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MASS-TRANSPORT LIMITATION TO IN-CLOUD REACTION RATES: IMPLICATIONS OF NEW ACCOMMODATION COEFFICIENT MEASUREMENTS

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ABSTRACT

Although it has been recognized for some time that the rate of reactive uptake of gases in cloudwater can depend on the value of the mass-accommodation coefficient (α) describing interfacial mass transport (MT), definitive evaluation of such rates is only now becoming possible with the availability of measurements of α for gases of atmospheric interest at air-water interfaces. Examination of MT limitation to the rate of in-cloud aqueous-phase oxidation of SO_2 by O_3 and H_2O_2 shows that despite the low value of α_{O_3} (5×10^{-4}), interfacial MT of this species is not limiting under essentially all conditions of interest; the high values of α for SO_2 (≥ 0.2) and H_2O_2 (≥ 0.08) indicate no interfacial MT limitation for these species also. Although gas- and aqueous-phase MT can be limiting under certain extremes of conditions, treating the system as under chemical kinetic control is generally an excellent approximation. Interfacial MT limitation also is found not to hinder the rate of H_2O_2 formation by aqueous-phase disproportionation of HO_2. Finally, the rapid uptake of N_2O_5 by cloud droplets implies that the yield of aqueous HNO_3 from in-cloud gas-phase oxidation of NO_2 by O_3 can be substantial even under daytime conditions.

This report consists of copies of viewgraphs prepared for this presentation.

IMPORTANCE

- Dissolution of gases in cloudwater followed by aqueous-phase reaction is an important type of atmospheric transformation process.
- Aqueous-phase reactions can be much faster than corresponding gas-phase reactions.
- Aqueous-phase reactions can concentrate gaseous pollutants and contribute to their removal from the atmosphere in precipitation.

OVERALL OBJECTIVE

- Describe (quantitatively) the rates of gas-aqueous reactions in liquid-water clouds:
    - Mechanisms.
    - Rate laws.
    - Reagent concentrations.
- Describe reagent concentrations as governed by:
    - Mass transport.
    - Chemical reaction.

INTERMEDIATE OBJECTIVES

- Assess the role of MT limitation to rate of uptake and reaction of gases in liquid-water clouds for representative environmental situations.

- Ascertain circumstances where MT limitation is unimportant vs. controlling.

- Assess the role of interfacial MT limitation vs. MT in gas and aqueous phases.

- Evaluate the rate of MT (or coupled MT and reaction) in pertinent environmental situations.

OUTLINE OF THIS TALK

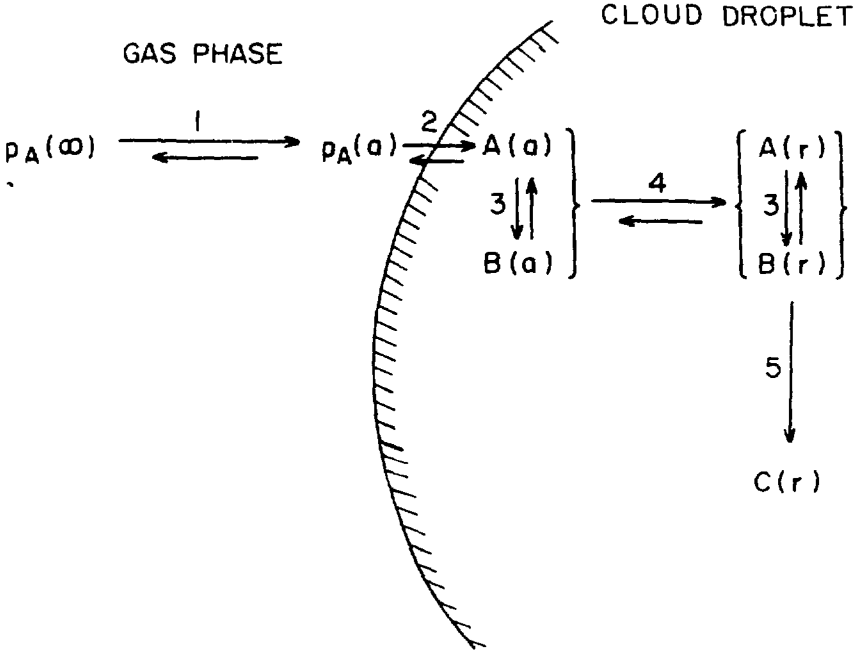
- Description of mass-transport mechanisms pertinent to reactions in clouds.
- Description of rates of coupled mass-transport and reaction in clouds.
- Examination of mass-transport limitation of in-cloud oxidation of SO_2 by H_2O_2 and O_3.
- Examination of uptake and reaction of N_2O_5 in daytime clouds.
- Examination of aqueous-phase H_2O_2 formation in clouds.

Mechanisms of Mass Transport

Gas Phase: Molecular diffusion

Interface: Gas-kinetic collision rate times mass-accommodation coefficient (α)

Aqueous Phase: Molecular diffusion



MASS-TRANSPORT MECHANISMS AND FLUXES

AIR

Molecular diffusion $F = -D_g \frac{dC}{dz}$

INTERFACE

Molecular collision $F = \frac{1}{4} C \bar{v} \alpha$

Mean molecular speed, $\bar{v}$.

Mass-accommodation coefficient, α.

WATER

Molecular diffusion Concurrent with $\boxed{\text{Chemical Reaction}}$

Drop radius, a

Effective first order rate coefficient, $k^{(1)}$

$$F = f\left(C(a), a, D_{aq}, k^{(1)}\right)$$

- - -

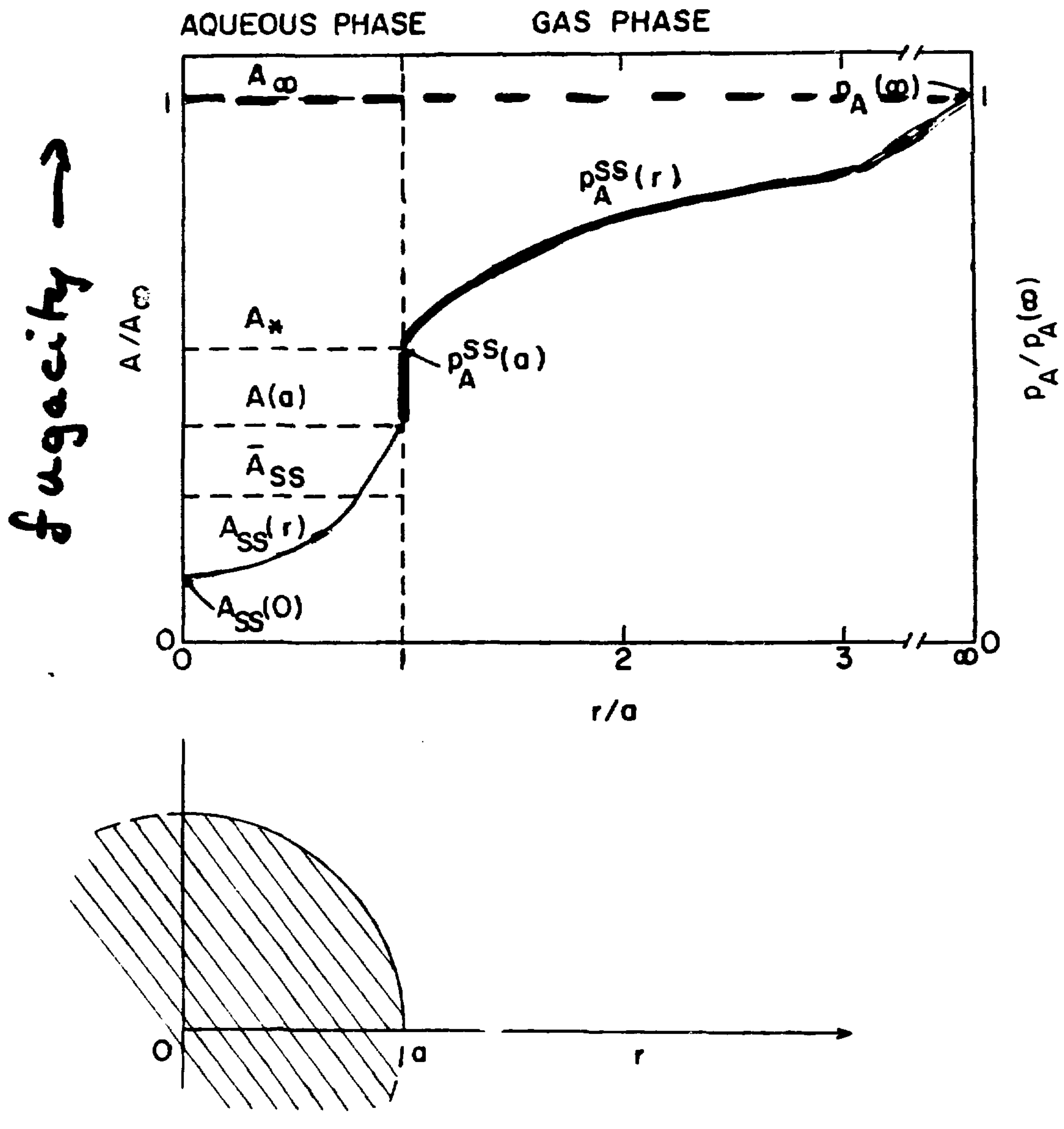
- These processes occur in series.
- Determine rates of individual processes.
- Ascertain rate-determining step.

Mass Transport Limitation

- Is mass transport sufficiently rapid that concentration of dissolved reagent gas is not appreciably less than Henry's law value as a consequence of depletion by reaction?

YES: Reaction rate is proportional to L, (and independent of mass-transport kinetics).

NO: Reaction rate depends on mass transport kinetics, and in turn on drop radius - must treat different radii separately.


