hspace{1cm} (13)

where \( B_i \) are functions of viscosity ratio in dispersed and continuous phases. Calculations for 60 \( \mu \)m droplets falling with terminal velocity 0.17 m/s.

\[ \begin{align*}
\begin{array}{c}
\Psi_i = (B_1 r^2 + B_2 r^3 + B_3 r^4) \sin^2 \theta + (B_4 r^2 + B_5 r^3 + B_6 r^4) \sin^2 \theta \cdot \cos \theta
\end{array}
\end{align*} \]

Fig. 19 Evolution of ammonia concentration inside a droplet. Low-pressure absorber, subcooling 14 °C and 19 °C.
Fig. 20  Dependence of evaporating droplet radius vs time for different initial ammonia concentrations inside a droplet. $T_{g0} = 293K$, RH = 88%
state of the art Moser and Tsotsas (2000)

Fig. 21 Normalized droplet temperature vs time for different initial ammonia concentrations inside a droplet
Tangential and radial fluid velocity component at gas-liquid interface (Pruppacher and Klett (1997)):

\[ v_\theta = -kU_\infty \sin \theta \quad v_y = \frac{2kU_\infty}{R} \cos \theta \]  

(1a)

where coefficient \( k \) varies from 0.009 up to 0.044 for different Reynolds numbers.
modelling

Equation of nonstationary convective diffusion:

\[
\frac{\partial x_A}{\partial t} + \frac{U_\infty k}{R} \left\{ -\sin \theta \frac{\partial x_A}{\partial \theta} + 2y \cos \theta \frac{\partial x_A}{\partial y} \right\} = D \frac{\partial^2 x_A}{\partial y^2} \tag{2a}
\]

Differential energy balance equation

\[
\frac{\partial T}{\partial t} + \frac{U_\infty k}{R} \left\{ -\sin \theta \frac{\partial T}{\partial y} + 2y \cos \theta \frac{\partial T}{\partial \theta} \right\} = a \frac{\partial^2 T}{\partial y^2} \tag{3a}
\]

boundary conditions

\[
x_B = x_B(t), \ T = T_B(t) \text{ at } y \to \infty \tag{4a}
\]
Solution is found by combining the similarity transformation method with Duhamel's Theorem

\[ \eta_c = \frac{y}{\delta_c(t, \theta)} = \frac{Y}{\Delta_c}, \quad \eta_T = \frac{y}{\delta_T(t, \theta)} = \frac{Y}{\Delta_T} \quad (5a) \]

\[ \Delta_c = \Delta_c(Pe_D, \theta, \tau_c) \quad (6a) \]

\[ x(y, \theta, t) = \frac{\partial}{\partial t} \int_0^t \left\{ \frac{d \cdot T_B(\lambda) + b - x_B(\lambda)}{1 - \sqrt{Le} / K} \text{erfc} \left[ \frac{y}{\delta_c(\theta, t - \lambda)} \right] + x_B(\lambda) \right\} d\lambda \quad (7a) \]

\[ T(y, \theta, t) = \frac{\partial}{\partial t} \int_0^t \left\{ \frac{(x_B(\lambda) - b) / d}{1 - K / \sqrt{Le}} \text{erfc} \left[ \frac{y}{\delta_T(\theta, t - \lambda)} \right] + T_B(\lambda) \right\} d\lambda \quad (8a) \]
modelling

\[- Vp_L \frac{dx_B}{dt} = 2\pi R^2 \rho_L D \int_0^{\theta_{sep}} \frac{\partial x}{\partial y}\bigg|_{y=0} \sin \theta d\theta \]

\[- Vc_p \rho_L \frac{dT_B}{dt} = 2\pi R^2 \lambda \int_0^{\theta_{sep}} \frac{\partial T}{\partial y}\bigg|_{y=0} \sin \theta d\theta \]

concentration and temperature in the bulk of liquid droplet:

\[X_B(T) = \frac{3}{\sqrt{\pi} \text{Pe}_D (1 - \sqrt{\text{Le}/K})} \int_0^T \left[ X_B(\lambda) - K/(1 - K) \right] \int_0^{\theta_{sep}} \frac{\sin \theta d\theta d\lambda}{\Delta_c(\theta, T - \lambda)} \]

\[T_B(T) = \frac{3(1 - K)}{\sqrt{\pi} \text{Pe}_D K (1 - \sqrt{\text{Le}/K})} \int_0^T \left[ T_B(\lambda) - 1/(1 - K) \right] \int_0^{\theta_{sep}} \frac{\sin \theta d\theta d\lambda}{\Delta_T(\theta, T - \lambda)} \]
When $t \to \infty$, values of concentration and temperature in a liquid droplet are determined by the following formulas:

\[
c(t \to \infty) = \frac{\frac{d \cdot T_0 + b - c_0 K^{-1}}{1 - K^{-1}}}{1 - K^{-1}}
\]  

