The Problem of Water in Vacuum Systems

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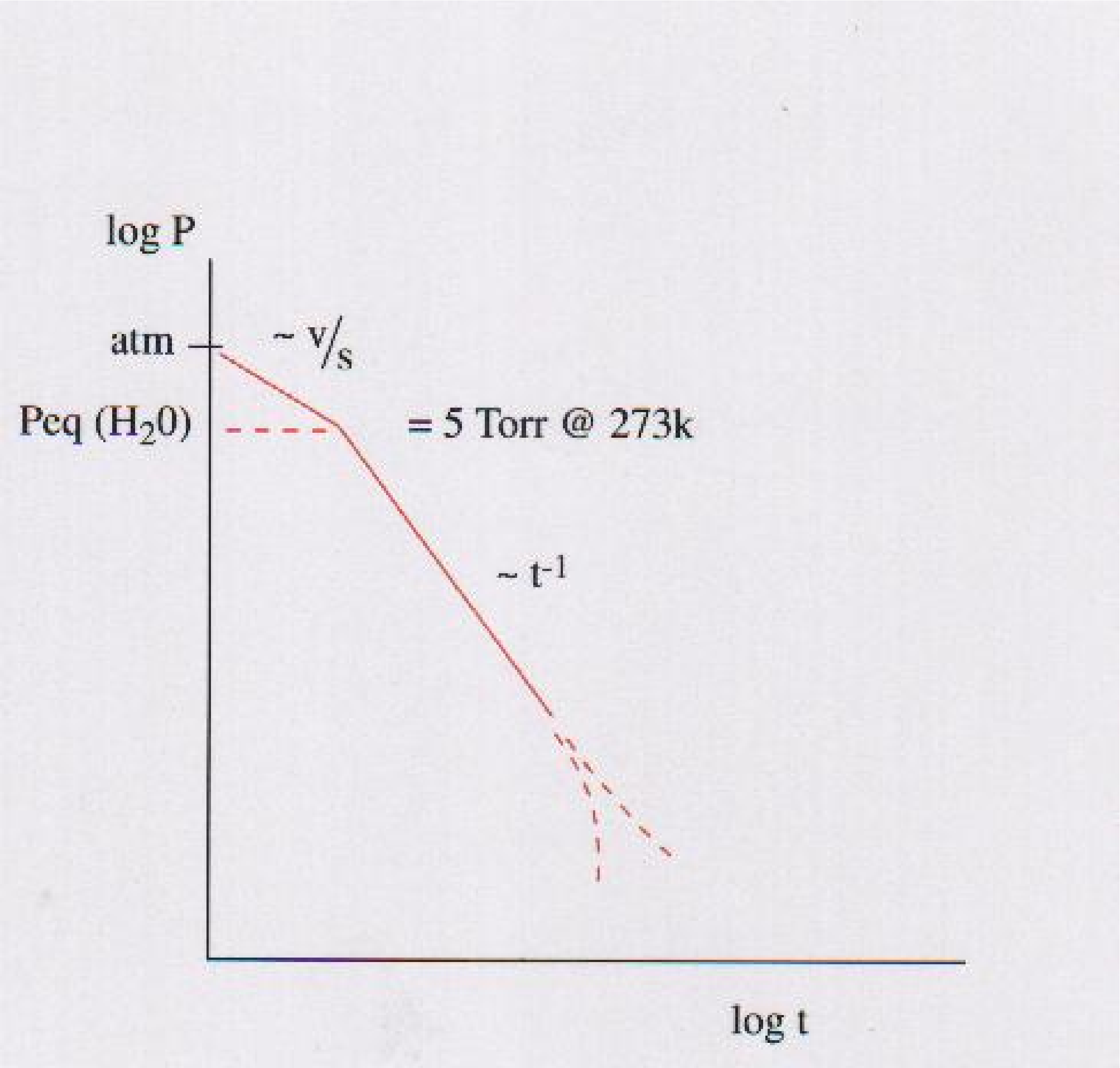
Introduction: H_20 in Vacuum

- From 5 Torr to the UHV boundary
  - the interaction of water on (metal) surfaces is the dominant problem in vacuum systems
- For unbaked systems, the pumping of H_2O determines the pumping time constant

$$P = P_0 t^{-\alpha} \text{ , where } \alpha \cong -1$$

- For baked systems, H_2O removal, and H_2O mediated C removal, dominate the gas removal
- For UHV/XHV system, H_2O interactions are still important
  - residual H,O from previously absorbed H_2O or oxide decomposition can account for the remaining residual gases (usually H_2, CH_4 and CO)

Outgassing Behavior of an Unbaked Vacuum System



Understand H_2O in Vacuum---Save $$

- With a better understanding of H_2O interactions on technical surfaces (mainly 300 series SS and 6000 series Al), e.g.
  - minimize H_2O adsorption (and re-adsorption) during gas exposure
  - minimize H_2O formation (from oxide decomposition)
  - maximize H_2O desorption and removal during pumping
- There would be significant time savings (i.e., COST SAVINGS) with the operation and maintenance of high performance vacuum systems:
  - turn-around time for large UHV systems used in science (ie, accelerators)
  - target changes in sputter source chambers in “cluster tools”
  - baking costs

H_2O /Surfaces: What have we studied?

- 50 years of outgassing measurements
  - predominately 300 series stainless steel (technical material of choice)
  - some data on Al, Cu, other UHV metals, various coatings (TiC, BN, etc.)
  - ceramics and glasses that have been qualified for vacuum use
- 35 years of surface science measurements
  - largely on model systems: single crystal metals (W, Mo, Fe, etc.)
- 40 years of theoretical studies
  - modeling of adsorption/desorption phenomena on both technical and model surfaces

H_2O on Stainless Steel

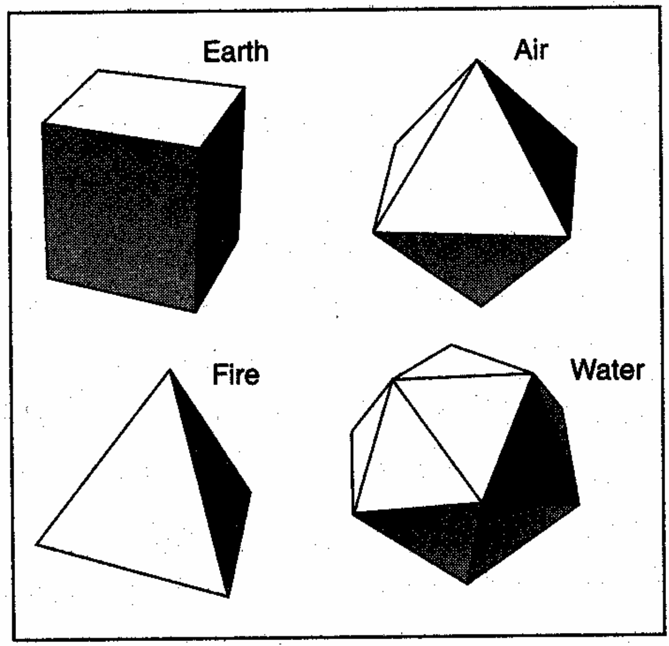
- Given the breadth of this subject, restrict the problem to a high priority subset that is relevant to the design, fabrication and operation of vacuum systems
  - the problem of H_2O adsorption/desorption from stainless steel
  - the practical, relatively inexpensive, widely used structural material for vacuum systems

Let’s analyze the problem in three parts:

- the H_2O molecule
- H_2O interacting with the surface
- H_2O interacting with bulk material

H_2O: from the Greeks to Kauzmann

- The first Physicists (Democritus et al) recognized the importance of H_2O
  - One of the Four Elements

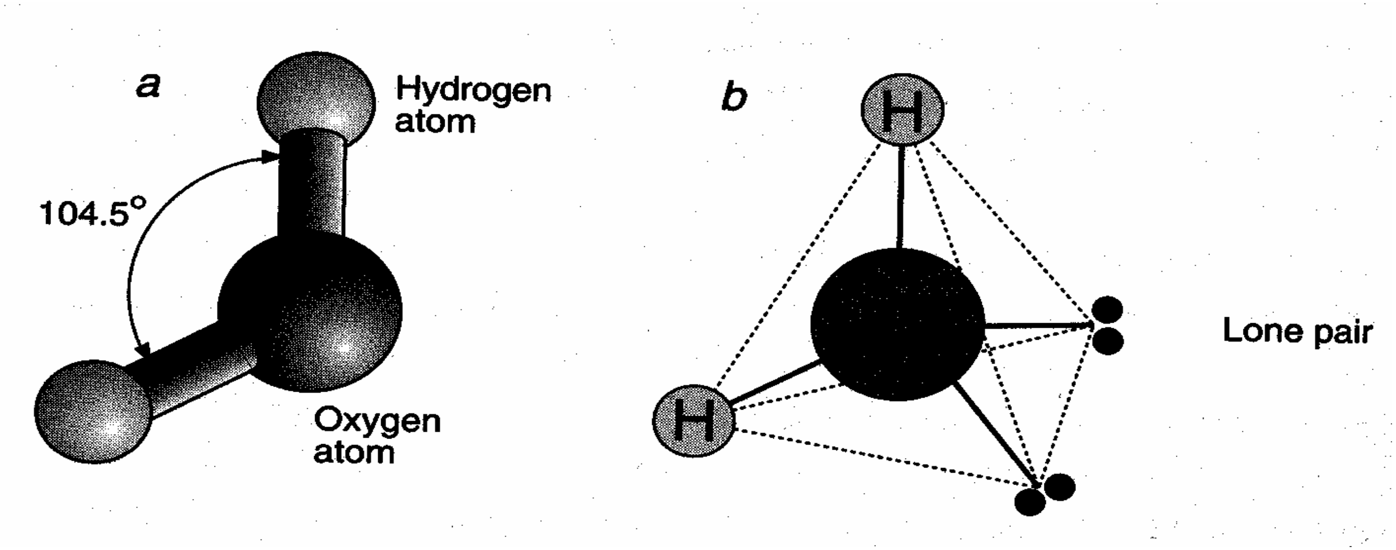


H_2O: from the Greeks to Kauzmann, cont.

