

HISTORICAL PERSPECTIVE ON HETEROGENEOUS GAS-PARTICLE INTERACTION

Stephen E. Schwartz



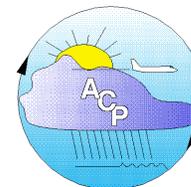
<http://www.ecd.bnl.gov/steve/schwartz.html>

Mass Accommodation Workshop

Billerica MA

February 25 - 28, 2002

Acknowledgment: DOE Atmospheric Chemistry Program



OUTLINE

Interfacial mass flux

Detailed balance – The Hertz-Langmuir-Marcelin-Knudsen equation

Mass accommodation coefficient

State of knowledge of accommodation coefficients circa 1980

Water on water - a special case: latent heat

Volatile gases as solutes

Importance of mass accommodation coefficients in atmospheric science?

Coupling interfacial and diffusion fluxes

Mass transport and reaction in liquid-water clouds

Coupled mass transport and reaction

Criteria governing saturation of reacting gases

Low solubility gases

Conclusions and future directions

GAS KINETIC COLLISION RATE AT INTERFACE

$$J_{\text{coll}} = \frac{1}{4} \bar{v} c_g$$

J_{coll} = Collision rate, amount area⁻¹ time⁻¹

\bar{v} = Mean molecular speed, length time⁻¹; $\bar{v} = (8R_g T / \pi M)^{1/2}$

c_g = Concentration on gas side of interface, amount volume⁻¹

CONDENSATION FLUX AT INTERFACE

$$J_c = \frac{1}{4} \bar{v} \alpha_c c_g$$

α_c = Condensation coefficient, dimensionless

EVAPORATION FLUX AT INTERFACE

$$J_e = \frac{1}{4} \bar{v} \alpha_e c_g^*$$

α_e = Evaporation coefficient

c_g^* = Hypothetical equilibrium gas-phase concentration on condensed-phase side of interface

NET FLUX AT INTERFACE

$$J = J_c - J_e = \frac{1}{4} \bar{v} (\alpha_c c_g - \alpha_e c_g^*)$$

J = Net flux (gas phase to condensed phase)

DETAILED BALANCE ARGUMENT

At equilibrium $c_g^* = c_g$ and $J = 0$, whence $\alpha_c = \alpha_e = \alpha_m$, where

α_m = Mass accommodation coefficient

Whence we obtain the

HERTZ-LANGMUIR-MARCELIN-KNUDSEN EQUATION FOR INTERFACIAL MASS TRANSPORT

$$J = \frac{1}{4} \bar{v} \alpha_m (c_g - c_g^*)$$

MASS ACCOMMODATION COEFFICIENT

CHIMIE PHYSIQUE. — *Échange de matière entre un liquide ou un solide et sa vapeur saturée.* Note de M. R. MARCELIN, présentée par M. Lippmann.

$$x = \frac{C}{N} = \frac{P}{4} \sqrt{\frac{8}{\pi MRT}}$$

Si d est la densité du liquide on a pour la hauteur évaporée pendant l'unité de temps

$$v = \frac{XM}{d} = \frac{P}{4d} \sqrt{\frac{8M}{\pi RT}} = 4,38 \cdot 10^{-3} \frac{P}{d} \sqrt{\frac{M}{T}}$$

III. *Échange de matière entre un liquide ou un solide et sa vapeur saturée.* — Si le liquide doit être touché par λ molécules gazeuses avant d'être capable d'en prendre une, la vitesse d'évaporation dans le vide sera seulement

$$v = \frac{v}{\lambda}$$

EQUIVALENT EXPRESSION IN TERMS OF PARTIAL PRESSURES

By ideal gas law, $c_g = p / R_g T$, whence

$$J = \frac{1}{4} \bar{v} \alpha_m \frac{(p - p^*)}{R_g T}$$

p = Partial pressure on gas side of interface

p^* = Hypothetical equilibrium gas-phase partial pressure on condensed-phase side of interface (fugacity)

EVAPORATION RATE OF WATER

What is the evaporation rate of water assuming $\alpha = 1$ and no other mass transport limitation?



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ANSWER

At 25 °C, 20 cm min⁻¹

The mean residence time of a water molecule on the surface is 70 ns.

The surface of water is a region of “heavy traffic.”

- *Adamson*

EXTENSION TO AQUEOUS CONCENTRATIONS OF DILUTE VOLATILE SOLUTES

According to Henry's law $p^* = c_{\text{aq}}/H$

p^* = Hypothetical equilibrium gas-phase partial pressure on solution side of interface (fugacity)

c_{aq} = Concentration of solute on solution side of interface

H = Henry's law coefficient, commonly in M atm^{-1} (SI: $\text{mol kg}^{-1} \text{Pa}^{-1}$)

Whence

$$J = \frac{1}{4} \bar{v} \alpha_m \frac{(p - c_{\text{aq}}/H)}{R_g T} = \frac{1}{4} \bar{v} \alpha_m (c_g - c_{\text{aq}}/HR_g T)$$

↑
Dimensionless
Henry's law coefficient

REMARKS ON MASS ACCOMMODATION COEFFICIENT

$$\alpha \equiv \frac{J_{\text{gross}}}{J_{\text{coll}}} \geq \frac{J_{\text{net}}}{J_{\text{coll}}}$$

The mass accommodation coefficient is a *phenomenological quantity*.

The definition *assumes no properties of the surface* — how sharply defined, how rapidly bonds are being made or broken or the like.

The definition *assumes no mechanism of accommodation*.

In particular, there is *no presumption one way or the other* of a potential energy well at the surface.

REASONS FOR WANTING TO KNOW α

Discovery-oriented science: Grand quest for knowledge about the universe — the physics and chemistry of matter.

Practical: Rate of sublimation of tungsten lamp filaments.

Practical: Influence on rates of gas-liquid reactions in chemical engineering.

Practical: Rate of uptake and reaction of reactive gases in the stratosphere.

Practical: The role of interfacial mass transport in limiting the rates of aqueous-phase reactions in clouds.

SYSTEMS OF INTEREST

Solids

Pure substances

Uptake of trace gases

Liquids

Pure substances

Water!!

Solutions - solvent

Solvent

Solute - ***dilute solutions of volatile gases***

Non-reacting

Reacting

Liquids with surface films

Solvent

Solute

CONDENSATION COEFFICIENT FOR WATER

Pruppacher and Klett, *Microphysics of Clouds and Precipitation* (1978)

(a)

Evaporation From A Quasi-Quiescent Water Surface

OBSERVER	TEMPERATURE (°C)	α_c
Alty (1931)	18 to 60	0.006 to 0.016
Alty and Nicole (1931)	18 to 60	0.01 to 0.02
Alty (1933)	-8 to +4	0.04
Alty and Mackay (1935)	15	0.036
Baramaev (1939)	-	0.033
Pruger (1940)	100	0.02
Yamamoto and Miura (1949)	-	0.023
Hammeke and Kappler (1953)	20	0.045
Delaney <i>et al.</i> (1964)	0 to 43	0.0415
Kiriukhin and Plaude (1965)	7	0.019
Chodes <i>et al.</i> (1974)	20	0.033
Rogers and Squires (1974)	-	0.065
Narusawa and Springer (1975)	18 to 27	0.038
Sinarwalla <i>et al.</i> (1975)	22.5 to 25.7	0.026

(b)

Evaporation From A Rapidly Renewing Water Surface

OBSERVER	TEMPERATURE (°C)	α_c
Hickman (1954)	0	0.42
Berman (1961)	-	1.0
Nabavian and Bromley (1963)	10 to 50	0.35 to 1.0
Jamieson (1965)	0 to 70	0.35
Mills and Seban (1967)	7 to 10	0.45 to 1.0
Tamir and Hasson (1971)	50	0.20
Narusawa and Springer (1975)	18 to 27	0.18

Experimental values for α_c are listed in two categories: (a) those derived from observations on a quiescent or quasi-quiescent water surface, and (b) those derived from a rapidly renewing surface. Since the latter conditions are not likely to be realized in clouds, we recommend the values for α_c given in (a) for cloud physics computations. These values range approximately from 0.01 to 0.07, with an average of $\overline{\alpha_c} \approx 0.035$.

CONDENSATION COEFFICIENT FOR WATER

Why so hard to measure?

1. *Diffusion limitation.* Water vapor has a high equilibrium vapor pressure.
2. *Latent heat.* Water condensation/evaporation releases/takes up a large amount of heat.
3. *Clausius-Clapeyron.* The large latent heat implies a strong temperature dependence of equilibrium vapor pressure.
4. *Le Chatelier.* The change in vapor pressure acts to resist the condensation or evaporation, thus masquerading as a surface resistance.

So every mass-transfer problem involving water condensation or evaporation is inherently also a heat-transfer problem!

