CU BKK 2010

CHEMICAL DURABILITY OF GLASS

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Bangkok 14th September 2010

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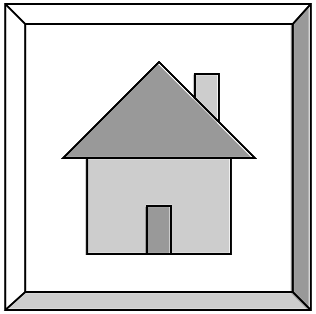 = load down & read at home

data sources

AQUEOUS SYSTEMS

- Pourbaix: Atlas of Electrochemical Equilibria in Aqueous Solutions
  aq. pH-Eh speciation of the entire periodic table of elements
- Iler: The Chemistry of Silica (1979) *more than 2600 references!*
- Baes & Mesmer: The thermodynamics of cation hydrolysis (1981)
- Brinker & Scherer: Sol-Gel Science (1990)
- H.E. Bergna: The colloid Chemistry of Silica (1994)
- G. Sposito: The Environmental Chemistry fo Alumina (1996)

SYSTEMS

Atlas of Electrochemical Equilibria in Aqueous Solutions

speciation of the entire periodic table of elements

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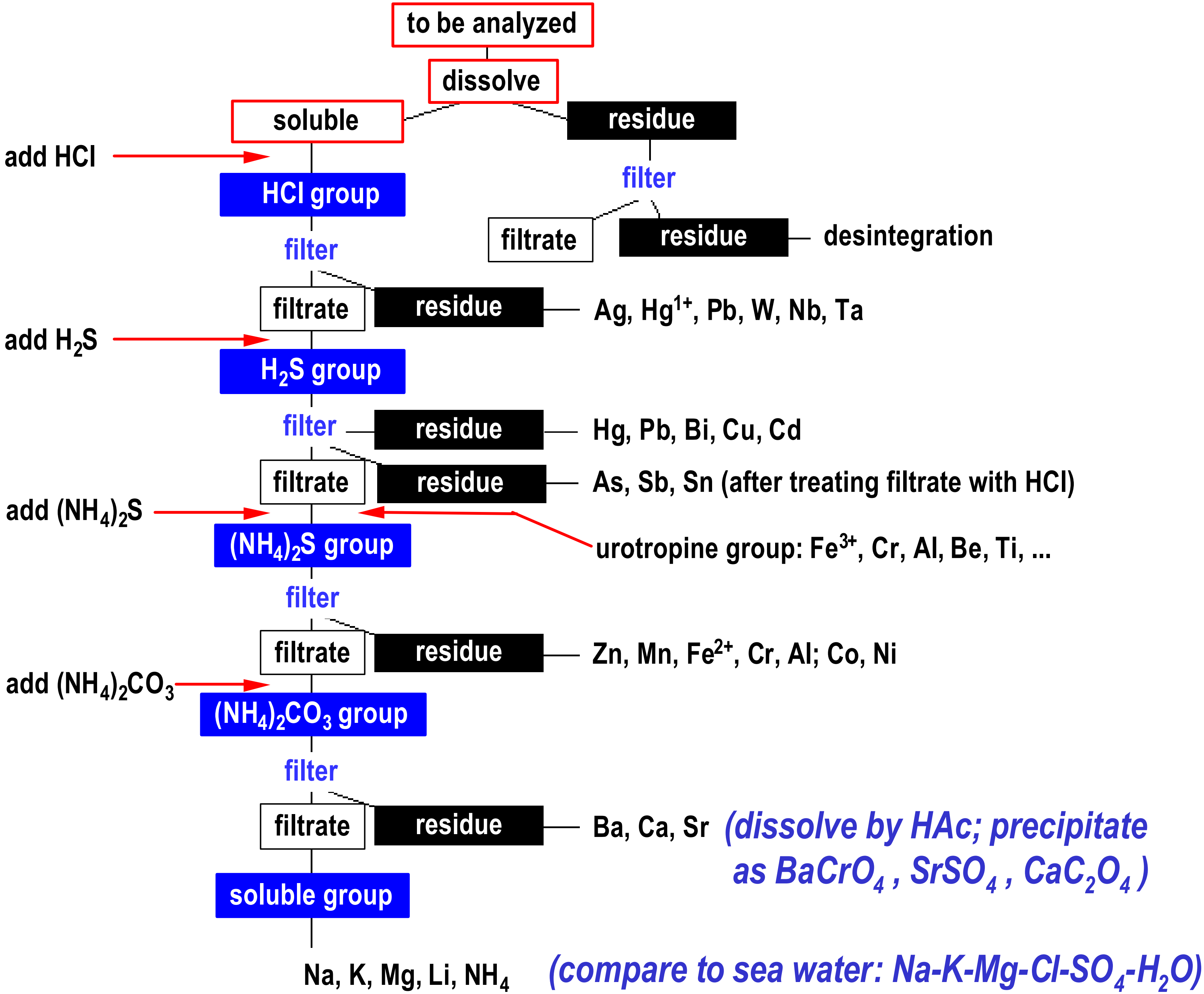
- H.E. Bergna: The colloid Chemistry of Silica (1994)
- G. Sposito: The Environmental Chemistry fo Alumina (1996)

GLASS CORROSION

- ICG compilation of literature (1972) *almost 1000 references!*
- Holland (1964)
- Besborodow (1972)
- Clark, Pantano & Hench (1979)
- Doremus & Tomozawa (1977-82)
- Scholze (1964-91)
- Paul (1982)
- Clark & Zoitos (1992)


to be analyzed
dissolve
soluble
residue
filter
filtrate
residue
desintegration
add HCl
HCl group
filter
filtrate
residue
Ag, Hg1+, Pb, W, Nb, Ta
add H2S
H2S group
filter
residue
Hg, Pb, Bi, Cu, Cd
filtrate
residue
As, Sb, Sn (after treating filtrate with HCl)
add (NH4)2S
(NH4)2S group
urotropine group: Fe3+, Cr, Al, Be, Ti, ...
filter
filtrate
residue
Zn, Mn, Fe2+, Cr, Al; Co, Ni
add (NH4)2CO3
(NH4)2CO3 group
filter
filtrate
residue
Ba, Ca, Sr
(dissolve by HAc; precipitate as BaCrO4 , SrSO4 , CaC2O4)
soluble group
Na, K, Mg, Li, NH4
(compare to sea water: Na-K-Mg-Cl-SO4-H2O)

phenomena observed

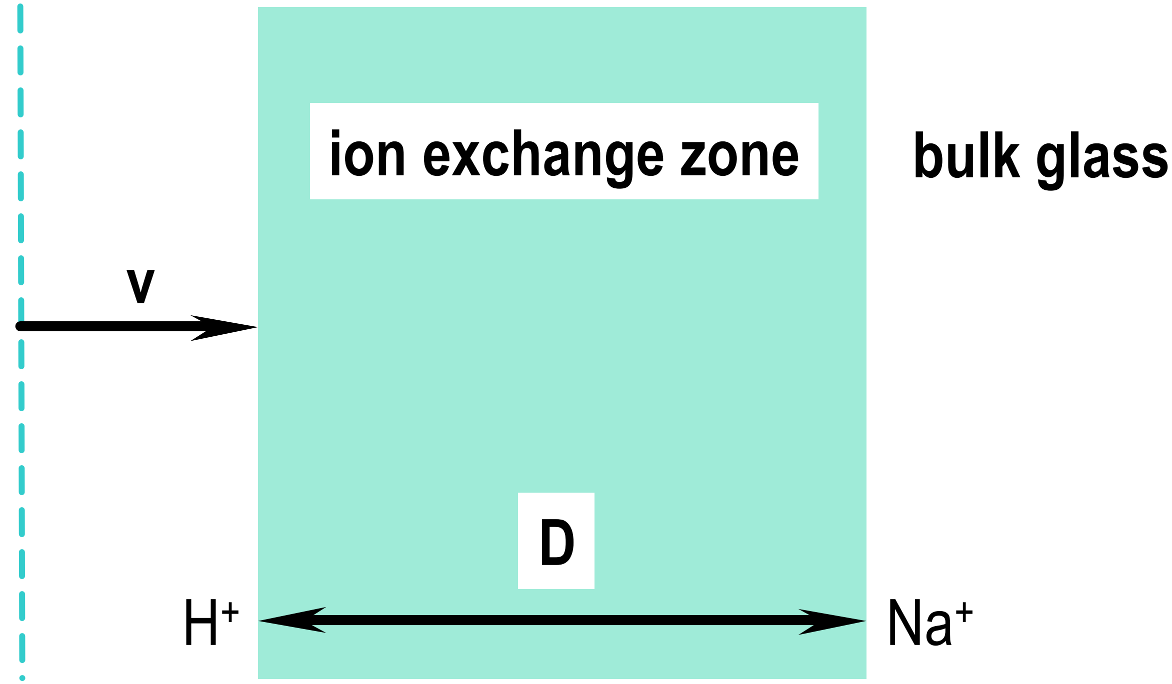
standard model

glass surface at t = 0

network dissolution
(q ∝ t)

$SiO_2 + H_2O = H_4SiO_4$

≡Si-O-Si≡ + H_2O
→ 2 ≡Si-OH

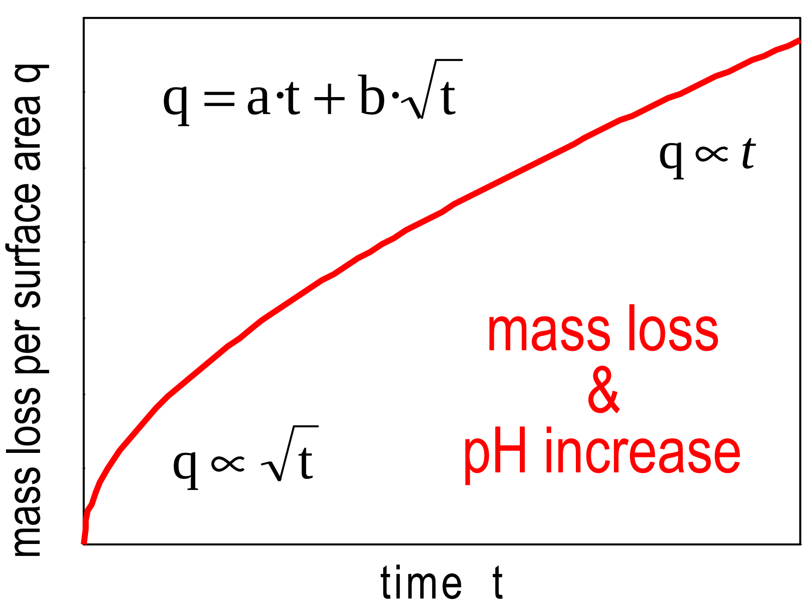


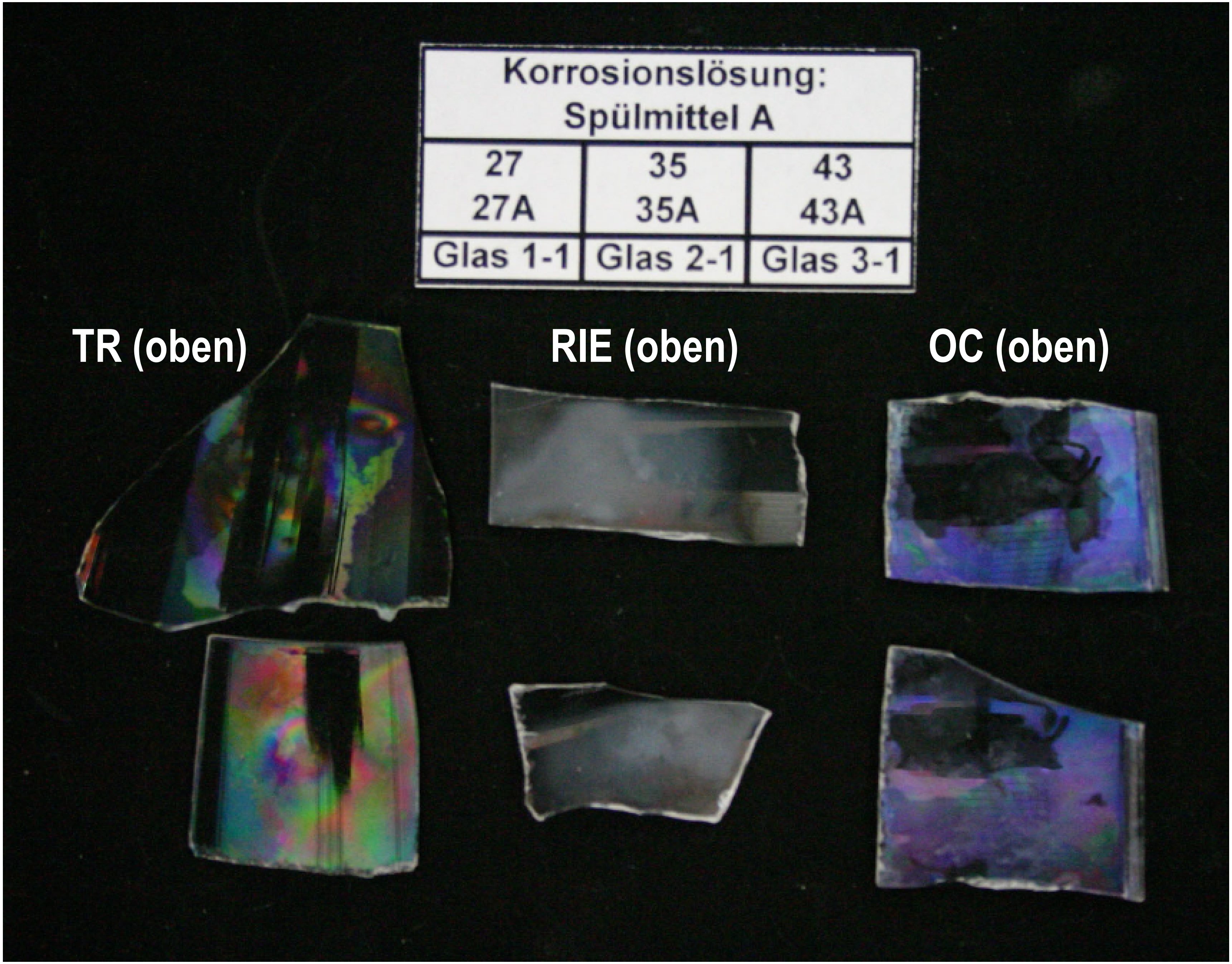
leaching
(q ∝ √t)

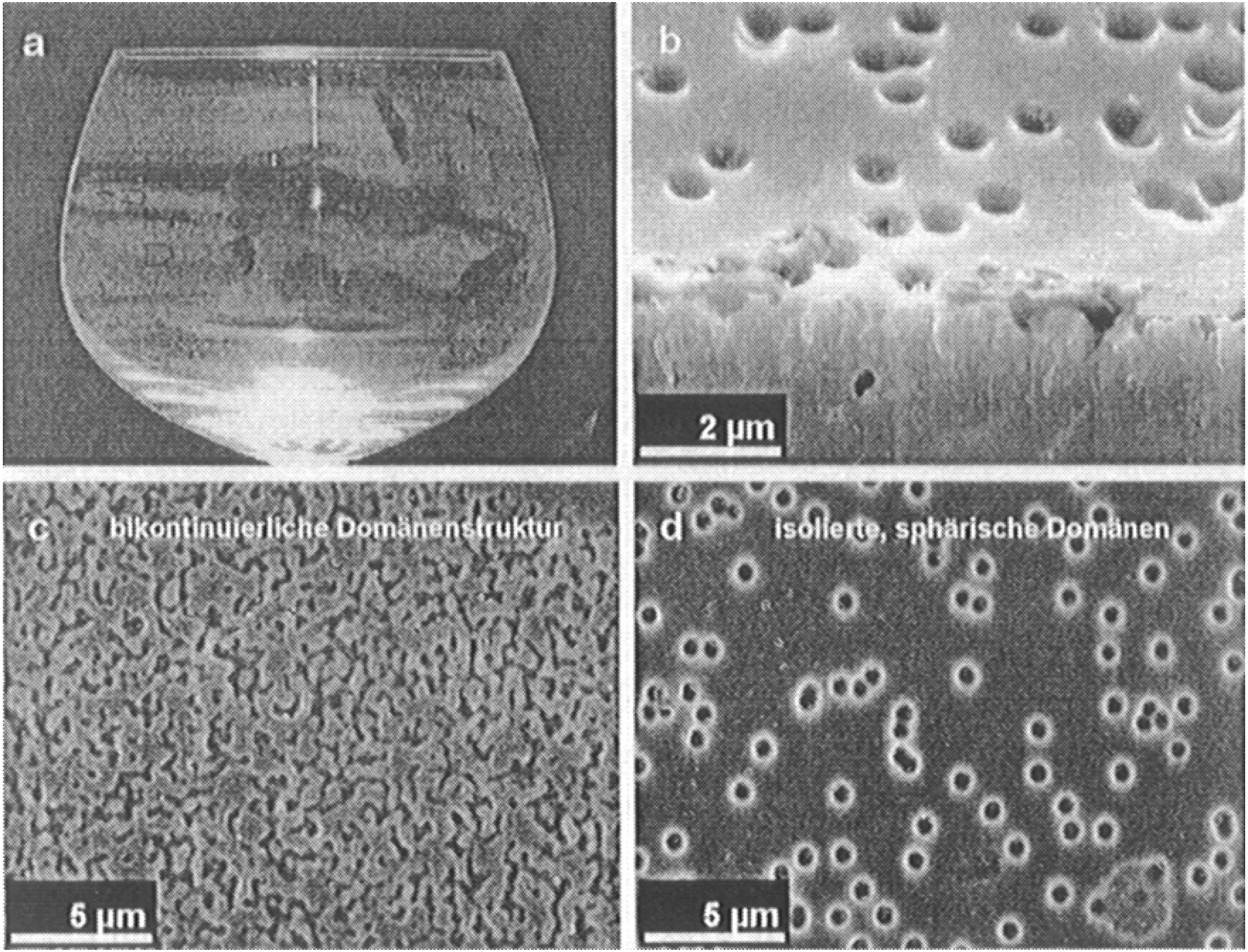
≡Si-O⁻Na⁺(gl) + H⁺(aq)
→≡Si-OH(gl) + Na⁺(aq)