The early Chemists Cavendish and Lavoisier (1783-84 identified the elemental composition of H_2O)

The modern physical-chemical view of H_2O (Kauzman et al.*)

- large dipole moment—polarizability→H-bonding
- unique solid and liquid structures
- universal solvent/structural component for chemistry/biology



*D. Eisenberg and W. Kauzmann, The Structue and Properties of Water (Oxford, 1969)

Water on Stainless Steel: Sources

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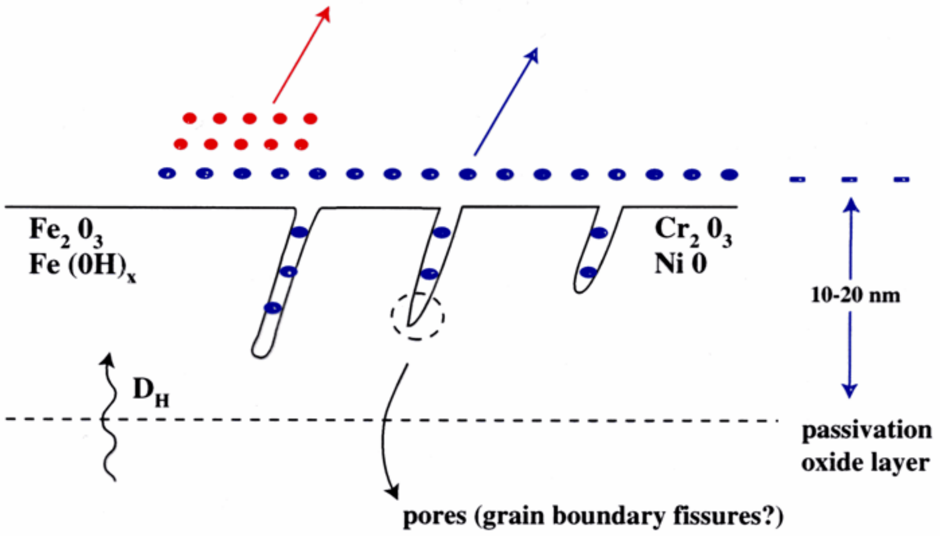
physisorbed H_2O

- multilayer
- weakly bound
- desorbs in vacuum easily



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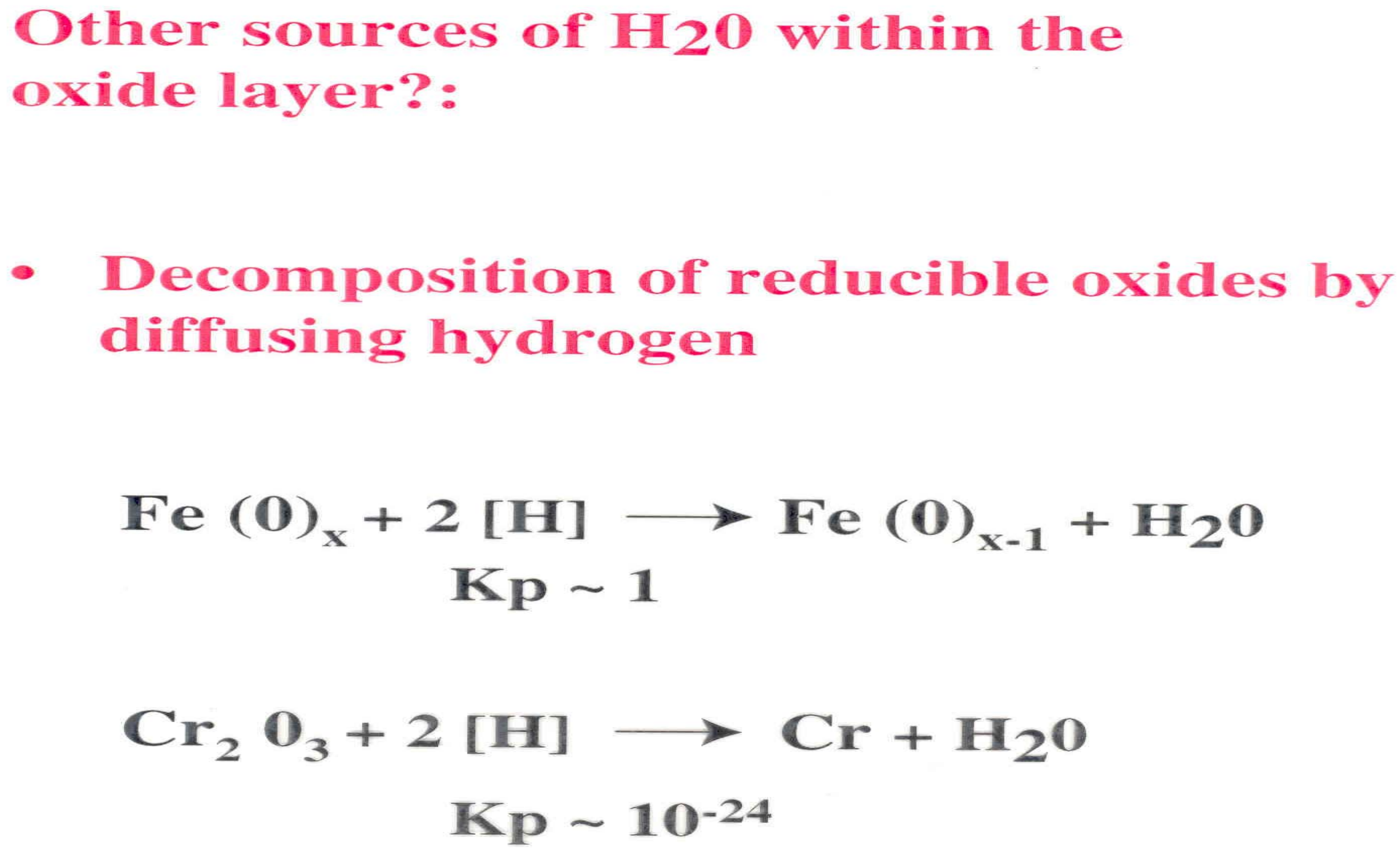
chemisorbed H_2O

- ≤ 1 monolayer on "accessible" surface
- > 5 monolayers compared to geometric surface
- Strongly bound (15-25 kcal/mole)
- Easily recharged by atmospheric exposure

Other sources of H_2O



Other sources of H_2O within the oxide layer?:

- **Decomposition of reducible oxides by diffusing hydrogen**

$$Fe\ (O)_x + 2\ [H] \longrightarrow Fe\ (O)_{x-1} + H_2O$$

$$Kp \sim 1$$

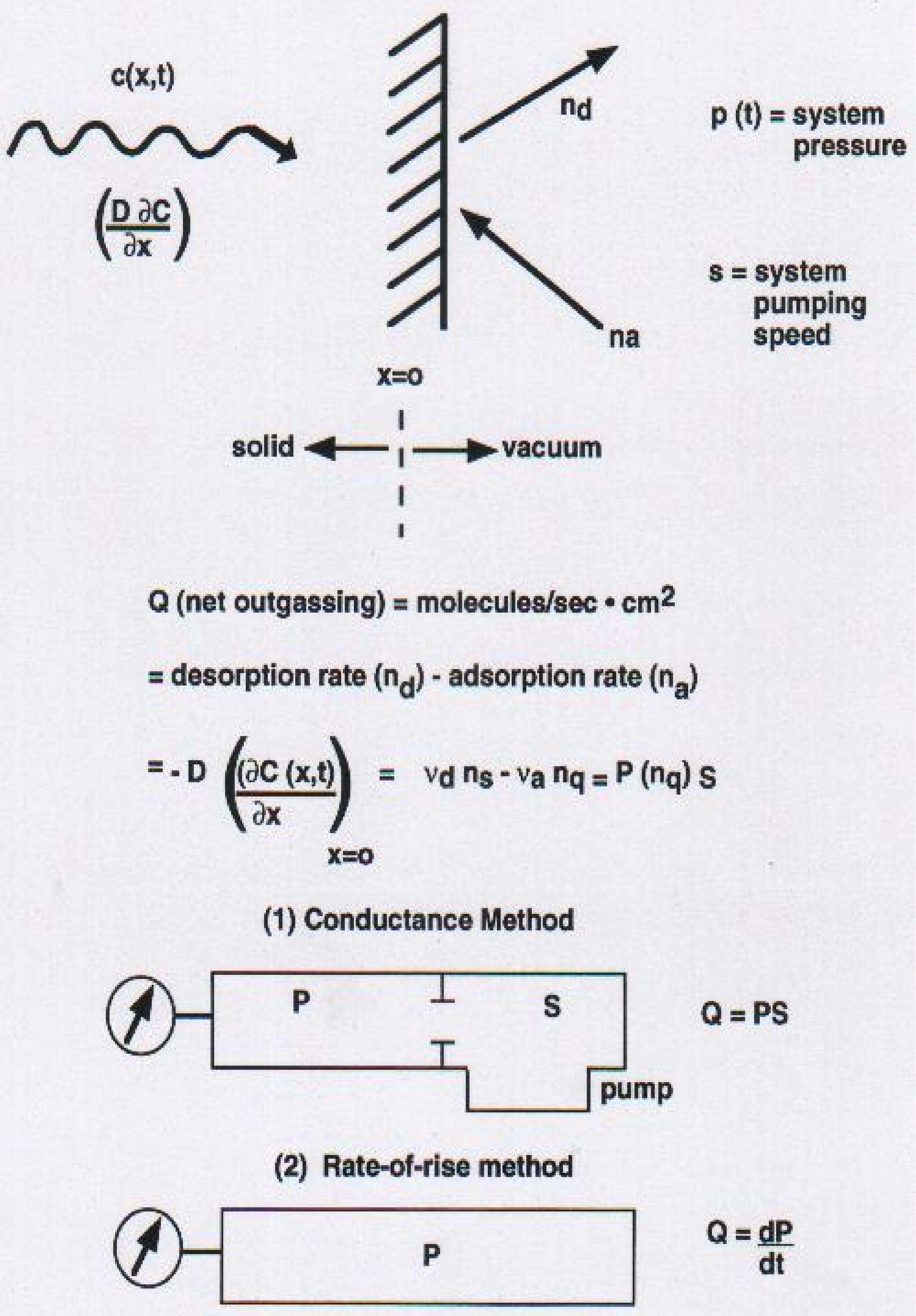
$$Cr_2\ O_3 + 2\ [H] \longrightarrow Cr + H_2O$$

$$Kp \sim 10^{-24}$$

H_2O/Stainless Steel Studies

- What is known about H_2O /SS adsorption/desorption phenomena?
  - large record of outgassing measurements from 300 series SS from which empirical relations and some fundamental kinetic data can be extracted
- Outgassing data generally fit $Q = Q_o\, t^{-\alpha}$
  - large variation in Q_o, α from the literature
- Comparisons of data difficult because:
  - different measurement techniques: throughput (S=finite) vs static(S=0)
  - poorly documented calibration techniques
  - ill defined starting conditions
  - poorly documented surface conditions

Outgassing Measurements



Q (net outgassing) = molecules/sec • cm^2

= desorption rate (n_d) - adsorption rate (n_a)

$$= - D \left(\frac{\partial C\,(x,t)}{\partial x}\right)_{x=o} = \nu_d\, n_s - \nu_a\, n_q = P\,(n_q)\, S$$

