Lecture 10: Nucleation or new particle formation in the atmosphere

1

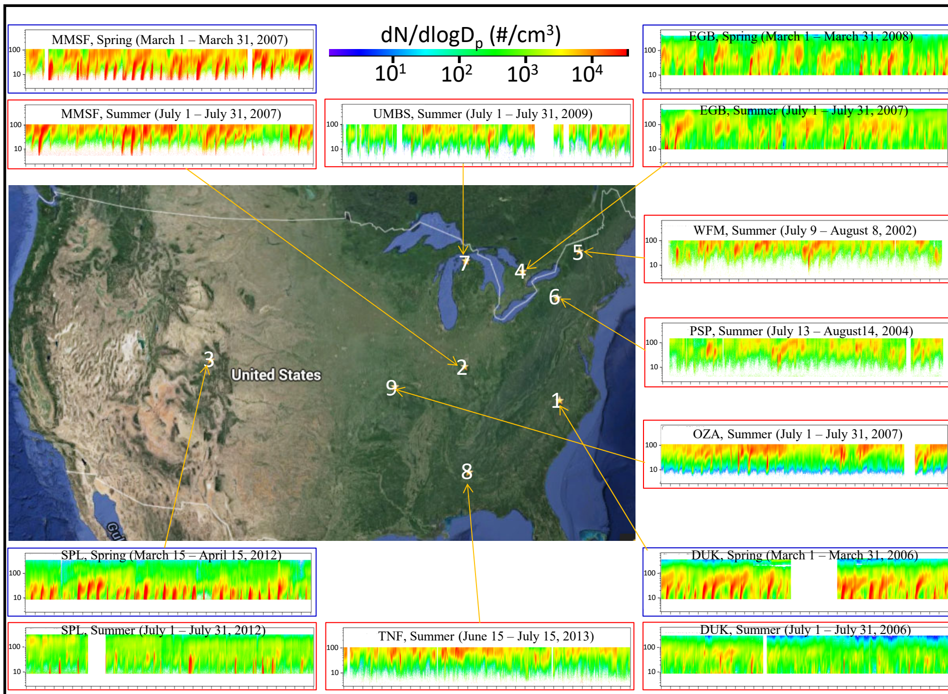


Figure 1

2

communications
earth & environment

ARTICLE

https://doi.org/10.1038/s43247-022-00653-w OPEN

Nucleation of jet engine oil vapours is a large source of aviation-related ultrafine particles

Florian Ungeheuer[1], Lucía Caudillo[1], Florian Ditas[2], Mario Simon[1], Dominik van Pinxteren[3], Doğuşhan Kılıç[4,5], Diana Rose[2], Stefan Jacobi[2], Andreas Kürten[1], Joachim Curtius[1] & Alexander L. Vogel[1]

Large airports are a major source of ultrafine particles, which spread across densely populated residential areas, affecting air quality and human health. Jet engine lubrication oils are detectable in aviation-related ultrafine particles, however, their role in particle formation and growth remains unclear. Here we show the volatility and new-particle-formation ability of a common synthetic jet oil, and the quantified oil fraction in ambient ultrafine particles downwind of Frankfurt International Airport, Germany. We find that the oil mass fraction is largest in the smallest particles (10-18 nm) with 21% on average. Combining ambient particle-phase concentration and volatility of the jet oil compounds, we determine a lower-limit saturation ratio larger than 1×10^5 for ultra-low volatility organic compounds. This indicates that the oil is an efficient nucleation agent. Our results demonstrate that jet oil nucleation is an important mechanism that can explain the abundant observations of high number concentrations of non-refractory ultrafine particles near airports.

3

Properties of contrails from aircraft with modern engines and alternative fuels

Dissertation zur Erlangung des Grades
„Doktor der Naturwissenschaften"

am Fachbereich Physik, Mathematik und Informatik
der Johannes Gutenberg-Universität
in Mainz