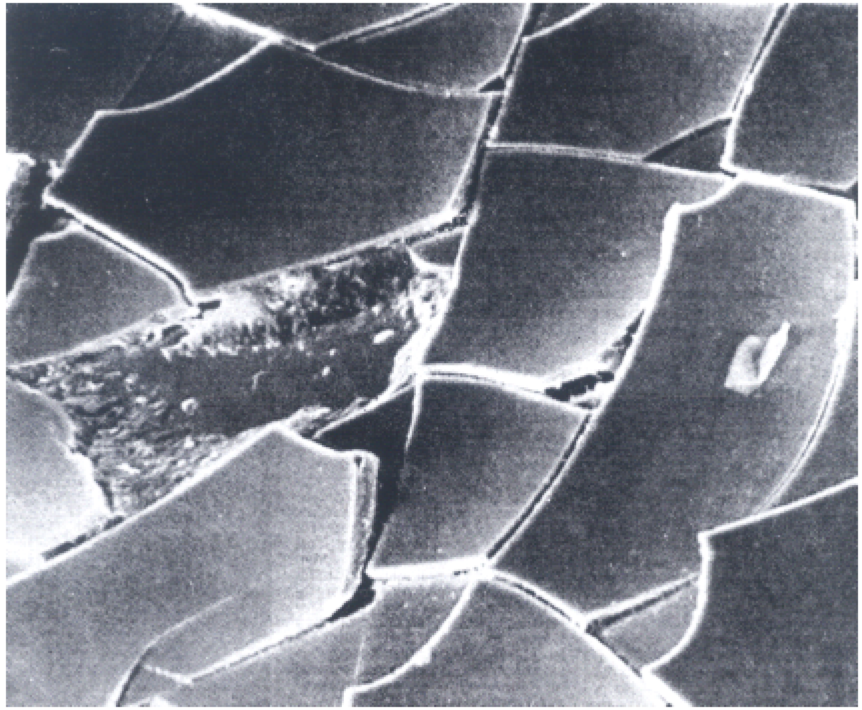
or

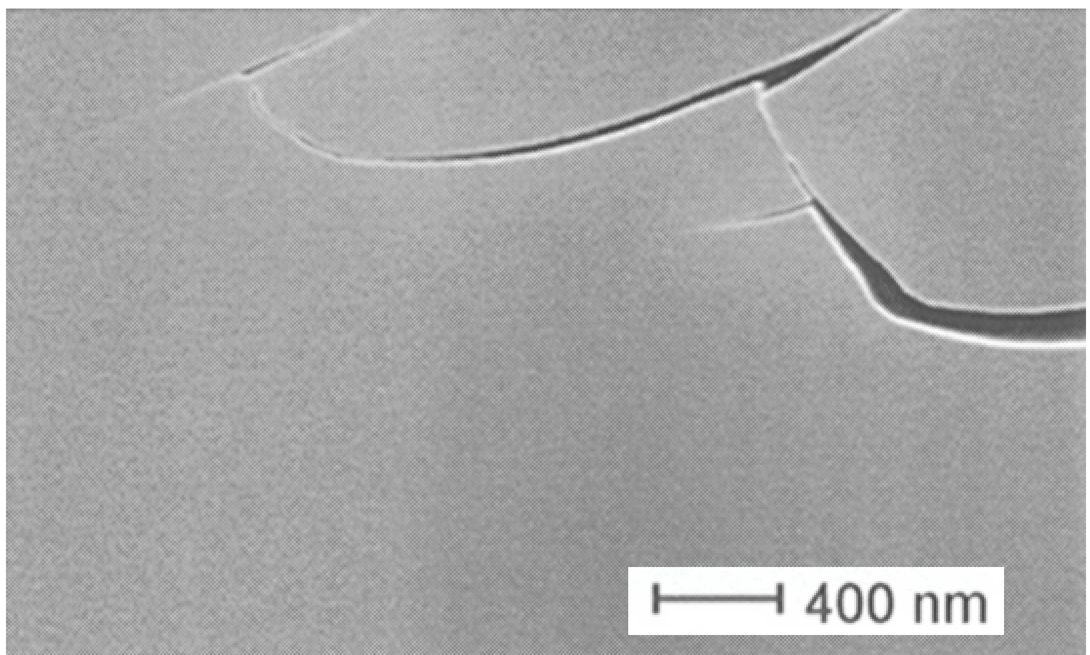
≡Si-O-Na+(gl) + H_3O^+(aq)
→≡Si-OH(gl) + H_2O(gl) + Na⁺(aq)

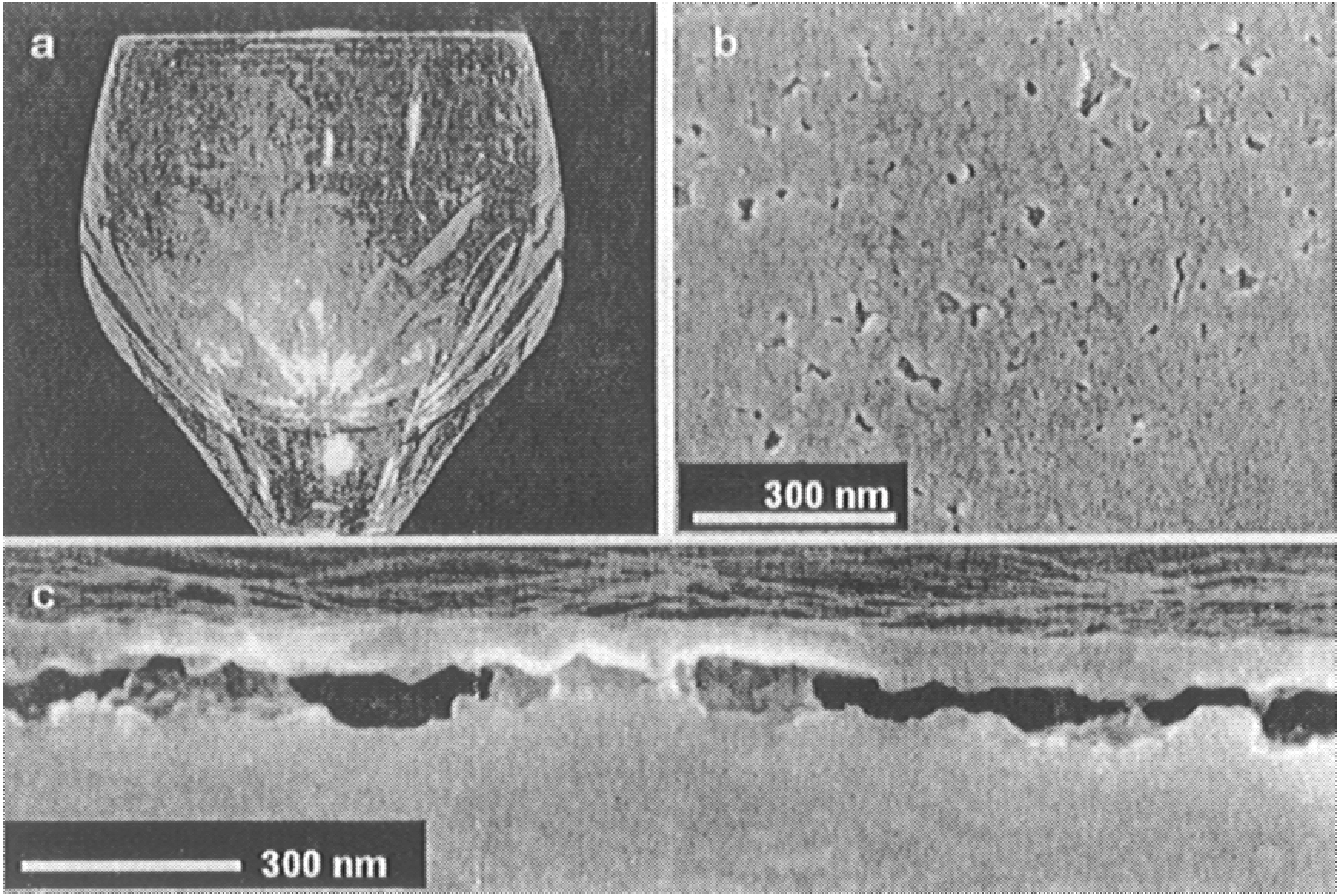


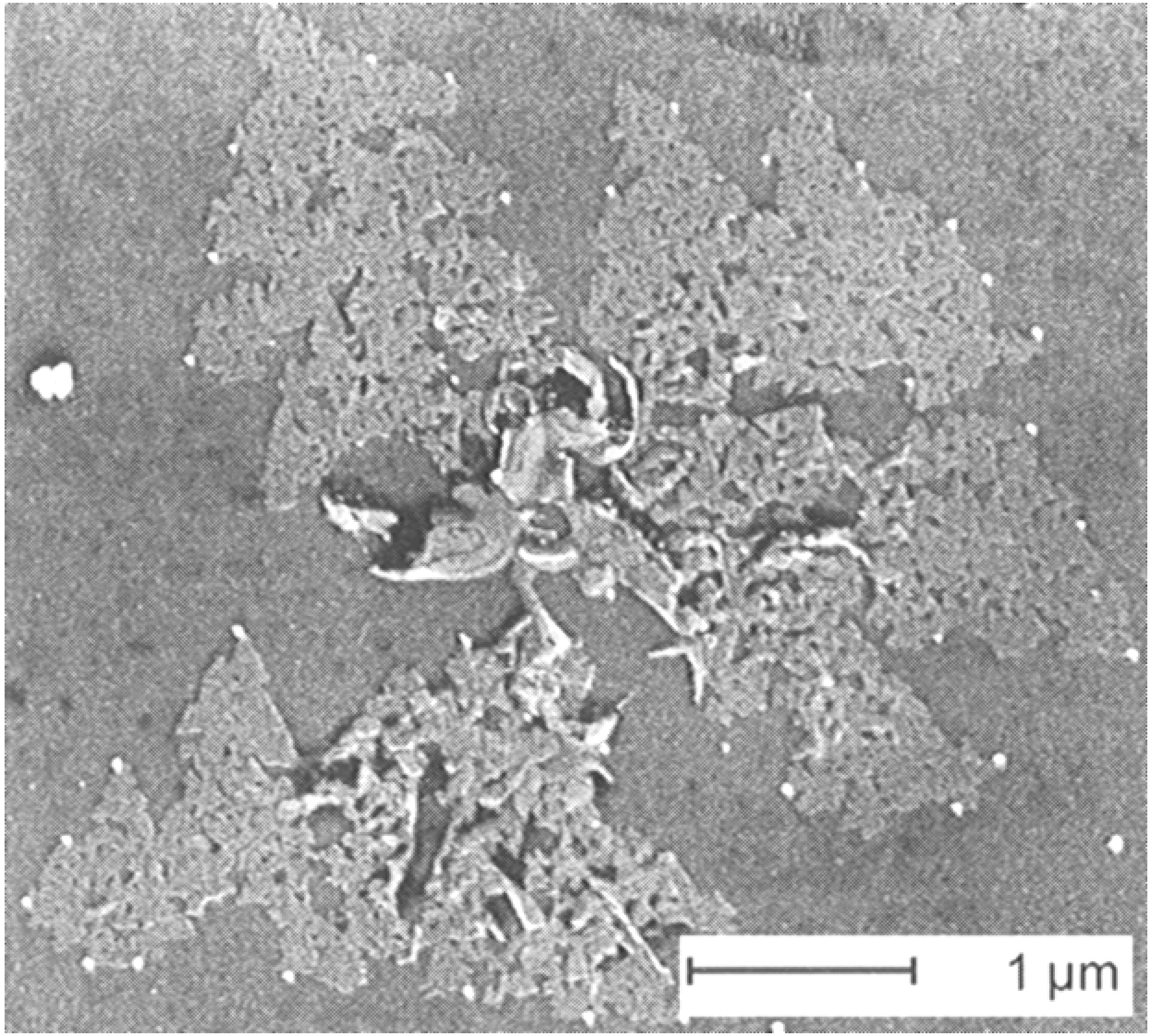

Korrosionslösung:
Spülmittel A
27
27A
35
35A
43
43A
Glas 1-1
Glas 2-1
Glas 3-1
TR (oben)
RIE (oben)
OC (oben)

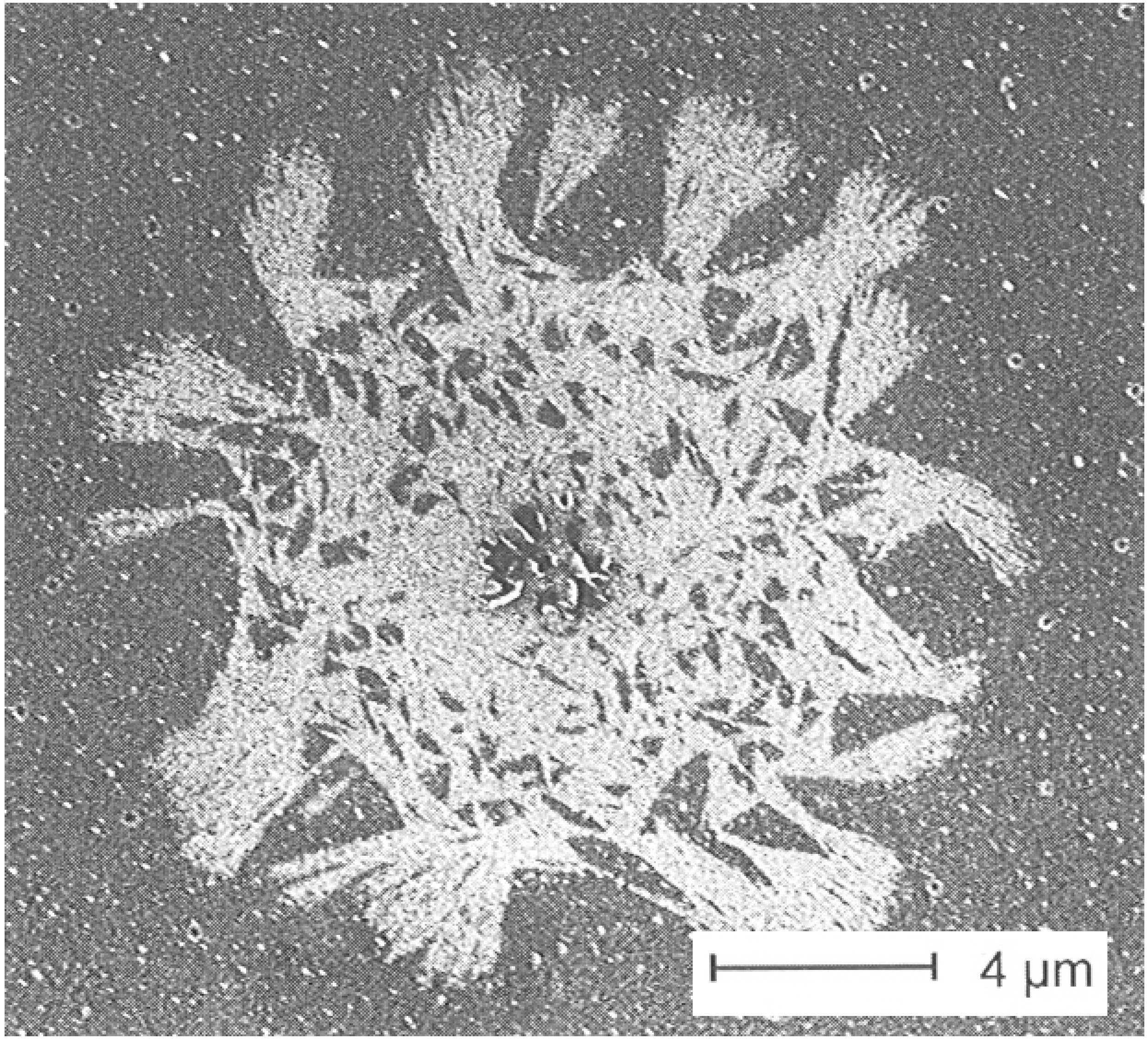

a
b
2 µm
c
bikontinuierliche Domänenstruktur
6 µm
d
isolierte, sphärische Domänen
5 µm

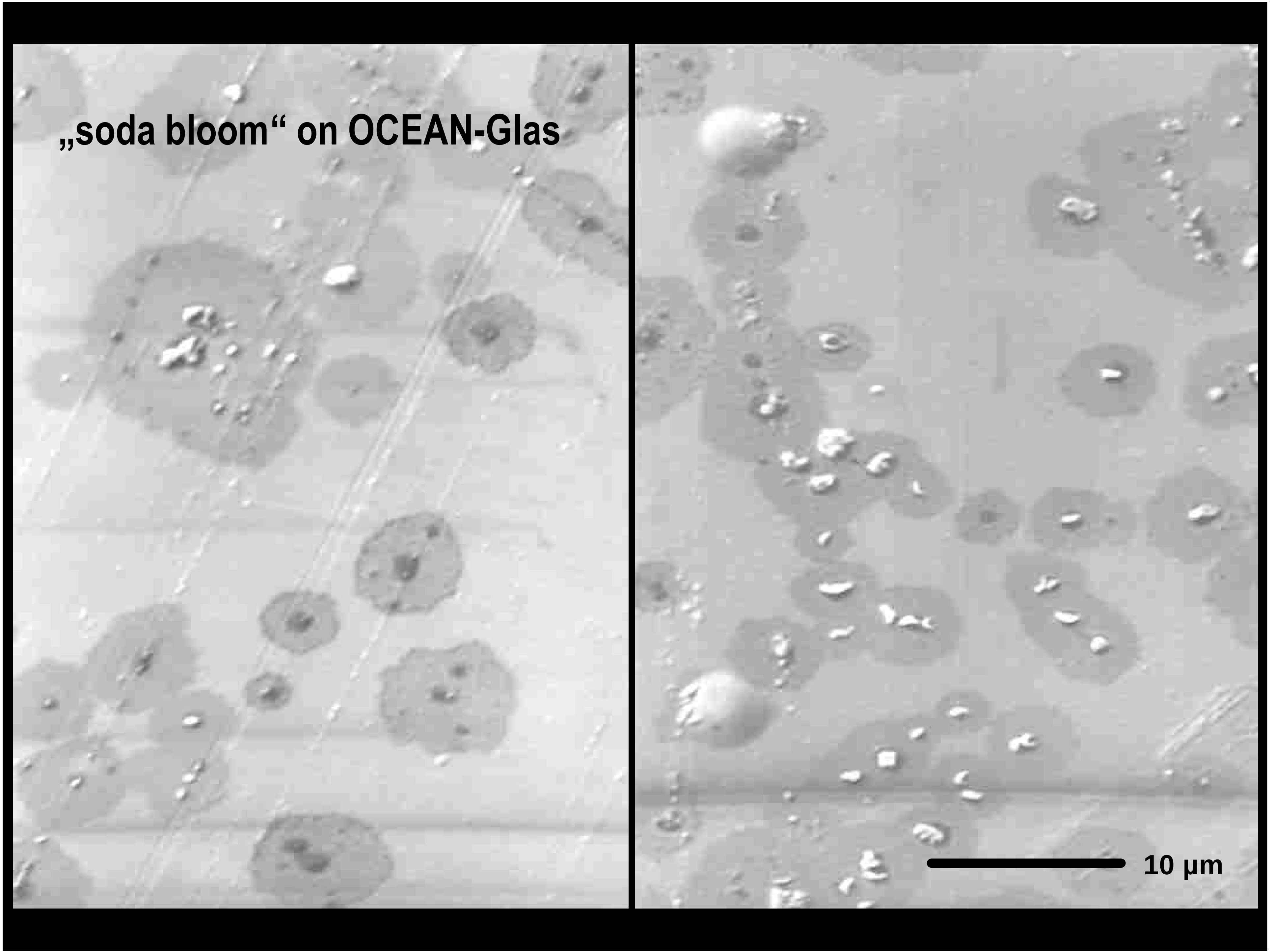



400 nm


a
b
300 nm
c
300 nm


1 µm


4 µm


„soda bloom“ on OCEAN-Glas
10 µm

vertical differentiation:

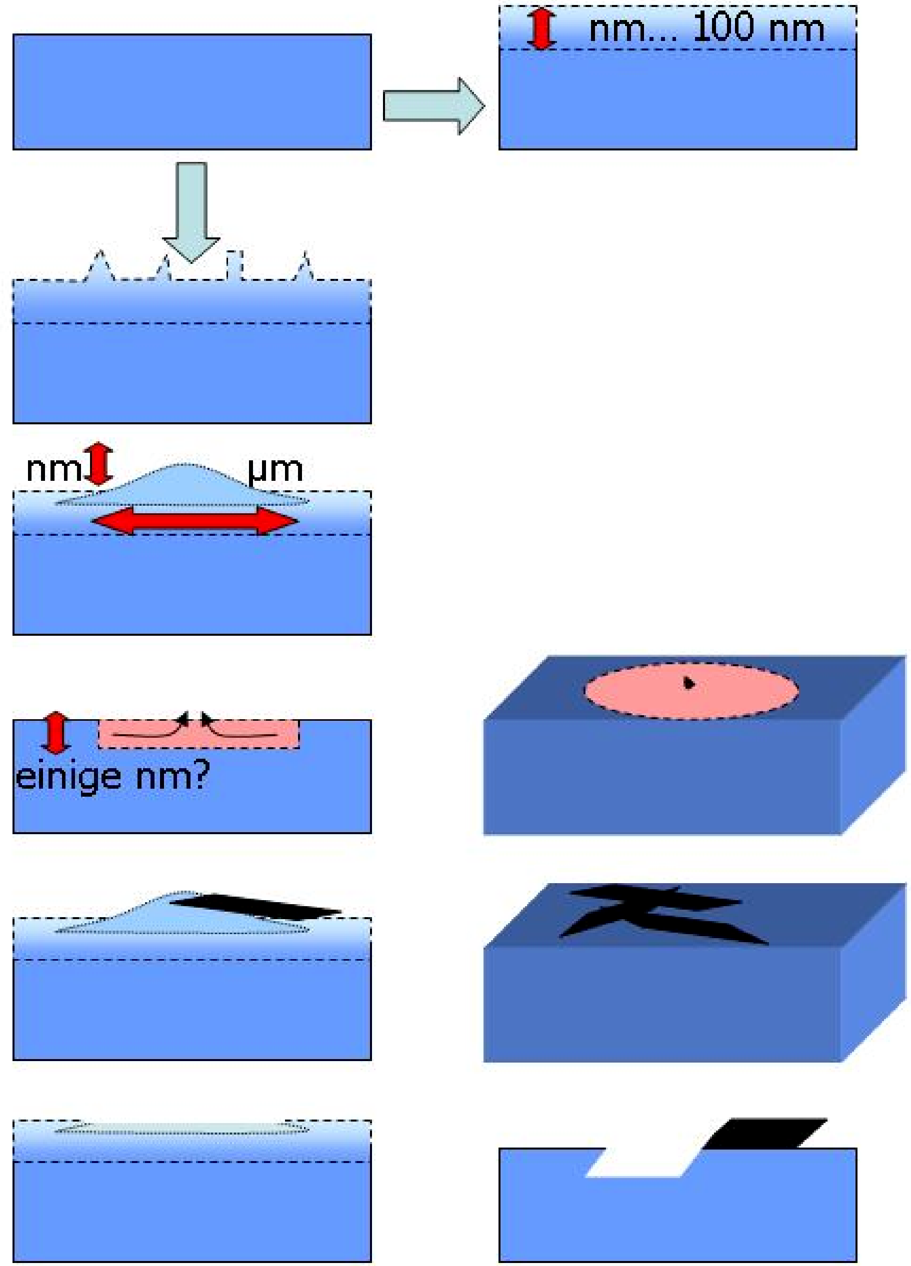
lateral differentiation:
emerging surface roughness

local swelling

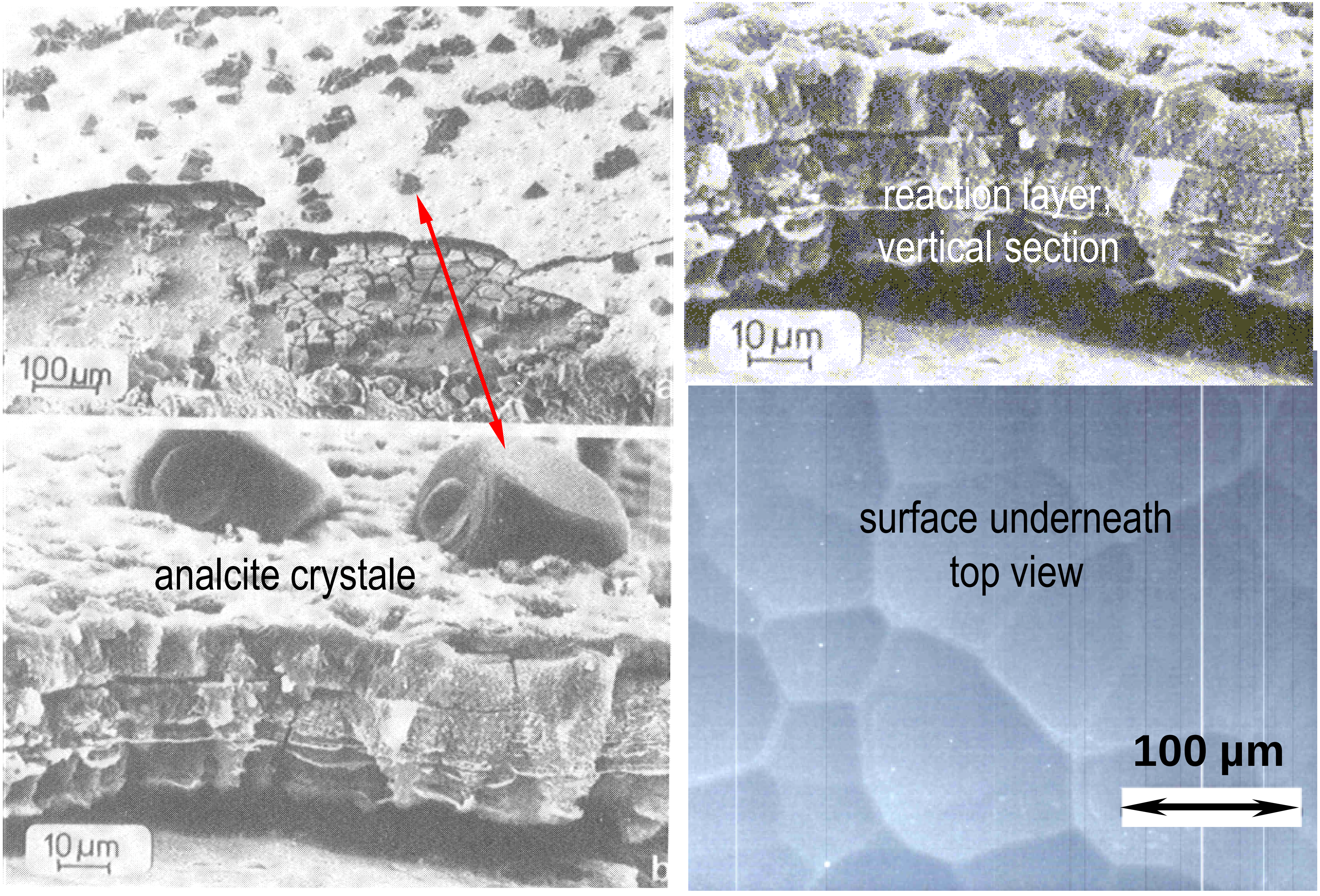
lateral diffusion zones

crystallization

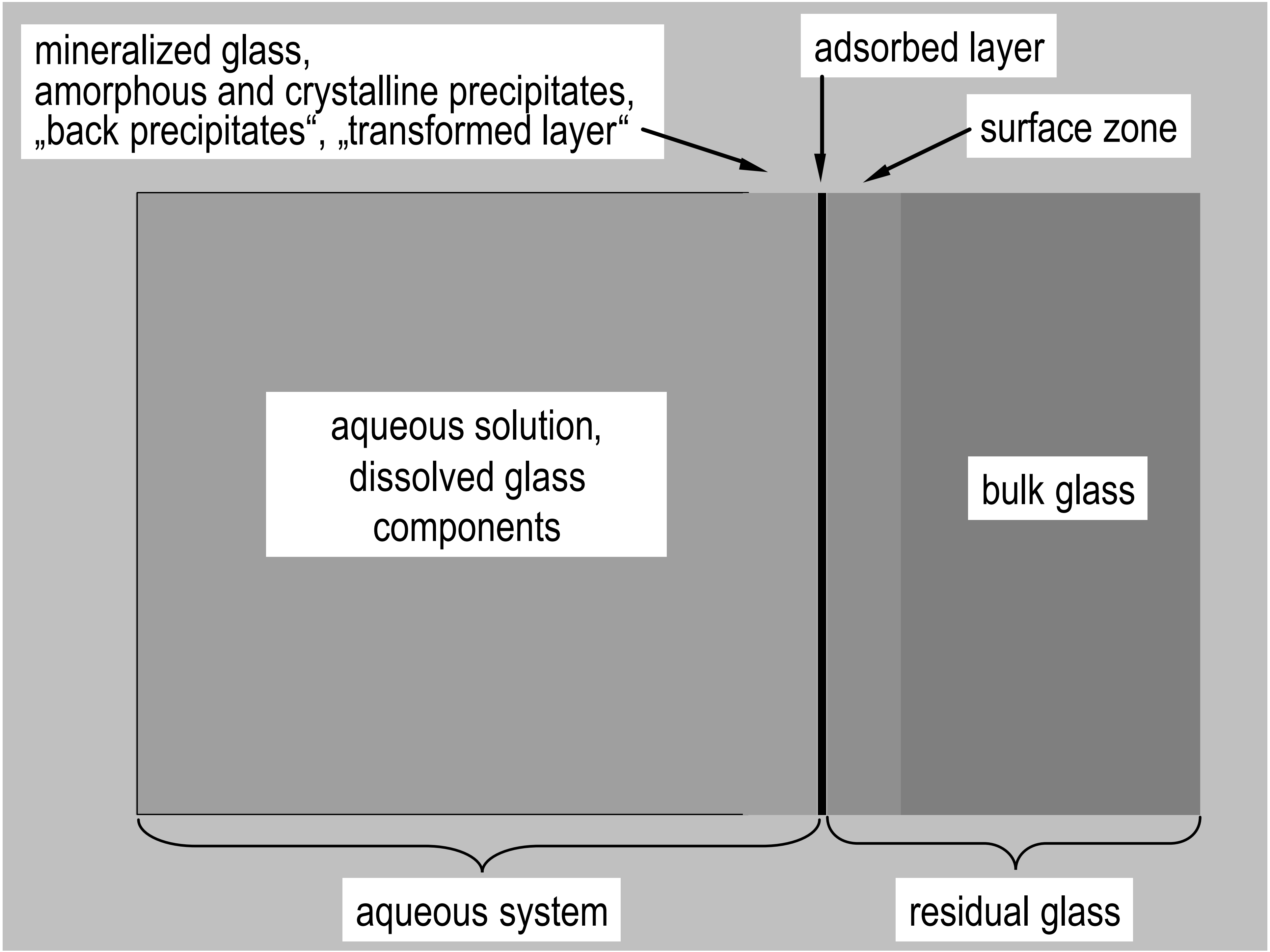
pitting



after: E. Rädlein



100 µm
a
analcite crystale
10 µm
b
reaction layer,
vertical section
10 µm
surface underneath
top view
100 µm


mineralized glass,
amorphous and crystalline precipitates,
„back precipitates", „transformed layer"
adsorbed layer
surface zone
aqueous solution,
dissolved glass
components
bulk glass
aqueous system
residual glass

standards

static tests

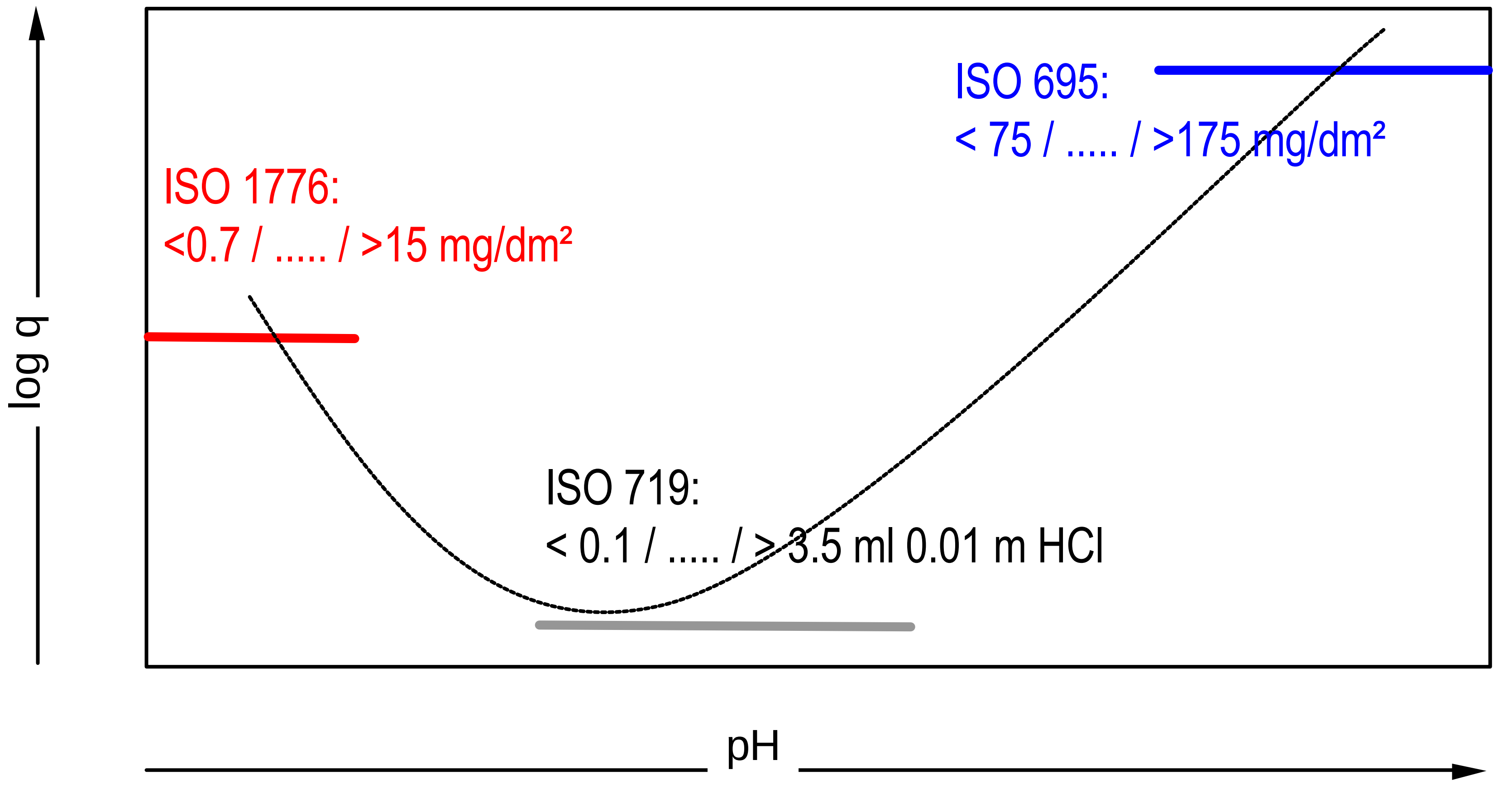
$$\frac{c}{\left[\frac{g}{cm^3}\right]} = \frac{q}{\left[\frac{g}{cm^2}\right]} \cdot \frac{s}{\left[\frac{cm^2}{cm^3}\right]}$$

s or “SA/V” in cm^{-1}

dynamic tests

$$\dot{c} = q \cdot \dot{s}$$

designed for the family of conventional silicate glasses



ISO standard tests:

ISO 1776 (stability against acidic attack)

area ≈ 300 cm²; boil in 6 m HCl (1.5 l) for 6 h

⇒ <0.7 / 1.5 / 15 / >15 mg/dm²

ISO 695 (stability against alkaline attack)

area 10=15 cm²; boil in 1 m NaOH + 1 m Na_2CO_3 (0.8 l) for 3 h ;

⇒ <75 / 175 / >175 mg/dm²

ISO 719 (stability against hydrolytic attack)

powder 315-500 µm (4x 2 g); expose to 30 ml water in 50 ml flask at 98 °C for 1 h; cool down; fill to 50 ml; titrate 25 ml aliquots by 0.01 m HCl

⇒ <0.1 / 0.2 / 0.85 / 2 / 3.5 ml HCl per g glass

ISO 720 (stability against hydrothermal attack)

powder 300-420 µm (4x 10 g); expose to 50 ml water in 10 ml flask at 121 °C for 0.5 h; cool down; fill to 10 ml; titrate by 0.02 m H_2SO_4

⇒ <0.1 / 0.85 / 1.5 ml H_2SO_4 per g glass

design of
glass corrosion experiments

solution: *)

pH (free, buffered
compensated);

salts (e.g., 9 g/l NaCl);

organics;

redox (e.g., $FeCl_2/FeCl_3$)

temperature:

37±1 or 98±1 °C

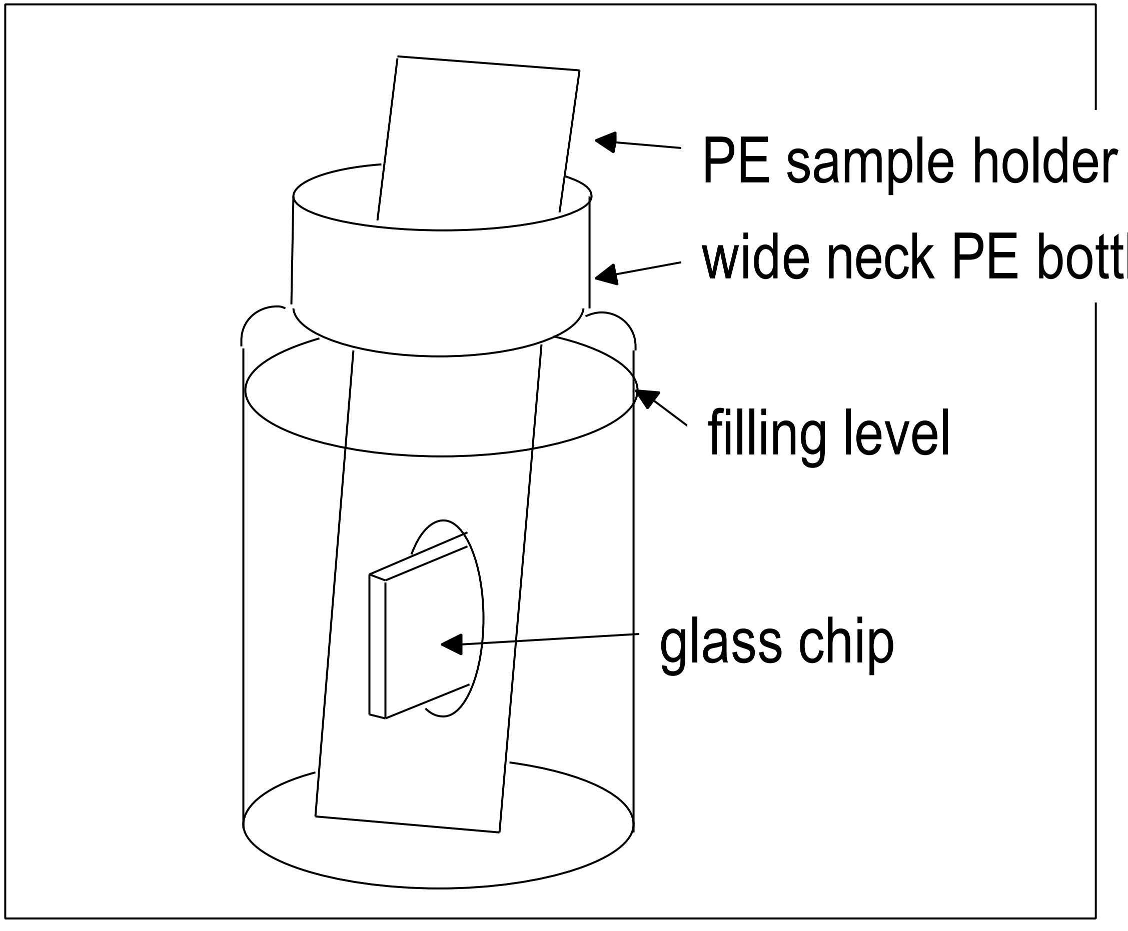
s parameter:

0.1 cm^{-1}

time intervals:

0.5, 1, 2, 4, 8, 16 hours;