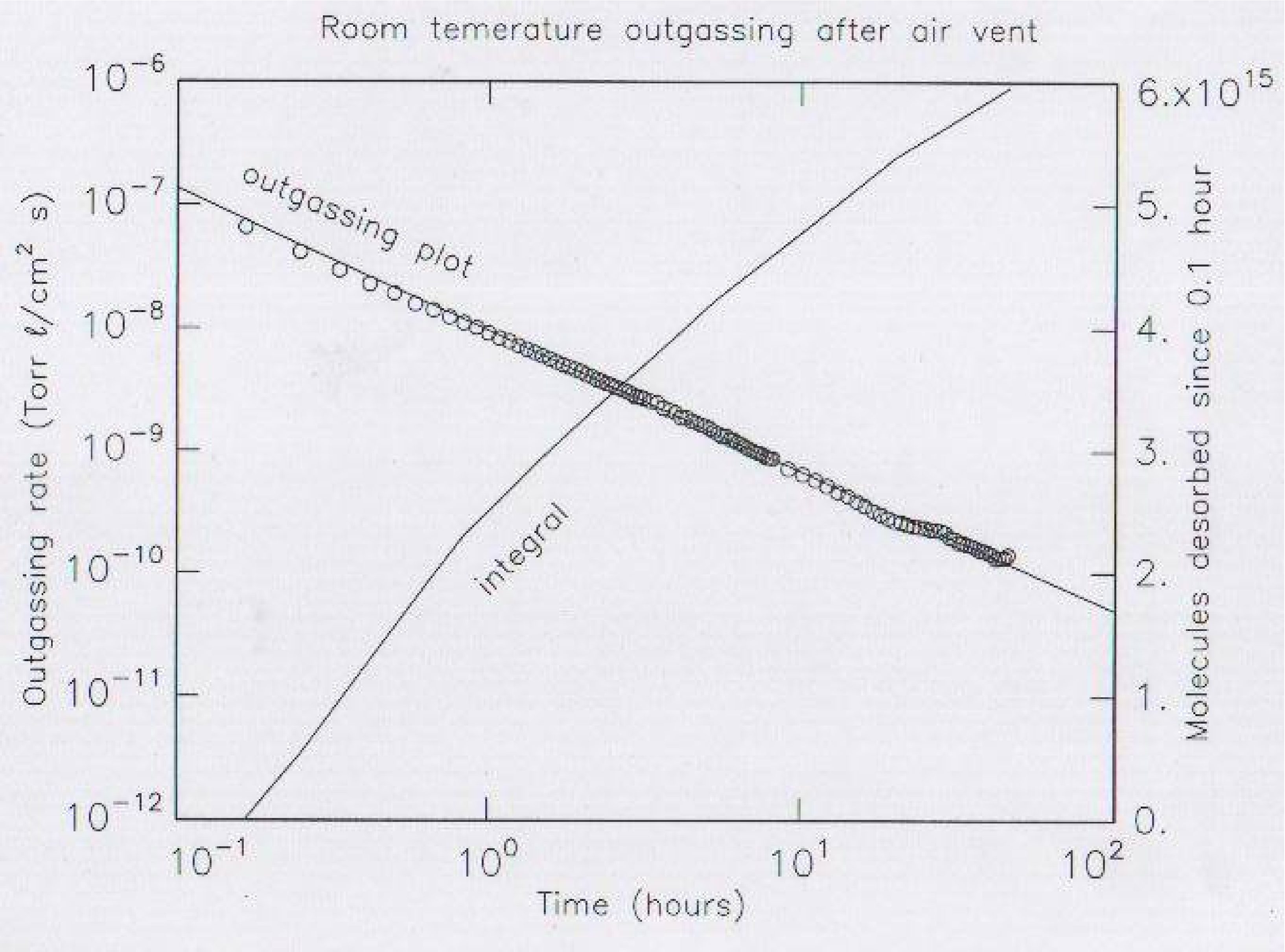
(1) Conductance Method

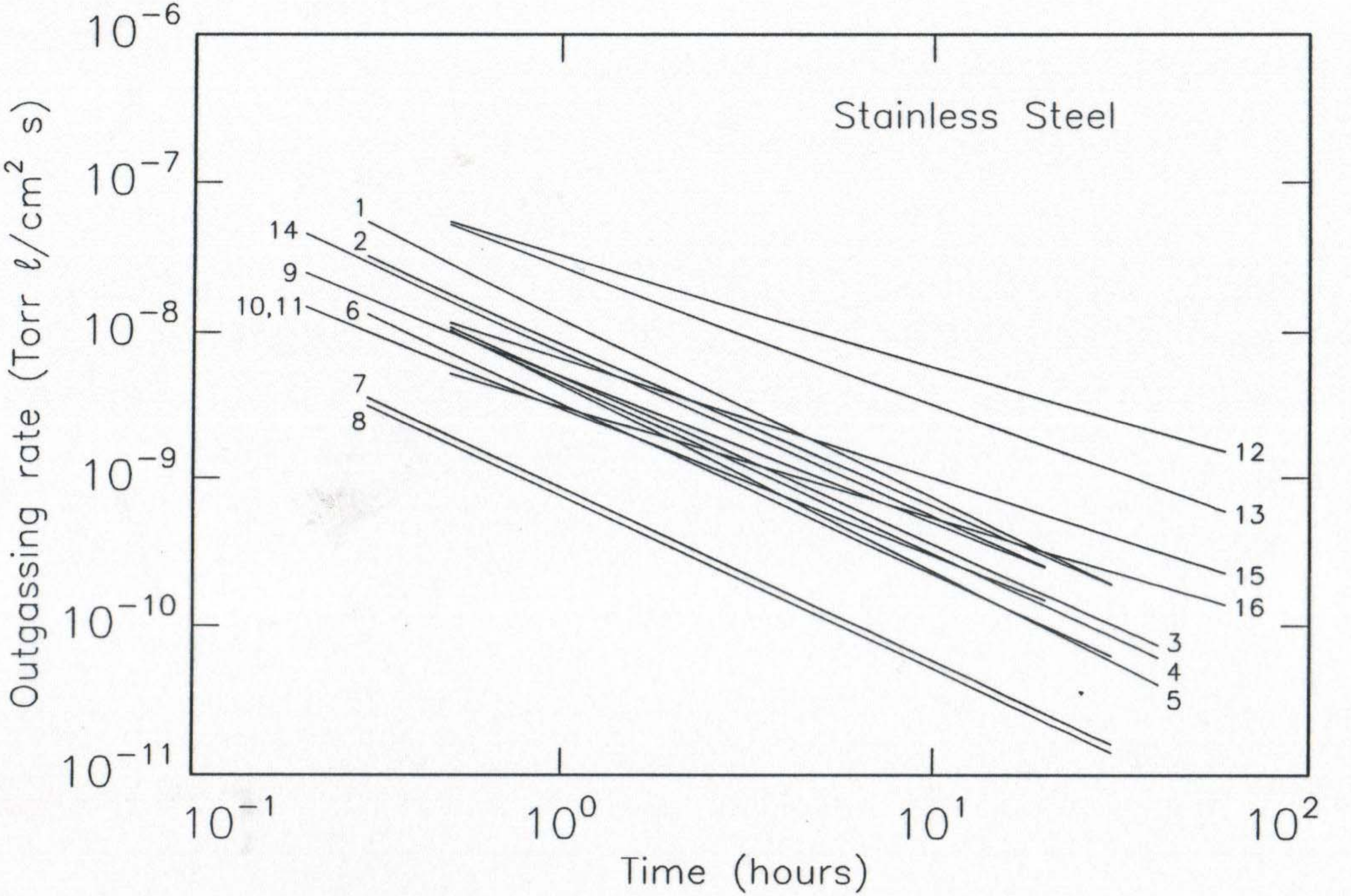
Q = PS

(2) Rate-of-rise method

$Q = \frac{dP}{dt}$

Typical Outgassing Data





1. Electropolish (Li and Dylla[1])

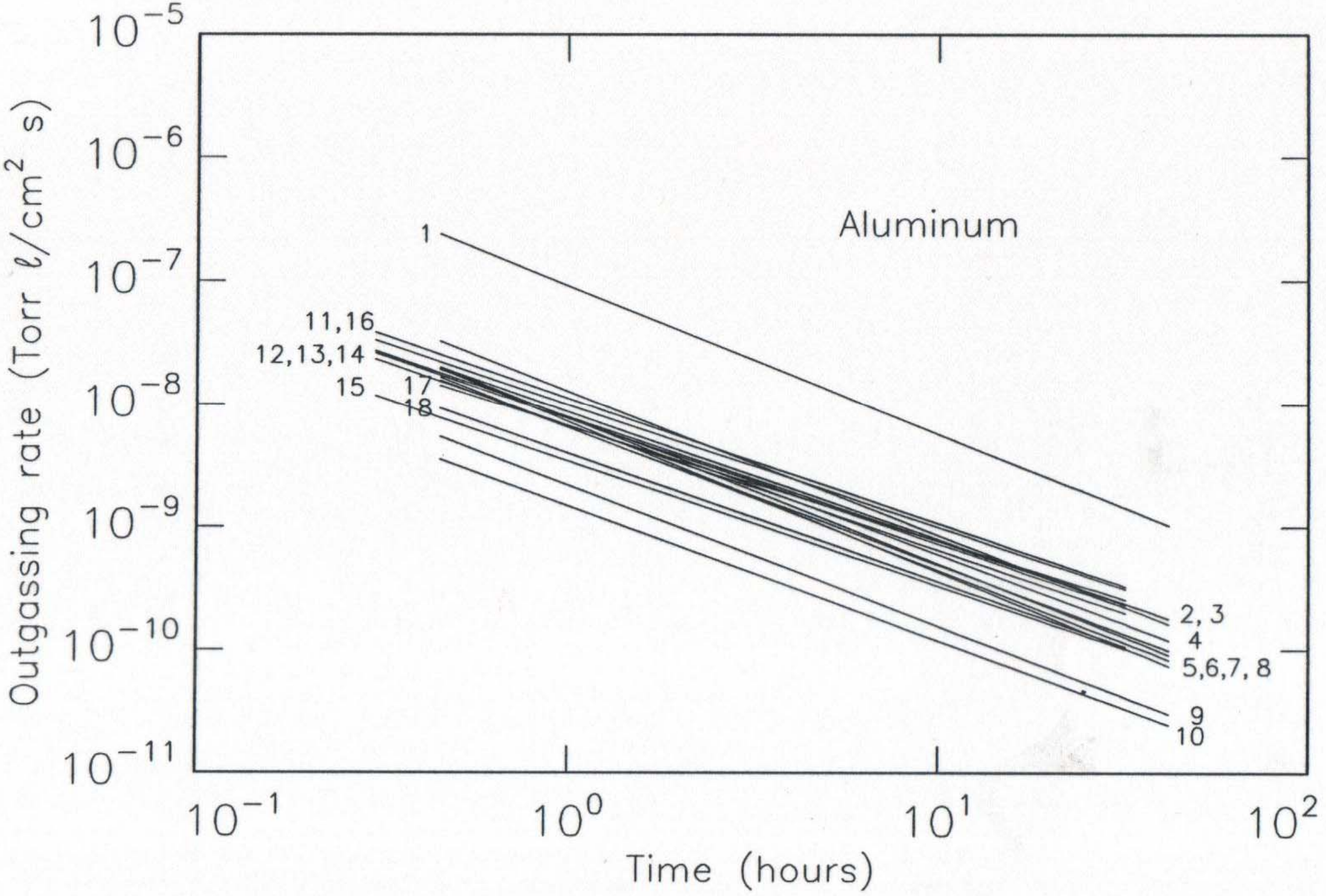
2. Electropolish; 3. Vac.Remelt/Detergent; 4. Mill Finish/Detergent; 5. Bake/Electropolish; 6. Compound Electropolish (Dylla et al[2])

7. SUS 304/Filled with H_2O for one day; 8. Normal air venting(Chen et al[3])

9. Electropolish (Edwards[4])

10. Literature average (Varian[5]); 11. Eletropolish (Barton & Govier[6])

12. Sulphidized; 13. Untreated; 14. Electropolished; 15. Treated with cord–brush 16. Cleaned Ultrasonically (Zilnin et al[7])