STATE OF KNOWLEDGE - 1970

Gas-Liquid Reactions, Danckwerts (1970)

- “ The rate of absorption [of a gas by a liquid] can never be larger than the rate at which molecules of the gas impinge on the surface. . . .
- “ [Neglecting gas-phase diffusion] the rate of impingement is given by

$$J_m = \frac{1}{4} \bar{v} p / R_g T$$

- “ If a fraction $(1-\alpha)$ of the incident molecules is reflected without entering the liquid, then gas molecules enter the liquid at a rate αJ_m .
- “ The net rate of transference, J , is not equal to αJ_m because there is simultaneous passage of molecules in the opposite sense.
- “ If $\alpha = 1$, none of the impinging molecules is reflected and the ‘surface resistance’ has its lowest possible value.

cont'd . . .

STATE OF KNOWLEDGE - 1970 (*cont'd*)

Gas-Liquid Reactions, Danckwerts (1970)

- “ If the fraction of molecules reflected, $1 - \alpha$, were to approach unity it might be possible to detect the resulting surface-resistance by measuring Q [the amount of uptake; time integral of R] for short enough contact times.
- “ Although some experiments have suggested the existence of a measurable resistance, this was probably due to experimental error.
- “ Other experiments with laminar jets . . . and with CO_2 diffusing into quiescent water . . . have revealed no appreciable resistance.
- “ Surfactants give rise to a measurable resistance.

STATE OF KNOWLEDGE - MID 1970'S

Mass Transfer, Sherwood, Pigford & Wilke (1975)

- ““ Published values of α for liquids range from 1.0 to 0.02, or even lower, and values as low as 10^{-9} have been reported for solids.
- ““ . . . Values of α for water of 0.042 at 0°C and 0.027 at 43°C.
- ““ Experimental determination of α requires the measurement of the surface temperature. . . . This leads to errors, since the temperature gradient at the surface can be very steep.
- ““ . . . Question the validity of most of the values of α reported because of questionable surface temperatures.
- ““ . . . Using a laminar jet and an ingenious method to measure surface temperature obtained $\alpha \approx 1.0$ for water.
- ““ It is conceivable that most of the published data are in error, and that α is essentially unity for all simple liquids.
- ““ Not only is there no useful theory to employ in predicting α , there is also no easy way to experimentally measure it.

Heterogeneous Atmospheric Reactions: Sulfuric Acid Aerosols as Tropospheric Sinks

ALAN C. BALDWIN

DAVID M. GOLDEN

SCIENCE, VOL. 206, 2 NOVEMBER 1979

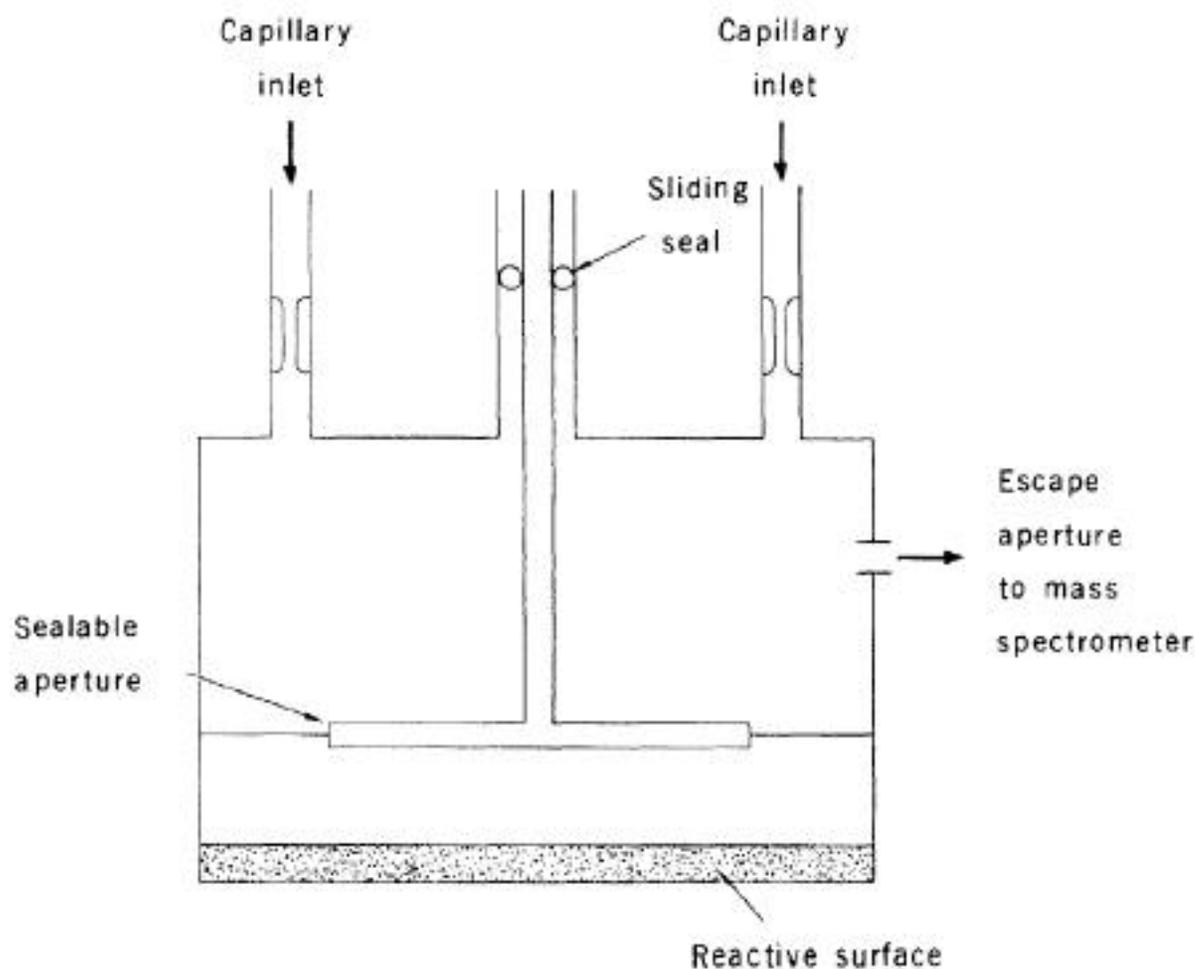


Fig. 1. The two-chamber Knudsen cell reactor.

Table 1. Collisional reaction probabilities on a H_2SO_4 surface at 300 K.

Species	Collisional reaction probability (γ)	Reference
H_2O_2	7.8×10^{-4}	
HNO_3	$\geq 2.4 \times 10^{-4}$	(7)
HO_2NO_2	2.7×10^{-5}	
ClONO_2	1.0×10^{-5}	
N_2O_5	$\geq 3.8 \times 10^{-5}$	(7)
H_2O	$\sim 2.0 \times 10^{-3}$	(8)
NH_3	$> 1.0 \times 10^{-3}$	(9)
O_3	$< 1.0 \times 10^{-6}$	
NO	$< 1.0 \times 10^{-6}$	
NO_2	$< 1.0 \times 10^{-6}$	
SO_2	$< 1.0 \times 10^{-6}$	
Alkenes	$< 1.0 \times 10^{-6}$	
Alkanes	$< 1.0 \times 10^{-6}$	
CF_4	$< 1.0 \times 10^{-6}$	
CCl_2F_2	$< 1.0 \times 10^{-6}$	

7. We monitored HNO_3 and N_2O_5 in terms of their mass peak at a mass-to-charge ratio (m/e) of 46; a product, presumably NO_2 , also having a mass peak at m/e 46, formed in the reaction; thus the measured γ values were upper limits.
8. Water reacted almost completely within the minimum number of collisions obtainable with our present apparatus.
9. In our system, NH_3 reacted completely; γ may be much larger than 10^{-3} .

Baldwin and Golden, *Science*, 1979

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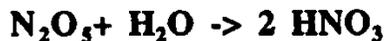
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Baldwin and Golden, *Science*, 1979

STEVE: WOULD YOU PLEASE SEND ME THE REFERENCE FOR THIS.

HA

Let me communicate to you, a member of the family so to speak, a topic that I have not presented in recent years.

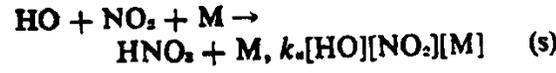


In the 1950s, I did a great deal of work with N_2O_5 , and I found that it did not react with water in the gas phase but that it reacted strongly with adsorbed water on glass or metal surfaces. During 1971-1972, I heard about the Junge layer of sulfuric acid haze in the stratosphere, and I felt sure N_2O_5 would react with it to produce nitric acid, but I did not know the surface area of the aerosol nor the collision efficiency. During and after 1972, I strongly advocated that CIAP (Climatic Impact Assessment Program, SST research program, 1972-1975) fund a laboratory study of N_2O_5 reactions on sulfuric acid surfaces. After my continued heavy persuasion, they reluctantly and late in the program had SRI make one test. SRI reported that the reaction coefficient per collision was less than 10^{-5} . Such a low value meant that the reaction would have no significant effect on stratospheric chemistry. At this point I gave up. There are quotes from my publications below, and I have saved relevant correspondence.