AQUEOUS PHASE
GAS PHASE
fugacity →
A/A_∞
p_A/p_A(∞)
A_∞
p_A(∞)
p_A^SS(r)
A_*
p_A^SS(a)
A(a)
Ā_SS
A_SS(r)
A_SS(O)
1
O
2
3
∞
r/a
O
a
r

DIMENSIONAL CONSIDERATIONS

Consider a spherical drop, radius a

Gaseous diffusive flux at a: $F_g = \frac{D_g(C_\infty - C_a)}{a}$

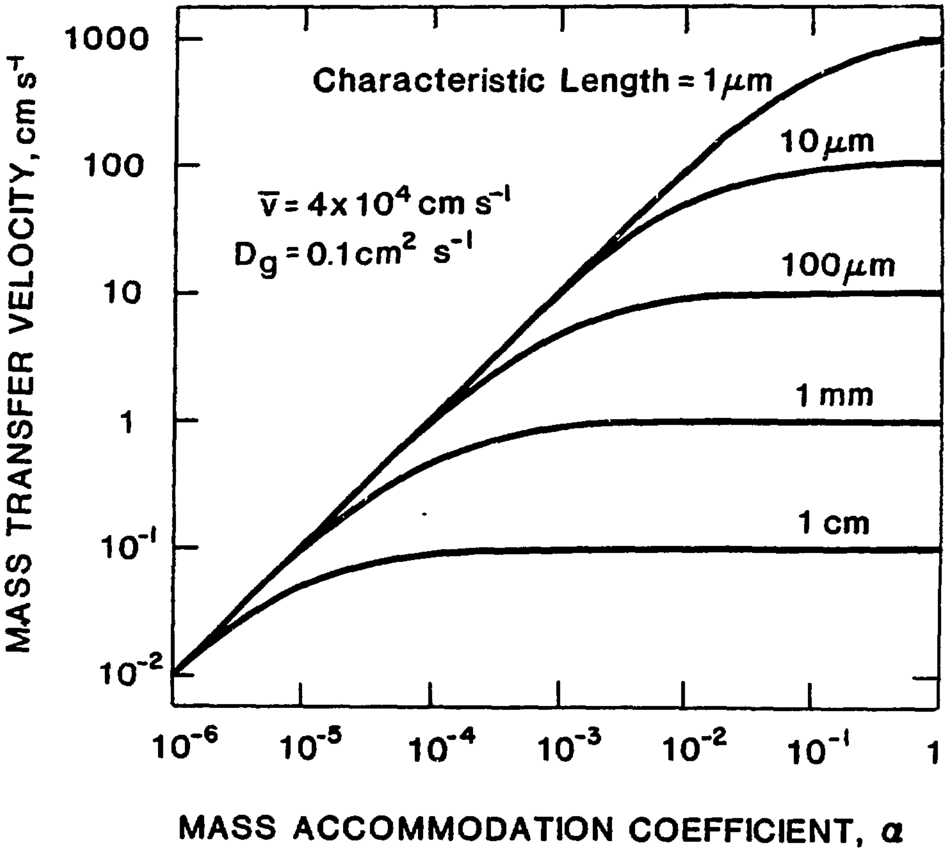
Interfacial flux at a: $F_i = \frac{1}{4}\alpha\bar{v}C_a$

Equate to obtain resultant flux at a:

$$F = C_\infty \frac{1}{\frac{1}{\frac{1}{4}\alpha\bar{v}} + \frac{a}{D_g}}$$

(Add as conductances in series.)

DIMENSIONAL DEPENDENCE OF MASS ACCOMMODATION EFFECT



VOLATILE SOLUTES

- Characterized by Henry's law:

  The equilibrium concentration of a gas dissolved in a liquid is proportional to the partial pressure of the gas.

  $$[X(aq)] = H_X p_X$$

- H_X: Henry's law coefficient.

  Units: M atm^{-1}

- There are a variety of units commonly employed.

- Dimensionless:

  $$C_{aq} = \underset{\sim}{H}_X C_g$$

  $$\underset{\sim}{H}_X = H_X \underset{\sim}{R} T$$

INTERFACIAL MT OF VOLATILE SOLUTES

$$F_{g\rightarrow aq} = \frac{1}{4} C_g \bar{v} \alpha$$

What is $F_{aq\rightarrow g}$?

$$F_{aq\rightarrow g} = k_{aq\rightarrow g}\, C_{aq}$$

At equilibrium:

$$F_{aq\rightarrow g} = F_{g\rightarrow aq} = \frac{1}{4} C_g \bar{v} \alpha$$

Whence:

$$k_{aq\rightarrow g} = \frac{1}{4} \bar{v} \alpha \left(\frac{C_g}{C_{aq}} \right)_{eq}$$

$$= \frac{1}{4} \bar{v} \alpha \underset{\sim}{H}^{-1}$$

Whence:

$$F_{\text{net } g\rightarrow aq} = \frac{1}{4} \bar{v} \alpha (C_g - C_{aq}/\underset{\sim}{H})$$

SCIENCE, VOL. 206, 2 NOVEMBER 1979

Heterogeneous Atmospheric Reactions: Sulfuric Acid Aerosols as Tropospheric Sinks

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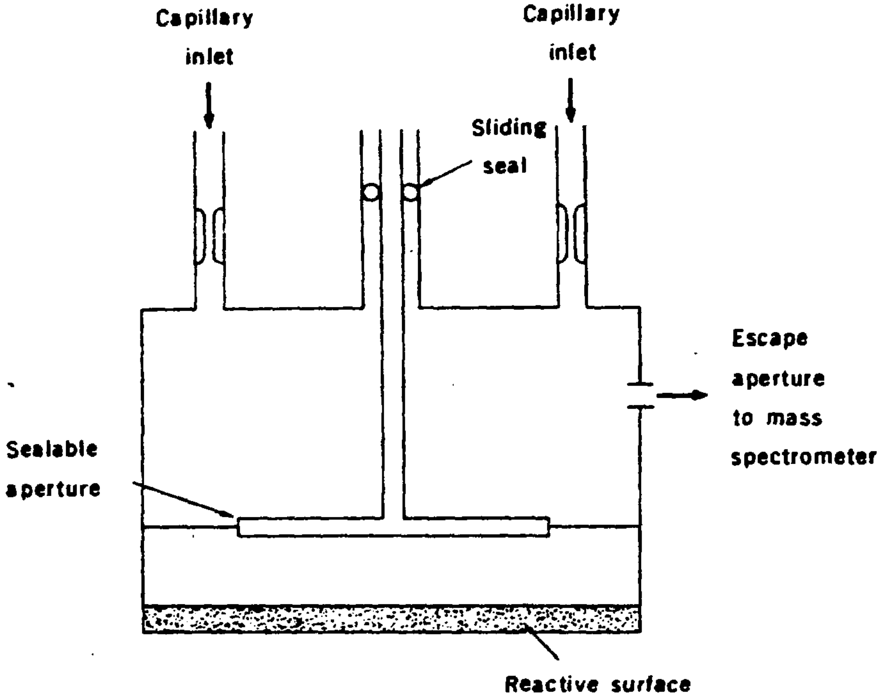


Table 1. Collisional reaction probabilities on a H_2SO_4 surface at 300 K.

Species	Collisional reaction probability (γ)
H_2O_2	7.8×10^{-4}
HNO_3	$\geq 2.4 \times 10^{-4}$
HO_2NO_2	2.7×10^{-5}
$ClONO_2$	1.0×10^{-5}
N_2O_5	$\geq 3.8 \times 10^{-5}$
H_2O	$\sim 2.0 \times 10^{-3}$
NH_3	$> 1.0 \times 10^{-3}$
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	$< 1.0 \times 10^{-6}$

DESCRIPTION OF GAS-AQUEOUS KINETICS

Master Rate Equations

$$\frac{dp}{dt} = - p \int k_{mt}(a)\, dL(a) + \frac{1}{H} \int k_{mt}(a)\, C(a)\, dL(a)$$

$$\frac{dC(a)}{dt} = \frac{k_{mt}(a)}{\underset{\sim}{R}T}\, p - \frac{k_{mt}(a)}{H\, \underset{\sim}{R}T}\, C(a) - \overline{R}(a)$$

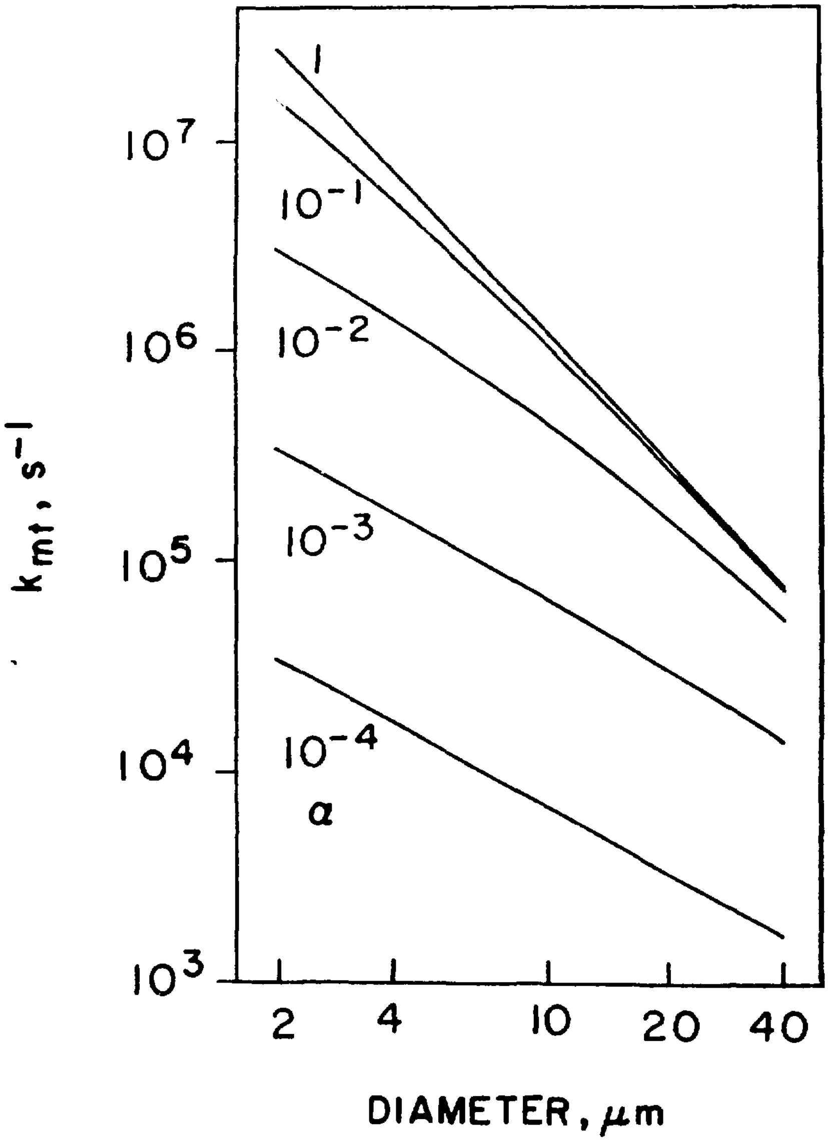
Nomenclature

a	Drop radius.
p	Bulk partial pressure of reagent gas.
C(a)	Aqueous concentration of dissolved reagent gas, at interface.
$\overline{R}(a)$	Aqueous-phase reaction rate, average over drop volume.
dL	Differential liquid-water volume fraction.