Raphael Satoru Märkl
geb. in München
Mainz, den 28. November 2024

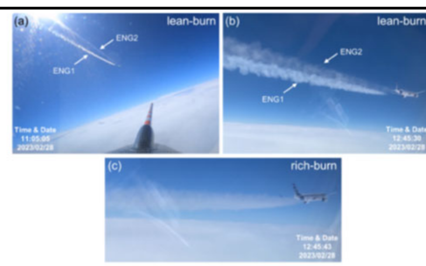


Figure 6.17: *Photographs of contrails produced by the A321 source aircraft during flight 03 on February 28, 2023 of VOLCAN2. (a) Falcon cockpit mounted GoPro camera footage of contrails with visually different appearance from engine 1 (ENG1) and engine 2 (ENG2) while operating in the lean-burn combustion mode. (b-c) Photograph taken from the ice instrument operator seat onboard the Falcon with (b) differences visually apparent between the two engines while operating in the lean-burn combustion mode and (c) differences between engines not discernible due to the perspective while operating in the rich-burn combustion mode. The time and date of recording is indicated in UTC in every panel. Image in panel (a) courtesy of Monika Scheibe.*

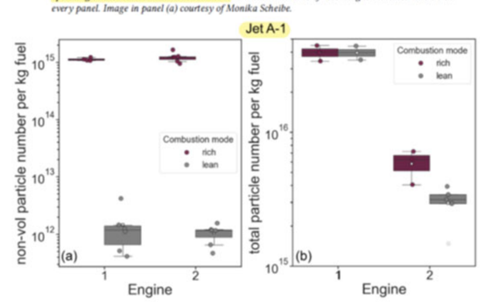


Figure 6.16: *VOLCAN2 comparison of engines during near-field measurements of (a) nvPM EIs and (b) total particle EIs. Courtesy of and with permission from Rebecca Dischl and Daniel Sauer. Note that the lowest lean-burn total particle value for engine 2 is likely affected by large uncertainties due to coincidence effects and is therefore faded.*

4

Nucleation

1. Homogeneous–homomolecular: self-nucleation of a single species. No foreign nuclei or surfaces involved.
2. Homogeneous–heteromolecular: self-nucleation of two or more species. No foreign nuclei or surfaces involved.
3. Heterogeneous–homomolecular: nucleation of a single species on a foreign substance.
4. Heterogeneous–heteromolecular: nucleation of two or more species on a foreign substance.

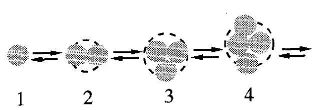
Classical Homogeneous Nucleation

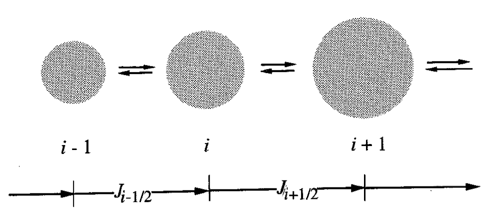
Kinetic approach

Constrained equilibrium approach (or classical approach)

5

Kinetic approach





$$\frac{dN_i}{dt} = \beta_{i-1}N_{i-1}(t) - \gamma_i N_i(t) - \beta_i N_i(t) + \gamma_{i+1}N_{i+1}(t)$$

Net Flux $J_{i+1/2} = \beta_i N_i - \gamma_{i+1} N_{i+1}$

Steady State $J_{i+1/2} = J, \quad$ all i

Let us define a quantity f_i by

$$\beta_i f_i = \gamma_{i+1} f_{i+1}$$

setting $f_1 = 1$

$$f_i = \frac{\beta_1}{\gamma_2}\frac{\beta_2}{\gamma_3}\cdots\frac{\beta_{i-1}}{\gamma_i} = \prod_{j=1}^{i-1}\frac{\beta_j}{\gamma_{j+1}}$$

$$\frac{J}{\beta_i f_i} = \frac{N_i}{f_i} - \frac{N_{i+1}}{f_{i+1}}$$

$$J\sum_{i=1}^{i_{max}}\frac{1}{\beta_i f_i} = N_1 - \frac{N_{i_{max}}}{f_{i_{max}}}$$

$$J = N_1\left(\sum_{i=1}^{i_{max}}\frac{1}{\beta_i f_i}\right)^{-1}$$

$$J = N_1\left(\sum_{i=1}^{\infty}\frac{1}{\beta_i f_i}\right)^{-1}$$

6

The Forward Rate Constant β_i

Collision rate (# cm^{-3} s^{-1}) between a monomer and an i-mer

$$Z_{AB} = \left(\frac{8\pi kT}{m_{AB}}\right)^{1/2} \sigma_{AB}^2 N_A N_B$$

$$Z_{1i} = (8\pi kT)^{1/2} \left(\frac{1}{m_1} + \frac{1}{m_i}\right)^{1/2} (r_1 + r_i)^2 N_1 N_i$$