1, 3, 7, 14, 28, 60, 120, ... days



similar procedures: see MCC-1, MCC-2 tests

**) no „natural“ reference solution for corrosion experiments*

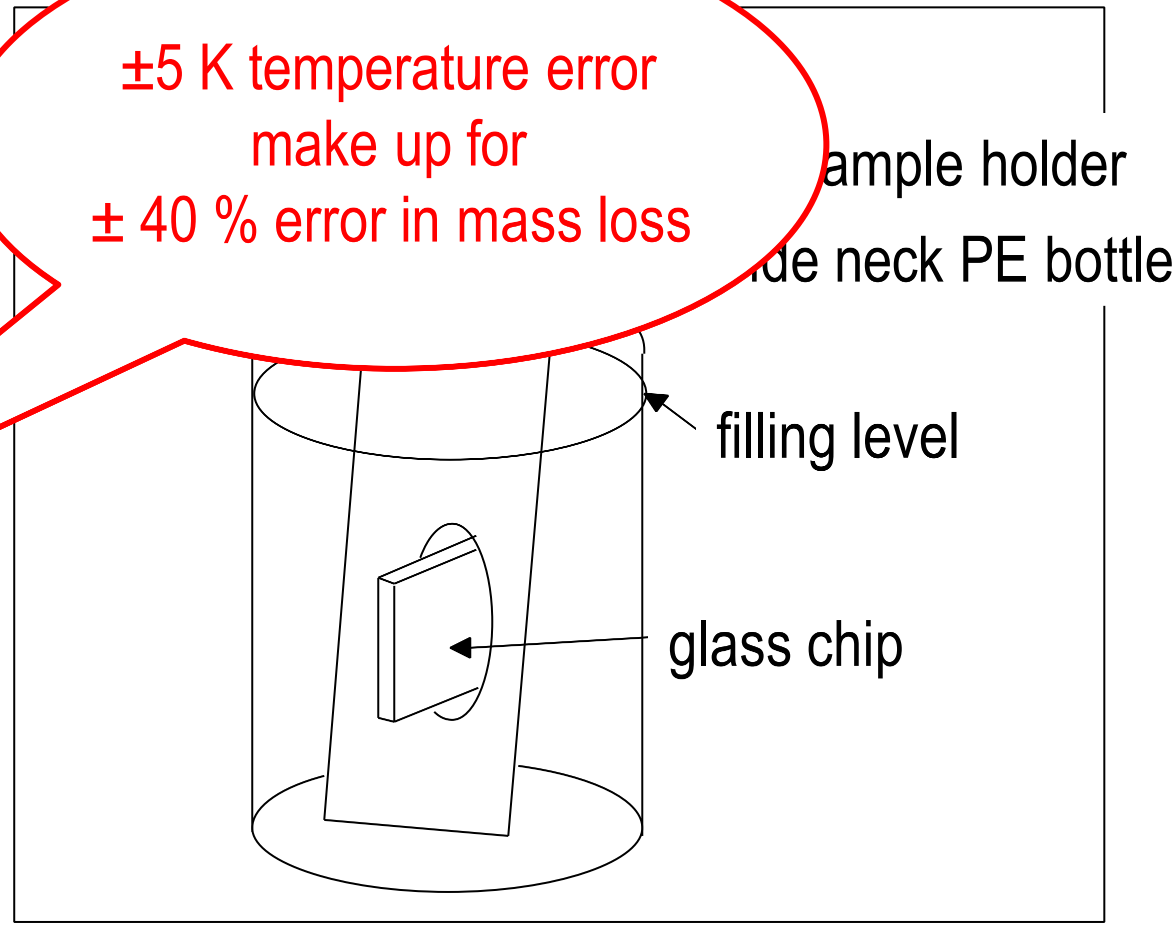
solution: *)
pH (free, buffered
compensated);
salts (e.g., 9 g/l NaCl);
organics;
redox (e.g., $FeCl_2$/FeC

±5 K temperature error
make up for
± 40 % error in mass loss

temperature:
37±1 or 98±1 °C

s parameter:
0.1 cm^{-1}

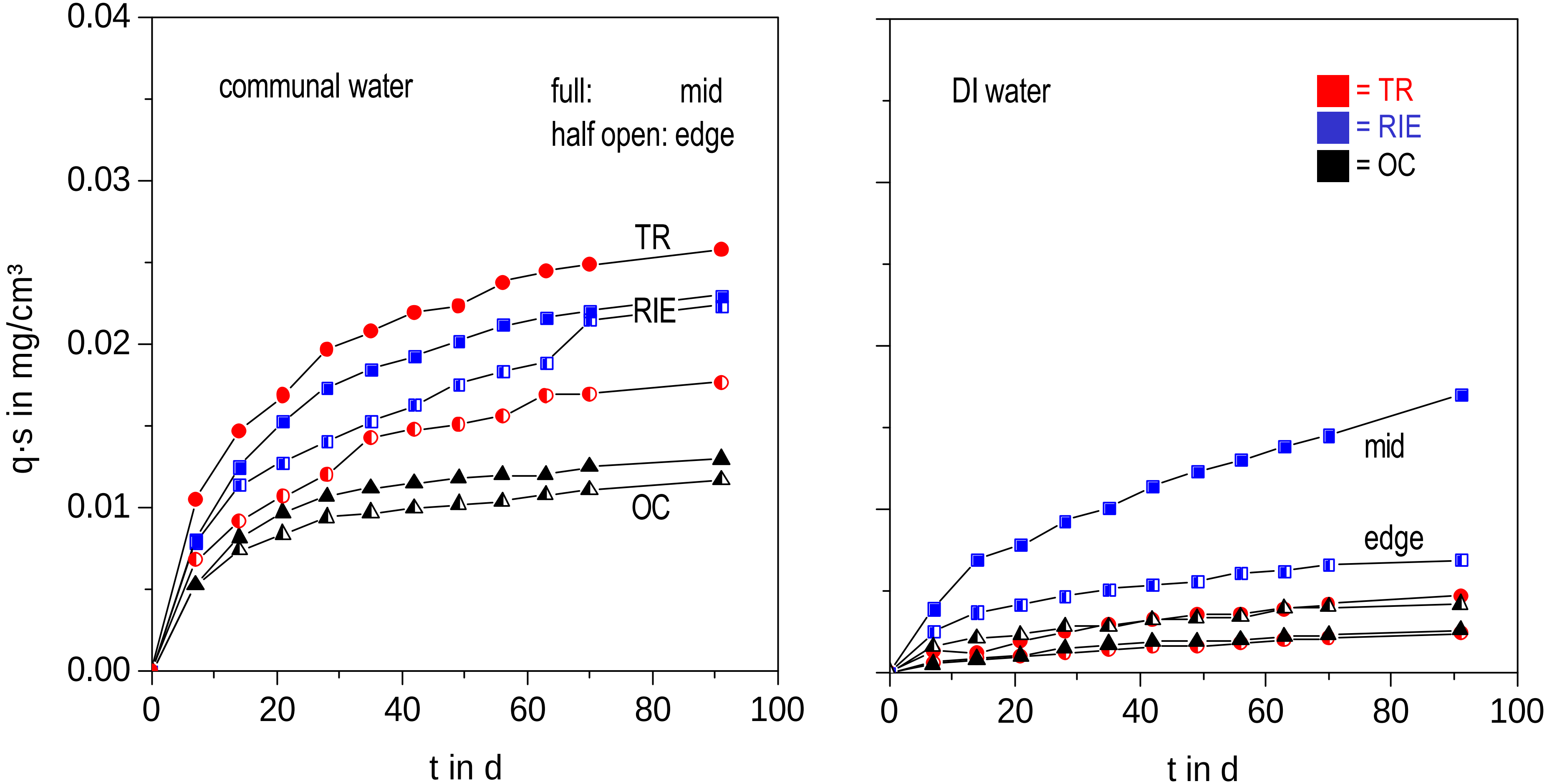
time intervals:
0.5, 1, 2, 4, 8, 16 hours;
1, 3, 7, 14, 28, 60, 120, ... days

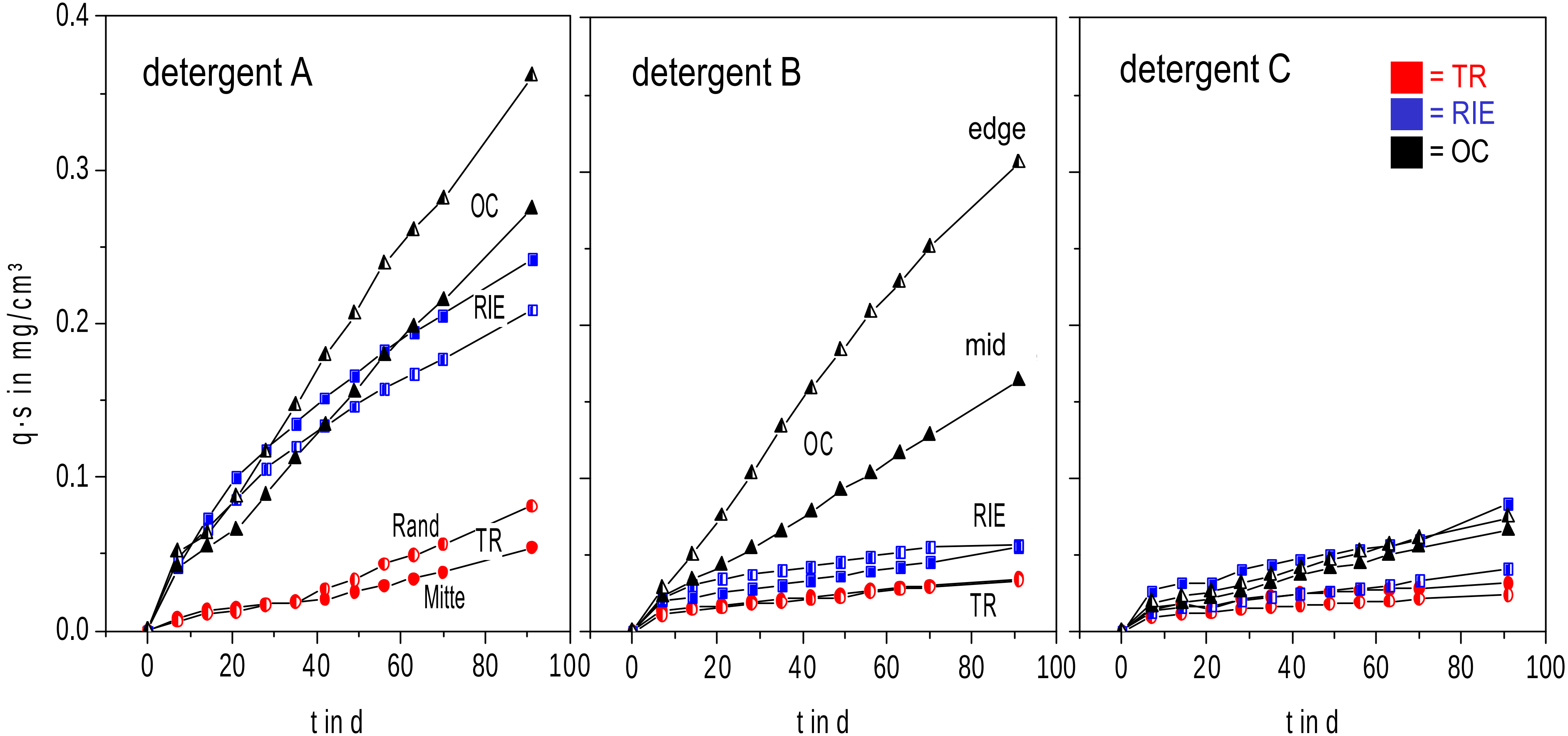


similar procedures: see MCC-1, MCC-2 tests

**) no „natural“ reference solution for corrosion experiments*

	RIE	OC	TR
oxide composition			
SiO_2	60.20	72.50	69.30
ZrO_2	-	-	1.50
TiO_2	-	-	0.60
Al_2O_3	1.00	1.00	1.00
B_2O_3	0.70	-	-
MgO	-	4.11	-
CaO	-	7.10	4.90
ZnO	-	-	2.30
PbO	24.60	-	-
Na_2O	5.30	14.10	9.10
K_2O	8.70	-	10.00
sum	100.50	98.81	98.70
constitutional composition			
$2ZnO \cdot SiO_2$	-	-	3.16
$ZrO_2 \cdot SiO_2$	-	-	0.90
$CaO \cdot TiO_2$	-	-	2.56
$PbO \cdot SiO_2$	31.35	-	-
$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	0.55	-	5.05
$K_2O \cdot 2SiO2$	19.67	-	20.88
$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	-	7.26	5.56
B_2O_3	0.70	-	-
$MgO \cdot SiO_2$	-	10.32	-
$Na_2O \cdot 2SiO_2$	15.64	31.50	20.72
$Na_2O \cdot 3CaO \cdot 6SiO_2$	-	25.13	13.55
SiO_2	32.10	25.80	27.63
sum	100.00	100.00	100.00


communal water
full: mid
half open: edge
TR
RIE
OC
q·s in mg/cm³
t in d
DI water
= TR
= RIE
= OC
mid
edge
t in d



detergent A
detergent B
detergent C
= TR
= RIE
= OC
OC
RIE
Rand
TR
Mitte
edge
mid
OC
RIE
TR
q·s in mg/cm³
t in d
t in d
t in d
0.0
0.1
0.2
0.3
0.4
0
20
40
60
80
100

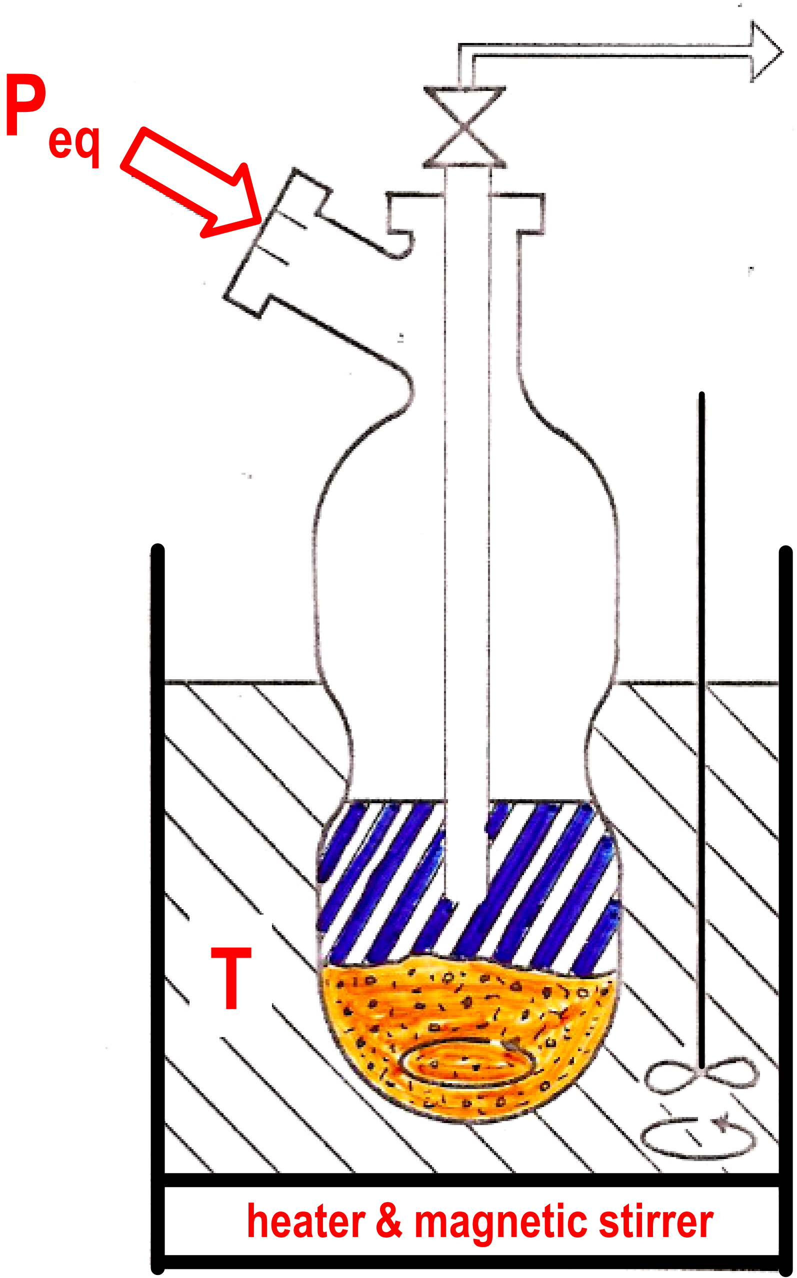
H_2O dest. → rapid change of pH takes place
(specified by el. conductivity)

buffered solutions → may interfere with the corrosion mechanism

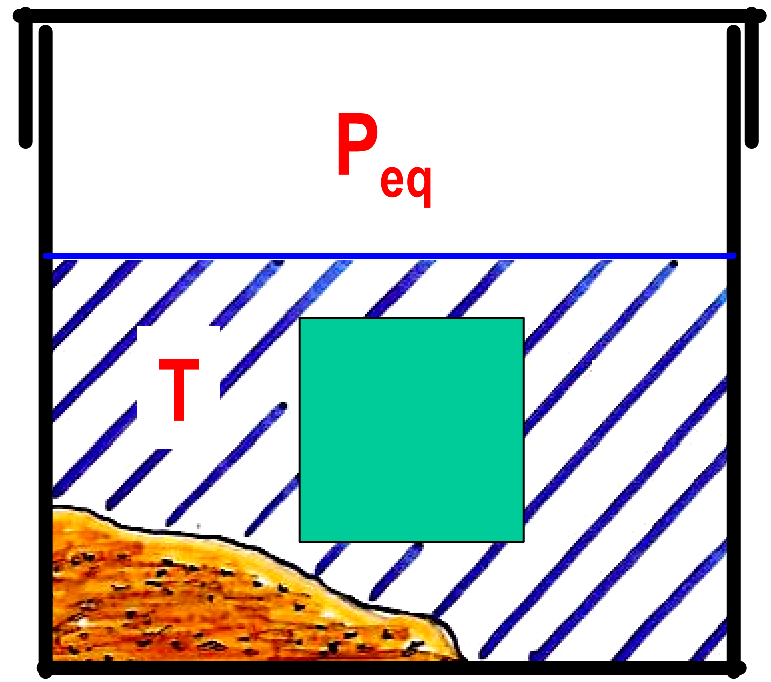
special corrosion media → for specific corrosion scenarios, e.g.,
- salt brines „Q“, „R“, ...;
- granitic or clay waters;
- simulated physiological fluids (9 g/l NaCl, Gamble‘s solution, ...)
- water with dish washing agents

water pre-saturated with glass powder

example:
how to perform a corrosion test
under conditions „close to saturation“



pre-saturation



corrosion test under saturation conditions example: buffered solutions

citrate buffers

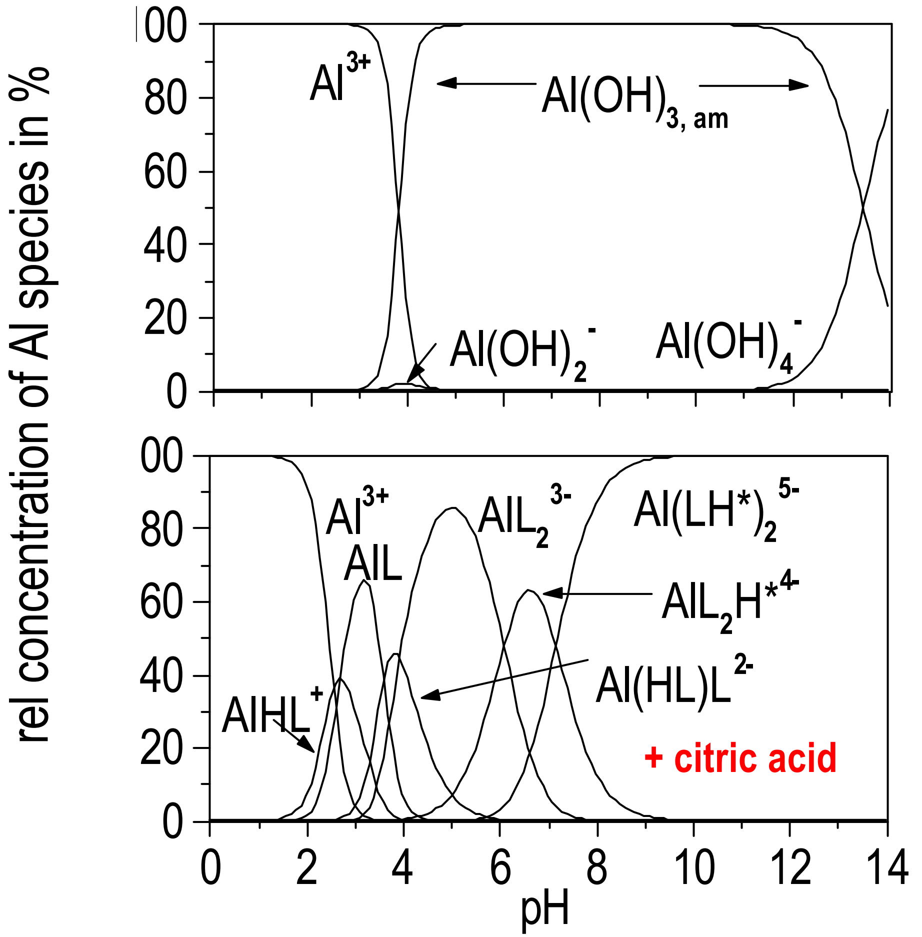
pH	$C_6H_8O_7 \cdot H_2O$ [g]	NaCl [g]	Zusatz *) [ml]	
2	6.43	3.58	8.2	HCl
3	8.47	3.49	20.6	NaOH
4	11.75	2.57	68.0	NaOH
5	20.26	-	196.4	NaOH
6	12.53	-	159.6	NaOH

*) concentration 1 mol/l

Is a buffered constant pH solution
a good reference medium for corrosion tests?