$$L = \int dL = \int \left(\frac{dL}{da} \right) da$$

Mass-Transport Rate Coefficient (Gas and Interface)

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



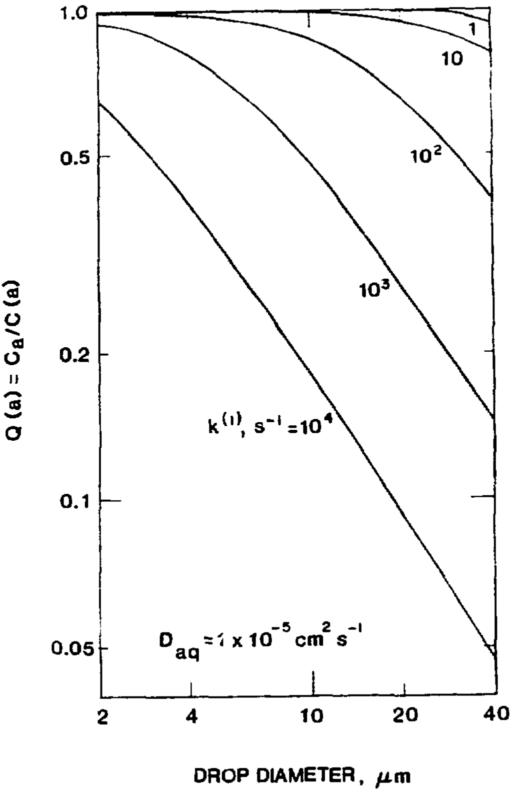
AQUEOUS-PHASE RATE

$$\overline{R}(a) = k^{(1)}\, \overline{C}_a = k^{(1)}\, C(a)\, Q(a)$$

Aqueous-Phase Mass-Transport Limitation

$$Q(a) = \frac{\overline{C}_a}{C(a)} = 3\left(\frac{\coth q}{q} - \frac{1}{q^2}\right) \le 1$$

where $$q = a\left(\frac{k^{(1)}}{D_{aq}}\right)^{1/2}$$



Criteria for Absence of Mass-Transport Limitation

Gas Phase $\quad Hk^{(1)} \leq \varepsilon \dfrac{3\,D_g}{\underset{\sim}{R}T\,a^2}$

Interface $\quad Hk^{(1)} \leq \varepsilon \dfrac{3\,\bar{v}\alpha}{4a\,\underset{\sim}{R}T}$