When Jack Calvert and others restudied this problem almost 15 years later, they found the reaction of N_2O_5 with sulfuric acid aerosols would occur at a rate 10,000 times faster than that reported by the hurried SRI study.

"Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysts from Supersonic Transport Exhaust." Harold Johnston, *Science*, 173, 517-522 (1971).

the H_2O emitted from the SST would be expected to have much less effect than the NO_x emitted (this statement is subject to further considerations about the rate of conversion of NO_x to N_2O_5 and to HNO_3 ; see below). The importance of H_2O in the stratosphere so far as O_3 is concerned is more in its role in removing NO_x (reactions r and s) than in its direct reaction with O_3 (reactions



"Catalytic Reduction of Stratospheric Ozone by Nitrogen Oxides, Harold S. Johnston, 263-380, from Advances in

WHY DID BALDWIN AND GOLDEN GET SUCH LOW VALUES OF γ ?

Collision reaction probabilities γ for uptake of O_3 , SO_2 , NO , NO_2 , alkenes, alkanes, CF_4 , CCl_2F_2 on concentrated sulfuric acid all less than 10^{-6} .

Because there was no sink in the condensed phase!

They were measuring (and reporting) an uptake coefficient γ , not a mass accommodation coefficient α .

REQUIREMENTS FOR MEASURING α

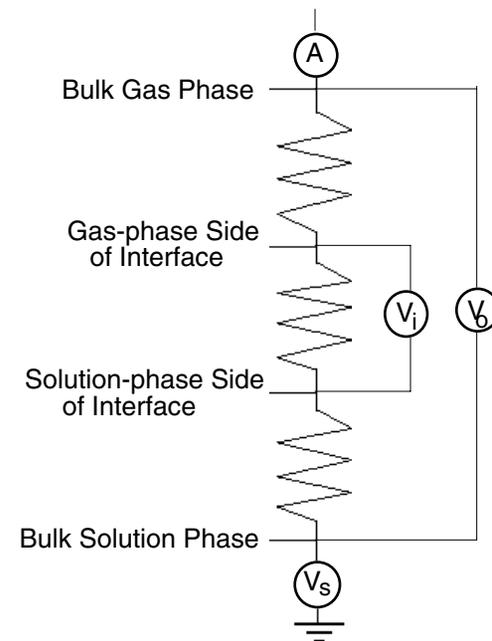
What you want: $\alpha = \frac{J_{\text{gross},i} / (\frac{1}{4}\bar{v})}{c_{\text{gas},i}}$ or $\frac{J_{\text{net},i} / (\frac{1}{4}\bar{v})}{(c_{\text{gas},i} - c_{\text{soln},i}^*)}$

What you measure: $\Gamma = \frac{J_{\text{net}} / (\frac{1}{4}\bar{v})}{(c_{\text{gas}} - c_{\text{soln}}^*)}$.

Resistance (Conductance) Analogy

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{\text{gas}}} + \frac{1}{\alpha} + \frac{1}{\Gamma_{\text{soln}}}$$

Measure steady state or transient



Minimize or account for gas and solution resistances. Do not assume $V_s = 0$.

IMPORTANCE OF α TO CLOUD CHEMISTRY AND MICROPHYSICS

- *Cloud formation processes*

What role does the mass accommodation coefficient of water on liquid water play in the kinetics of cloud formation?

- *Uptake and reaction of gases in liquid water clouds*

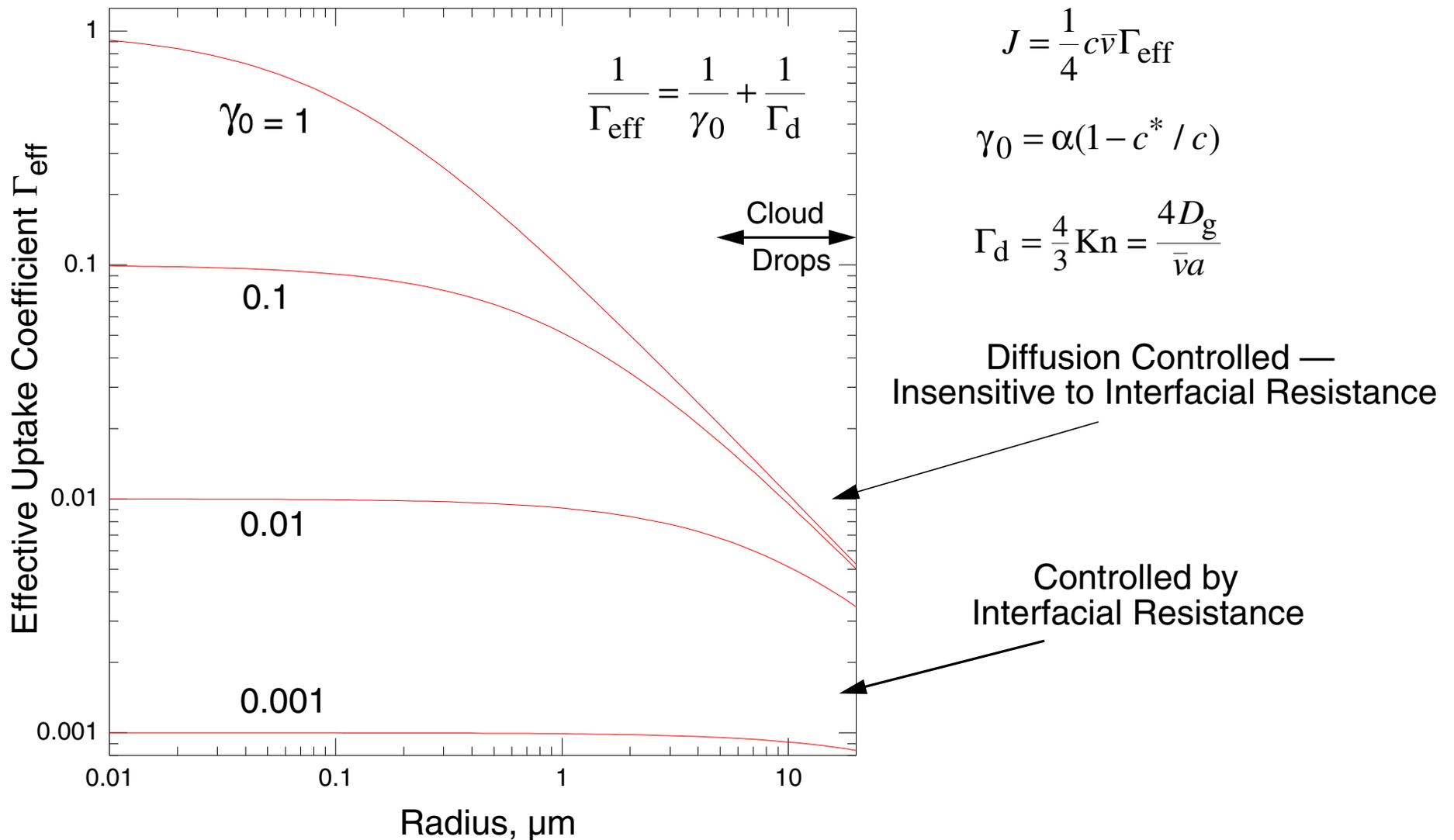
Knowledge of the mass accommodation coefficient is essential to describing the coupled reaction and mass transport kinetics in liquid-water clouds.

- *Uptake and reaction of gases in polar stratospheric clouds*

Knowledge of the mass accommodation coefficient is essential to describing uptake and reaction of gases in PSCs.