NO WAY!

Citrate buffers, for example, destablize the otherwise very stable alumina. Thus, very corrosion resistant glasses may appear to be very weak in a solution buffered with a citrate buffer.



surface pre-treatment:

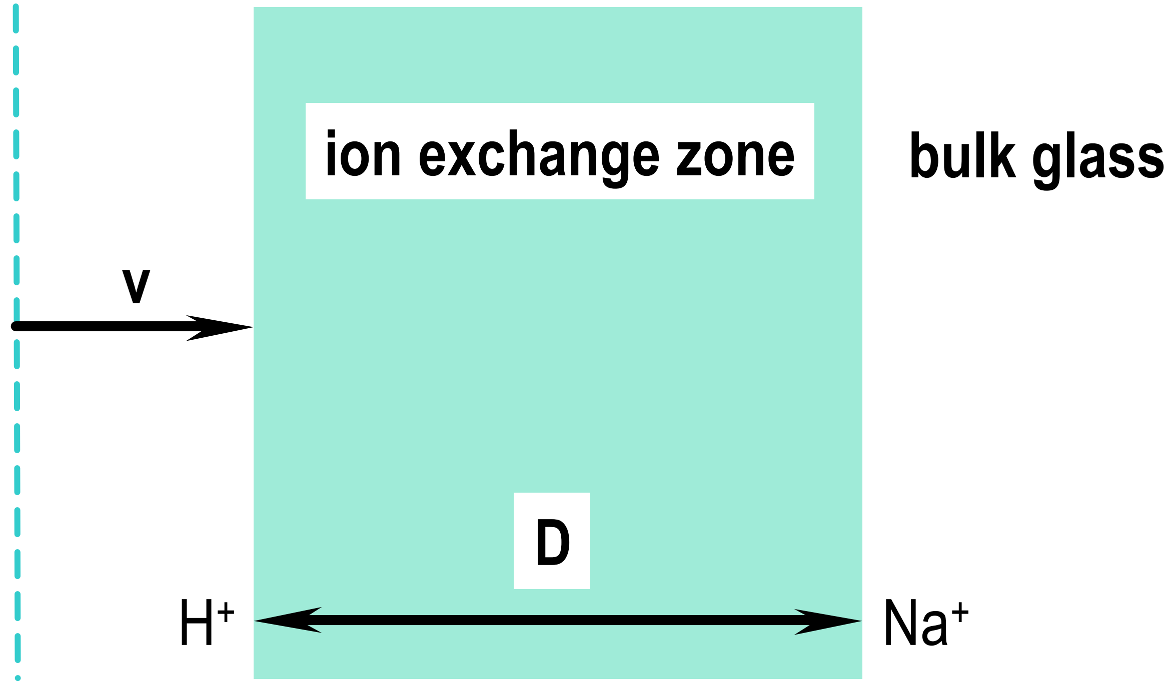
- cut by a low-speed saw in petroleum;
- cut, ground, polished, etched in HF-HNO_3
- as received from the production process
- fire polished
- blown glass foils

etc. etc.

empirical knowledge

standard model

glass surface at $t = 0$



network dissolution
($q \propto t$)

$SiO_2 + H_2O = H_4SiO_4$

$\equiv$Si-O-Si$\equiv$ + H_2O
$\rightarrow$ 2 $\equiv$Si-OH

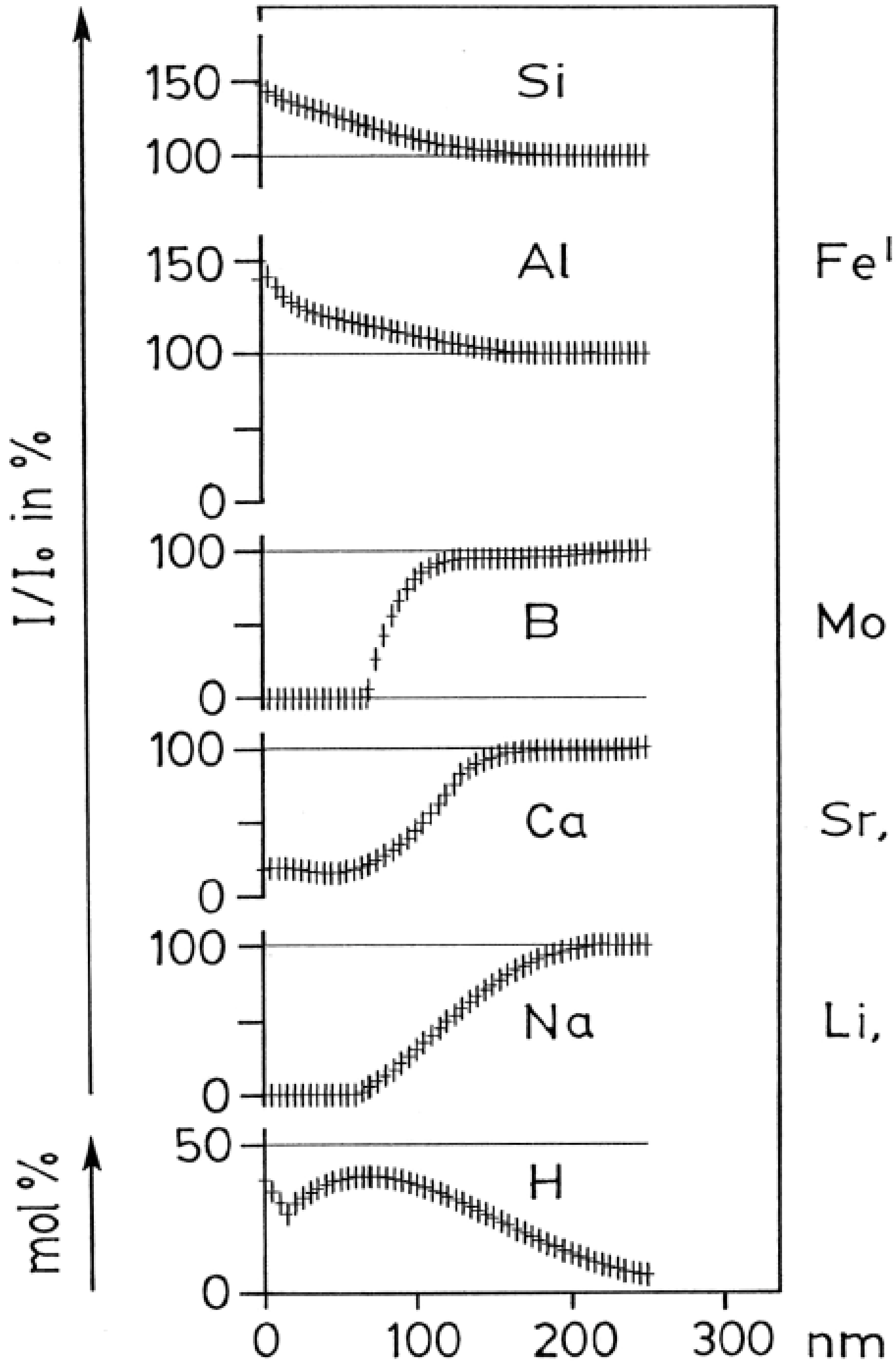
leaching
($q \propto \sqrt{t}$)

$\equiv$Si-O^-Na^+(gl) + H^+(aq)
$\rightarrow$ $\equiv$Si-OH(gl) + Na^+(aq)

The conclusion

„the network modifiers are leached preferentially, the network formers are left behind as a scaffold dissolving slowly“ is misleading.

The covalent / ionic nature of the metal-oxygen bond has almost **<u>nothing</u>** to do with its stability against aqueous attack. Think of Si-O vs. P-O! Think of pure P_2O_5 vs. natural bones.
How would a MgO-B_2O_3 glass behave?



Fe^{III}, Zn, Mg

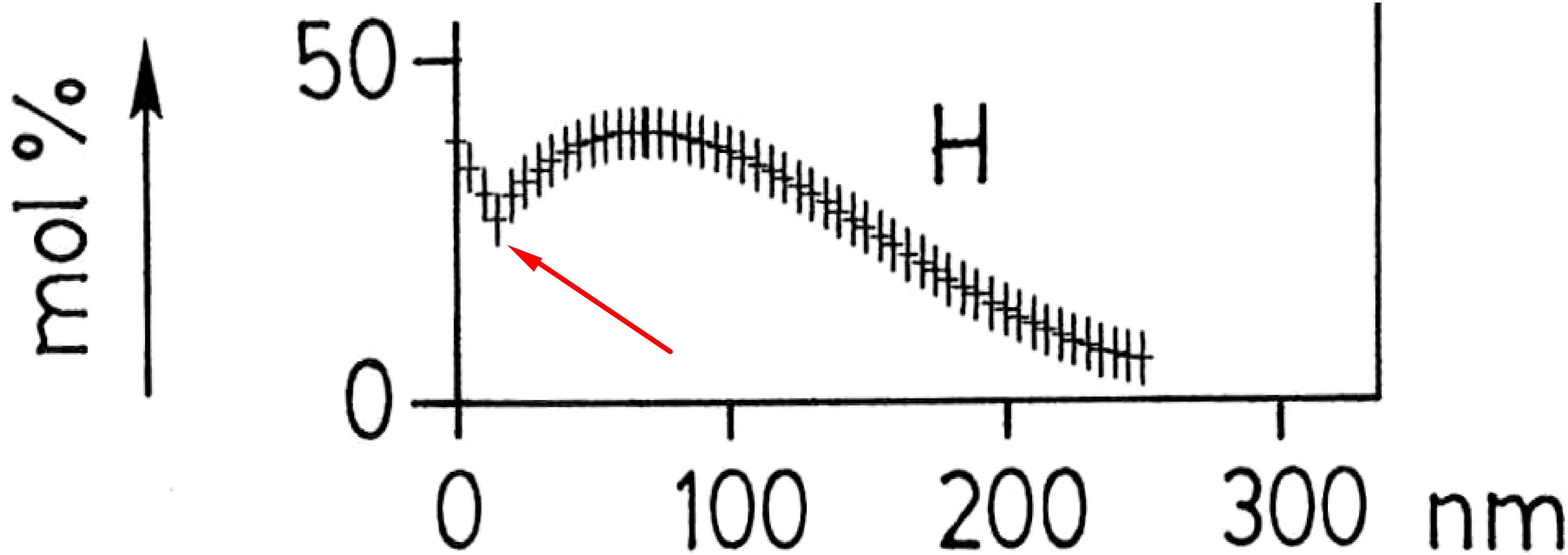
Mo

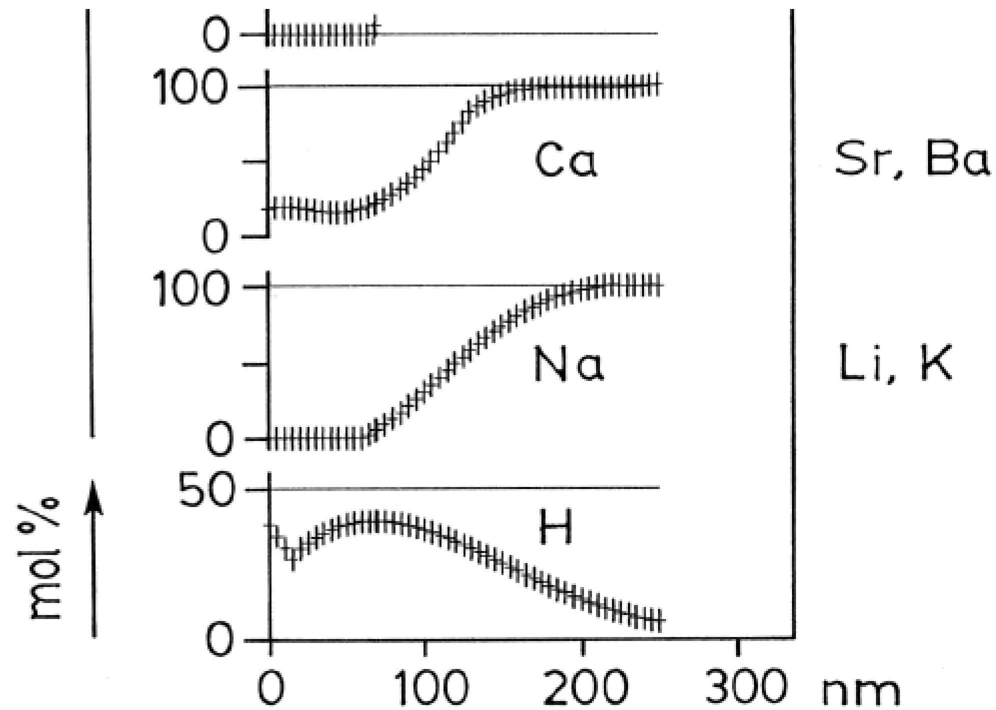
Sr, Ba

Li, K

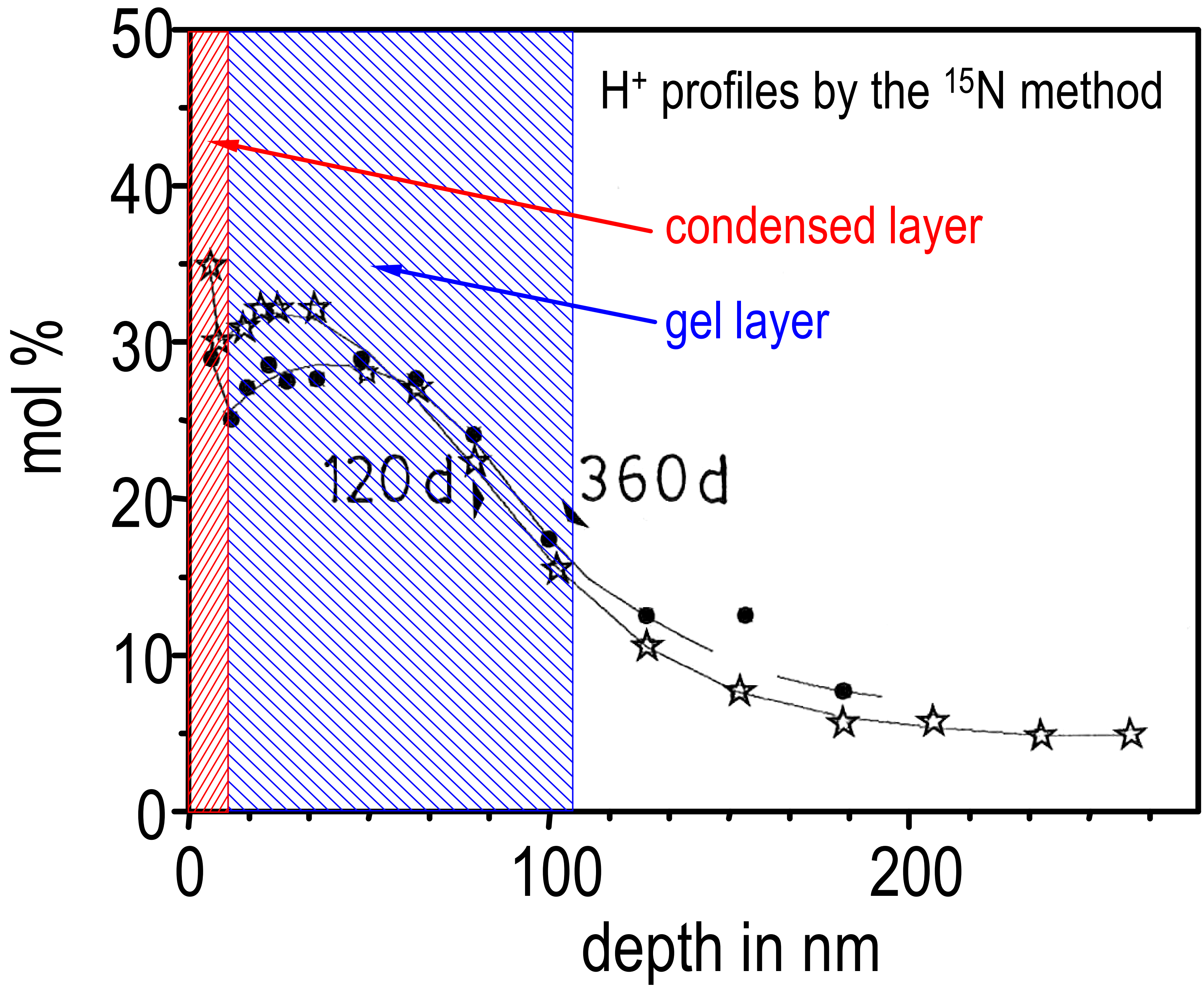
misleading view:
network modifiers are depleted,
network formers are enriched

correct view:
an incongruent dissolution process takess place;
the glass components are enriched or depleted according to their solubility in the aqueous system