Aqueous Phase $\quad k^{(1)} \leq 15\varepsilon \dfrac{D_a}{a^2}$

ε: Maximum tolerable mass-transport limitation

H: Henry's law or effective Henry's law coefficient

$k^{(1)}$: Pseudo first-order rate coefficient

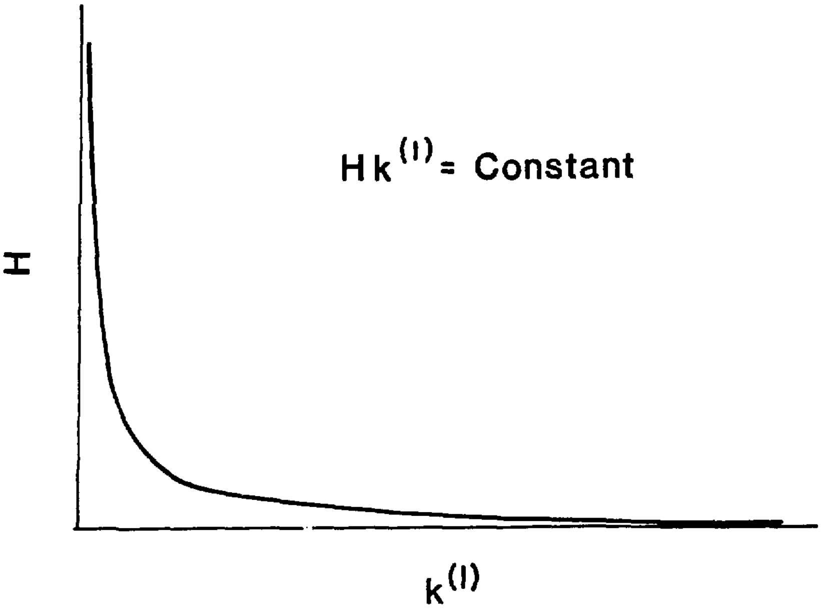
a: Drop radius

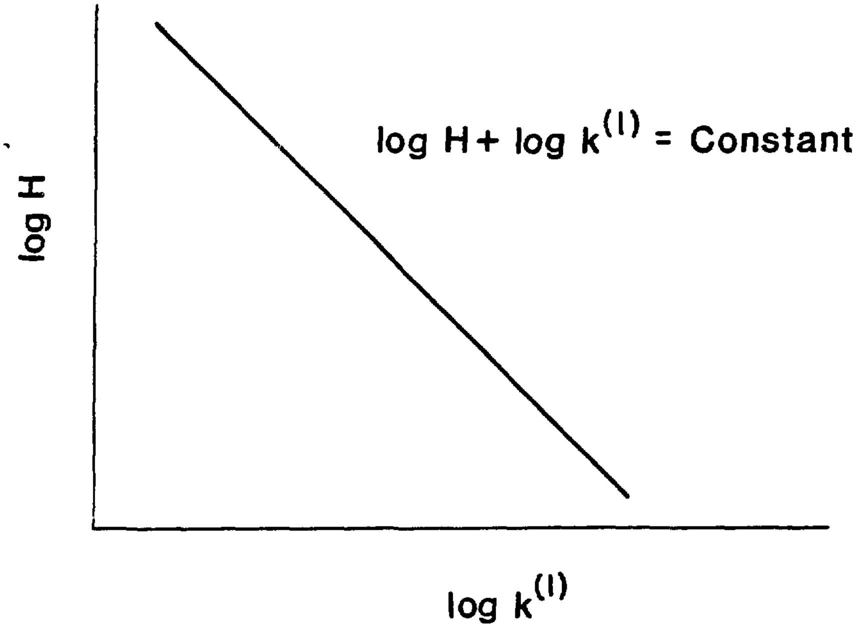
$\bar{v}$: Mean molecular speed

α: Mass accommodation coefficient

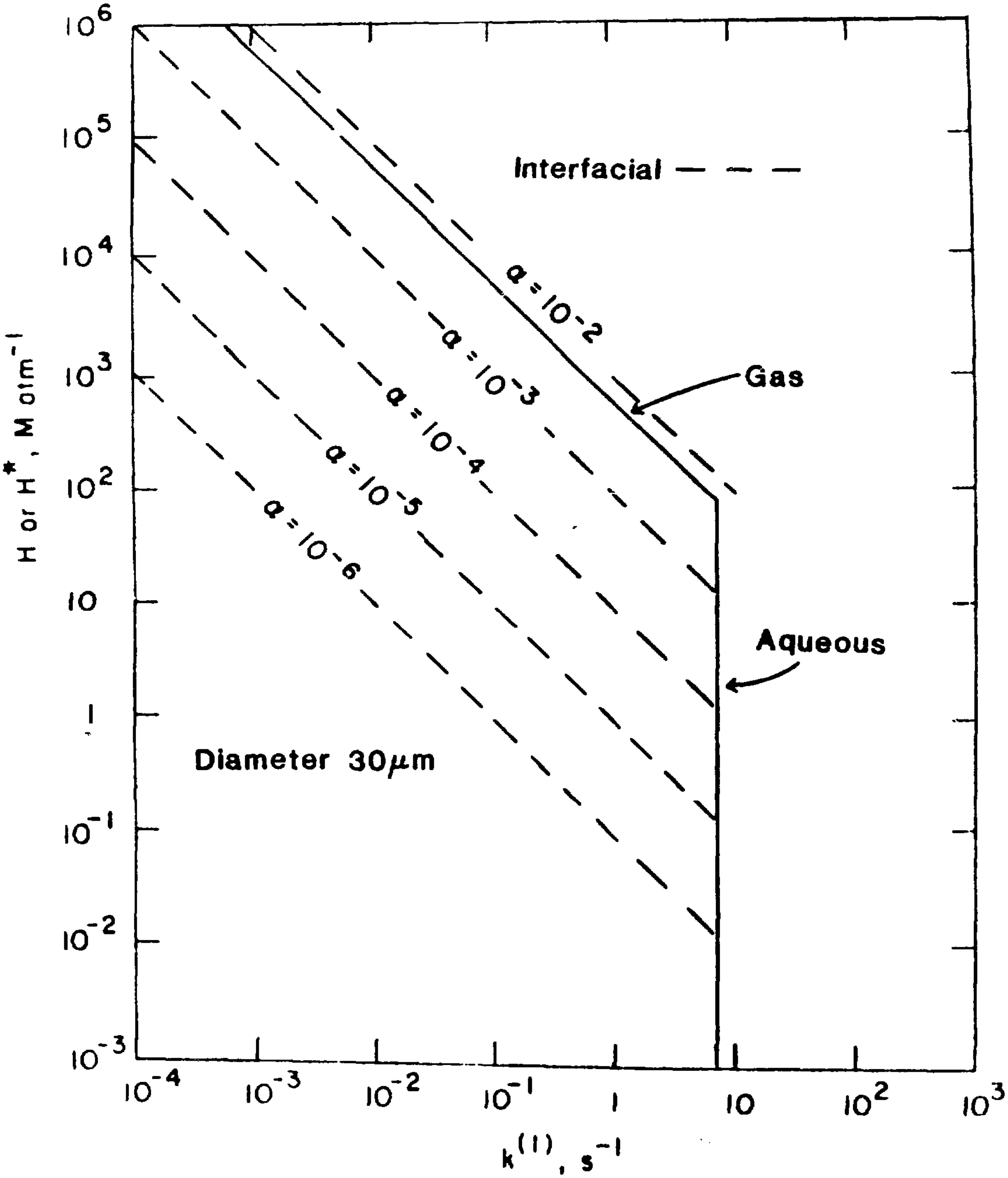
D_g: Gas-phase diffusion coefficient

D_a: Aqueous-phase diffusion coefficient


Hk^(l) = Constant
H
k^(l)


log H + log k^(l) = Constant
log H
log k^(l)

CRITERIA FOR ABSENCE OF MASS-TRANSPORT LIMITATION



APPLICATION TO SO_2 OXIDATION IN CLOUDS

- Clouds are an important gas-liquid atmospheric system.
- Wish to evaluate rates of SO_2 oxidation

$$S(IV) + O_3 \rightarrow S(VI)$$

$$S(IV) + H_2O_2 \rightarrow S(VI)$$

- Aqueous phase rate:

$$R_{S(IV)\text{-}O_3} = k_{O_3}^{(2)} [S(IV)] [O_3]$$

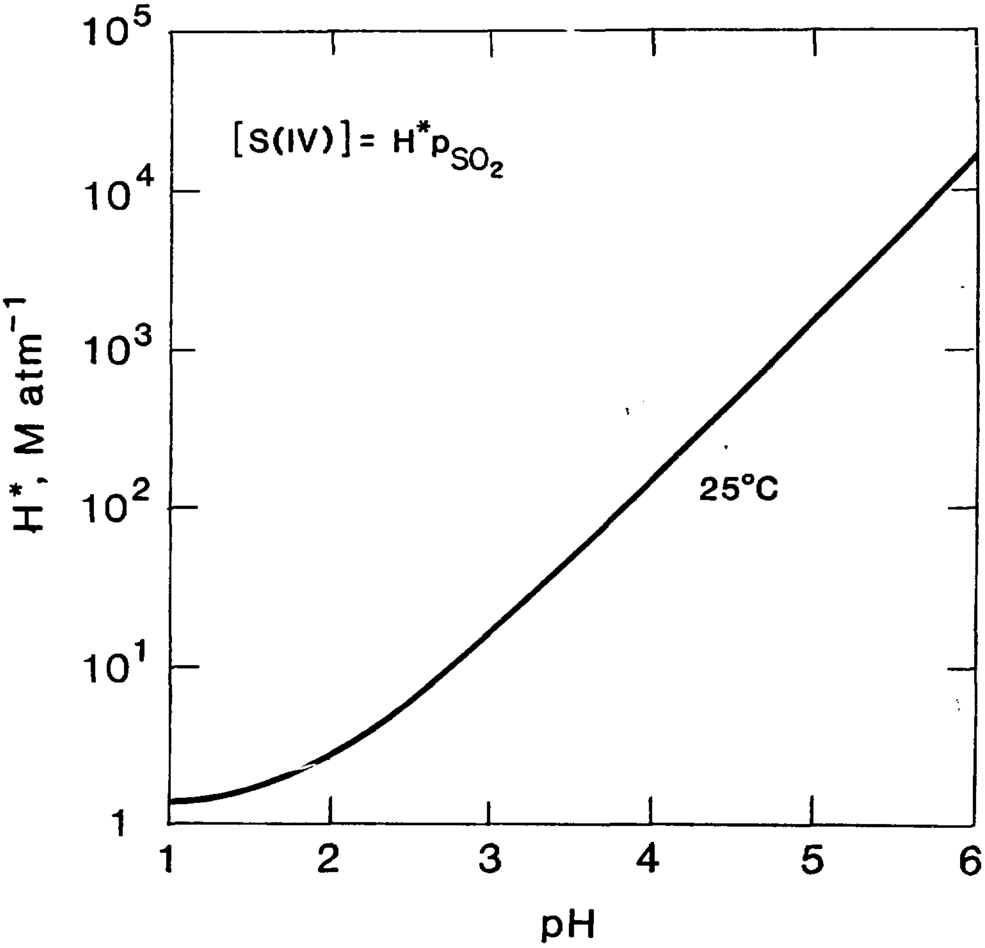
- Define

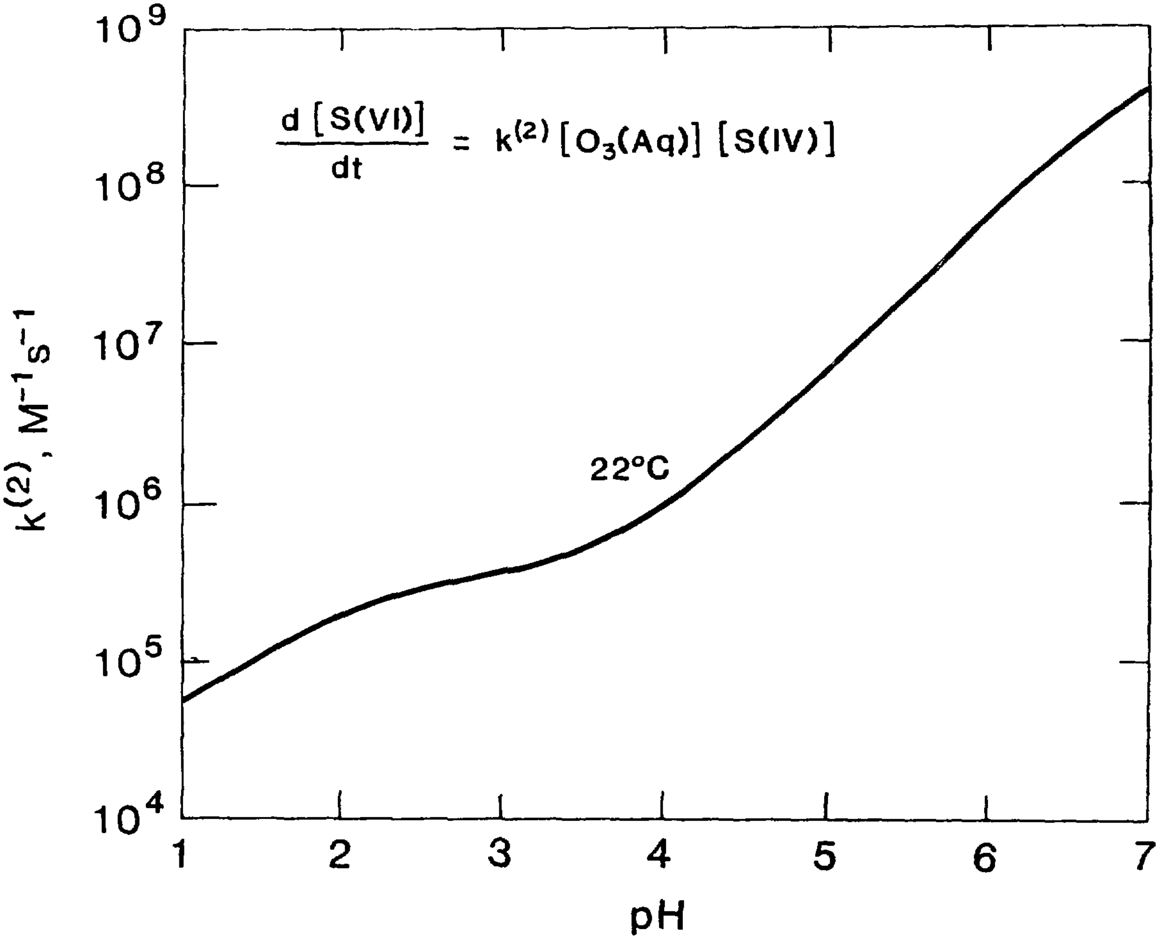
$$k_{S(IV)}^{(1)} = k_{O_3}^{(2)} [O_3] = k_{O_3}^{(2)} H_{O_3} p_{O_3}$$