$$m_i = i m_1 \qquad v_i = i v_1 \qquad a_1 = 4\pi \left(\frac{3v_1}{4\pi}\right)^{2/3}$$

$$Z_{1i} = \left(\frac{kT}{2\pi m_1}\right)^{1/2} a_1 \left(1 + \frac{1}{i}\right)^{1/2} (1 + i^{1/3})^2 N_1 N_i \qquad \text{(\# cm}^{-3}\text{ s}^{-1}\text{)}$$

$$\beta_i = \left(\frac{kT}{2\pi m_1}\right)^{1/2} \left(1 + \frac{1}{i}\right)^{1/2} (1 + i^{1/3})^2 a_1 N_1 \qquad \text{(\# s}^{-1}\text{)}$$

7

The Reverse Rate Constant γ_i

$$\gamma_i = \gamma_i^s$$

Kelvin Equation:

$$p_1 = p_1^s \exp\left(\frac{2\sigma v_1}{kT r_i}\right)$$

i-mer in equilibrium with surrounding vapor

$$\gamma_i = \beta_i$$

$$= \frac{p_1}{(2\pi m_1 kT)^{1/2}} \left(1 + \frac{1}{i}\right)^{1/2} (1 + i^{1/3})^2 a_i$$

$$= \frac{p_1^s}{(2\pi m_1 kT)^{1/2}} \left(1 + \frac{1}{i}\right)^{1/2} (1 + i^{1/3})^2 a_i \exp\left(\frac{2\sigma v_1}{kT r_i}\right)$$

8

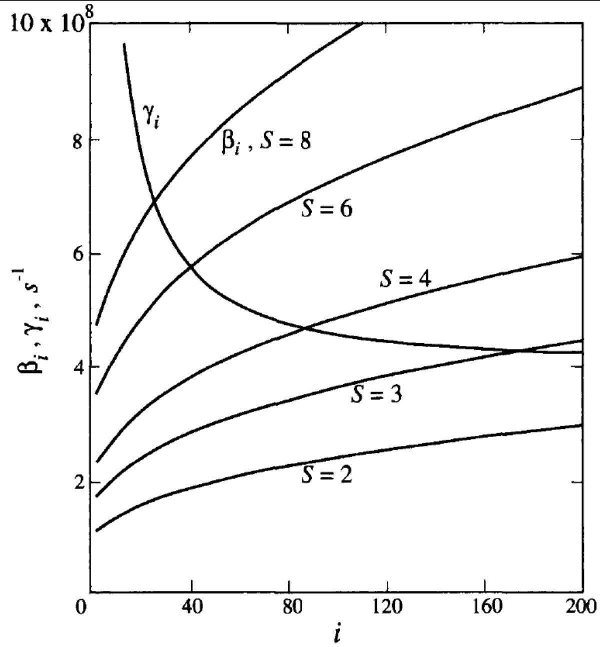


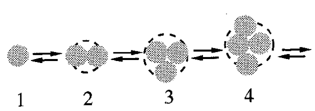
FIGURE 11.3 β_i and γ_i as a function of i for various values of the saturation ratio S. The two quantities are equal at the critical i values.

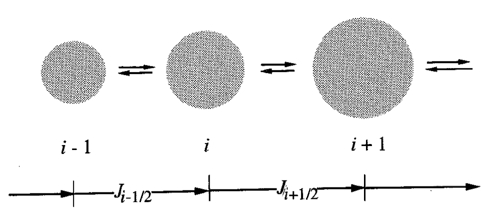
9

Derivation of the Nucleation Rate

Net Flux $J_{i+1/2} = \beta_i N_i - \gamma_{i+1} N_{i+1}$

Steady State $J_{i+1/2} = J, \quad \text{all } i$





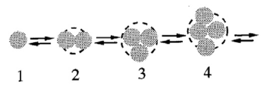
$$J = N_1 \left(\sum_{i=1}^{\infty} \frac{1}{\beta_i f_i} \right)^{-1}$$