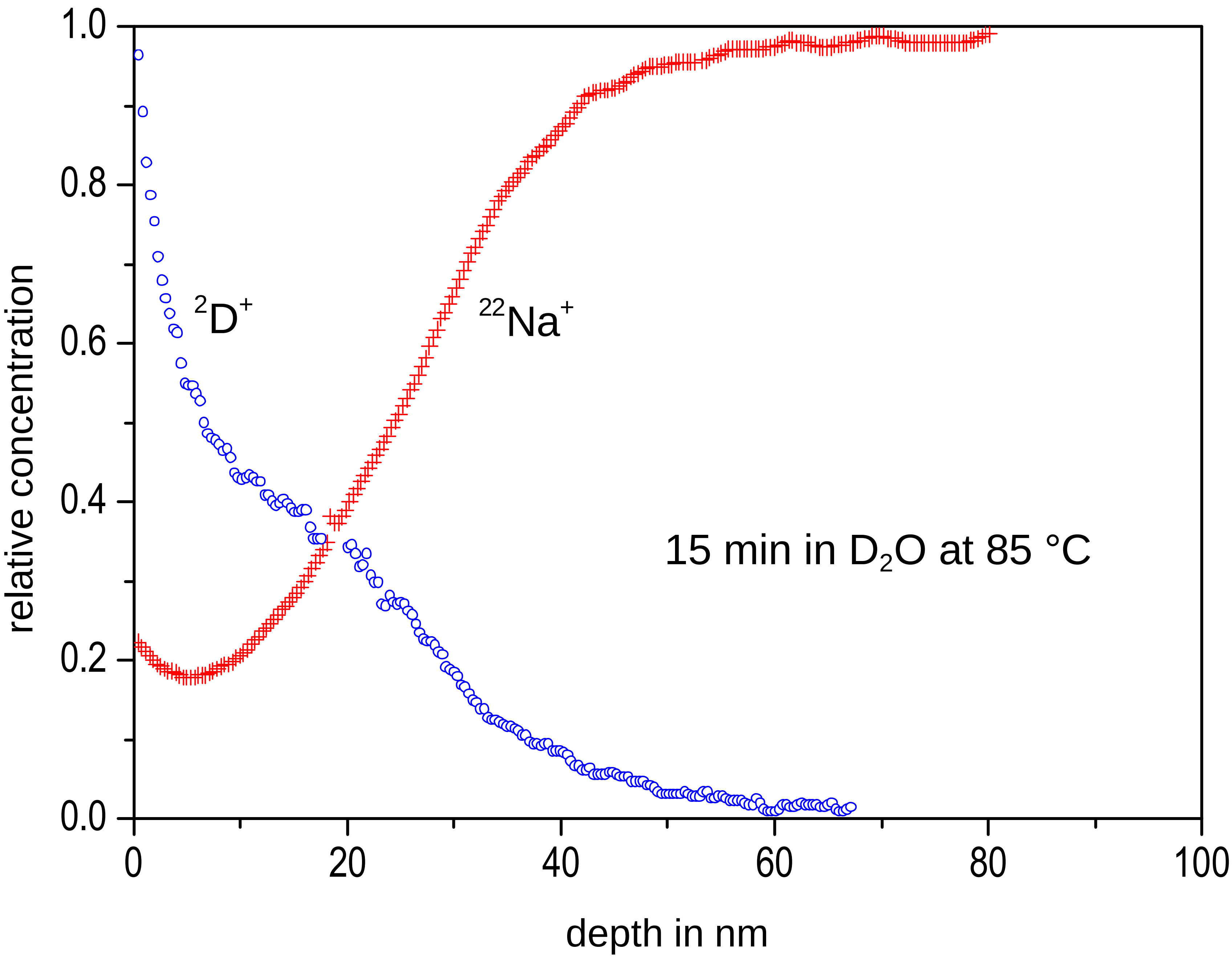


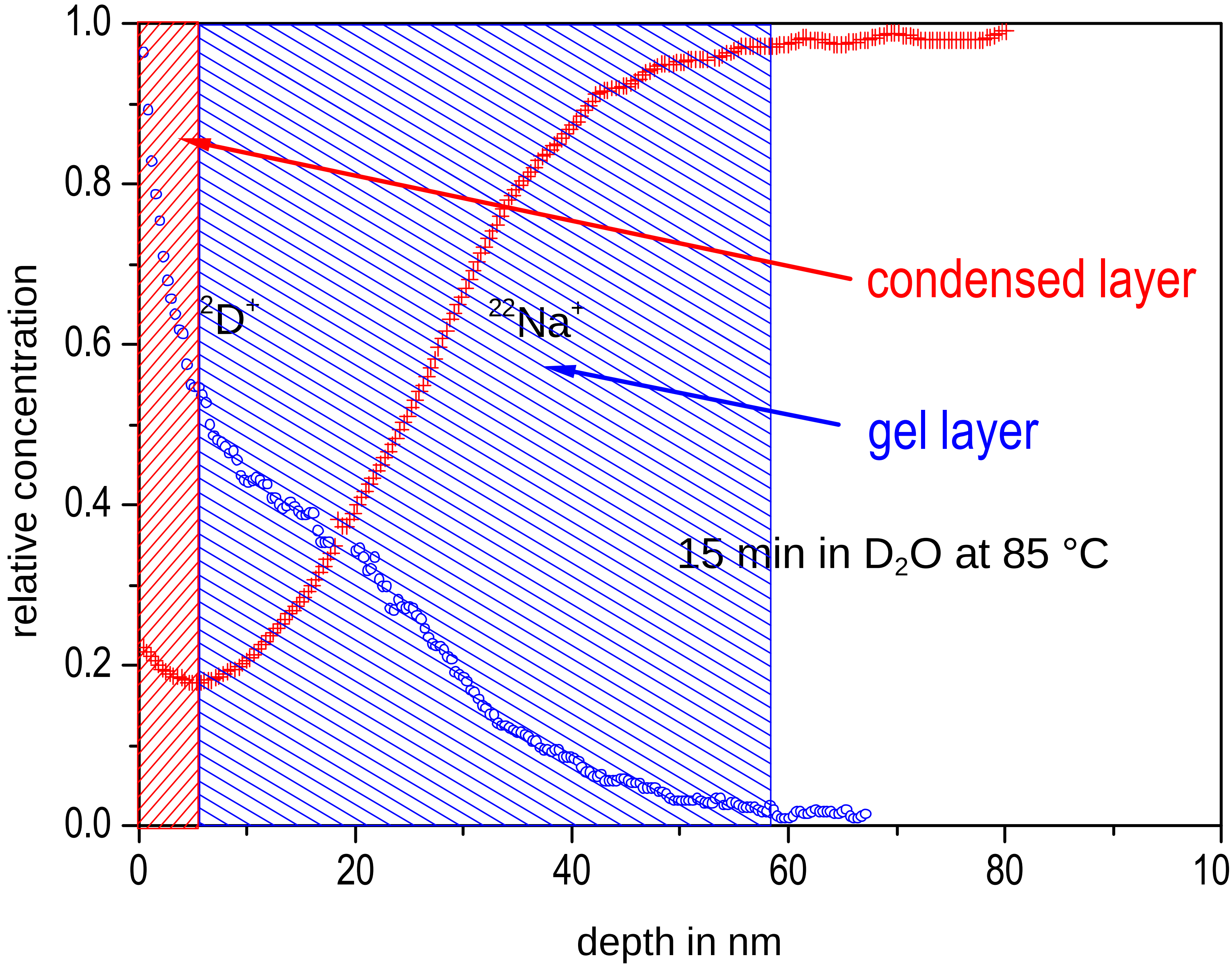


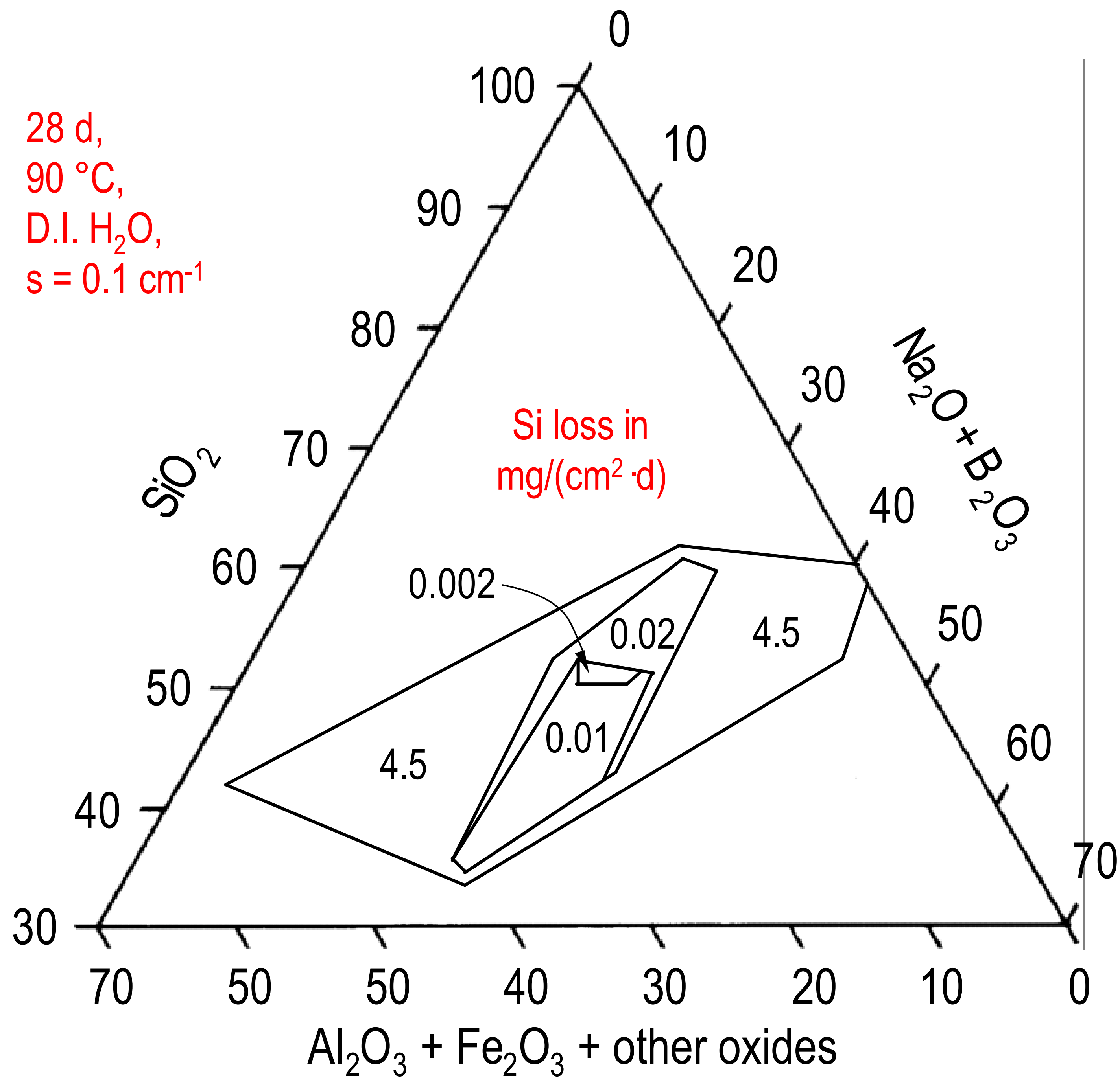
new paradigm:
incongruent dissolution
according to the solubility
of individual oxides



H+ profiles by the 15N method
condensed layer
gel layer
120 d
360 d
mol %
depth in nm
0
10
20
30
40
50
0
100
200


1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
relative concentration
depth in nm
$^{2}D^{+}$
$^{22}Na^{+}$
15 min in D_2O at 85 °C


1.0
0.8
0.6
0.4
0.2
0.0
relative concentration
0
20
40
60
80
100
depth in nm
condensed layer
gel layer
2D+
22Na+
15 min in D2O at 85 °C



28 d,
90 °C,
D.I. H2O,
s = 0.1 cm-1
Si loss in
mg/(cm2 ·d)
0.002
0.02
0.01
4.5
4.5
SiO2
Na2O+B2O3
Al2O3 + Fe2O3 + other oxides
100
90
80
70
60
50
40
30
0
10
20
30
40
50
60
70
70
50
50
40
30
20
10
0

Let us learn from metallurgy:

corrosion resistance =

f (thermodynamic stability, layer formation, passivation)

metals

the elementary process of metal corrosion is ***electron transfer*** (redox reactions):

in air

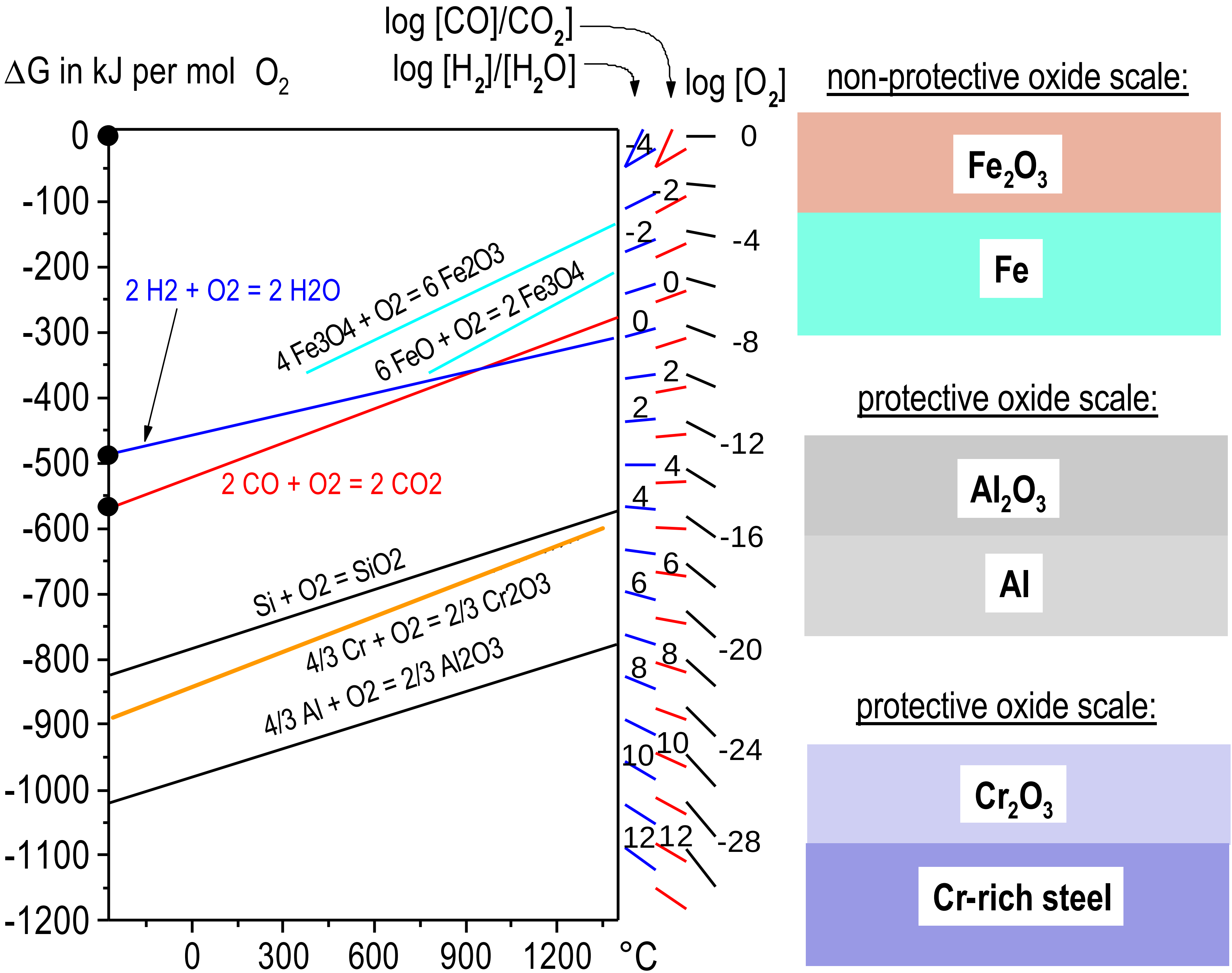
$2Fe^0$	$\rightarrow$	$2Fe^{2+} + 4e^-$
$O_2 + 4e^-$	$\rightarrow$	$2O^{2-}$
$2Fe^0 + O_2$	$\rightarrow$	$2FeO$

in water

$2Fe^0$	$\rightarrow$	$2Fe^{2+} + 4e^-$
$2H_2O + 4e^-$	$\rightarrow$	$2H_2 \quad + 4\ OH^-$
$2Fe^0 + 2H_2O$	$\rightarrow$	$2Fe(OH)_2(aq) + 2H_2$

in a slag

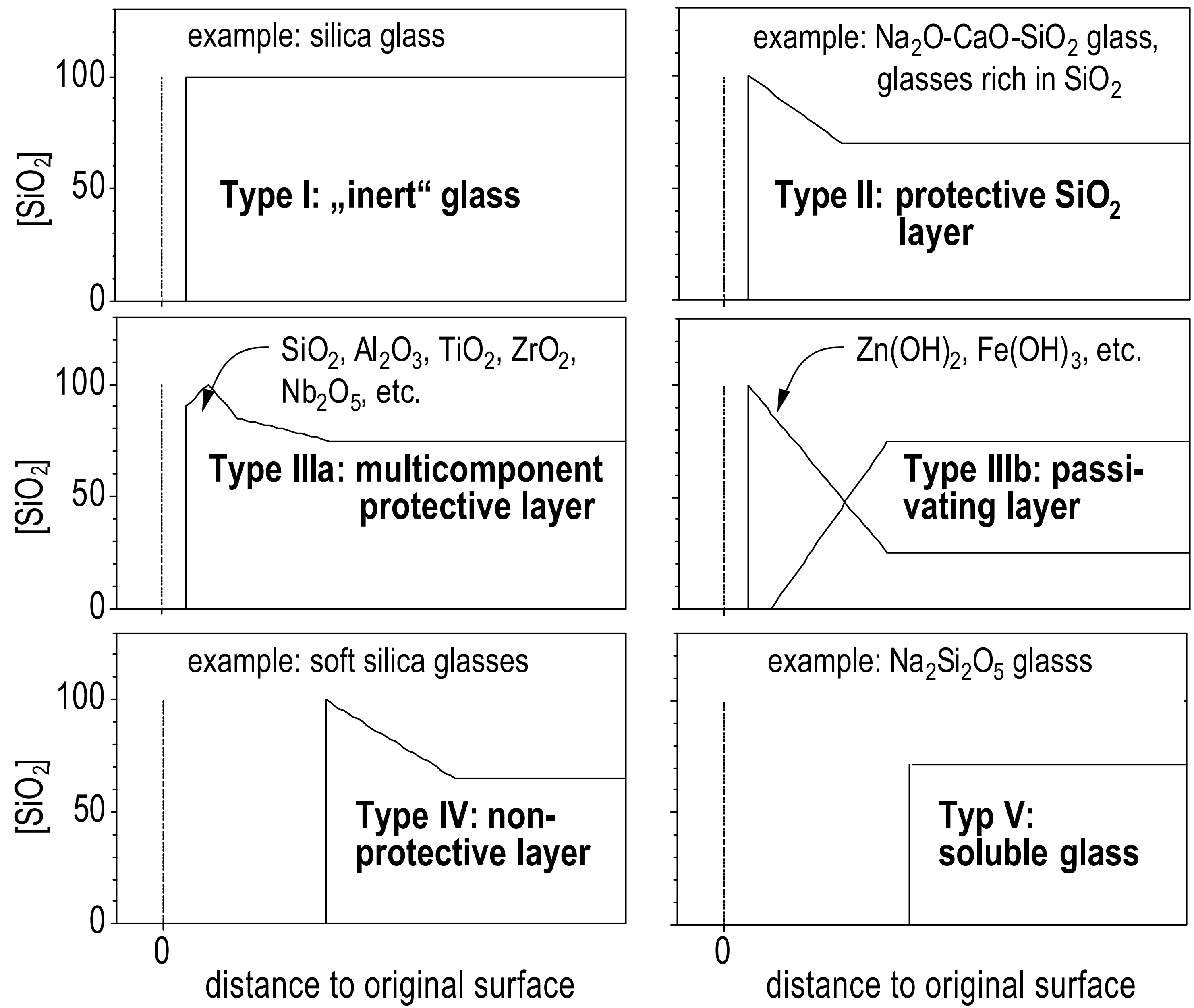
$2Fe^0$	$\rightarrow$	$2Fe^{2+} + 4e^-$
$O_2 + 4e^-$	$\rightarrow$	$2O^{2-}$
$2Fe^0 + O_2$	$\rightarrow$	$2FeO(slag)$



ΔG in kJ per mol O2
log [CO]/CO2]
log [H2]/[H2O]
log [O2]
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
-1100
-1200
0
300
600
900
1200
°C
2 H2 + O2 = 2 H2O
2 CO + O2 = 2 CO2
4 Fe3O4 + O2 = 6 Fe2O3
6 FeO + O2 = 2 Fe3O4
Si + O2 = SiO2
4/3 Cr + O2 = 2/3 Cr2O3
4/3 Al + O2 = 2/3 Al2O3
-4
-2
0
2
4
6
8
10
12
0
-4
-8
-12
-16
-20
-24
-28
non-protective oxide scale:
Fe2O3
Fe
protective oxide scale:
Al2O3
Al
protective oxide scale:
Cr2O3
Cr-rich steel

The layer must

- be an effective diffusion barrier
- adhere well to the metal
- passivate the metal (forestall the e^- transfer)