$$k_{O_3}^{(1)} = k_{O_3}^{(2)} [S(IV)] = k_{O_3}^{(2)} H_{S(IV)}^{*} p_{SO_2}$$

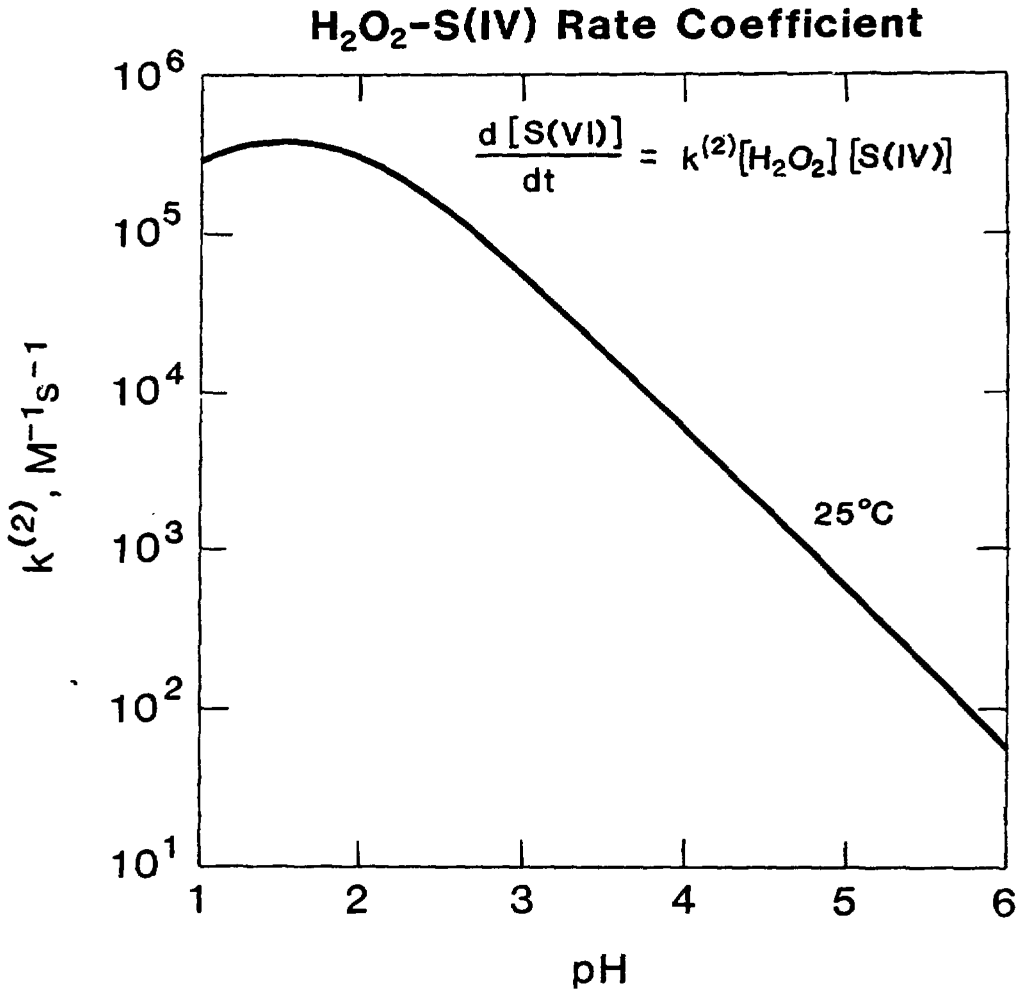
- Similarly for H_2O_2-S(IV) reaction.

Sulfur (IV) Solubility



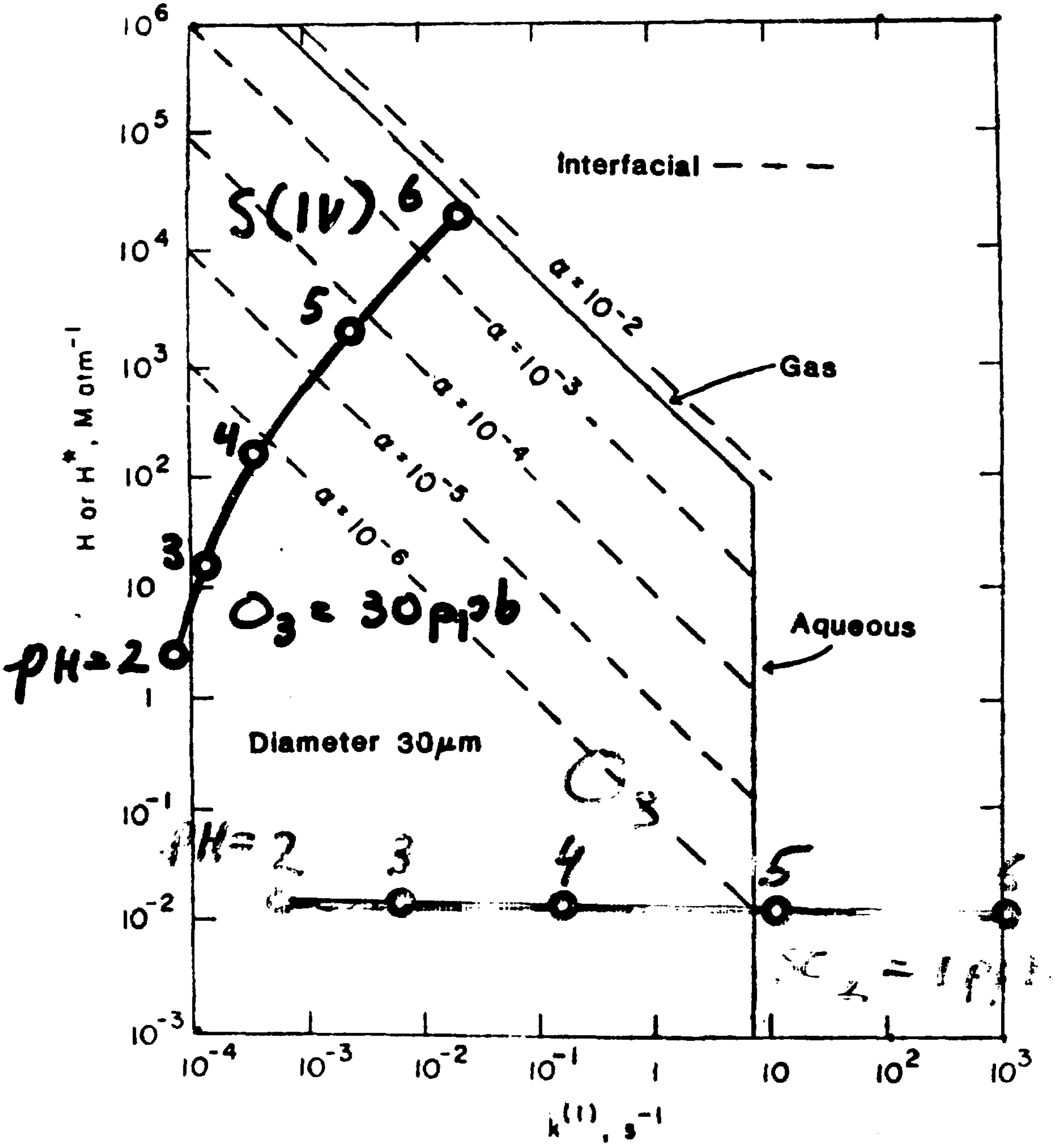


O_3-S(IV) Rate Coefficient


H_2O_2-S(IV) Rate Coefficient
$\frac{d[S(VI)]}{dt} = k^{(2)}[H_2O_2][S(IV)]$
25°C
$k^{(2)}$, $M^{-1}s^{-1}$
10^6
10^5
10^4
10^3
10^2
10^1
1
2
3
4
5
6
pH

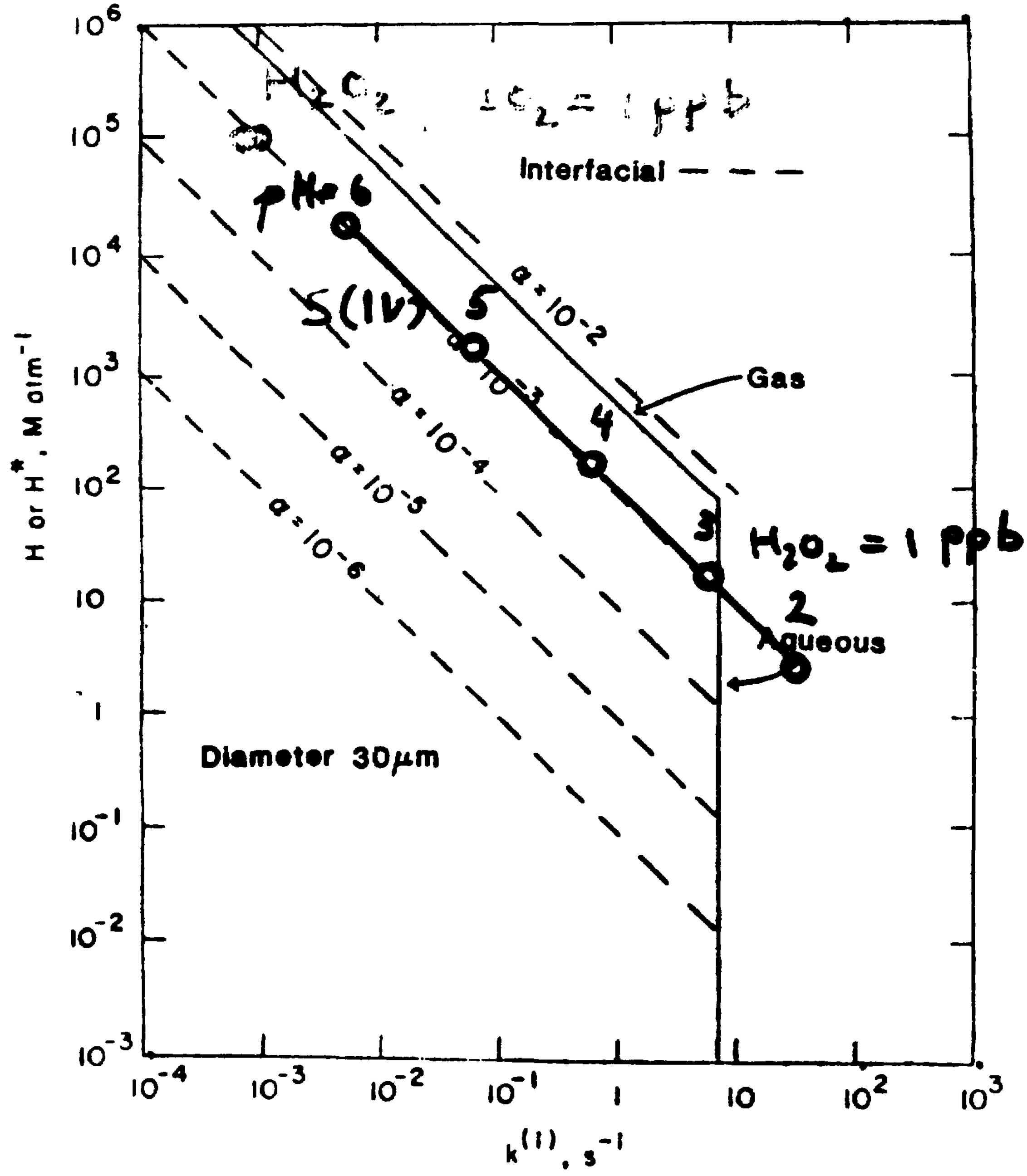
O_3 - S(IV) REACTION (25°C)