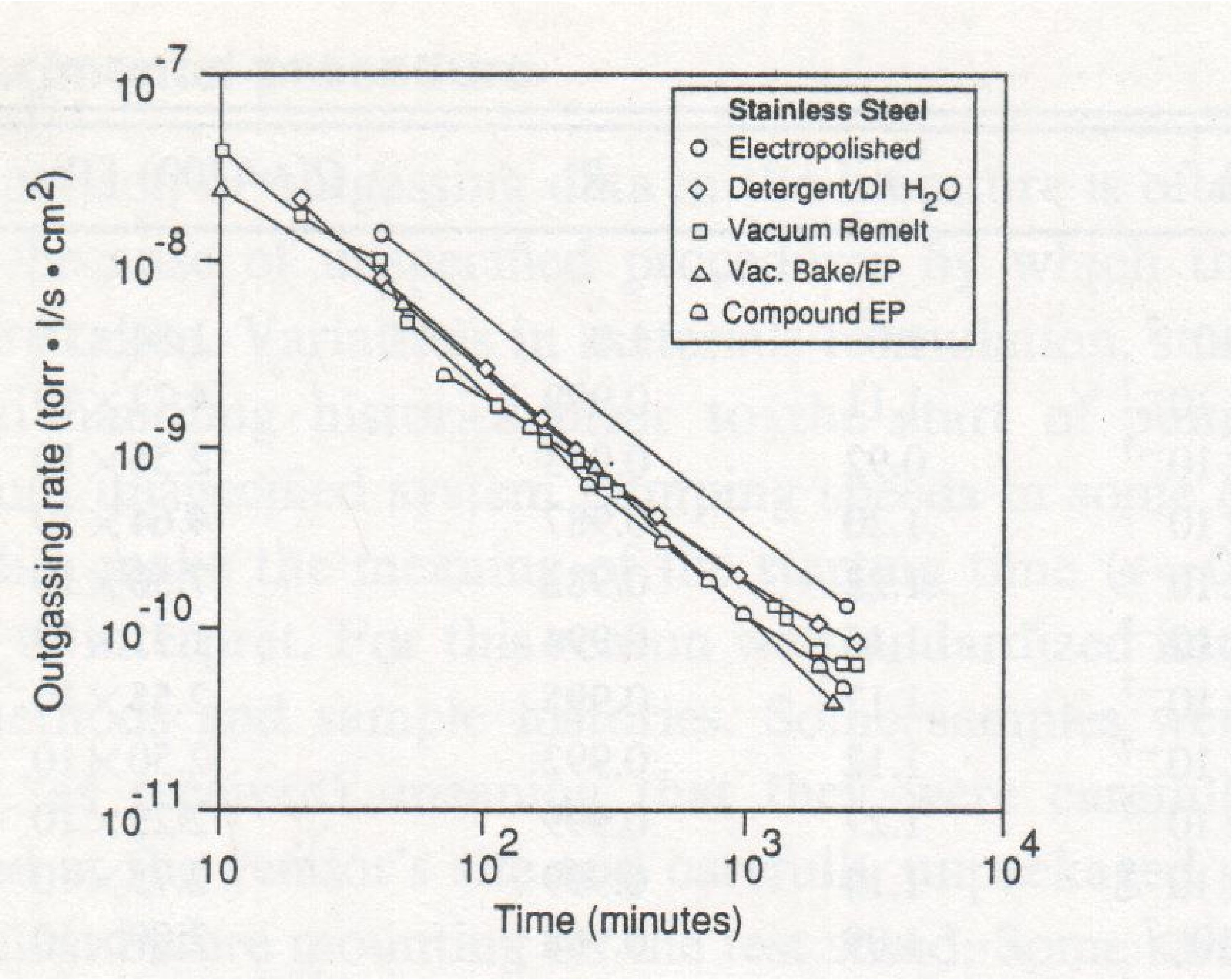


1. A6063−EX/H_2O, one week; 2. A6063−EX/H_2O, one day;
6. A6063−EX/Normal air; 7. A6063−EX/Air, one and half years;
9. A6063+1050 clading/Fresh;
10. A6063+1050 clading/Air, one day (Chen et al[3,8])
3. Innert Extrude(EX)/EBW; 4. Innert EXtrude(EX)/TIG;
5. Mirror Finish; 8. Mill Finish/Detergen (Dylla et al[2])
11. IPL−hs; 12. EL−hs; 13. EL−dia; 14. IPL−dia; 15. OMCP (Suemitsu et al[9])
16. Clean (Varian[5])
17. Untreated; 18. Extrusion, Chemically polished (Zilnin et al[7])

Outgassing vs. Surface Treatment

- A study in 1993 (Dylla, Manos and LaMarche, JVST, A11, 2623, 1993) tried to quantify outgassing vs. surface treatment

- Observed a factor of 4 variation in outgassing rate with 5 different surface treatments with surface roughness factor varying a factor of 100
  - Electropolish
  - Vacuum remelt
  - Vacuum bake/EP
  - Compound EP

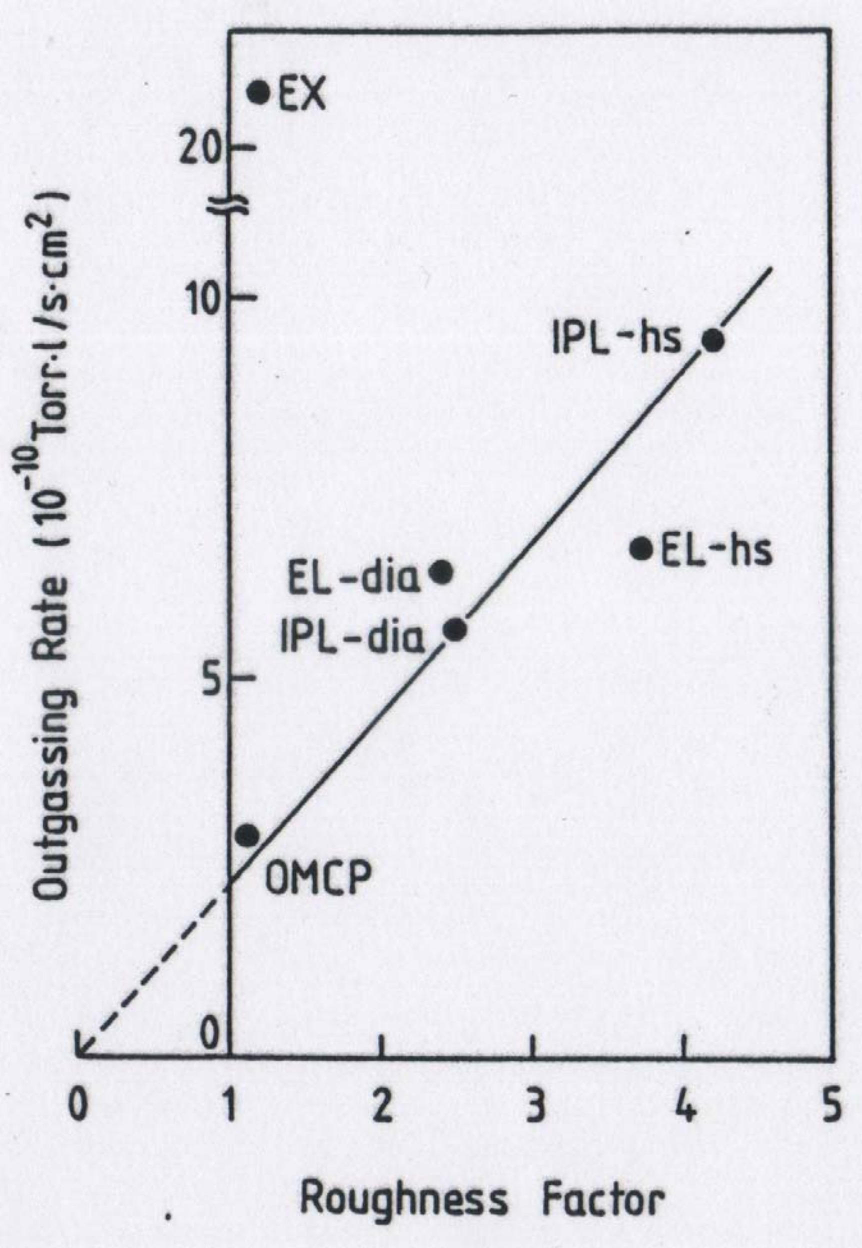


Outgassing results for the stainless steel surface treatments

Outgassing vs. surface roughness

- Uncontrolled variables were surface roughness and water content of initial atmospheric exposure

- Suemitsu et al (JVSTA 10, 570 1992) showed that for well defined oxides on Al, the outgassing rate scaled with surface roughness



Outgassing rate after 10 h of evacuation vs. roughness factor defined by Eq. (1).

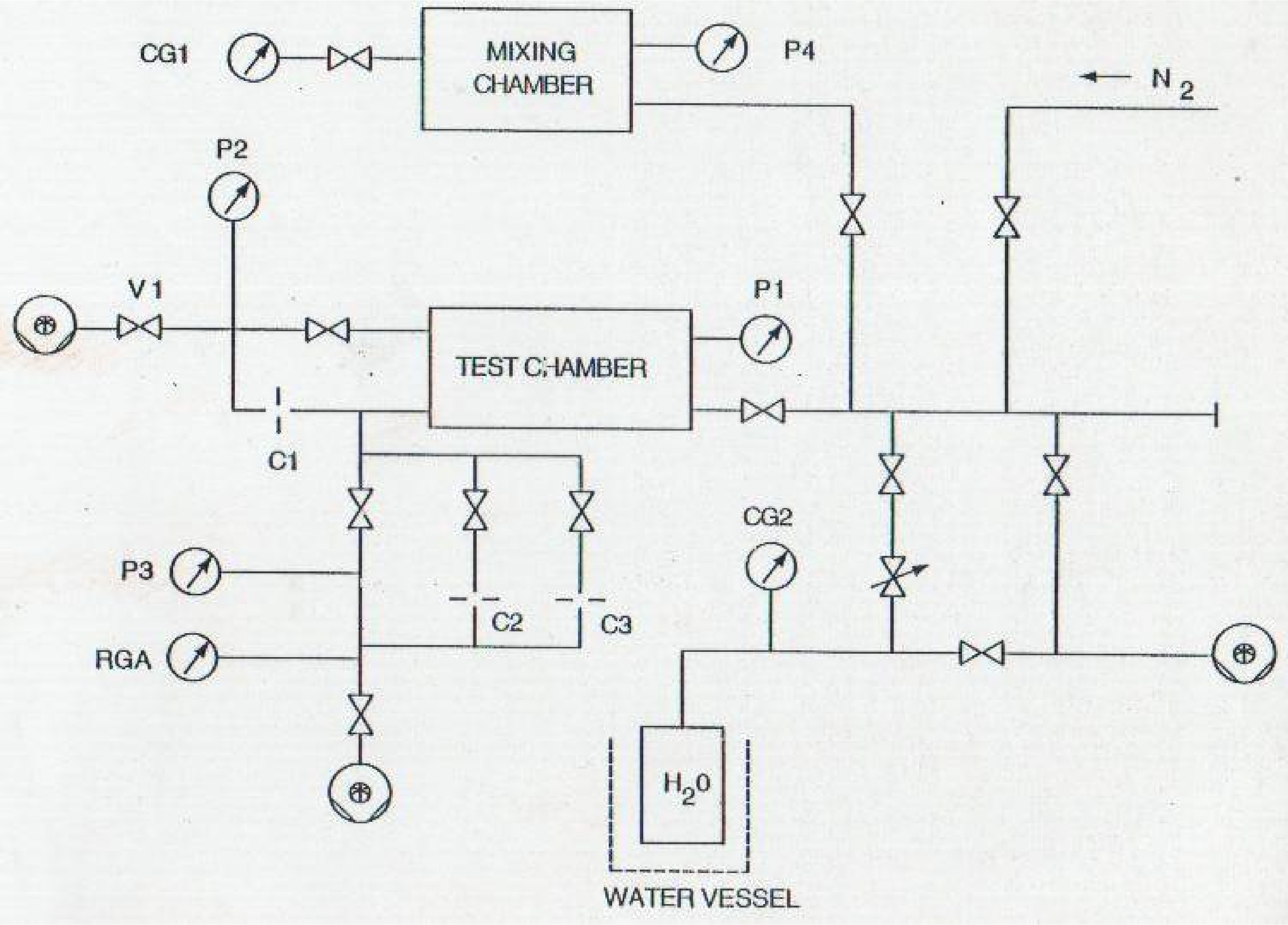
Outgassing vs. H_2O exposure

- With carefully controlled exposures to H_20 of previously degassed stainless steel surfaces, the empircal data set became reproducible:

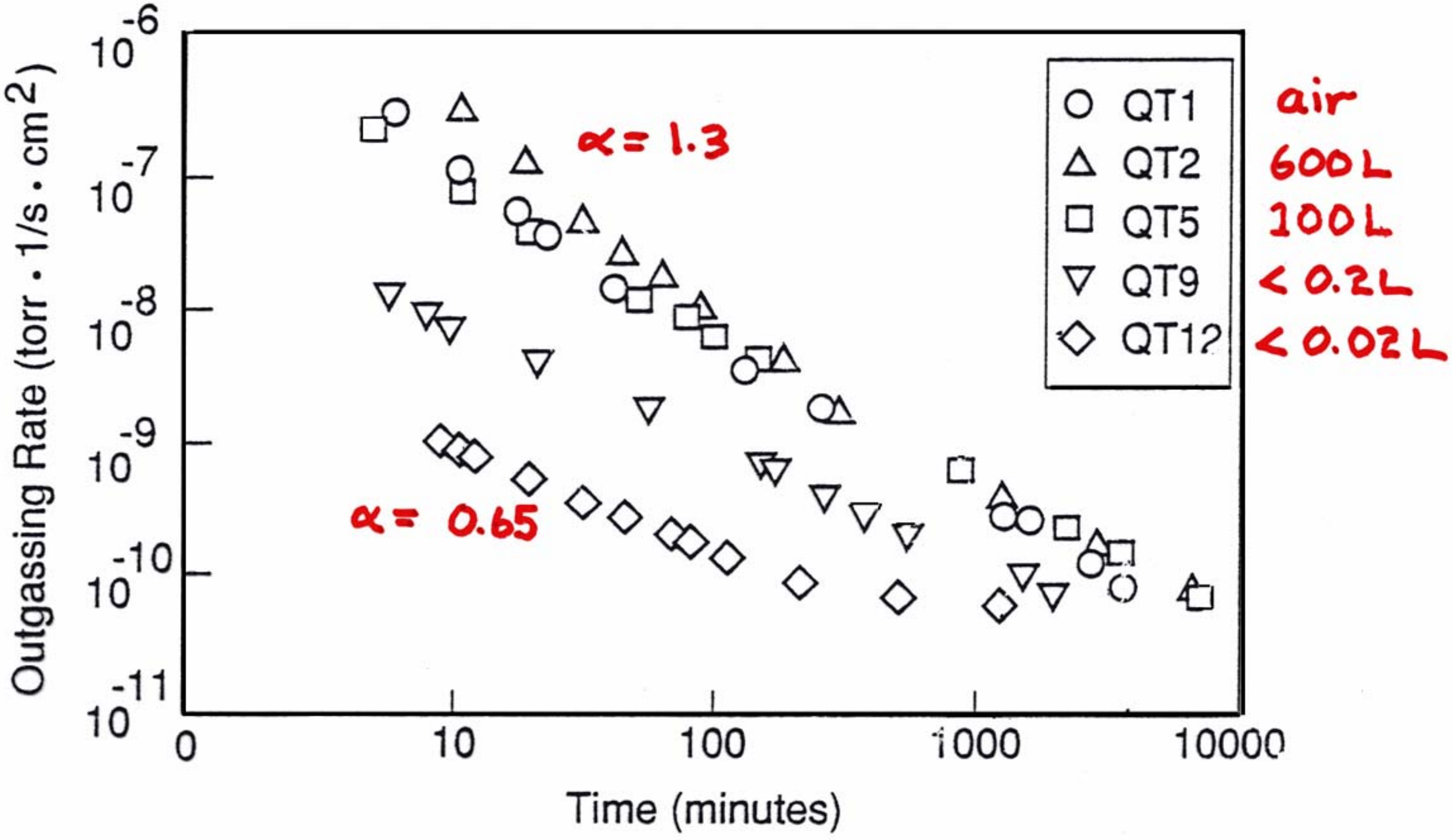
- $\alpha \longrightarrow$ 1/2 for low exposures (< 0.01 ML)
- $\alpha \dashrightarrow$ 3/2 for large exposures (>100 ML)

(Ref: Li and Dylla, JVST 11, 1702, 1993; A12, 1772, 1994)

Water Outgassing Apparatus



Water Outgassing on SS as Function of Exposure

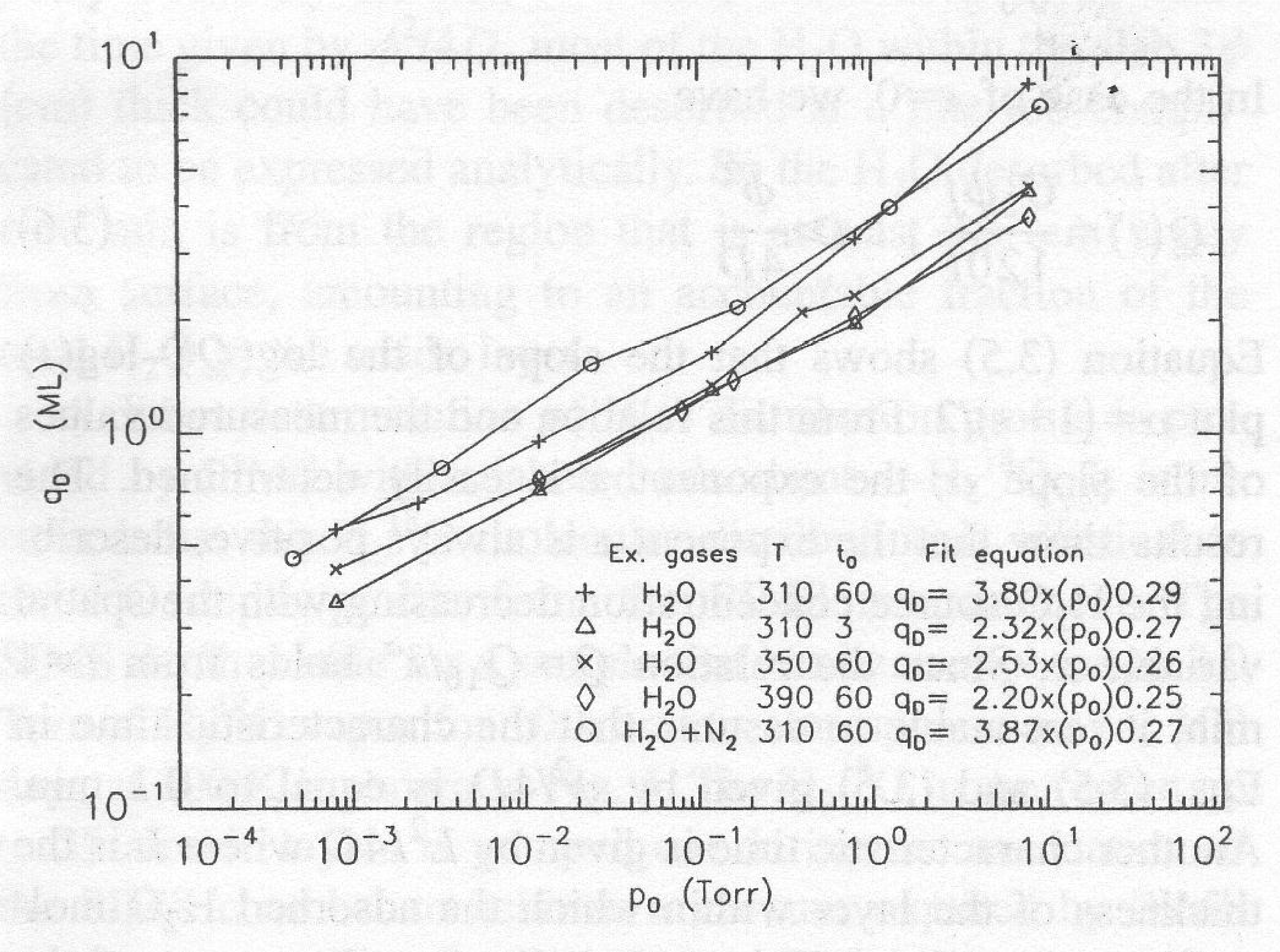


Li and Dylla

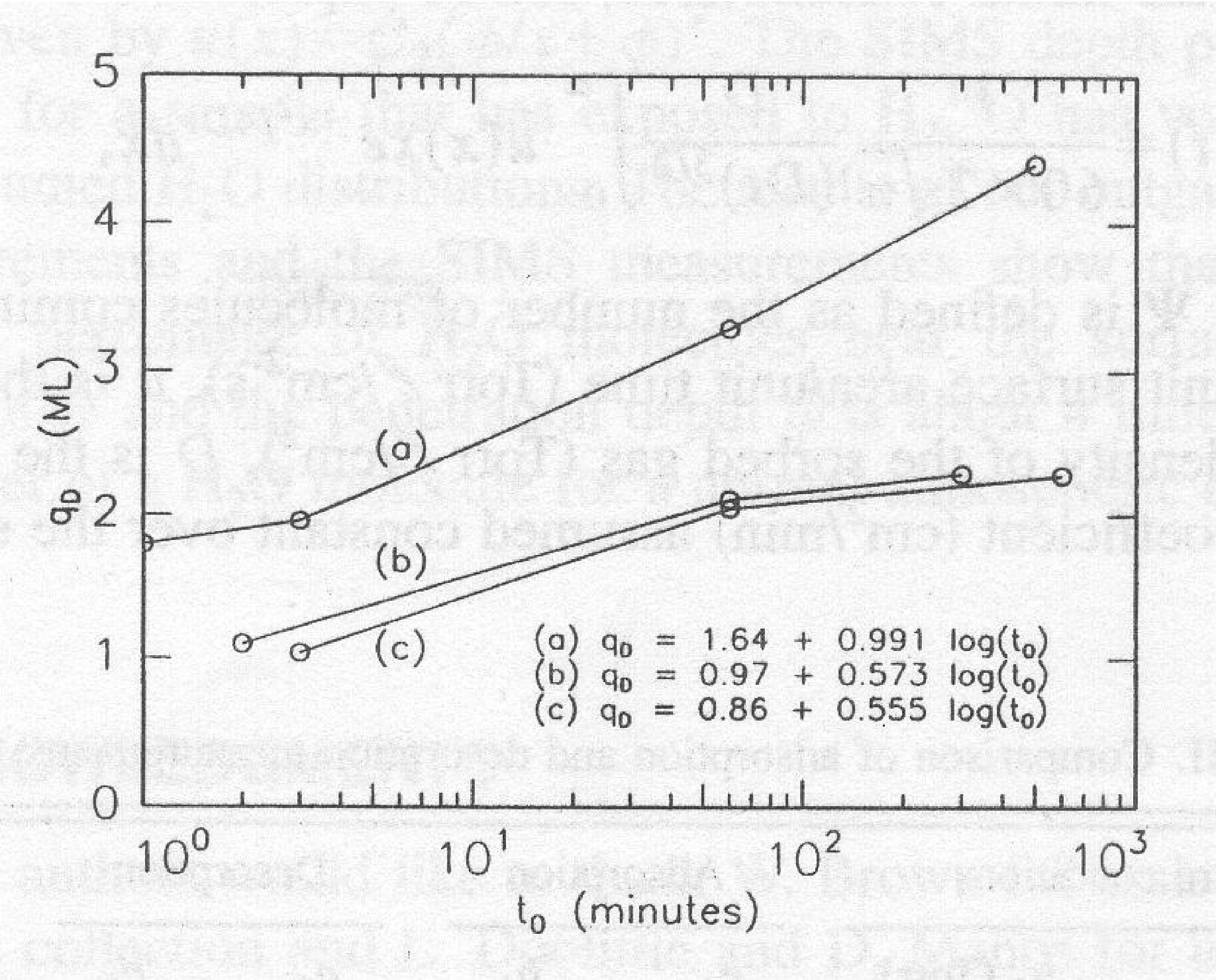
H_2O/SS Engineering Formula

These measurements resulted in series of empircal formulae that can be used to predict the adsorption/desorption rates from SS vacuum systems knowing:

- water exposure (P_o x t_{exp})
- chamber area (A)/ pumping speed (S)
- chamber temperature



Relation between the quantity desorbed and the H_20 exposure pressure



The dependence of the quantity desorbed on the exposure duration under different exposure conditions (a) T=310 K, p_0=0.8 Torr, (b) T=350 K, p_0=0.4 Torr; (c) T=390 K, p_0=0.8 Torr.