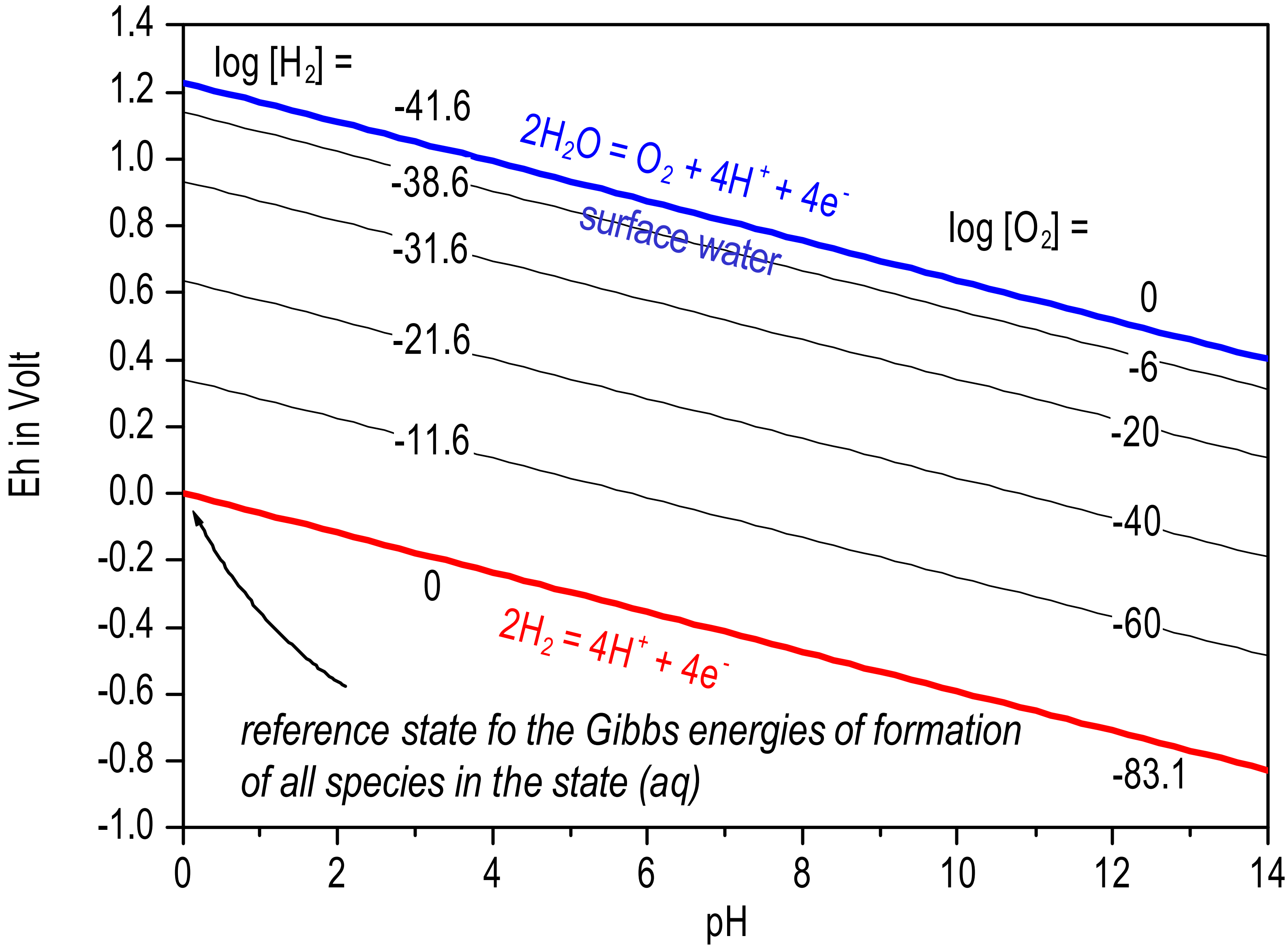
example: silica glass
Type I: „inert“ glass
example: Na_2O-CaO-SiO_2 glass, glasses rich in SiO_2
Type II: protective SiO_2 layer
SiO_2, Al_2O_3, TiO_2, ZrO_2, Nb_2O_5, etc.
Type IIIa: multicomponent protective layer
$Zn(OH)_2$, $Fe(OH)_3$, etc.
Type IIIb: passi-vating layer
example: soft silica glasses
Type IV: non-protective layer
example: $Na_2Si_2O_5$ glasss
Typ V: soluble glass
[SiO_2]
100
50
0
distance to original surface

L.L. Hench

The layer must

- be an effective diffusion barrier
- adhere well to the residual glass
- passivate the glass (forestall the H^+ transfer)

the driving force of glass corrosion



$2H_2O = 2H_2 + O_2$; $G^f = 474.360$ kJ/mol; $K_f = 7.8 \cdot 10^{-84}$

$H_2O = H^+ + OH^-$; $G_w = 79.880$ kJ/mol; $K_w = 1.0 \cdot 10^{-14}$

species	-Gf_e (kJ/mol)
$H_2O(l)$	237.180
$H^+(aq)$	0.000
$H_2O - OH^-(aq) = H^+(aq)$	79.880
$OH^-(aq)$	157.300
$HO_2^-(aq)$	67.362
$H_2O_2(l)$	134.097
$H_2(aq)$	-17.573
$O_2(aq)$	-16.318
$H_2(g)$	0.000
$O_2(g)$	0.000

The state „dissolved in water“ is a state like the states „solid“, „liquid“, and „gas“. It is denoted by (aq).

Spezies	$-G^f_e$ (kJ/mol)	Spezies	$-G^f_e$ (kJ/mol)
$CO_2(g)$	394.570	$F_2(g)$	0.000
$CO_2(aq)$	386.016	F^-	279.993
HCO_3^-	586.848	$HF(aq)$	298.110
CO_3^{2-}	527.895	HF_2^-	581.492
$SiO_2(s)$	854.910	$P_2O_5(s)$	1349.570
$SiO_2(aq)$	1307.760	$H_3PO_4(aq)$	1142.650
$H_3SiO_4^-$	1251.990	$H_2PO_4^-$	1130.391
$H_2SiO_4^{2-}$	1185.460	HPO_4^{2-}	1089.263
$HSiO_4^{3-}$	1116.547	PO_4^{3-}	1018.804
SiO_4^{4-}	1048.230	$H_4P_2O_7(aq)$	2032.160
$H_6[H_2SiO_4]_4^{2-}$	5153.236	$H_3P_2O_7^-$	2026.830
$H_4[H_2SiO_4]_4^{4-}$	5025.951	$H_2P_2O_7^{2-}$	2003.410
$HSiO_3^-$	1005.46	$HP_2O_7^{3-}$	1961.710
SiO_3^{2-}	938.51	$P_2O_7^{4-}$	1919.200
		$H_5P_3O_{10}(aq)$	2921.670
$Al_2O_3(s)$	1583.150	$H_4P_3O_{10}^-$	2923.190
Al^{3+}	492.000	$H_3P_3O_{10}^{2-}$	2917.480
$Al(OH)^{2+}$	700.653	$H_2P_3O_{10}^{3-}$	2094.550
$Al(OH)_2^+$	907.384	$HP_3O_{10}^{4-}$	2872.550
$Al(OH)_3(aq)$	1111.061	$P_3O_{10}^{5-}$	2821.490
$Al(OH)_3(am)$	1137.630		
$Al(OH)_4^-$	1305.410	B_2O_3	1194.270
		$H_3BO_3(aq)$	968.638
$Fe_2O_3(s)$	739.960	$H_2BO_3^-$	917.564
Fe^{3+}	17.866	HBO_3^{2-}	845.695
$FeOH^{2+}$	240.413	BO_3^{3-}	769.182
$Fe(OH)_2^+$	457.228		
$Fe(OH)_3(aq)$	670.695	TiO_2	889.940
$Fe(OH)_3(s)$	696.636	TiO^{2+}	577.392
$Fe(OH)_4^-$	841.821	TiO_2OH^-	467.353
		$TiO(OH)_2$ s	1058.552
FeO	250.990		
Fe^{2+}	92.257	ZrO_2	1036.870
$FeOH^+$	279.951	Zr^{4+}	594.128
$Fe(OH)_2(aq)$	457.102	ZrO^{2+}	843.076
$Fe(OH)_2(s)$	486.599	ZrO_2OH^-	1203.737
$Fe(OH)_3^-$	619.232	$ZrO(OH)_2$ s	1303.316

Spezies	$-G^f_e$ (kJ/mol)	Spezies	$-G^f_e$ (kJ/mol)
$MgO(s)$	569.840	$PbO(s)$	188.489
Mg^{2+}	455.261	Pb^{2+}	24.393
$MgOH^+$	638.064	$PbOH^+$	226.354
$Mg(OH)_2(aq)$	769.438	$Pb(OH)_2(aq)$	400.827
$Mg(OH)_2(s)$	833.746	$Pb(OH)_3^-$	575.718
$MgCO_3(aq)$	1002.486		
$MgCO_3(s)$	1012.110	$BaO(s)$	528.690
$MgHCO_3^-$	1050.602	Ba^{2+}	547.518
$CaO(s)$	604.460	$Li_2O(s)$	561.760
Ca^{2+}	552.706	Li^+	292.629
$CaOH^+$	716.970		
$Ca(OH)_2(aq)$	868.138	$Na_2O(s)$	376.740
$Ca(OH)_2(s)$	897.008	Na^+	262.211
$CaCO_3(aq)$	1081.438		
$CaCO_3(s)$	1128.760	$K_2O(s)$	322.200
$CaHCO_3^-$	1145.035	K +	282.671
$SrO(s)$	562.680	$Cs_2O(s)$	308.300
Sr^{2+}	571.451	Cs^+	292.001
$SrOH^+$	733.455		
$Sr(OH)_2(aq)$	871.109	$Nd_2O_3(s)$	1721.700
$Sr(OH)_2(s)$	881.987	Nd^{3+}	671.532
$SrCO_2(aq)$	1087.338	$Nd_2(OH)_2^{4+}$	1738.230
$SrCO_3(s)$	1140.140	$Nd(OH)^{2+}$	863.126
		$Nd(OH)_3(s)$	1259.221
$MnO(s)$	363.340	$Nd(OH)_4^-$	1407.096
Mn^{2+}	229.953		
$MnOH^+$	406.685	$MoO_3(s)$	655.778
$Mn(OH)_2(s)$	615.048	MoO_2^{2+}	411.287
$Mn(OH)_3^-$	746.426	$MoO_2(OH)^+$	645.884
		$H_2MoO_4(aq)$	877.134
$ZnO(s)$	318.470	$HMoO_4^-$	866.632
Zn^{2+}	147.193	MoO_4^{2-}	838.055
$ZnOH^+$	333.256		
$Zn(OH)_2(aq)$	535.385	$Nb_2O_5(s)$	1765.82
$Zn(OH)_3^-$	704.711	$Nb(OH)_5(aq)$	1448.50
$Zn(OH)_4^{2-}$	871.276	NbO_3^-	932.20

Spezies	$-G^{f}_{e}$ (kJ/mol)	Spezies	$-G^{f}_{e}$ (kJ/mol)	Spezies	$-G^{f}_{e}$ (kJ/mol)	Spezies	$-G^{f}_{e}$ (kJ/mol)
CO_2(g)	394.570	F_2(g)	0.000	MgO(s)	569.840	PbO(s)	188.489
CO_2(aq)	386.016	F^-	279.993	Mg^{2+}	455.261	Pb^{2+}	24.393
HCO_3^-	586.848	HF(aq)	298.110	$MgOH^+$	638.064	$PbOH^+$	226.354
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SiO_3^{2-}	938.51	$P_2O_7^{4-}$	1919.200	$CaCO_3$(aq)	1081.438		
		$H_5P_3O_{10}$(aq)	2921.670	$CaCO_3$(s)	1128.760	K_2O(s)	322.200
Al_2O_3(s)	1583.150	$H_4P_3O_{10}^-$	2923.190	$CaHCO_3^-$	1145.035	K +	282.671
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$Al(OH)_3$(am)	1137.630			$Sr(OH)_2$(aq)	871.109	Nd_2O_3(s)	1721.700
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$Fe(OH)_2$(aq)	457.102	ZrO^{2+}	843.076	$Zn(OH)_2$(aq)	535.385	Nb_2O_5(s)	1765.82
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$Fe(OH)_3^-$	619.232	$ZrO(OH)_2$ s	1303.316	$Zn(OH)_4^{2-}$	871.276	NbO_3^-	932.20

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Al^{3+}	492.000
$Al(OH)^{2+}$	700.653
$Al(OH)_2^{+}$	907.384
$Al(OH)_3(aq)$	1111.061
$Al(OH)_3(am)$	1137.630
$Al(OH)_4^{-}$	1305.410

$$Al_2O_3 + 6\,H^+ \rightarrow 2\,Al^{3+} + 3\,H_2O$$

$$+ 4\,H^+ \rightarrow 2\,AlOH^{2+} + H_2O$$

$$+ 2\,H^+ + H_2O \rightarrow 2\,Al(OH)_2^{+}$$

$$+ 3\,H_2O \rightarrow 2\,Al(OH)_3$$

$$+ 5\,H_2O \rightarrow 2\,Al(OH)_4^{-} + 2\,H^+$$

$$Al_2O_3 + n\cdot H^+ + m\cdot H_2O \leftrightarrow 2\cdot i$$

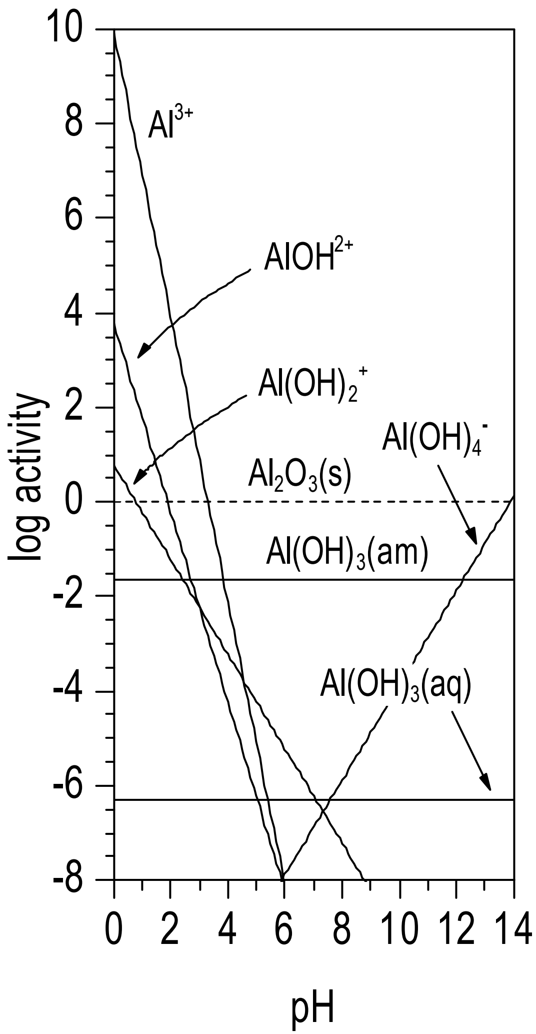
$$K_i = \frac{a_i^2}{[Al_2O_3]\cdot[H^+]^n\cdot[H_2O]^m}$$

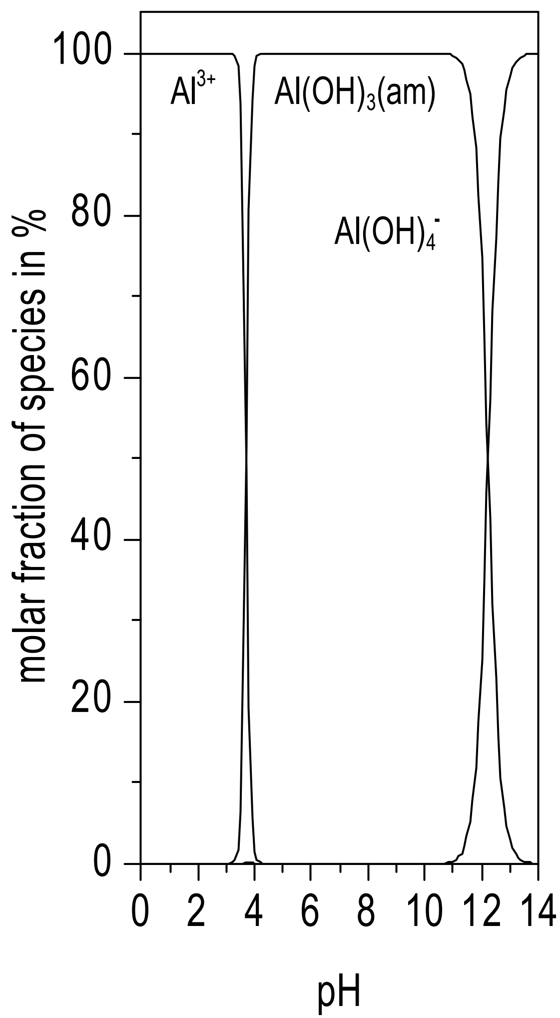
$$\log a_i = \frac{1}{2}\cdot\log K_i - \frac{n}{2}\cdot pH$$

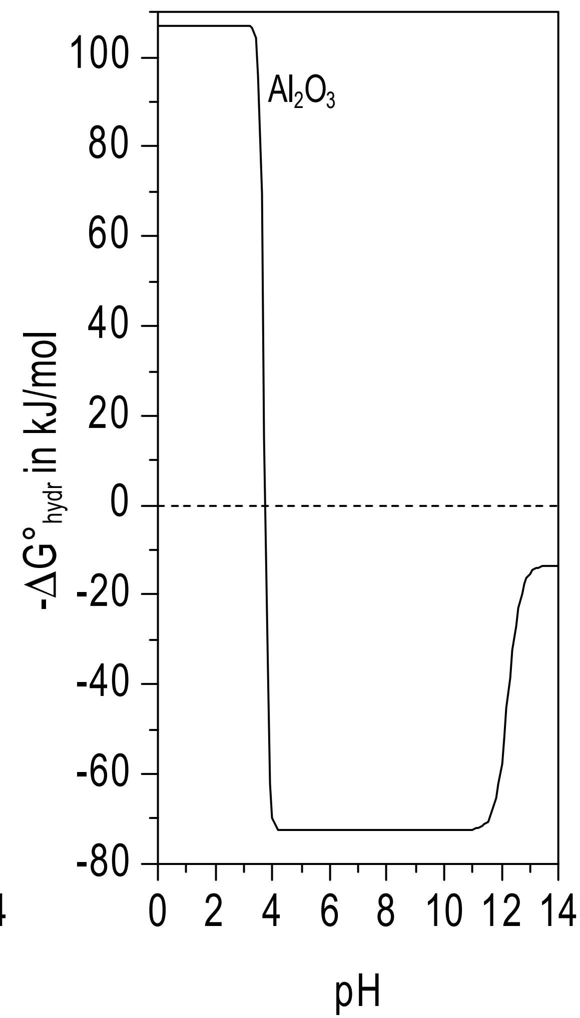
$$x_i = \frac{10^{\log a_i}}{\sum 10^{\log a_i}}$$