CRITERIA FOR ABSENCE OF MASS-TRANSPORT LIMITATION



H_2O_2 - S(IV) REACTION (25 °C)

CRITERIA FOR ABSENCE OF MASS-TRANSPORT LIMITATION

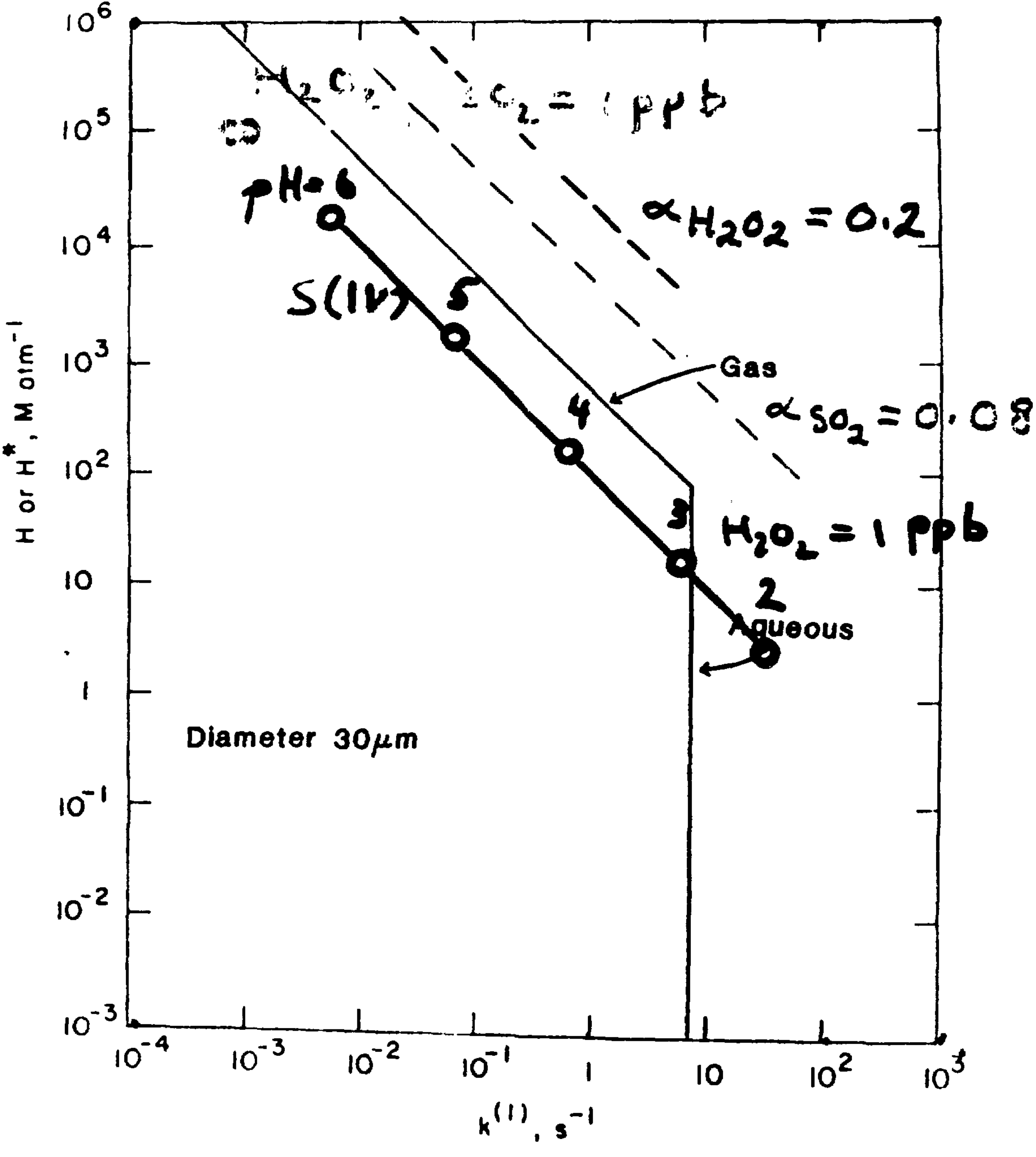


MASS ACCOMMODATION COEFFICIENT MEASUREMENTS AT AIR-WATER INTERFACE

SO_2	$\geq$	0.002	Tang and Lee (1986)
	$\geq$	0.08	Gardner et al. (1987a)
	$=$	0.11 ± 0.02	Worsnop et al. (1988)
H_2O_2	$\geq$	0.2	Gardner et al. (1987b)
	$=$	$0.12 - 0.30$ (293 - 263K)	Worsnop et al. (1988)
O_3	$=$	5×10^{-4}	Tang and Lee (1986)

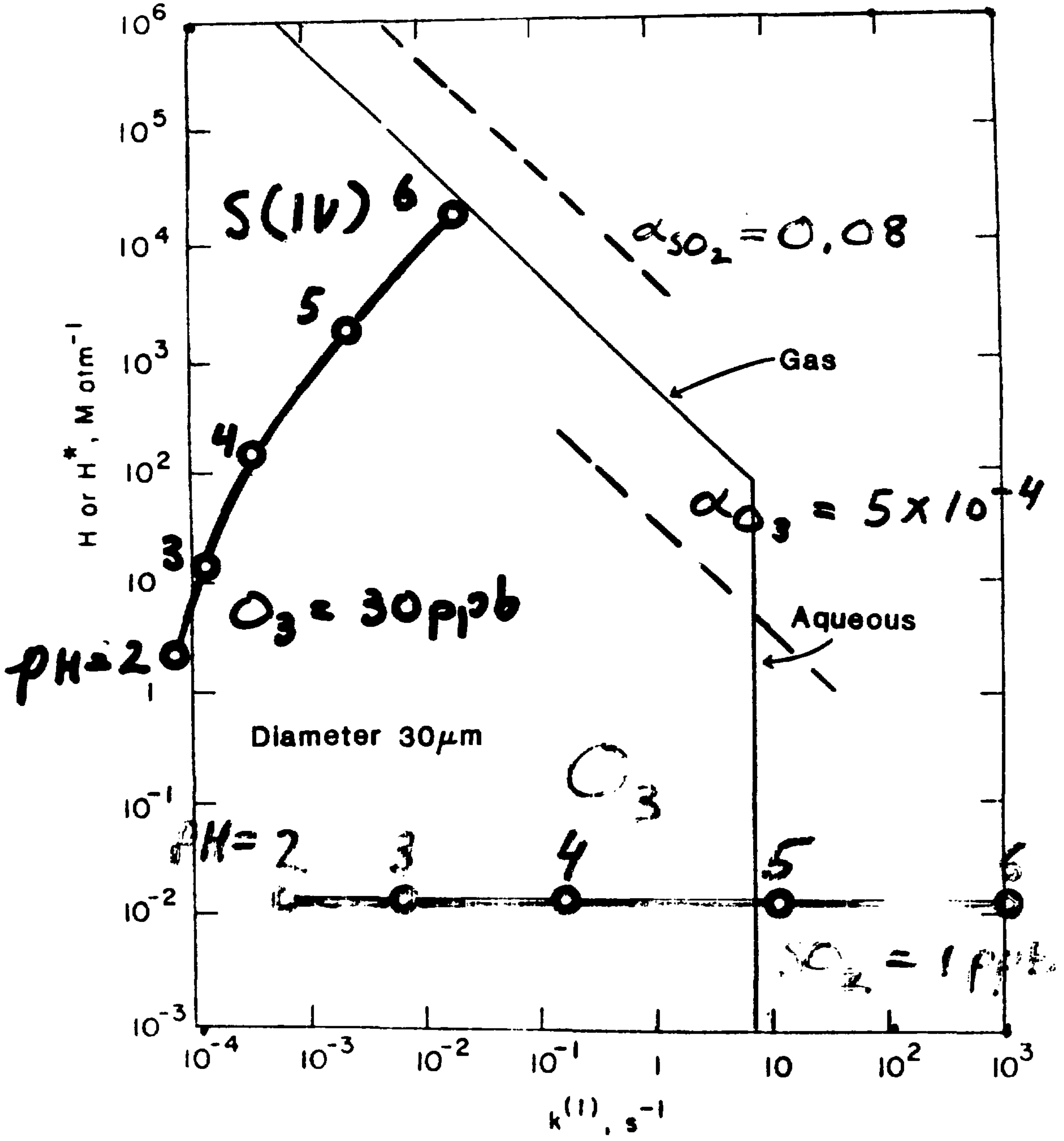
H_2O_2 - S(IV) REACTION (25 °C)

CRITERIA FOR ABSENCE OF MASS-TRANSPORT LIMITATION



O_3 - S(IV) REACTION (25°C)

CRITERIA FOR ABSENCE OF MASS-TRANSPORT LIMITATION



RESULTS OF MASS-TRANSFER EXAMINATION FOR SO_2 OXIDATION IN CLOUDS

- The high values of α for SO_2 (≥ 0.08) and H_2O_2 (≥ 0.2) indicate that interfacial MT is less restrictive than diffusive, and thus not limiting.

- Despite the low value of α for O_3 (5×10^{-4}), interfacial MT is not limiting for most situations of interest.