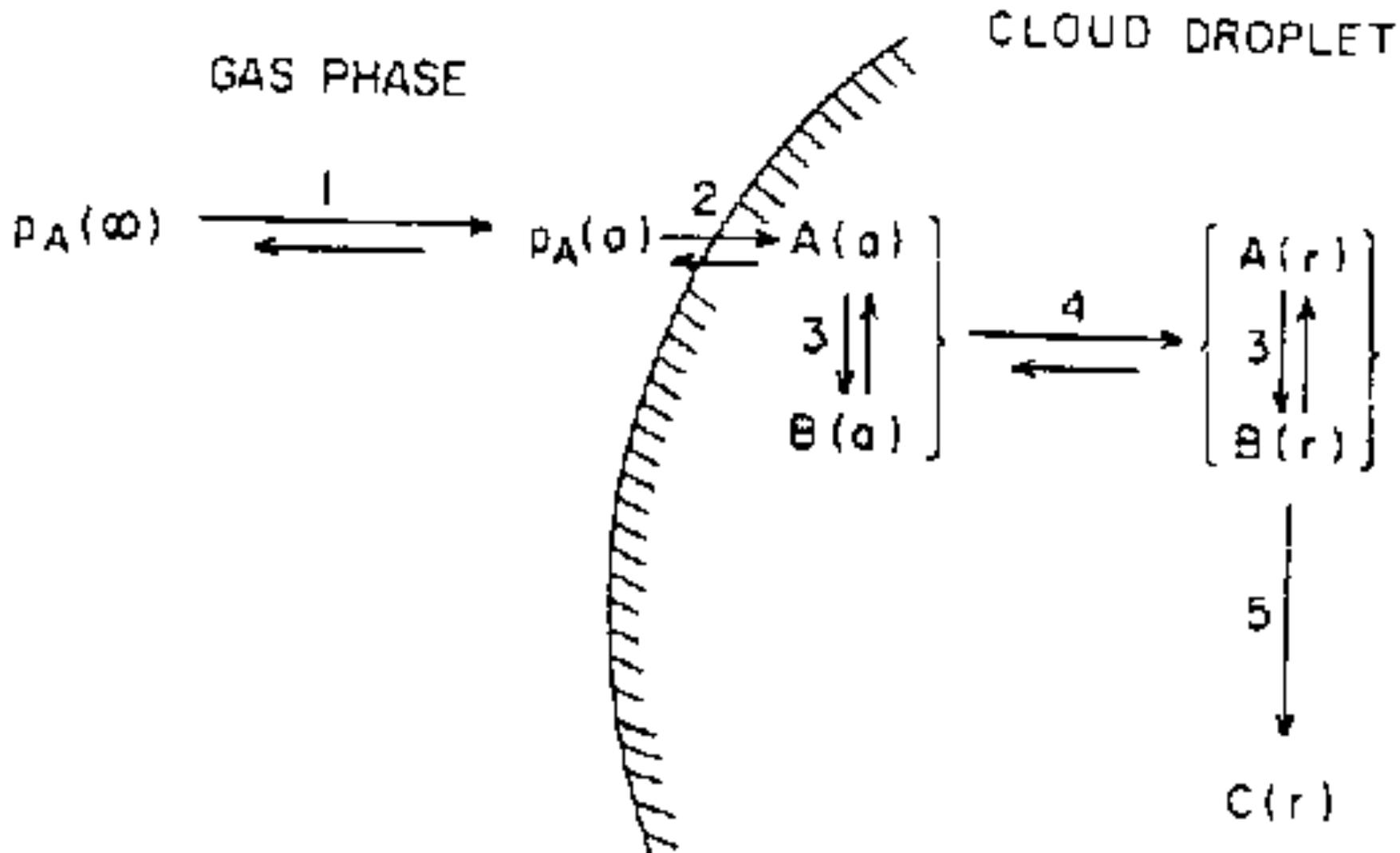
UPTAKE FLUX

Dependence on radius for various uptake coefficients



AQUEOUS-PHASE REACTIONS IN CLOUDS

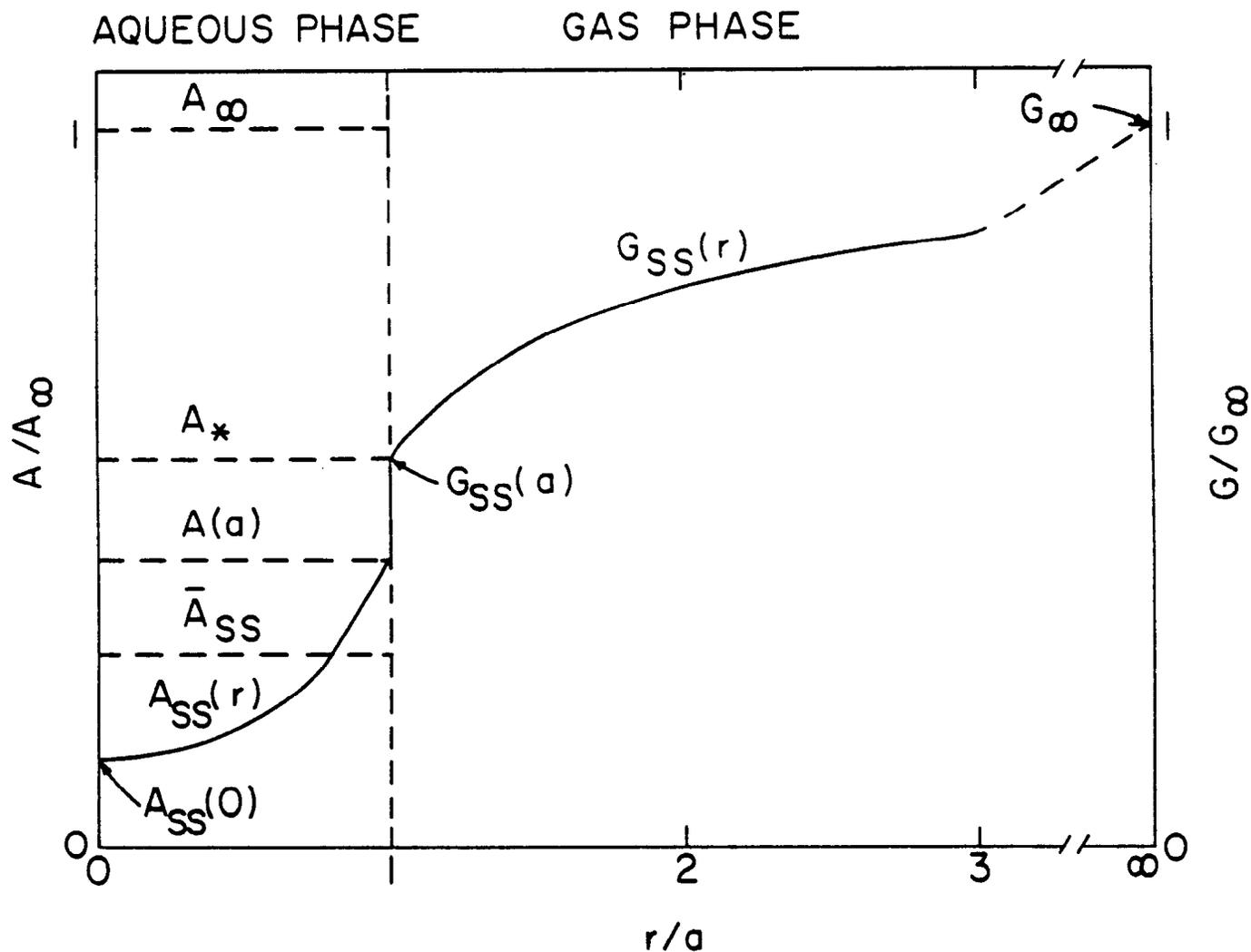
Coupled mass-transport and reaction system



MASS-TRANSPORT LIMITATION TO THE RATE OF REACTION OF GASES IN LIQUID DROPLETS: APPLICATION TO OXIDATION OF SO₂ IN AQUEOUS SOLUTIONS*

S. E. SCHWARTZ and J. E. FREIBERG †

Atmospheric Environment, Vol. 15, No. 7, pp. 1129-1144, 1981.



REFEREE FORM

ATMOSPHERIC ENVIRONMENT

MS. No 1822-L.....(80/112)

TITLE OF PAPER: "Mass-Transport Limitation to the Rate of Reaction of Gases..."

AUTHOR(S): S.E. Schwartz and J.E. Freiberg

You are invited to referee the enclosed paper. If you are able to do this please return the enclosed card. If you cannot report within ten days, please return the paper without delay.

REFEREE'S REPORT

It will be of great assistance to the Editors if the Referee will answer the following questions:

1. Should the paper be accepted for publication? Not in its present form

If the paper is scientifically unsound or does not contain any material which is of sufficient interest and originality to merit publication, then the paper will normally be rejected. If the referee is of the opinion that the paper falls within either of these categories would he please state his reasons for this opinion.

Although scientifically sound, the paper is very long and doesn't really seem to say anything which isn't already well known to workers in the field.

Another reason for publication would be if it synthesised a mass of previous work in a new and innovative way. However, this does not seem to be the case for this paper. It might be worth encouraging the authors to resubmit the mss. in a shortened form, but the contraction would need to be substantial.

I felt that Section II was more worthwhile than Section III.

If the answer to Question 1 is "Yes", then would the referee please indicate:

ATMOSPHERIC ENVIRONMENT

An International Journal

From the Editor: Dr. J. P. Lodge, Jr.
385 Broadway
Boulder, Colorado 80303, U.S.A.