H_2O/SS Adsorption/Desorption Modelling

The outgassing measurements in the literature have spawned modelling efforts since Dayton's pioneering study in 1962 (B.Dayton, Trans.Vac.Symp., 1962)

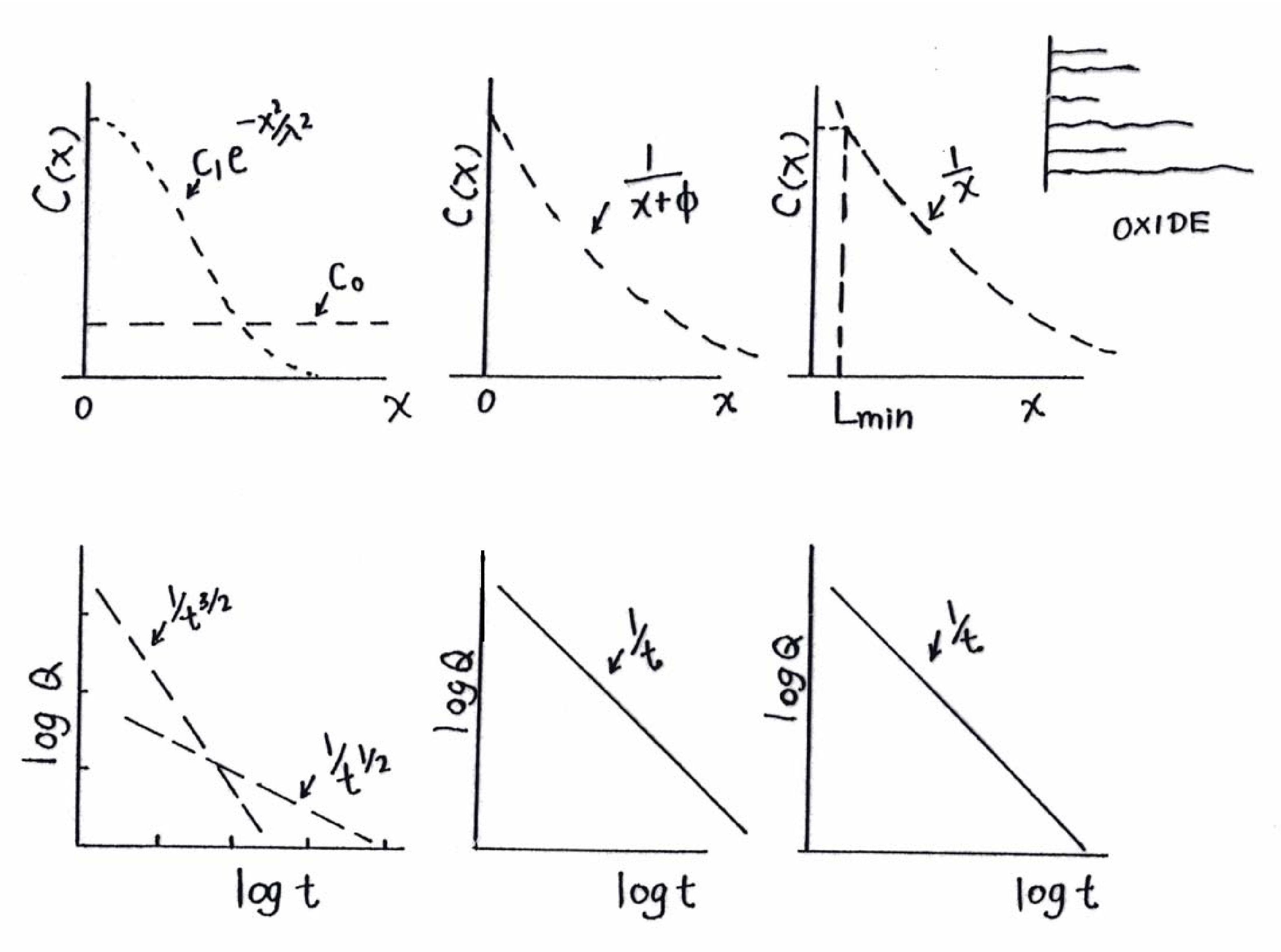
Models of H_2O Outgassing

Diffusion Limited	**Assumption**
Dayton	multivarible D
Malev	non-uniform source function
Li and Dylla	non-uniform source function
Surface Limited	
Edwards	multivariable wall pumping
Weiss	Dubinin-Radushkevich isotherm
Redhead	Tempkin isotherm

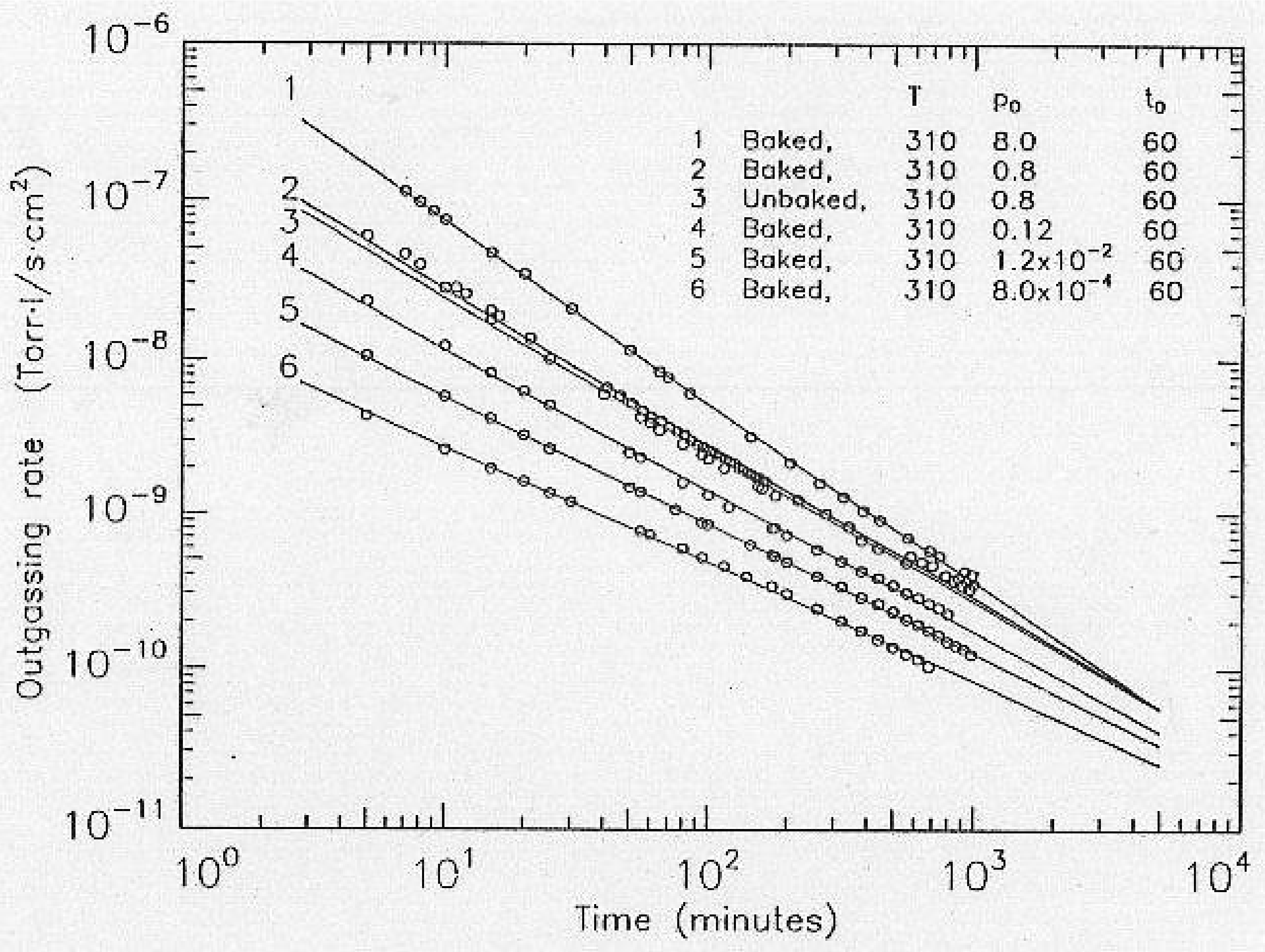
MODEL 1 MODEL 2 MODEL 3

Source Distribution

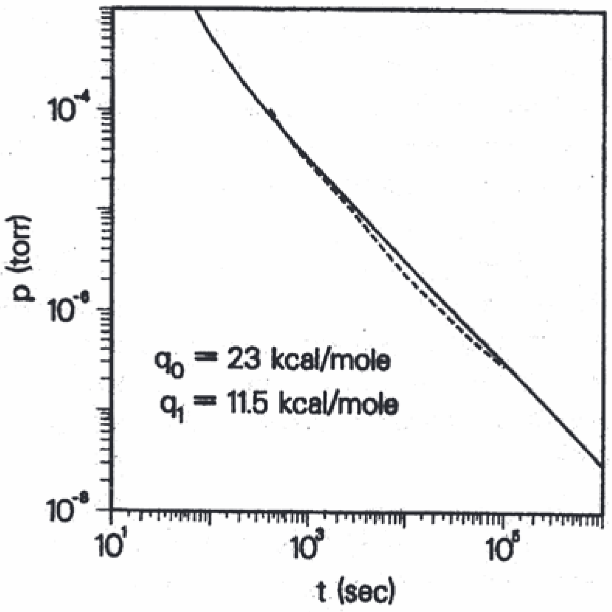
Outgassing Rate

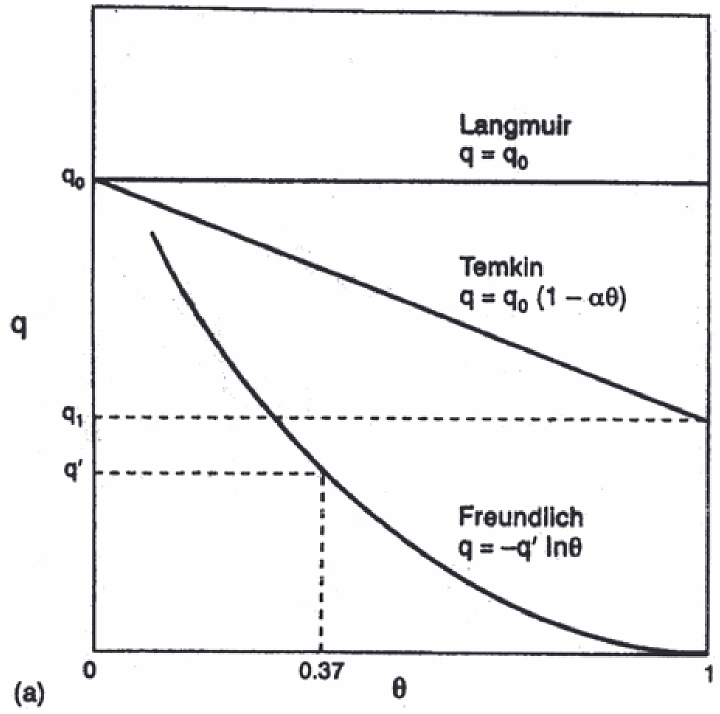


Li & Dylla Outgas Data and Fits



P. Redhead Analysis





JVST A , 13, 467 (1995)