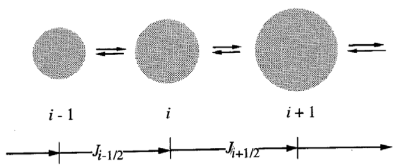
$$f_i = \prod_{j=1}^{i-1} \frac{\beta_j}{\gamma_{j+1}}$$

$$\frac{dN_i}{dt} = \beta_{i-1} N_{i-1}(t) - \gamma_i N_i(t) - \beta_i N_i(t) + \gamma_{i+1} N_{i+1}(t)$$

10

Derivation of the Nucleation Rate





$$J = N_1 \left(\sum_{i=1}^{\infty} \frac{1}{\beta_i f_i} \right)^{-1}$$

$$f_i = \prod_{j=1}^{i-1} \frac{\beta_j}{\gamma_{j+1}}$$

$$f_i = S^{i-1} \prod_{j=1}^{i-1} \frac{\beta_j^s}{\gamma_{j+1}^s}$$

β_1^s is forward rate at saturation

$$A_1 + A_1 \rightleftharpoons A_2$$
$$A_1 + A_2 \rightleftharpoons A_3$$

$$\left(\frac{\beta_1^s}{\gamma_2^s}\right)\left(\frac{\beta_2^s}{\gamma_3^s}\right)$$

equilibrium constant for

$$3A_1 \rightleftharpoons A_3$$

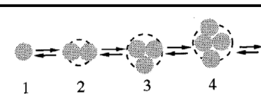
$$iA_1 \rightleftharpoons A_i$$

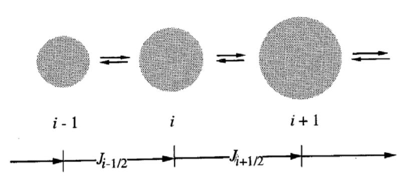
$$f_i = S^{i-1} \exp(-\Delta G_i / kT)$$

ΔG_i **is the Gibbs free energy change for formation of a cluster of size *i* at saturation (*S*=1)**

11

How to calculate ΔG_i $\longrightarrow$ **Major assumption of classical nucleation theory**





Capillarity Approximation:
Clusters of a small number of molecules exhibit the same surface tension as the bulk liquid

$$\Delta G_i = \sigma a_i$$
$$a_i = (36\pi)^{1/3}\, v_1^{2/3}\, i^{2/3}$$

a_i is the surface area of a cluster of size i.

dimensionless surface tension,

$$\theta = (36\pi)^{1/3}\, v_1^{2/3}\, \sigma / kT$$

$$\Delta G_i = \theta k T i^{2/3}$$

12

$$J = N_1 \left(\sum_{i=1}^{\infty} \frac{1}{\beta_i^s S^i \exp(-\theta i^{2/3})} \right)^{-1}$$

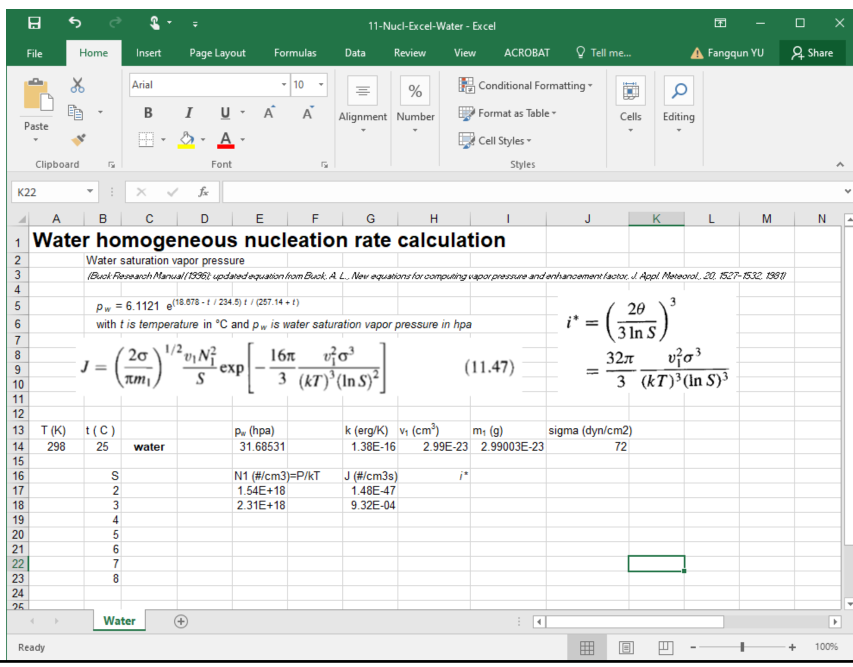
(see textbook 11.1.3 for mathematical derivation)