1 July 1980

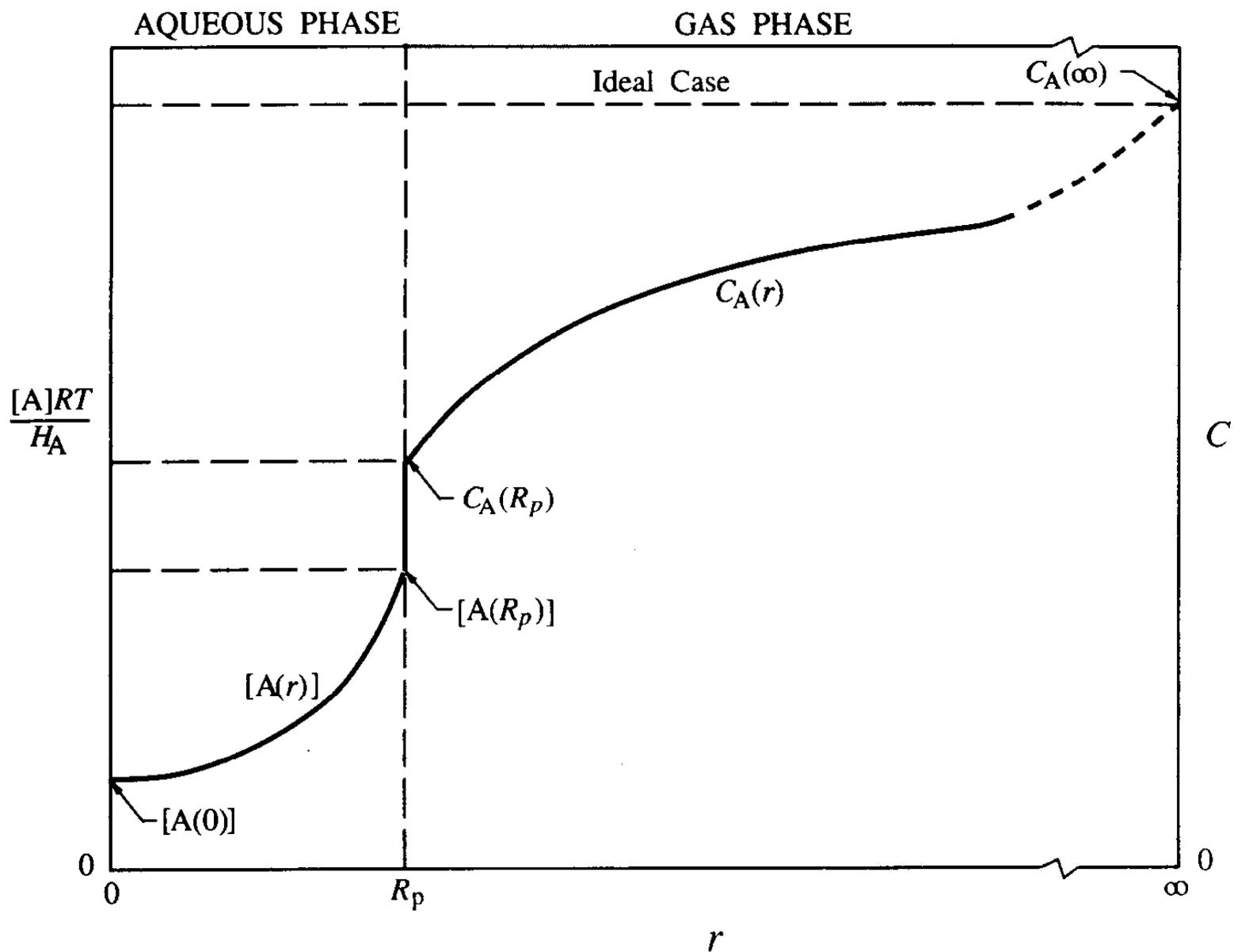
Dr. Stephen E. Schwartz
Chemist
Environmental Chemistry Division
Department of Energy & Environment, Bldg. 426
Brookhaven National Laboratory
Upton, New York 11973

Dear Dr. Schwartz:

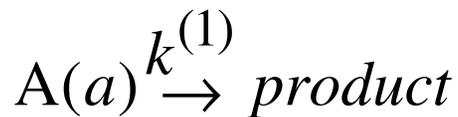
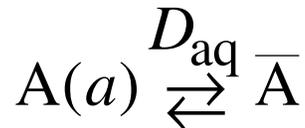
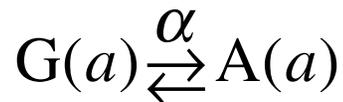
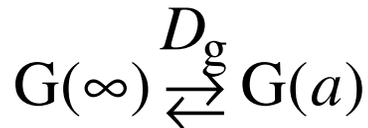
I have now heard from two referees concerning your paper, "Mass-Transport Limitation...." I have also heard from one referee, but not the second, on the companion paper. The comments on this paper are enclosed herewith; obviously, you will get the other one as soon as I have the second review.

Here I am faced with a rather difficult situation. The favorable reviewer is of my own selection. The one who says it is "uninteresting" is a reviewer selected by a fellow editor, D. J. Moore. In each case, of course, it is necessary for us to keep our reviewers happy so that there is some hope that they will serve again.

TEXTBOOK MATERIAL



COUPLED MASS TRANSPORT AND AQUEOUS REACTION KINETICS



At steady state:

$$[A(a)] = Hp \frac{(HR_g T)^{-1} k_{mt}}{(HR_g T)^{-1} k_{mt} + k^{(1)}}$$

$$\text{where } k_{mt} = \left(\frac{a^2}{3D_g} + \frac{4a}{3\bar{v}\alpha} \right)^{-1}$$

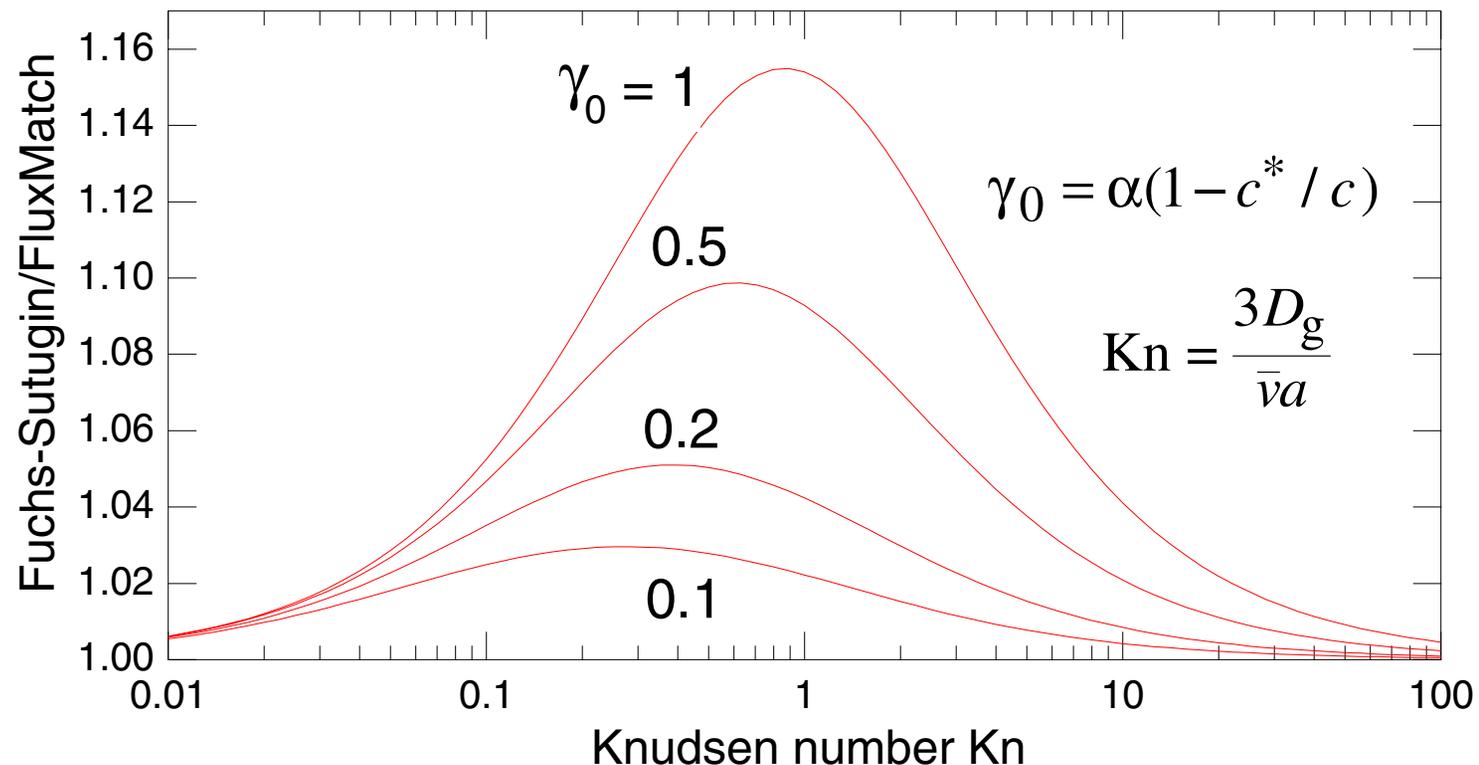
k_{mt} derived by matching diffusive and interfacial fluxes at the interface.