(13a)

\[
T(t \to \infty) = \frac{(c_0 - b) / d - T_0 K}{(1 - K)}
\]  

(14a)

\[
d \cdot T(t \to \infty) + b = c(t \to \infty)
\]  

(15a)
Fig. 1a  Dependence of concentration in the bulk of a droplet from time
Fig. 2a  Dependence of droplet temperature from time

$T_B(T) = \left[ T_B(t) - T_0 \right] / \left[ (x_0 - b) / d - T_0 \right]$
modelling

Fig. 3a Absorption of water vapor by water solution of LiBr
Fig. 4a Absorption of water vapor by water solution of LiBr
modelling

**Effect of thermal diffusion** on the rates of heat and mass transfer during nonisothermal absorption

A differential mass balance for the absorbing component in spherical coordinates reads

\[
\frac{\partial x_A}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 N_{Ar} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( N_{A\theta} \sin \theta \right) = 0
\]  

(16a)

Expression for mass flux of a component \( N_{Ar} \) and \( N_{A\theta} \) in Eq. (16a) reads:

\[
N_{Ar} = -D\rho \frac{\partial x_A}{\partial r} - D'\rho \cdot x_A \frac{\partial T}{\partial r} + x_A \rho v_r,
\]  

(17a)

\[
N_{A\theta} = -D\rho \frac{1}{r} \frac{\partial x_A}{\partial \theta} - \frac{x_A D' \rho}{r} \frac{\partial T}{\partial \theta} + x_A \rho v_\theta
\]  

(18a)

D'- thermal diffusion coefficient of solution
modelling

\[
\frac{\partial x}{\partial t} + \frac{U \cdot k}{R} \left\{ - \sin \theta \frac{\partial x}{\partial \theta} + 2y \cos \theta \frac{\partial x}{\partial y} \right\} = D \left\{ \frac{\partial^2 x}{\partial y^2} + \sigma \frac{\partial x}{\partial y} \frac{\partial T}{\partial y} \right\}, \quad (19a)
\]

\[
\frac{\partial T}{\partial t} + \frac{U \cdot k}{R} \left\{ - \sin \theta \frac{\partial T}{\partial y} + 2y \cos \theta \frac{\partial T}{\partial \theta} \right\} = a \frac{\partial^2 T}{\partial y^2}. \quad (20a)
\]

where \( \sigma = D' / D \) - Soret coefficient.

\[
\frac{Q_c}{Q_{c0}} = \left[ 1 + \frac{2\sigma(T_0' - T_0) \text{Le}^{1/2}}{1 - \sqrt{\pi} \cdot K / \sqrt{\text{Le}}} \right]^{-1} \quad (21a)
\]

ignoring the effect of thermal diffusion results in overestimating the rate of mass transfer during nonisothermal absorption.
Unsolved problems

1. Finite dilution of absorbate in absorbent.

A differential mass balance for the absorbing component in spherical coordinates reads

\[ \frac{\partial x_A}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 N_{A_r}) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (N_{A_\theta} \sin \theta) = 0 \quad (1b) \]

Expression for mass flux of a component \( N_{A_r} \) in Eq. (1b) reads:

\[ N_{A_r} = -D \rho \frac{\partial x_A}{\partial r} + x_A \left( N_{A_r} + N_{B_r} \right) \quad (2b) \]

Finally expression for \( N_{A_r} \) can be written as follows:

\[ N_{A_r} = -D \rho \frac{\partial x_A}{\partial r} - \frac{D \rho x_A}{1 - x_{A_s}} \frac{\partial x_A}{\partial r} \bigg|_{r=R} + x_A \rho v_r \quad (3b) \]
unsolved problems

2. **Droplet motion with acceleration.**

Equation of motion for a spherical droplet of mass $m_d$:

$$m_d \frac{dv}{dt} = m_d g \left( 1 - \frac{\rho_a}{\rho_w} \right) - 6 \pi \eta_a \left( \frac{C_D N_{Re}}{24} \right) v$$  \hspace{1cm} (4b)

For very small droplet falling in Stokes regime

$$v(t) = U_\infty \left[ 1 - \exp \left( - \frac{6 \pi \eta_a t}{m_d} \right) \right]$$  \hspace{1cm} (5b)

Table 3  Distance the droplet must fall to reach 99% of its terminal velocity

<table>
<thead>
<tr>
<th>Droplet radius $[\mu m]$</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_{99%}[m]$</td>
<td>0.18</td>
<td>0.90</td>
<td>2.1</td>
<td>3.6</td>
<td>5.4</td>
<td>12.6</td>
<td>19.8</td>
</tr>
</tbody>
</table>
unsolved problems

3. Non sphericity of droplets
4. Inert admixtures
5. Droplet growth due to gas absorption

“The droplet erodes the stone not by its power, but by constantly falling”