$$J = \left(\frac{2\sigma}{\pi m_1} \right)^{1/2} \frac{v_1 N_1^2}{S} \exp\left[-\frac{16\pi}{3} \frac{v_1^2 \sigma^3}{(kT)^3 (\ln S)^2} \right] \tag{11.47}$$

$$i^* = \left(\frac{2\theta}{3 \ln S} \right)^3 = \frac{32\pi}{3} \frac{v_1^2 \sigma^3}{(kT)^3 (\ln S)^3} \tag{11.35}$$

13

Homogeneous nucleation rate calculation with excel sheet



14

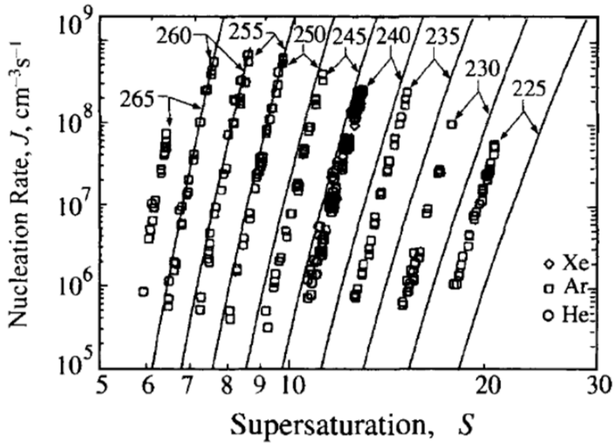


FIGURE 11.7 Nucleation rates measured in supersaturated *n*-butanol vapor as a function of saturation ratio for various temperatures ranging from 225 to 265 K (Viisanen and Strey 1994). Different symbols indicate different carrier gases at 240 K. Predictions of classical nucleation theory are shown by the lines. (Reprinted with permission from Viisanen, Y., and Strey, R., V. M. Homogeneous Nucleation Rates for *n*-Butanol, *J. Chem. Phys.* **101**. Copyright 1994 American Institute of Physics.)

15

TABLE 11.1 Critical Number and Radius for Water Droplets

	$T = 273$ K[a]		$T = 298$ K[b]	
S	r^*, Å	i^*	r^*, Å	i^*
1	∞	∞	∞	∞
2	17.3	726	15.1	482
3	10.9	182	9.5	121
4	8.7	87	7.6	60
5	7.5	58	6.5	39

[a] $\sigma = 75.6$ dyn cm^{-1}; $v_1 = 2.99 \times 10^{-23}$ cm^3 molecule^{-1}.
[b] $\sigma = 72$ dyn cm^{-1}; $v_1 = 2.99 \times 10^{-23}$ cm^3 molecule^{-1}.

16

TABLE 11.3 Critical Number and Radius for Five Organic Species at 298 K

Species		S = 2	3	4	5
Acetone	i^*	265	67	33	21
	r^* (Å)	19.8	12.5	9.9	8.5
Benzene	i^*	706	177	88	56
	r^* (Å)	29.2	18.4	14.6	12.6
Carbon tetrachloride	i^*	678	170	85	54
	r^* (Å)	29.6	18.7	14.8	12.7
Ethanol	i^*	147	37	18	12
	r^* (Å)	15.1	9.5	7.5	6.5
Styrene	i^*	1646	413	206	132
	r^* (Å)	42.2	26.6	21.1	18.2

17

Constrained equilibrium approach (or classical approach)

Free Energy of *i*-mer Formation

$$\Delta G_i = (\mu_l - \mu_v)\, i + 4\pi\sigma r^2$$

$$\mu_v - \mu_l = kT \ln S$$

$$\Delta G_i = 4\pi\sigma r^2 - \frac{4\pi}{3}\frac{kT \ln S}{v_1} r^3$$

$$r^* = \frac{2\sigma v_1}{kT \ln S}$$

$$\Delta G^* = \frac{4\pi}{3}\sigma r^{*2} = \frac{16\pi}{3}\frac{v_1^2\sigma^3}{(kT \ln S)^2}$$