H_2O/SS Models (continued)

- The available models are phenomenological and several can fit the available data

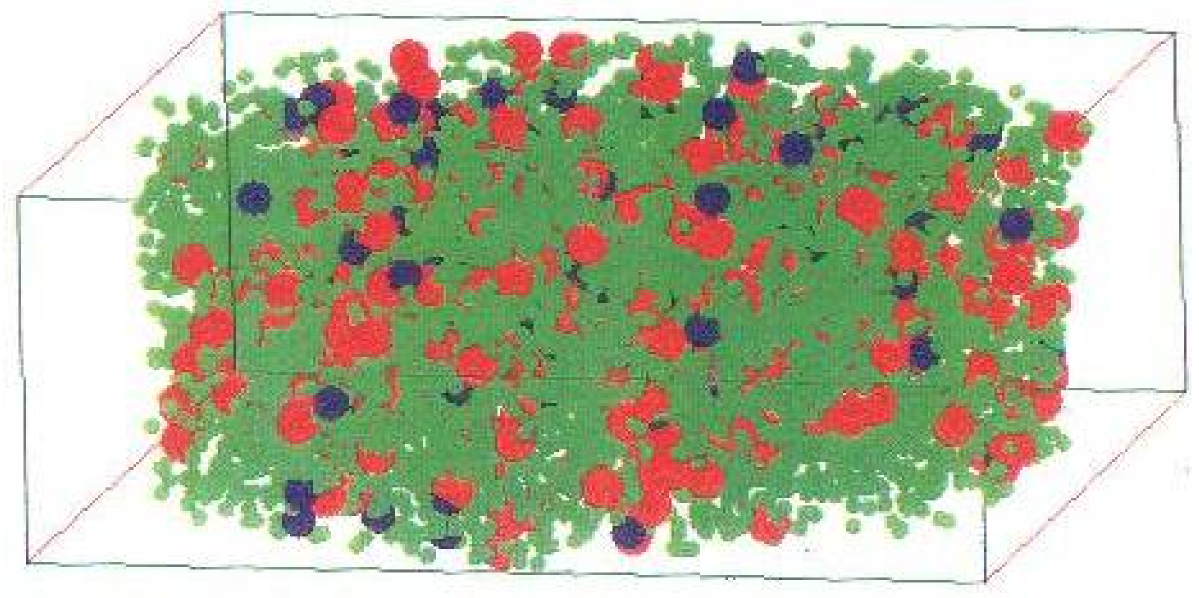
- Is adsorption/desorption diffusion limited or surface limited?

- What we don’t know?
- If diffusion limited:
  - nature of the diffusion constant D, source function c[x]
  - nature of the diffusant [O, H, OH, etc.]
  - bulk vs pore diffusion?
- If surface limited:
  - appropriate isotherm [adsorption energy E_d]
  - sticking coefficient
  - possibility of multilayer adsorption at room temperature

Connections to Fundamental Surface Studies

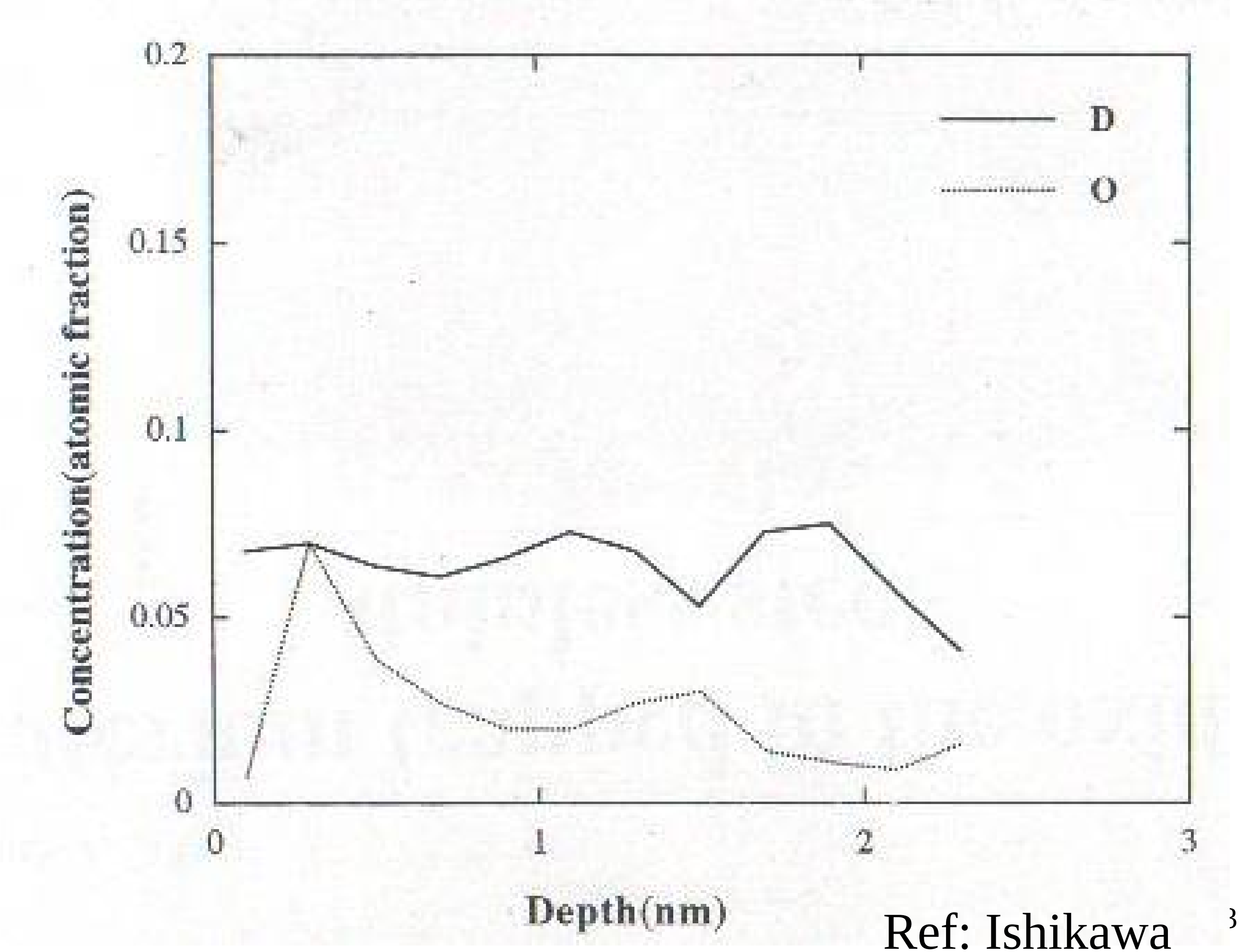
- Excellent body of fundamental surface studies of H_2O adsorption/desorption on metal surfaces:
  - see for example: P.A. Thiel and T.E. Madey, Surface Science Reports 7, 211-385 (1987) “The Interaction of Water with Surfaces: Fundamental Aspects”
- We have to make the connection between these fundamental studies on (typically) single crystal, pure metallic elements (Fe, Mo, etc.) to the macroscopic studies on adsorption/desorption from real world surfaces (stainless steel with its complicated chemical and “messy” physical structure)
- Approach the problem from both directions:
  - use of microscopic techniques on SS samples (FIM –Ishikawa; SIMS-Li)
  - use of radiotracer techniques for sorption/desorption (Drobrozemsky)

Deuterium trapped in the oxide in Stainless Steel (Ishikawa)



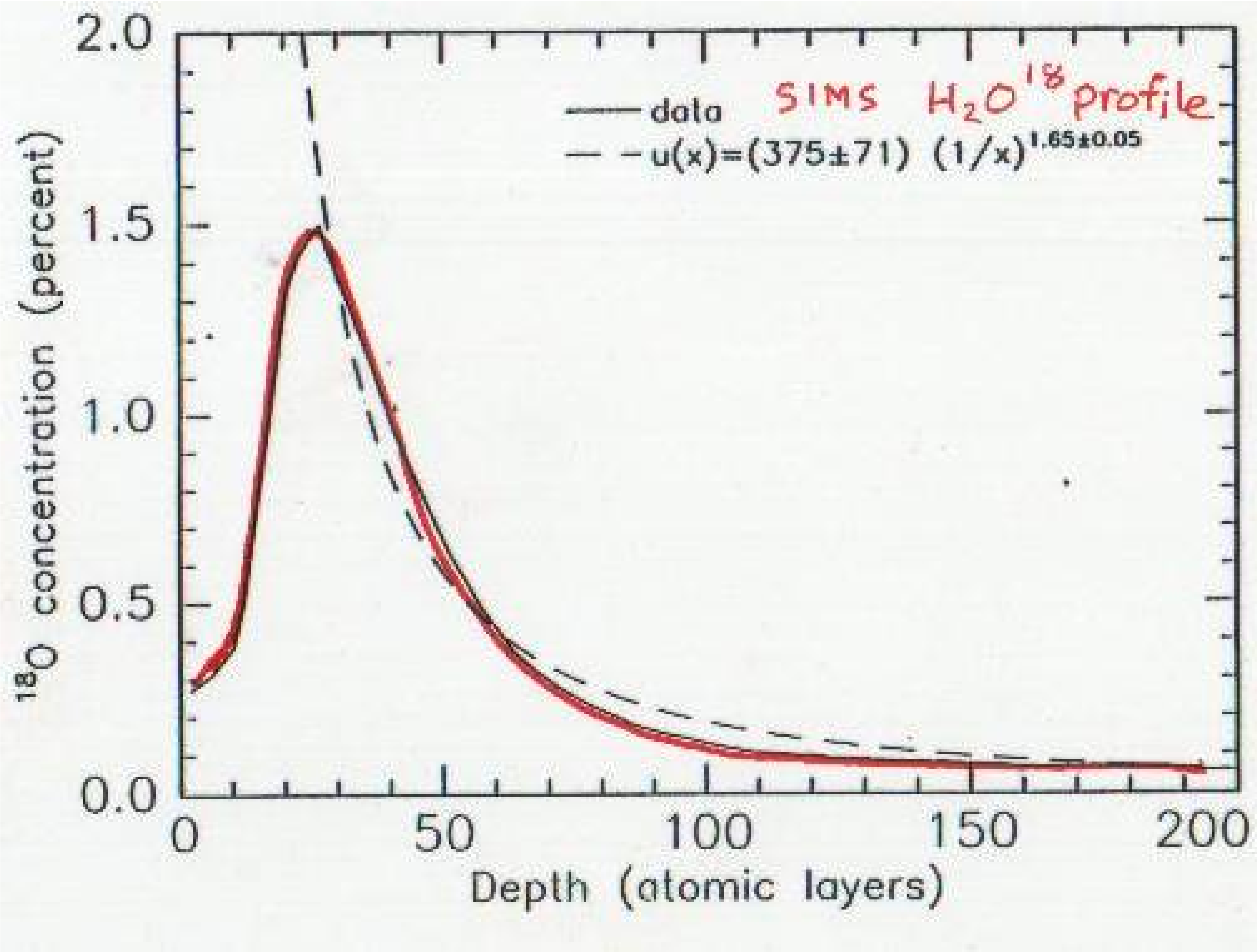
FIM Image (Metallic elements: green, Oxygen containing species: blue Deuterium: red spheres)