- Gas- and aqueous-phase diffusive MT is also not limiting for most situations of interest.

- Reaction rates in cloud droplets may be evaluated to good approximation by treating cloud droplets as saturated in the reagent gases.

UPTAKE AND REACTION OF N_2O_5 IN DAYTIME CLOUDS

$$NO_2 + O_3 \rightarrow NO_3 \qquad (1)$$

$$NO_3 + NO_2 \rightleftharpoons N_2O_5 \qquad (2)$$

$$NO_3 \xrightarrow{h\nu} NO_2 + O;\ NO + O_2 \qquad (3)$$

$$NO_3 + NO \rightarrow 2NO_2 \qquad (4)$$

$$N_2O_5 + \text{c.w.} \rightarrow 2H^+ + 2NO_3^- \qquad (5)$$

- What is yield of (5), per occurrence of (1), in competition with (3) and (4)?

- For 30 ppb O_3, 100% yield implies NO_2 oxidation rate of 8% hr^{-1} (298K), 17% hr^{-1} (273K).

- Compare OH + NO_2, ~5% hr^{-1} for $[OH] = 1 \times 10^6$ cm^{-3}

RATE AND YIELD OF REACTION

$$\boxed{\begin{array}{ll}
NO_2 + O_3 \rightarrow NO_3 & (1) \\
NO_3 + NO_2 \rightleftharpoons N_2O_5 & (2) \\
NO_3 \xrightarrow{h\nu} NO_2 + O;\ NO + O_2 & (3) \\
NO_3 + NO \rightarrow 2NO_2 & (4) \\
N_2O_5 + \text{c.w.} \rightarrow 2H^+ + 2NO_3^- & (5)
\end{array}}$$

$$R_5 = R_1 Y$$

$$R_1 = k_1[NO_2][O_3]$$

$$Y = \frac{k_2k_5[NO_2]}{k_{-2}k_3 + k_{-2}k_4[NO] + k_3k_5 + k_4k_5[NO] + k_2k_5[NO_2]}$$

$$k_5 = \int dL \frac{1}{\dfrac{a^2}{3D_g} + \dfrac{4a}{3\bar{v}\alpha} + \dfrac{1}{H\underset{\sim}{R}T\, k^{(l)}\, Q(a)}}$$

MOZURKEWICH - CALVERT
EXPERIMENT

- Flow tube.
- N_2O_5 + aqueous NH_4HSO_4 aerosol.
- Drop radius 0.05 - 0.12 µm, monodisperse.
- Variable relative humidity.
- N_2O_5 loss rate:

$$\frac{d[N_2O_5]}{dt} = -[N_2O_5]\left(\frac{\bar{v}\gamma}{4}\right)A$$

A: Specific surface area, cm^2/cm^3

γ: Reaction probability per collision

- For RH = 55 - 76%

$\gamma = 0.09 \pm 0.015$, T = 274K

$\gamma = 0.045 \pm 0.015$, T = 294K

INTERPRETATION OF MEASUREMENTS

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{H\underset{\sim}{R}T\left(\frac{4a}{3\bar{v}}\right)kQ}$$

Implies

$$\gamma \leq H\underset{\sim}{R}T\left(\frac{4a}{3\bar{v}}\right)k \qquad \text{(volume)}$$

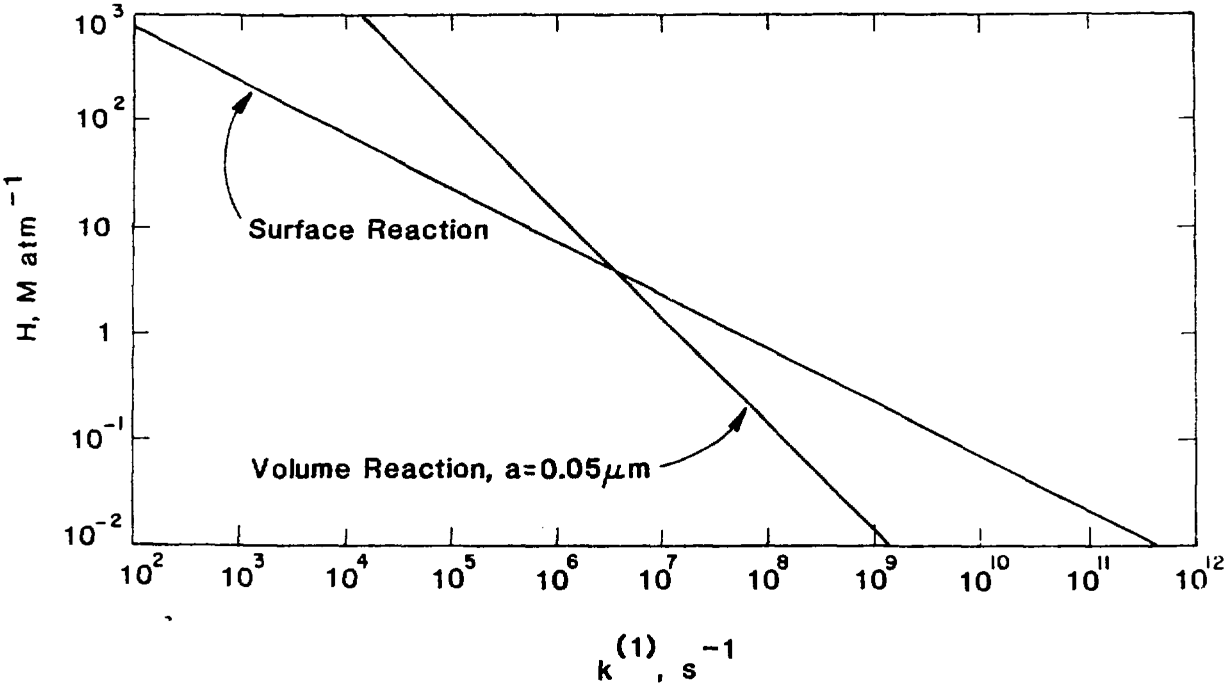
$$\gamma \leq H\underset{\sim}{R}T\frac{4}{\bar{v}}(k\ D_{aq})^{1/2} \qquad \text{(surface)}$$

whence

$$Hk \geq \frac{3\bar{v}}{4\underset{\sim}{R}Ta}\gamma \qquad \text{(volume)}$$

$$Hk^{1/2} \geq \frac{\bar{v}}{4\underset{\sim}{R}TD_{aq}^{1/2}}\gamma \qquad \text{(surface)}$$

LOWER BOUNDS FOR GAS-AQUEOUS REACTION OF N_2O_5

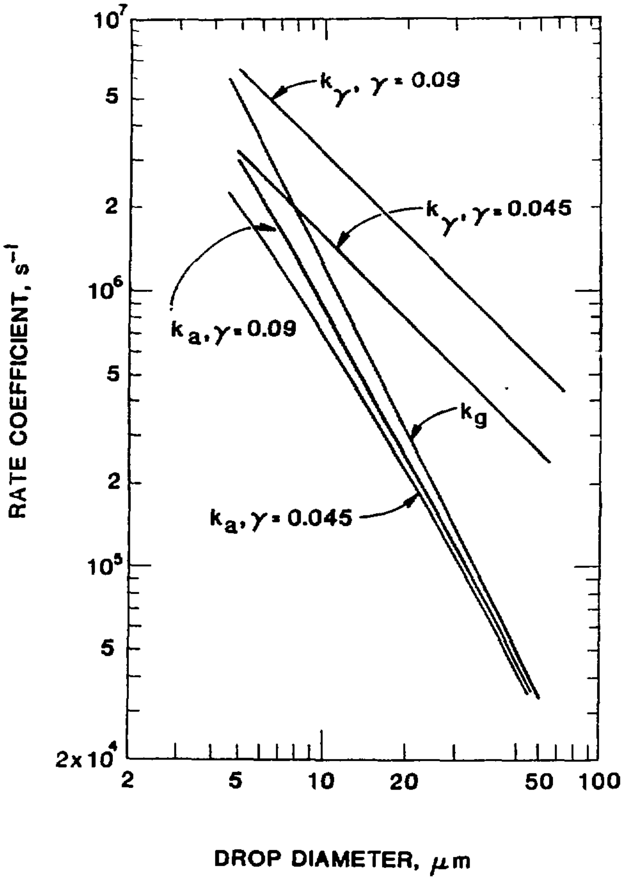


IN-CLOUD REACTION RATE

$$k_5 = \int dL\ k_a$$

$$k_a = \frac{1}{\frac{a^2}{3D_g} + \frac{4a}{3\bar{v}\gamma}}$$

GAS-AQUEOUS RATE COEFFICIENTS FOR N_2O_5



CONDITIONS

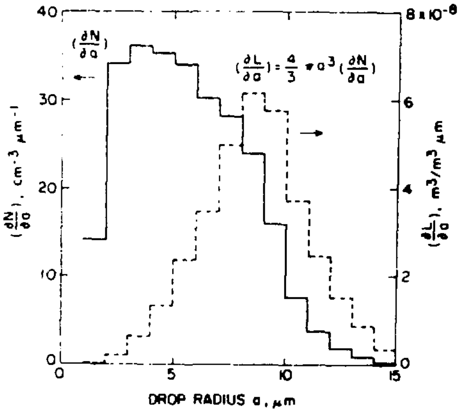
$p_{NO} = 0.2$ ppb

$p_{NO_2} = 0.8$ ppb

$p_{O_3} = 30$ ppb

$j_{NO_3} = 0.1\ s^{-1}$
(half Z = 0 rate)

RESULTS

a	k_a, s^{-1}	LWC, 10^{-6}	k_5, s^{-1}	Yield
5 μm	8×10^5	0.5	0.4	8%
10 μm	2×10^5	0.5	0.1	6%
		0.34	0.15	6%

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 89, NO. D7, PAGES 11,589-11,598, DECEMBER 20, 1984