18

Constrained Equilibrium Cluster Distribution

obeys the usual Boltzmann distribution

$$N_i^e = N_1 \exp(-\Delta G_i / kT)$$

$$\beta_i N_i^e = \gamma_{i+1} N_{i+1}^e$$

$$J = \beta_i N_i - \gamma_{i+1} N_{i+1}$$

$$= \beta_i N_i^e \left[\frac{N_i}{N_i^e} - \frac{N_{i+1}}{N_{i+1}^e} \right]$$

$$\sum_{j=1}^{i_{\max}-1} \frac{J}{\beta_j N_j^e} = \frac{N_1}{N_1^e} - \frac{N_{i_{\max}}}{N_{i_{\max}}^e}$$

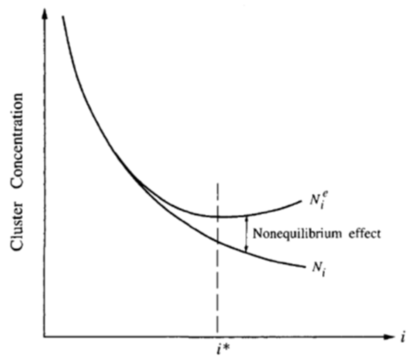


FIGURE 11.2 Constrained equilibrium and steady-state cluster distributions, N_i^e and N_i, respectively.

$$J = \left(\sum_{j=1}^{i_{\max}-1} \frac{1}{\beta_j N_j^e} \right)^{-1}$$

Thus the unknown steady-state cluster distribution N_i, disappears, allowing the nucleation rate to be expressed in terms of the constrained equilibrium distribution N_i^e

THE JOURNAL OF CHEMICAL PHYSICS **122**, 104511 (2005)

Simple correction to the classical theory of homogeneous nucleation

Alexey B. Nadykto[a)] and Fangqun Yu
Atmospheric Sciences Research Center, State University of New York at Albany, 251 Fuller Road, New York, New York 12203

(Received 2 July 2004; accepted 30 December 2004; published online 15 March 2005)

It is well known that the classical nucleation theory (CNT),[2] which is the most common tool to analyze the nucleation phenomena, fails in predicting the temperature dependence and absolute values of the critical supersaturations of a number of substances including water, alcohols, and high alkanes.[5–13,17] A large number of theories[7–9,14,15,18–23] to test against the experimental data have been reported in the literature in the last two decades, yet a major source of the discrepancies is not clearly identified.

$$J = K \exp\left(\frac{-\Delta G_i}{kT} \right)$$

$$\Delta G_i^{\mathrm{CNT}} = \Delta \mu i + \gamma A(i)$$

The Becker–Doring theory[2] expresses the nucleation rates as

$$J^{\mathrm{BD}} = \upsilon N_1^2 \left[\frac{2\gamma}{\pi m} \right]^{0.5} \exp\left[\frac{-\Delta G_i^{\mathrm{CNT}}}{kT} \right]$$
$$= K^{\mathrm{BD}} \exp\left[\frac{-\Delta G_i^{\mathrm{CNT}}}{kT} \right], \qquad (3)$$

Nucleation rates in the kinetically consistent version of CNT are given by the following equation:

$$J^{\mathrm{CNT}} = \upsilon N_1^2 \left[\frac{2\gamma}{\pi m} \right]^{0.5} \frac{1}{S} \exp\left[\frac{-\Delta G_i^{\mathrm{CNT}}}{kT} \right] = \frac{1}{S} J^{\mathrm{BD}}. \qquad (4)$$

In the self-consistency corrected model SCC the nucleation rate is

$$J^{\mathrm{SCC}} = \frac{1}{S} \exp\left(\frac{\gamma A(1)}{kT} \right) J^{\mathrm{BD}} = \exp\left(\frac{\gamma A(1)}{kT} \right) J^{\mathrm{CNT}}. \qquad (5)$$

Finally, the present study (CCNT) express the nucleation rate as

$$J^{\mathrm{CCNT}} = \frac{1}{S^2} \exp\left(\frac{\gamma A(1)}{kT} \right) J^{\mathrm{CNT}} = \frac{1}{S} \exp\left(\frac{\gamma A(1)}{kT} \right) J^{\mathrm{KCNT}}$$
$$= \frac{1}{S} J^{\mathrm{SCC}}. \qquad (11)$$