There is a suite of essentially equivalent such expressions that depend on the details of the flux matching, for example Fuchs-Sutugin.

The steady state expression allows criteria to be expressed for the absence of mass-transport limitation (very slow-reaction limit of Danckwerts).

MASS TRANSPORT RATE COEFFICIENT

Comparison of Fuchs-Sutugin and Simple flux match expressions



Difference never exceeds 16% and is usually much less. Use of Fuchs-Sutugin expression is hard to justify unless D_g is known to corresponding accuracy.

IF MASS TRANSPORT IS FAST. . .

- Replenishment by mass transport is much faster than depletion of the dissolved reagent gas by reaction on the water side.
- Aqueous phase can be treated as saturated in the reacting gas,

$$c_{\text{aq}} = Hp$$

- For aqueous rate law $R_{\text{aq}} = k^{(1)}c_{\text{aq}}$, then $R_{\text{aq}} = Hk^{(1)}p$.
- The rate per volume of air is $R_{\text{vol}} = LHk^{(1)}p$ where L is liquid water volume fraction.
- The saturation assumption requires criteria to establish that the mass transport is sufficiently fast.

CRITERIA FOR ABSENCE OF MASS-TRANSPORT LIMITATION

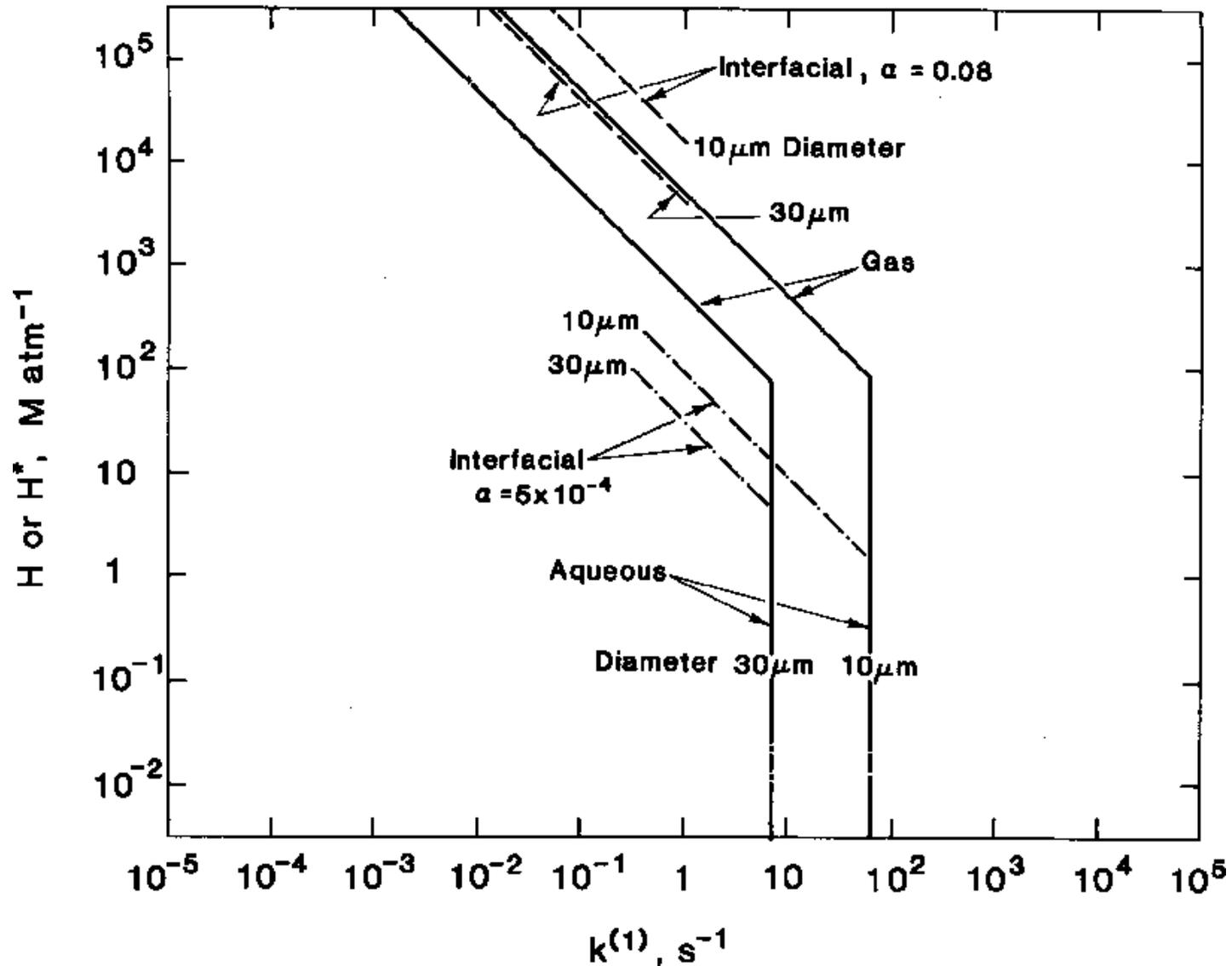
Phase	Criterion
Interface	$Hk^{(1)} \leq \varepsilon \frac{3\bar{v}\alpha}{4R_gTa}$
Gas	$Hk^{(1)} \leq \varepsilon \frac{3D_g}{R_gTa^2}$
Aqueous	$k^{(1)} \leq \varepsilon \frac{15D_{aq}}{a^2}$

$\varepsilon \leq 0.1$ represents maximum allowable fractional departure from uniformity. In the following $\varepsilon = 0.1$.

Schwartz, in *Chemistry of Multiphase Atmospheric Systems*, 1986

MASS-TRANSPORT LIMITATION INEQUALITIES

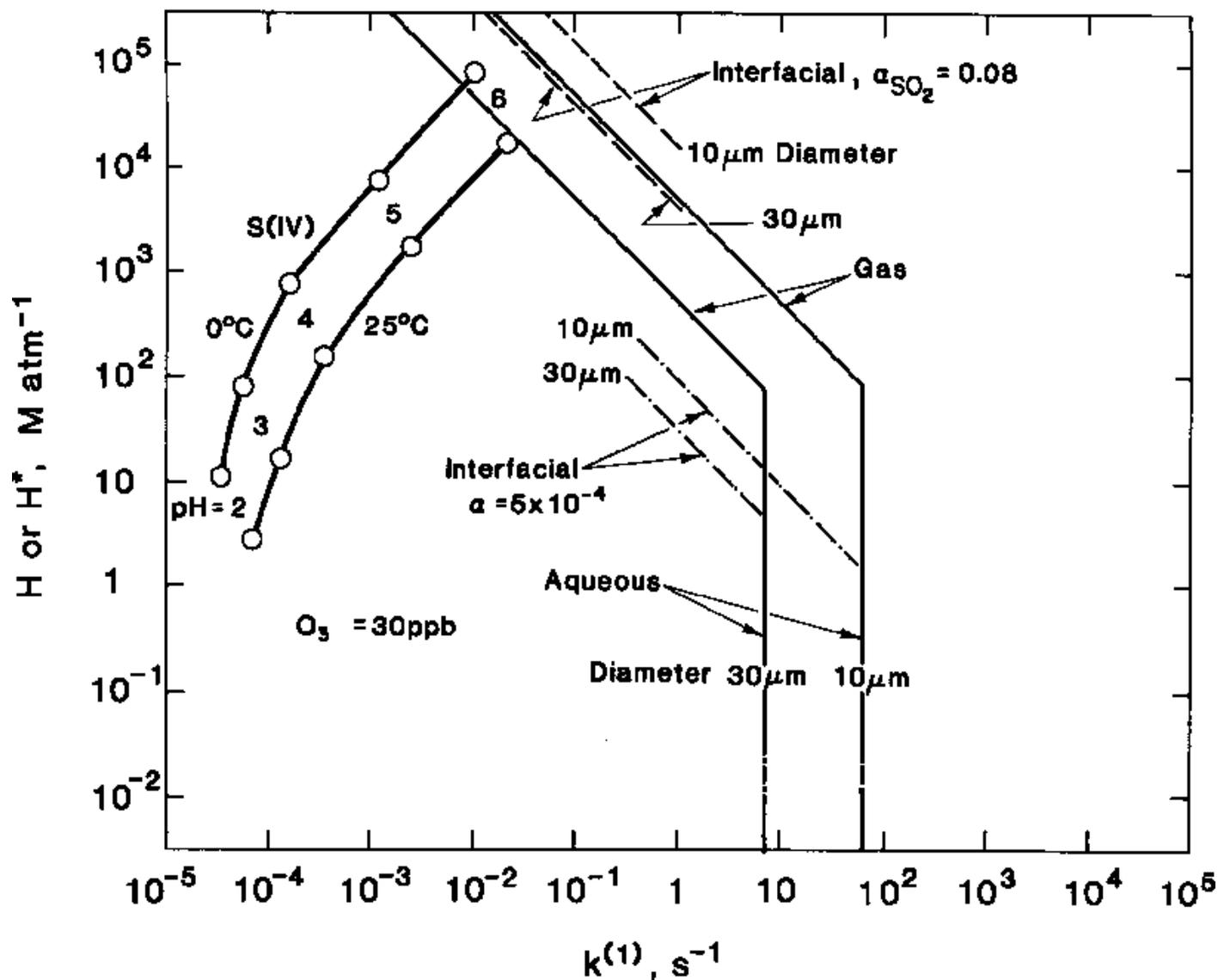
Mass-transport limitation is absent for points below and left of lines.