Deuterium and Oxygen Concentration Depth Profiles in Stainless Steel



Ref: Ishikawa

SIMS Profile of Adsorbed H_2O^{18} (Li)



Future Studies List:1

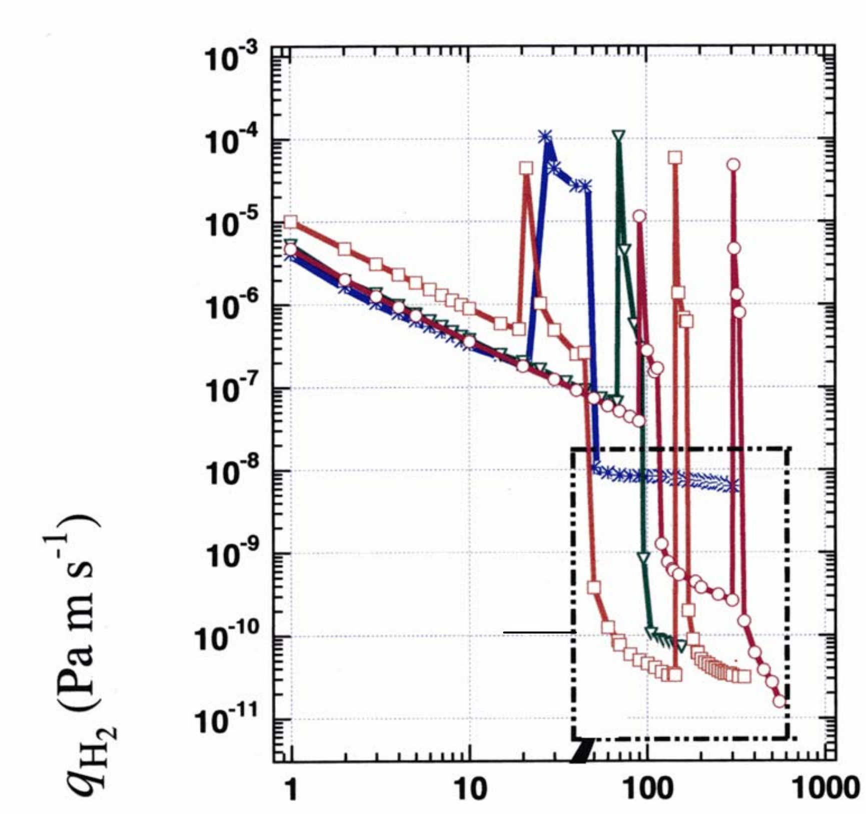
Two important experimental challenges:

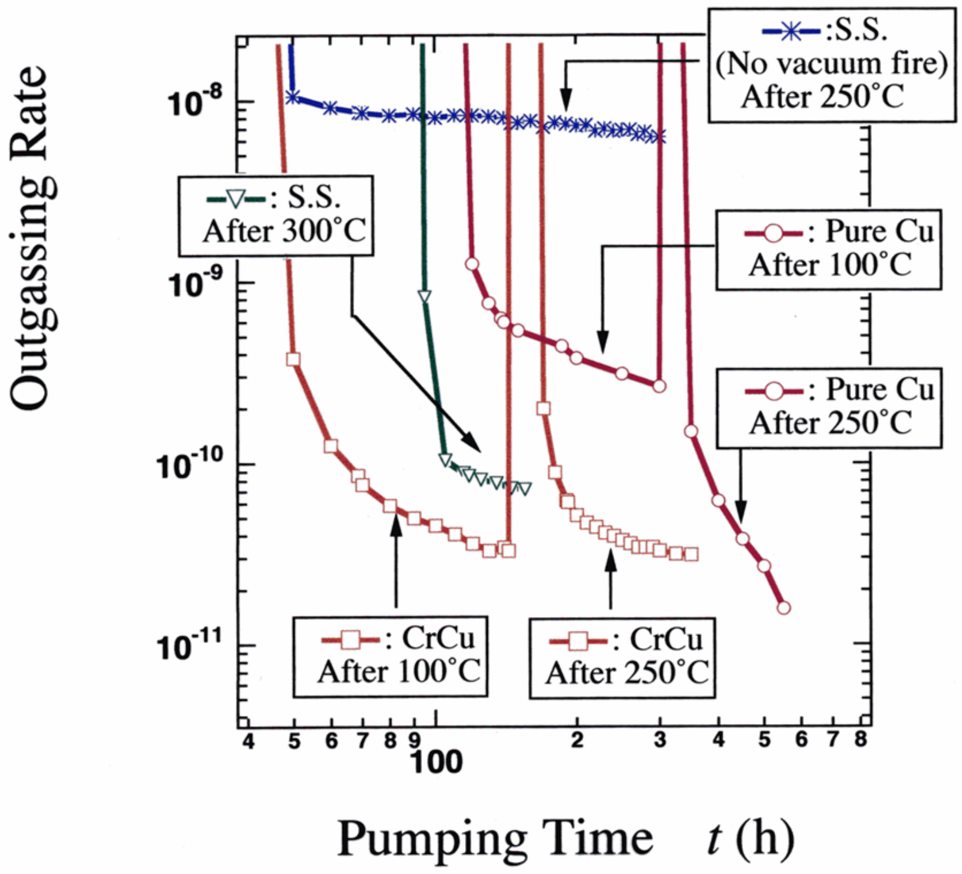
1) Can we design/apply a passivating surface to technical surfaces that minimize the adsorption (and sorption) of H_2O?
   - minimize surface adsorption (lower the adsorption energy)
   - minimize pore and grain boundary density which may represent bulk sorption sites

Examples: Au, Cr , Al , TiN coatings – not very successful

- grain boundary diffusion and chemistry can’t be shut down?

Cu/ CuCr as UHV/XHV Material (Watanabe)





Future Studies List: 2

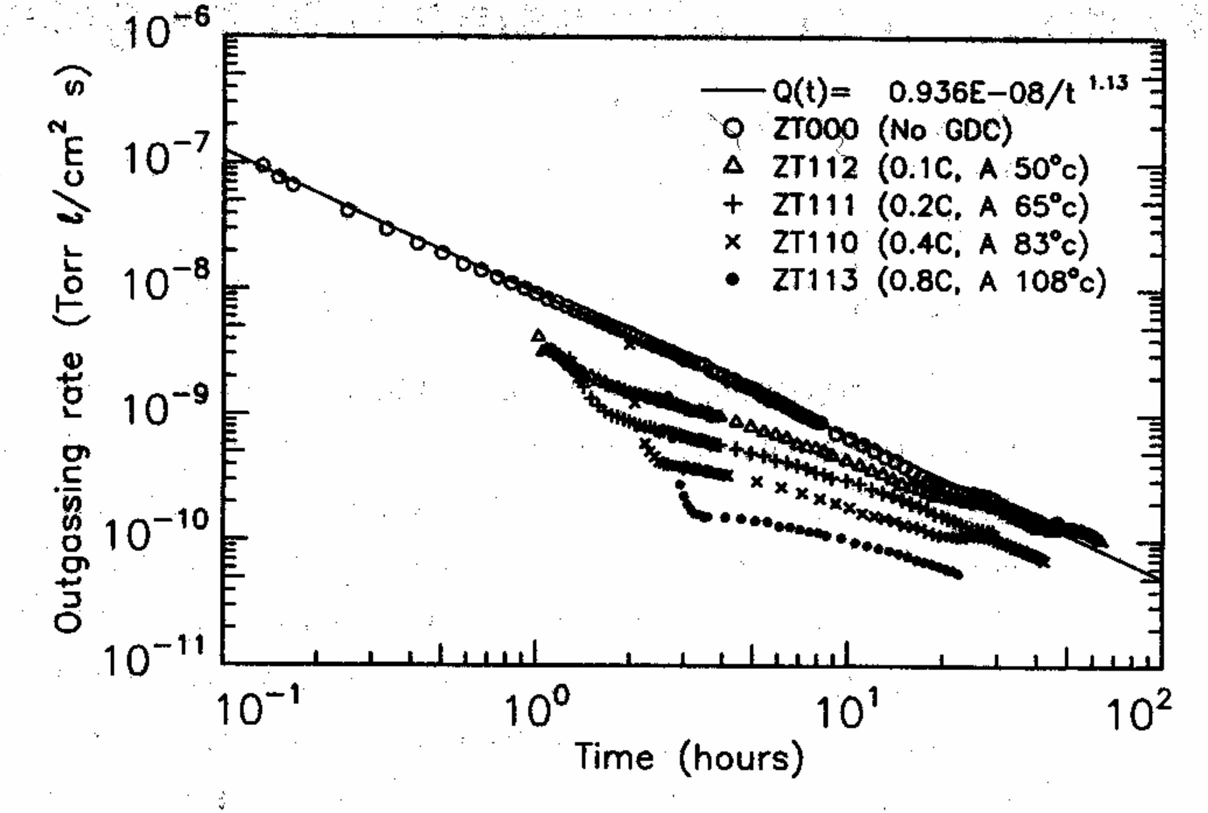
2) Can we design/apply techniques that enhance the desorption of H_2O during pump-down beyond the thermal desorption rate?

- some modest success here with :
  - glow discharges
  - UV-photodesorption
  - electron stimulated desorption

- experimental problems:
  - treating the entire internal surface area
  - formation of gas phase products that can be removed by the pump non-deleterious to other components in vacuum system

Outgassing after glow discharge treatment

(JVST A13, 571, 1995)



Summary

Measurements

- The outgassing of water from SS (Al) depends on the exposure pressure ($P_o^{0.25}$) and exposure time ($a_1+a_2\log t_o$)
- The observed power low dependence

$Q = Q_o t^{-\alpha}$ depends on the exposure, $P_o t_o$

$\alpha \sim \frac{1}{2}$ for low exposures, long times

$\alpha \sim 1$ typical air exposures

$\alpha \sim 3/2$ for high exposures

- Little difference among good cleaning methods
- Effects of surface roughness, oxide thickness, oxide conditions need more work

Modeling

- Several models can fit data from controlled experiments

More work needed on :

- Source distribution functions
- Realistic values for diffusion constants D (x, T)
- Relevant isotherms for H_2O/SS

References

- Dylla, Manos and La Marche, JVST A11, 2623 (1993)
- Li and Dylla, JVST A11, 1702 (1993); A12, 1772 (1994); A13,1872(1995)
- Redhead, JVST A13, 467 (1995)

Workshops

- NIST Workshop: H_2O in Vacuum (May 1994)
- IUVSTA Workshop: Conditioning of UHV Systems (Geneva, March 1995)
- IUVSTA Workshop: Outgassing Properties of Materials (Graftavellen, April 1997)
- AVS Workshop: Extreme High Vacuum (Newport News,VA, June 2000)

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