Gas- and Aqueous-Phase Chemistry of HO_2 in Liquid Water Clouds

STEPHEN E. SCHWARTZ

$$O_3 \xrightarrow{h\nu} O(^1D)$$

$$O(^1D) \longrightarrow O(^3P)$$

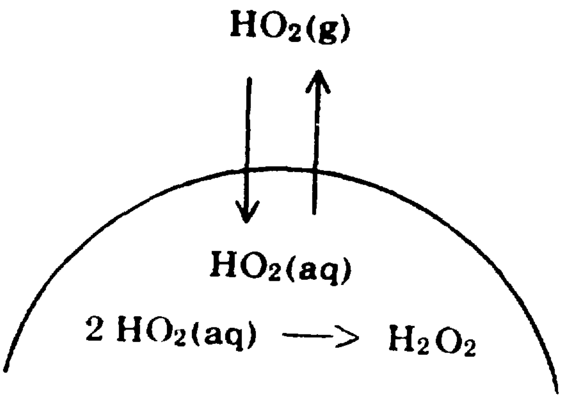
$$O(^1D) + H_2O \longrightarrow 2\,OH$$

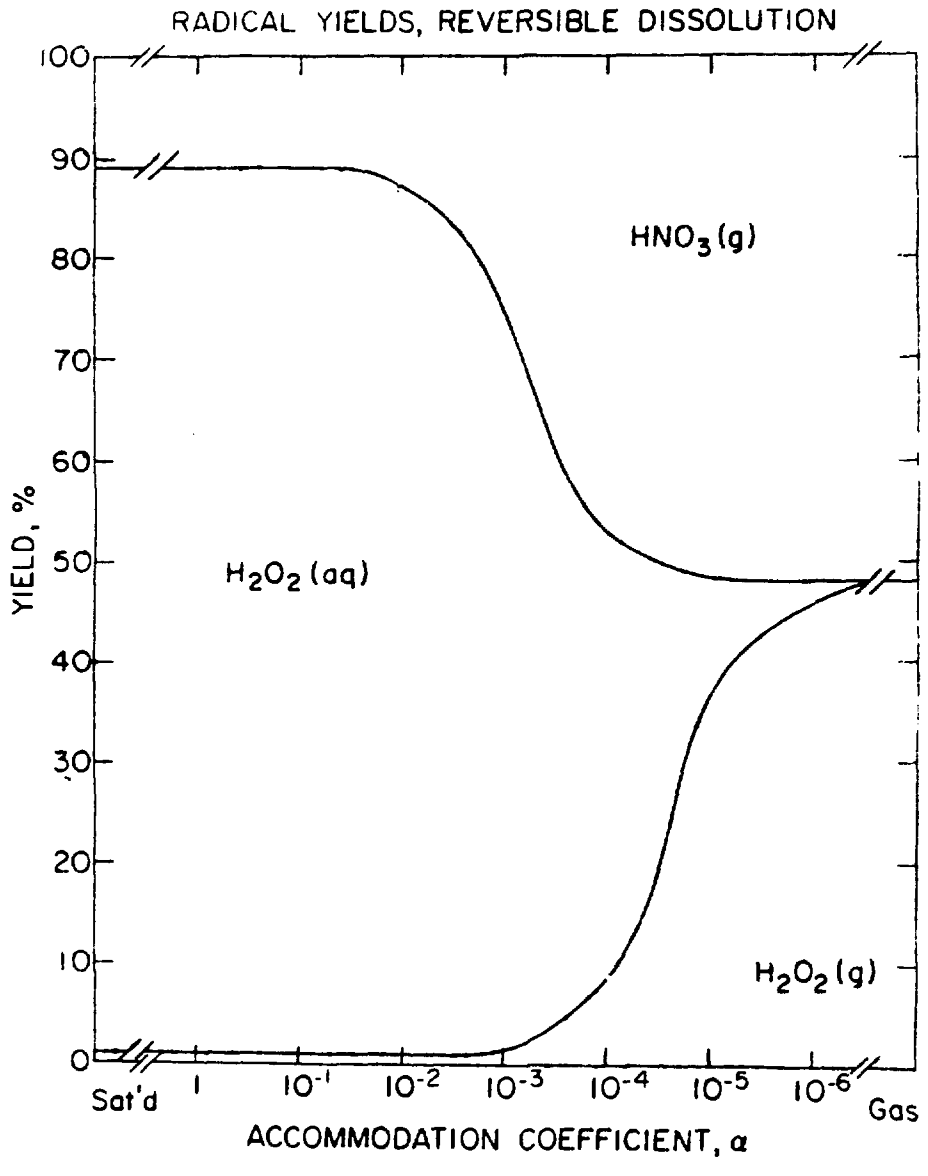
$$OH \longrightarrow \cdots HO_2$$

$$HO_2 \longrightarrow \cdots OH$$

$$OH + NO_2 \longrightarrow HNO_3$$

$$2\,HO_2 \longrightarrow H_2O_2 + O_2$$




RADICAL YIELDS, REVERSIBLE DISSOLUTION
YIELD, %
100
90
80
70
60
50
40
30
20
10
0
HNO_3(g)
H_2O_2(aq)
H_2O_2(g)
Sat'd
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
Gas
ACCOMMODATION COEFFICIENT, α

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 92, NO. D4, PAGES 4163–4170, APRIL 20, 1987

Mass Accommodation Coefficient for HO_2 Radicals on Aqueous Particles

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National Center for Atmospheric Research, Boulder, Colorado

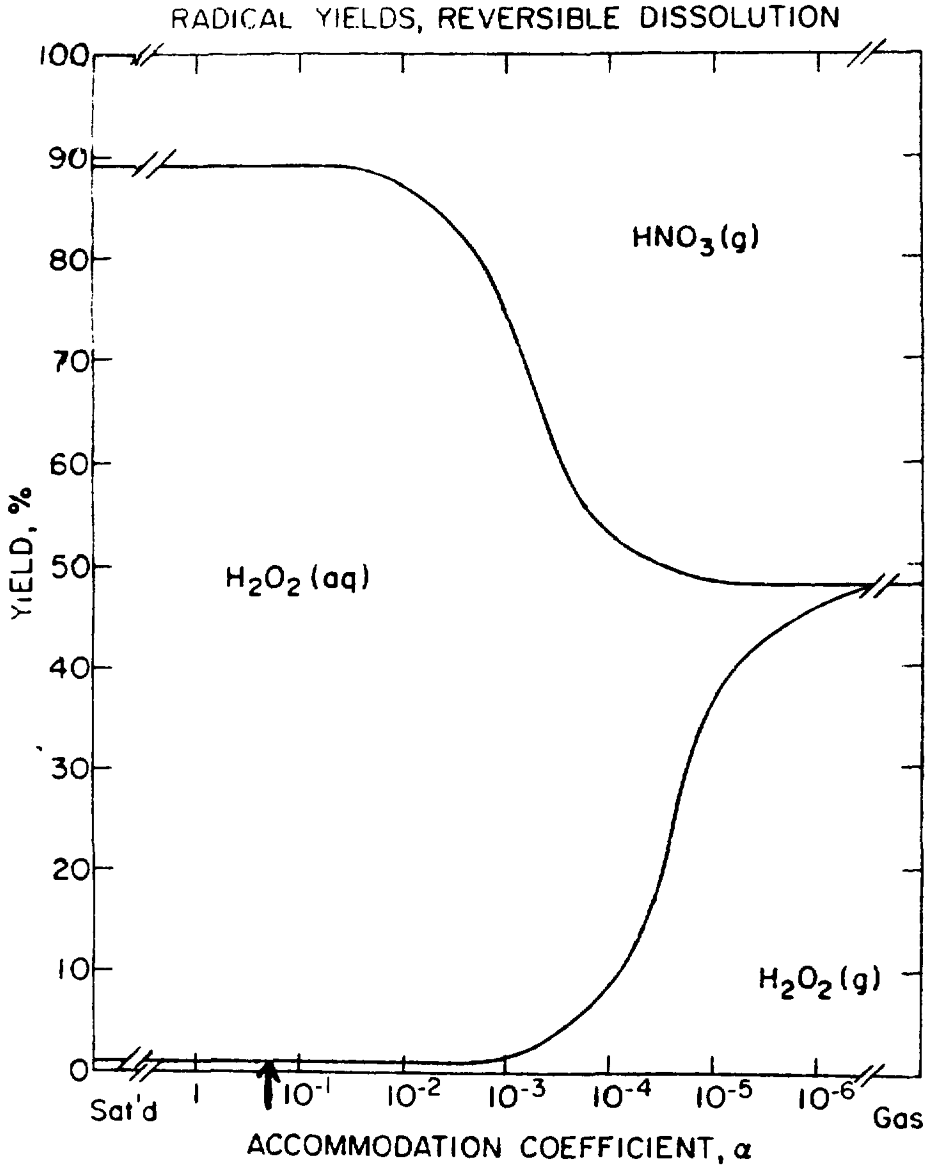
PETER H. MCMURRY AND ANAND GUPTA

Department of Mechanical Engineering, University of Minnesota, Minneapolis

JACK G. CALVERT

National Center for Atmospheric Research, Boulder, Colorado

The mass accommodation coefficient for HO_2 on aqueous particles was determined to be greater than 0.2.


RADICAL YIELDS, REVERSIBLE DISSOLUTION
YIELD, %
100
90
80
70
60
50
40
30
20
10
0
Sat'd
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
Gas
ACCOMMODATION COEFFICIENT, α
$HNO_3(g)$
$H_2O_2(aq)$
$H_2O_2(g)$

CONCLUSIONS

- Formalism is available to describe coupled mass-transport and chemical reaction in clouds.

- SO_2 oxidation by H_2O_2 and O_3 in clouds, for most situations, is controlled by aqueous reaction kinetics, not mass transport, including interfacial mass transport.

- Uptake of N_2O_5 by cloudwater is controlled largely by gas-phase mass transport, which is marginally competitive with other daytime sinks of NO_3.

- H_2O_2 formation by HO_2 disproportionation in cloudwater is not hindered by mass transport.