Schwartz, Atmos. Environ., 1988

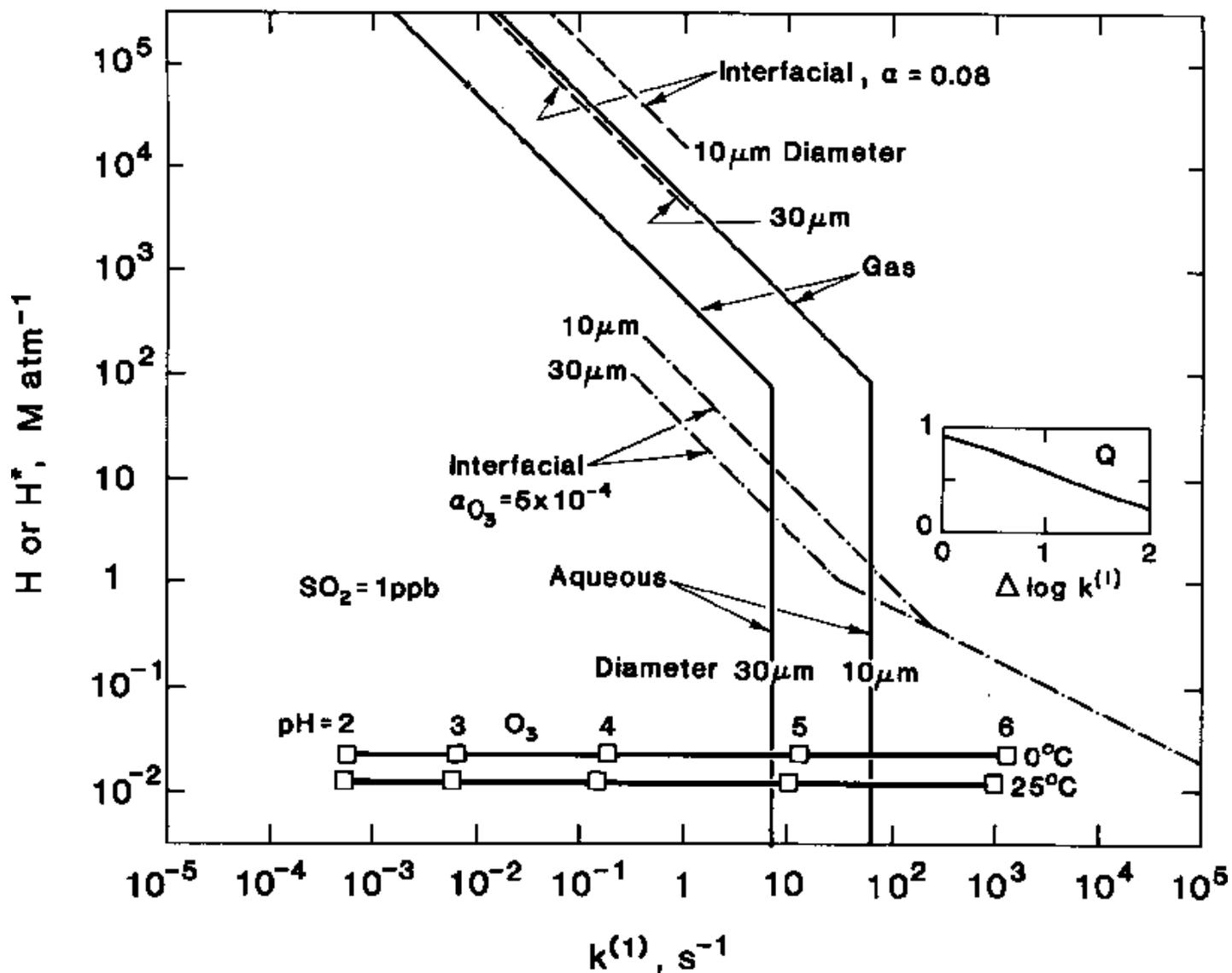
MASS-TRANSPORT LIMITATION INEQUALITIES

Mass-Transport Limitation of S(IV) in Ozone–Sulfur-IV Reaction



MASS-TRANSPORT LIMITATION INEQUALITIES

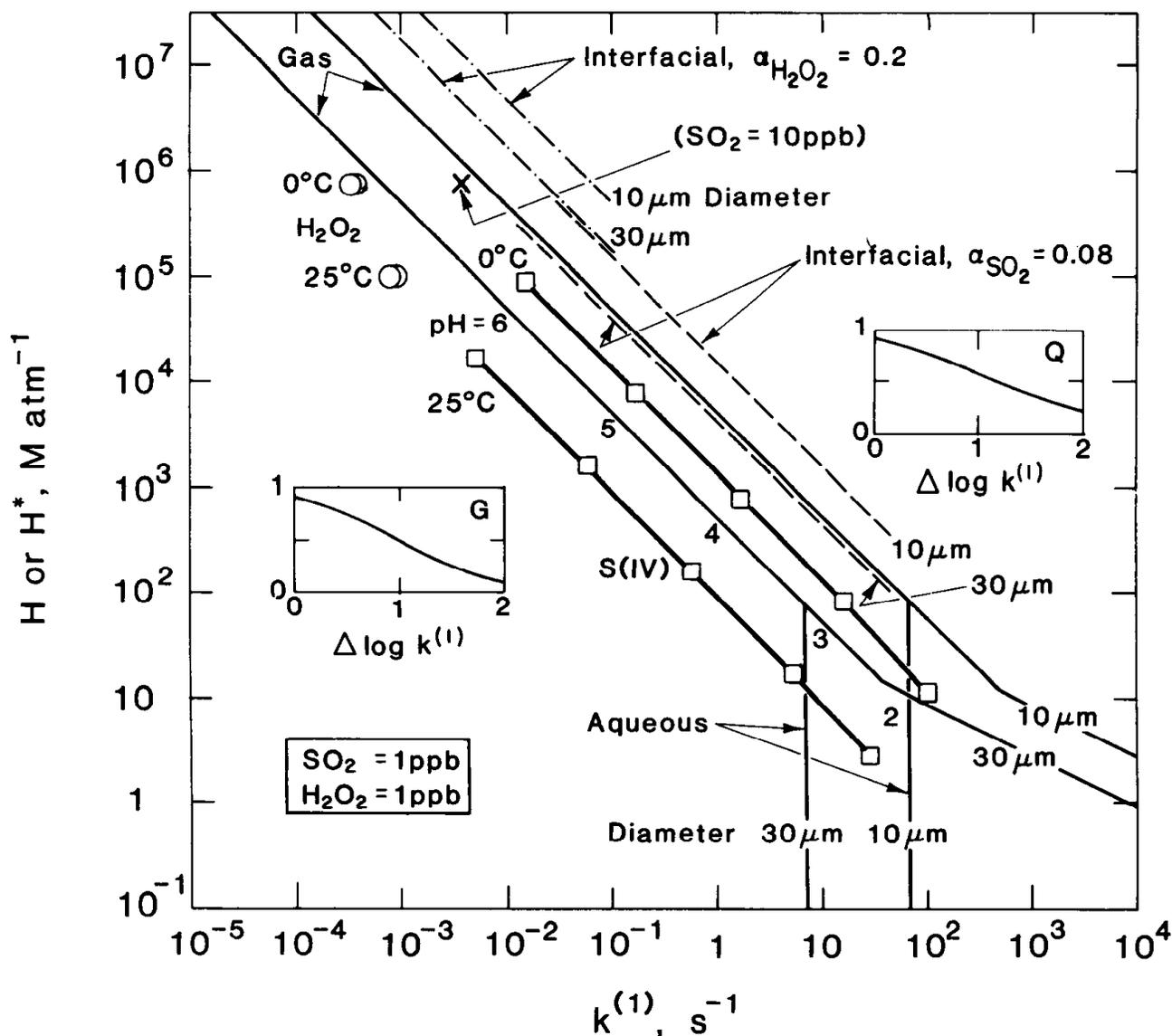
Mass-Transport Limitation of O₃ in Ozone-Sulfur-IV Reaction



Schwartz, Atmos. Environ., 1988

MASS-TRANSPORT LIMITATION INEQUALITIES

Mass-Transport Limitation in H_2O_2 -Sulfur-IV Reaction



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Table 63. Mass Accommodation Coefficients (α)

Gaseous Species	Surface Type	Surface Composition	T(K)	α	Uncertainty Factor
O ₃	Water Ice	H ₂ O(s)	195-262	>0.04	3
	Liquid Water	H ₂ O(l)	292	>2 x 10 ⁻³ †	
	Nitric Acid Ice	HNO ₃ • 3H ₂ O(s)	195	2.5 x 10 ⁻⁴ ‡	
	Sulfuric Acid	H ₂ SO ₄ • nH ₂ O(l) (50 wt.% H ₂ SO ₄) (97 wt.% H ₂ SO ₄)	195	See Note	
			196	See Note	
OH	Water Ice	H ₂ O(s)	205-253	>0.1	5
	Liquid Water	H ₂ O(l)	275	>4 x 10 ⁻³	
	Sulfuric Acid	H ₂ SO ₄ • nH ₂ O(l) (28 wt.% H ₂ SO ₄) (97 wt.% H ₂ SO ₄)	275	>0.07	
			298	>5 x 10 ⁻⁴ ‡	
			Alumina	Al ₂ O ₃ (s)	
HO ₂	Liquid Water	H ₂ O(l)	275	> 0.02	5
	Aqueous Salts	NH ₄ HSO ₄ (aq) and LiNO ₃ (aq)	293	> 0.2	
			Sodium Chloride	NaCl(s)	
	Potassium Chloride	KCl(s)	295	2 x 10 ⁻²	
H ₂ O	Water Ice	H ₂ O(s)	200	0.5	2
	Liquid Nitric Acid	HNO ₃ •nH ₂ O(l)	278	>0.3	
	Nitric Acid Ice	HNO ₃ • 3H ₂ O(s)	197	See Note	
	Sulfuric Acid	H ₂ SO ₄ • nH ₂ O (96 wt.% H ₂ SO ₄)	298	> 2 x 10 ⁻³ ‡	
			~298	See Note	
	Sodium Chloride	NaCl(s)	~299	> 0.5	
Carbon/Soot	NaCl(aq) (C(s))	~298	>4 x 10 ⁻⁴		
H ₂ O ₂	Liquid Water	H ₂ O(l)	273	0.18*	2

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Table 63. Mass Accommodation Coefficients (α)

Gaseous Species	Surface Type	Surface Composition	T(K)	α	Uncertainty Factor	
HNO ₃	Water Ice	H ₂ O(s)	200	0.3	3	
	Liquid Water	H ₂ O(l)	268	0.2*	2	
	Nitric Acid Ice	HNO ₃ • 3H ₂ O(s)	191-200	0.4	2	
	Liquid Nitric Acid	HNO ₃ • nH ₂ O(l)	278	0.6	2	
	Sulfuric Acid		H ₂ SO ₄ • nH ₂ O(l)	191-200	>0.3	2
			(57.7 wt.% H ₂ SO ₄)	283	0.1	
CH ₃ OH	Liquid Water	H ₂ O(l)	260-291	0.12-0.02*	2	
CH ₃ CH ₂ OH	Liquid Water	H ₂ O(l)	260-291	0.13-0.02*	2	
CH ₃ CH ₂ CH ₂ OH	Liquid Water	H ₂ O(l)	260-291	0.08-0.02*	2	
CH ₃ CH(OH)CH ₃	Liquid Water	H ₂ O(l)	260-291	0.10-0.02*	2	
HOCH ₂ CH ₂ OH	Liquid Water	H ₂ O(l)	260-291	0.13-0.04*	2	
CH ₂ O	Liquid Water	H ₂ O(l)	260-270	0.04	3	
	Sulfuric Acid	H ₂ SO ₄ • nH ₂ O(l)	235-300	0.04	3	
CH ₃ O ₂	Sodium Chloride	NaCl(s)	296	>4 × 10 ⁻³		
CH ₃ CHO	Liquid Water	H ₂ O(l)	267	>0.03*		
NH ₃	Liquid Water	H ₂ O(l)	~295	0.06*	3	

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Table 63. Mass Accommodation Coefficients (α)

Gaseous Species	Surface Type	Surface Composition	T(K)	α	Uncertainty Factor
CH ₃ OH	Liquid Water	H ₂ O(l)	260-291	0.12-0.02*	2
CH ₃ CH ₂ OH	Liquid Water	H ₂ O(l)	260-291	0.13-0.02*	2
CH ₃ CH ₂ CH ₂ OH	Liquid Water	H ₂ O(l)	260-291	0.08-0.02*	2
CH ₂ O	Liquid Water	H ₂ O(l)	260-270	0.04	3
	Sulfuric Acid	H ₂ SO ₄ • nH ₂ O(l)	235-300	0.04	3
HCl	Water Ice	H ₂ O(s)	191- 211	0.3	3
	Liquid Water	H ₂ O(l)	274	0.2*	2
	Nitric Acid Ice	HNO ₃ • 3H ₂ O(s)	191- 211	0.3	3
	Sulfuric Acid	H ₂ SO ₄ • nH ₂ O(l)	283 218	0.15* >0.005*	2
SO ₂	Liquid Water	H ₂ O(l)	260-292	0.11	2

UPPER LIMIT TO MASS ACCOMMODATION COEFFICIENT?

For mass accommodation the flux in is: $J_i = \frac{1}{4} \bar{v} \alpha_i c_g$

Consider mass de-accommodation. The flux out is : $J_o = \frac{1}{4} \bar{v} \alpha_o c_{aq}$

By detailed balance at equilibrium: $\alpha_i c_g = \alpha_o c_{aq}$

Note: $\frac{\alpha_i}{\alpha_o} = HR_g T$ is an equilibrium constant (Henry's law coefficient).

Aside: $\frac{\alpha_i}{1 - \alpha_i}$ is **not** an equilibrium constant.

Whence: $\alpha_i = \alpha_o \frac{c_{aq}}{c_g} = \alpha_o HR_g T$

Mass de-accommodation coefficient cannot exceed unity: $\alpha_o \leq 1$

Whence upper limit on α_i : $\alpha_i \leq HR_g T$ or 1, whichever is less.

WHERE DOES THIS KICK IN?

- $R_g T \approx 25 \text{ atm M}^{-1}$, so the solubility limit to α_i becomes restrictive for $H \lesssim 0.04 \text{ M atm}^{-1}$.
- For ozone, $H_{292} = 0.014 \text{ M atm}^{-1}$ implies an upper limit $\alpha_i \lesssim 0.5$.
Compare measurement: $\alpha_{292} \geq 2 \times 10^{-3}$.
- Certainly this is of no importance in atmospheric chemistry.
- Solubility limit to α_i would be well less than 1 for low solubility organics.
- Is this surprising? Doesn't $HR_g T < 1$ imply a free energy barrier to dissolution? This would imply at least as much barrier to α_i .
- Is this of any but academic importance? Is it even of academic importance?

CONCLUSIONS AND FUTURE DIRECTIONS

- The atmospheric science community now has a good understanding of the concept of mass-accommodation and its atmospheric implications.
- For uptake of reactive gases in liquid-water clouds mass accommodation *can be* controlling for $\alpha \lesssim 10^{-2}$ and increasingly likely controlling for $\alpha \lesssim 10^{-4}$.
- For a given value of α , whether or not mass accommodation is actually controlling depends on solubility and aqueous kinetics for the situation of interest.
- Work in the past 15 years has placed mass accommodation coefficients of volatile gases on water and aqueous solutions on a *firm foundation*, including dependence on temperature and composition.

cont'd . . .

CONCLUSIONS AND FUTURE DIRECTIONS

- Mass accommodation coefficients are available for key substances taken up by tropospheric liquid clouds.
- Mass accommodation does not appear to be controlling for SO₂ oxidation in tropospheric liquid clouds.
- Lab studies show mass accommodation is not controlling in lab drops.
What about the atmosphere? Real drops? Role of surface films?
- To what extent, if any, does mass accommodation control response of submicrometer particles to changes in relative humidity?
- Future work may focus more on understanding the chemical physics of mass accommodation than on practical applications.