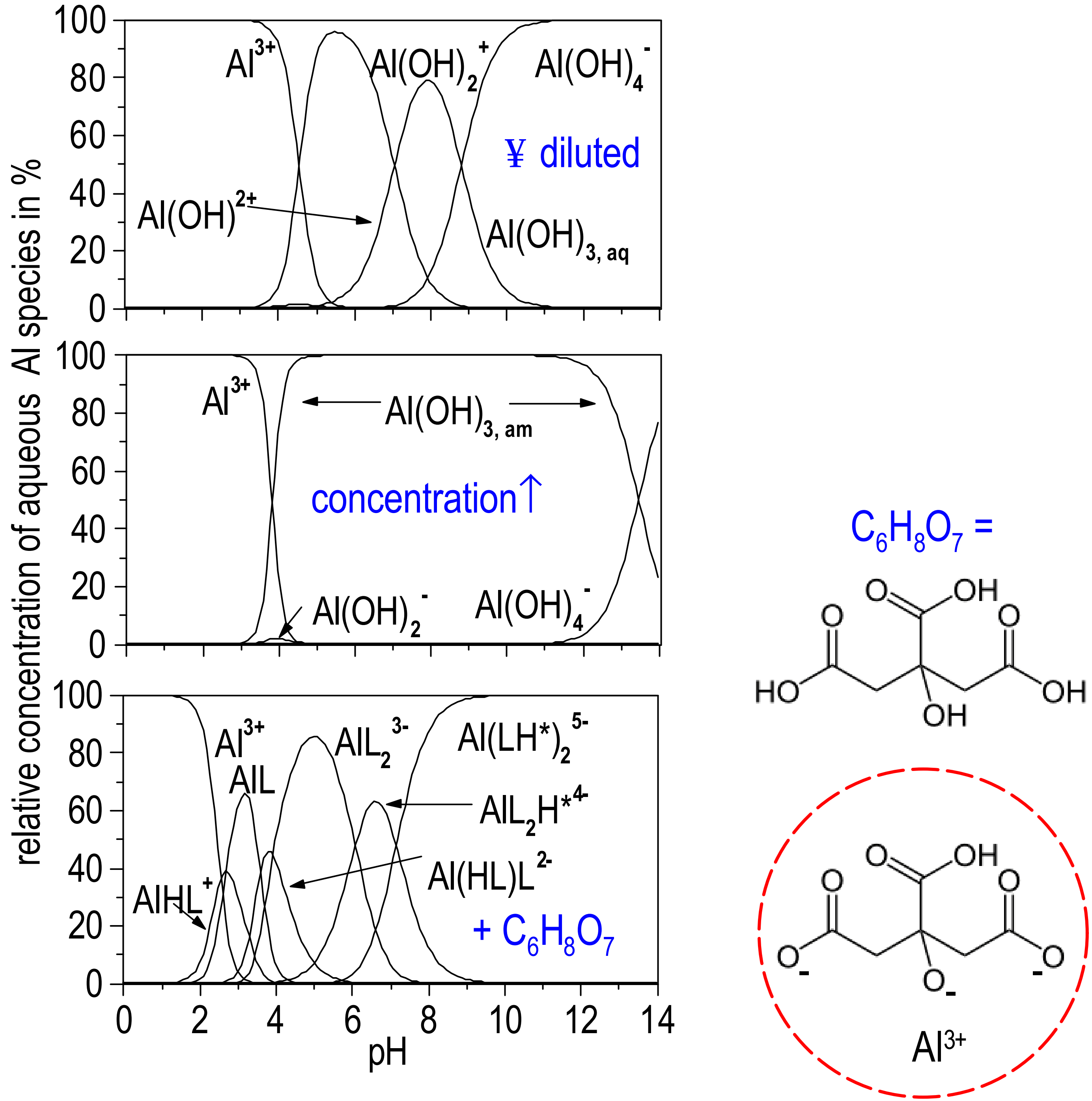
$$species\ \% = 100\cdot x_i$$

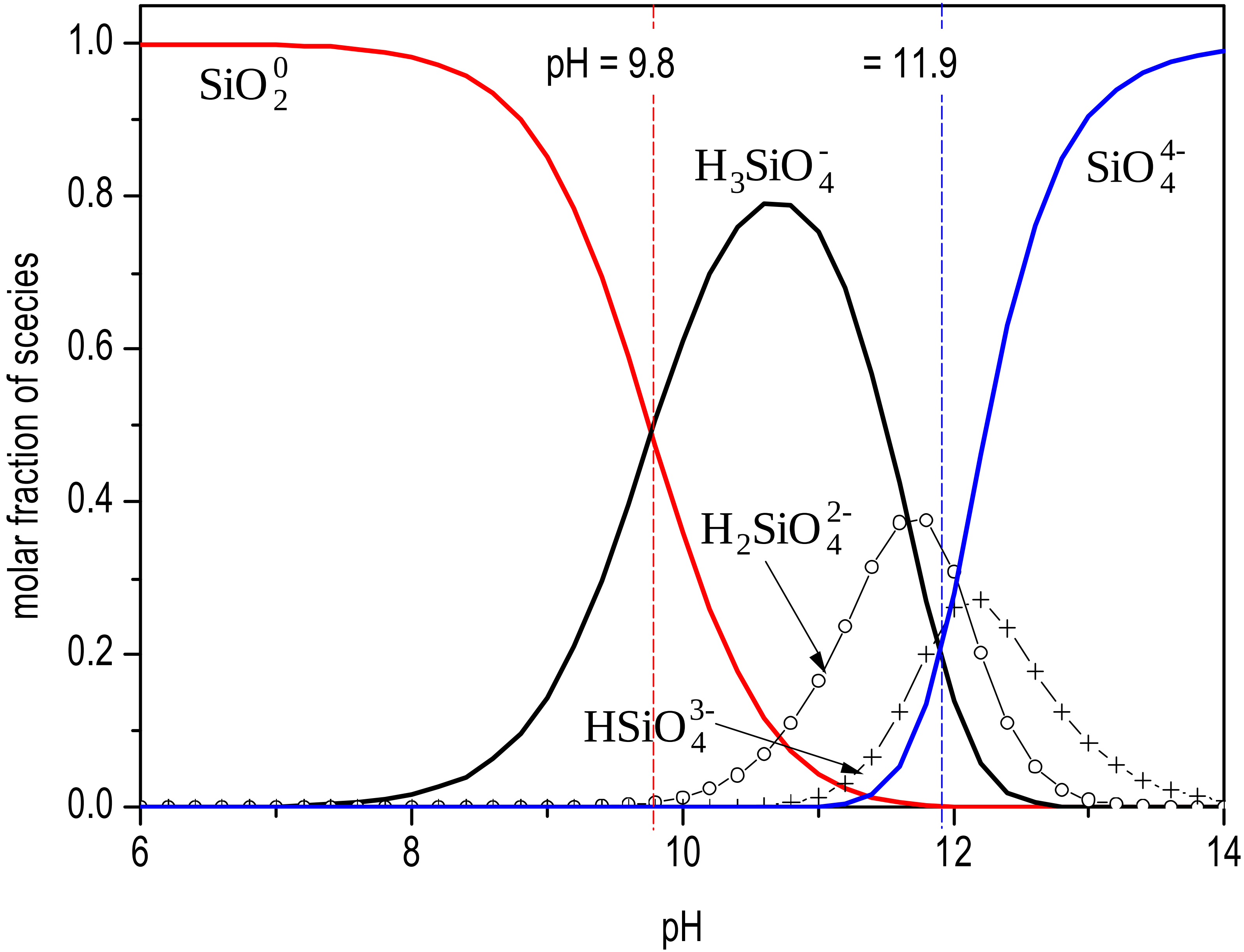
$$-\Delta G^o_{hydr}(Al_2O_3) = -RT\cdot\sum x_i\cdot\ln K_i$$



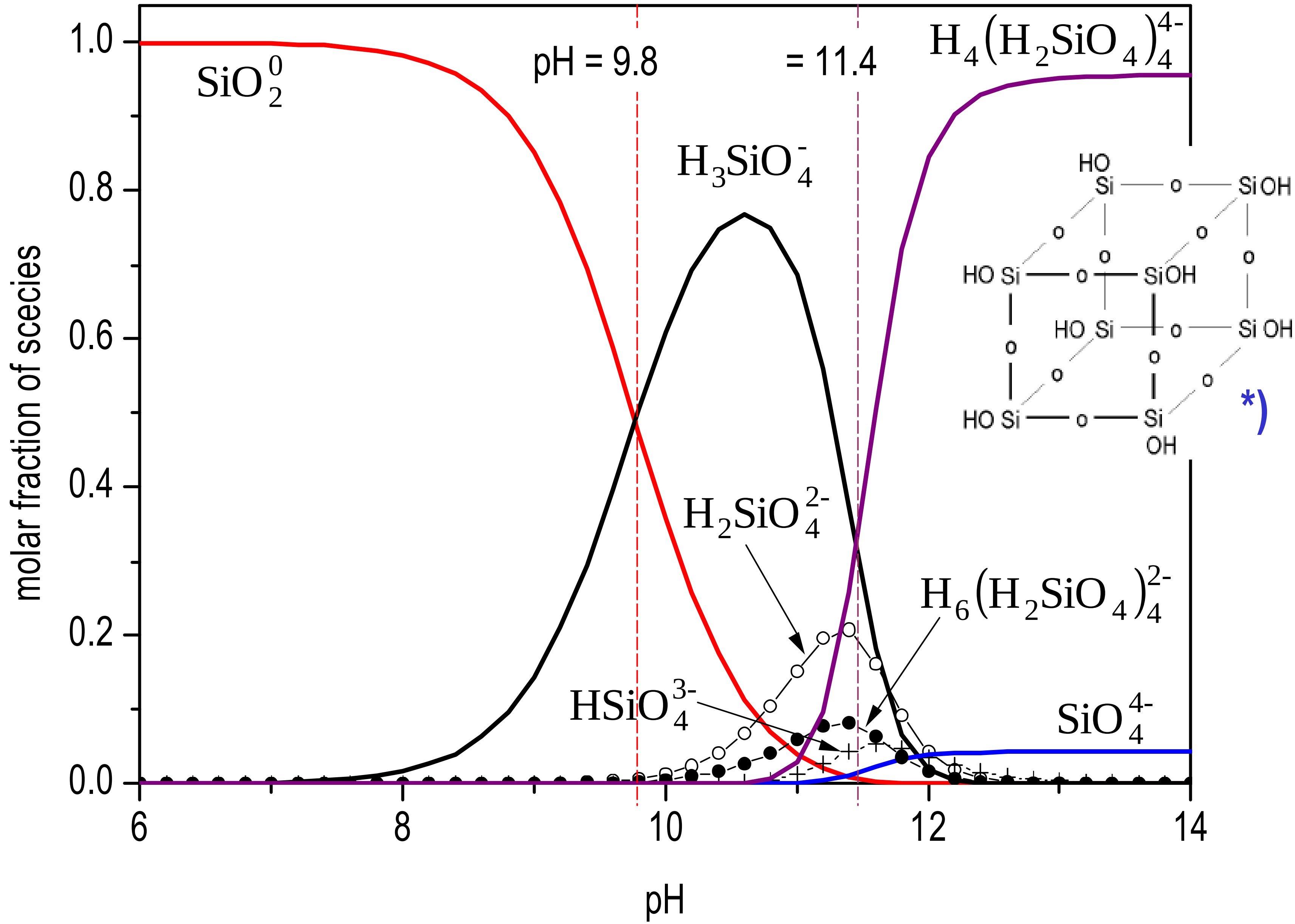




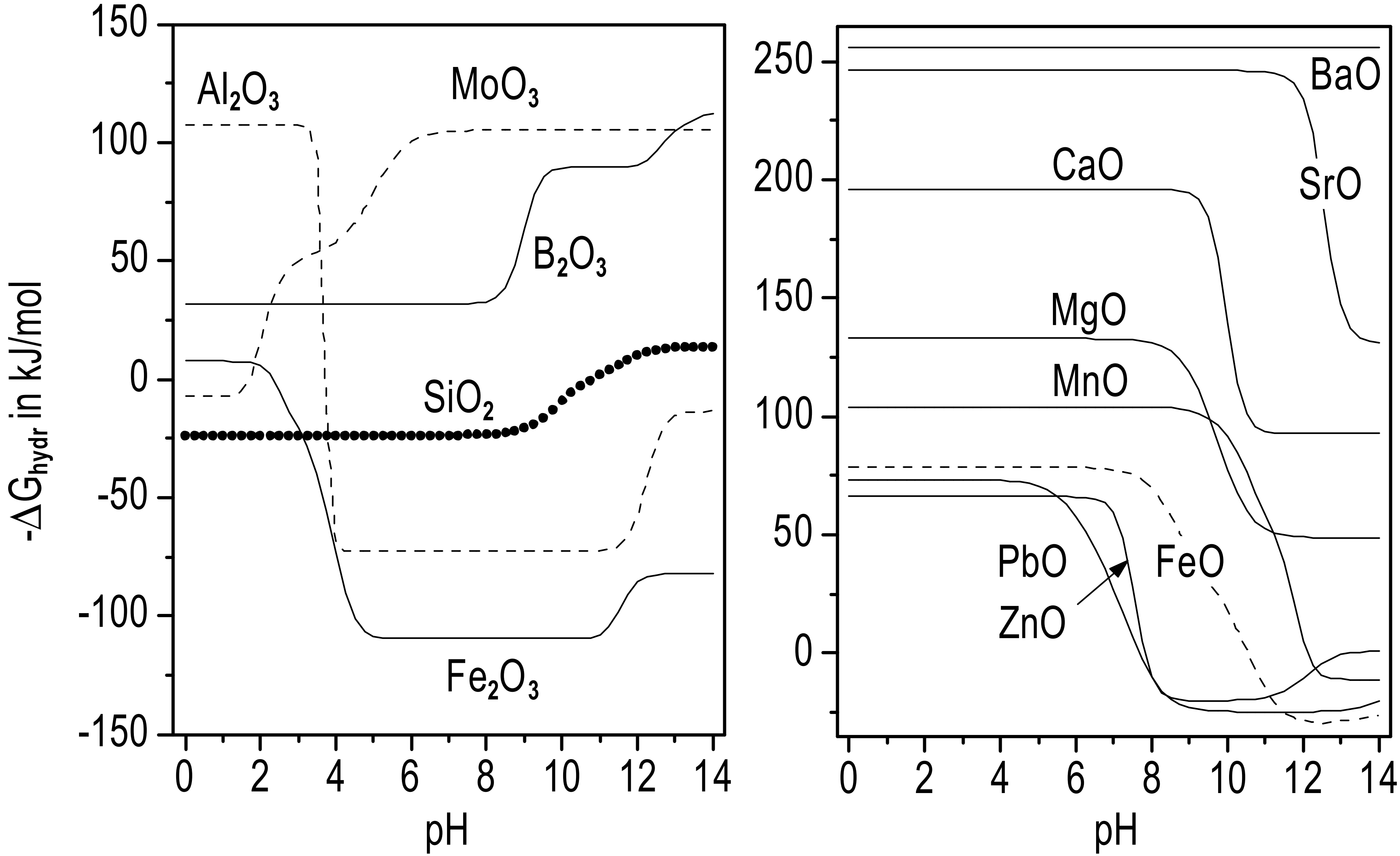

relative concentration of aqueous Al species in %
100
80
60
40
20
0
Al3+
Al(OH)2+
Al(OH)2+
Al(OH)4-
Al(OH)3, aq
¥ diluted
Al3+
Al(OH)3, am
concentration↑
Al(OH)2-
Al(OH)4-
Al3+
AlL
AlHL+
AlL2 3-
Al(LH*)2 5-
AlL2H*4-
Al(HL)L2-
+ C6H8O7
0
2
4
6
8
10
12
14
pH
C6H8O7 =
O
OH
HO
OH
Al3+



1.0
0.8
0.6
0.4
0.2
0.0
6
8
10
12
14
pH
molar fraction of scecies
pH = 9.8
= 11.9
SiO_2^0
$H_3SiO_4^-$
SiO_4^{4-}
$H_2SiO_4^{2-}$
$HSiO_4^{3-}$



*) Iler 1979; s.a. Roggendorf 2007



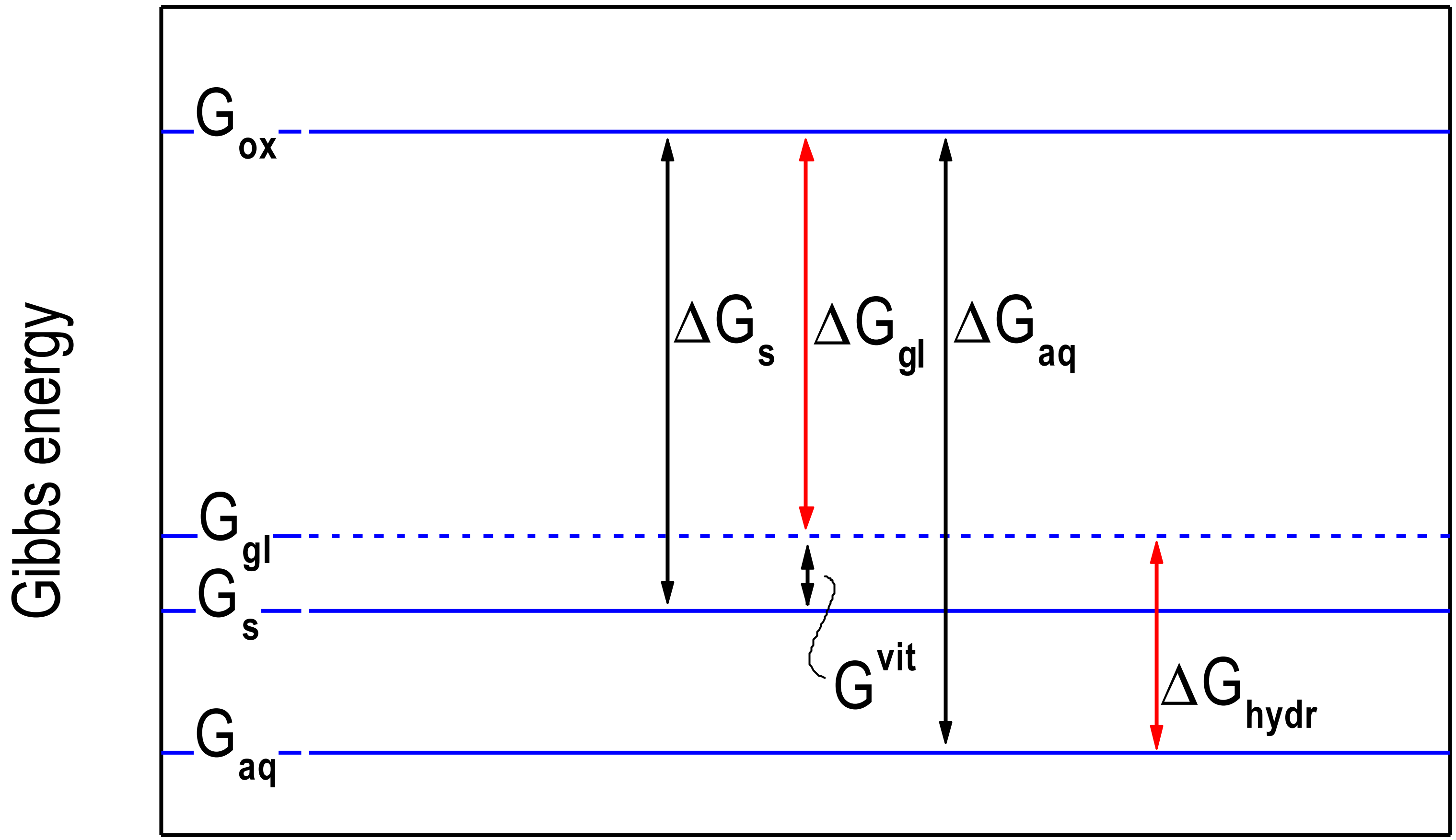
-ΔG_hydr in kJ/mol
150
100
50
0
-50
-100
-150
Al2O3
MoO3
B2O3
SiO2
Fe2O3
0
2
4
6
8
10
12
14
pH
250
200
150
100
50
0
BaO
SrO
CaO
MgO
MnO
PbO
FeO
ZnO
0
2
4
6
8
10
12
14
pH

The state „dissolved in water“ is a state like the states „solid“, „liquid“, and „gas“. It is denoted by (aq).
SiO_2(aq) = silica dissolved in water.

We may a glass like a „state“ - although it is not an equilibrium state like:
SiO_2(gl) = silica glass.

Let us discuss a glass like
[74SiO_2 + 10CaO + 16 Na_2O](gl)

What state corresponds to
[74SiO_2 + 10CaO + 16 Na_2O](aq) ?



(1) oxides + aqueous solution $\rightarrow$ aqueous species =

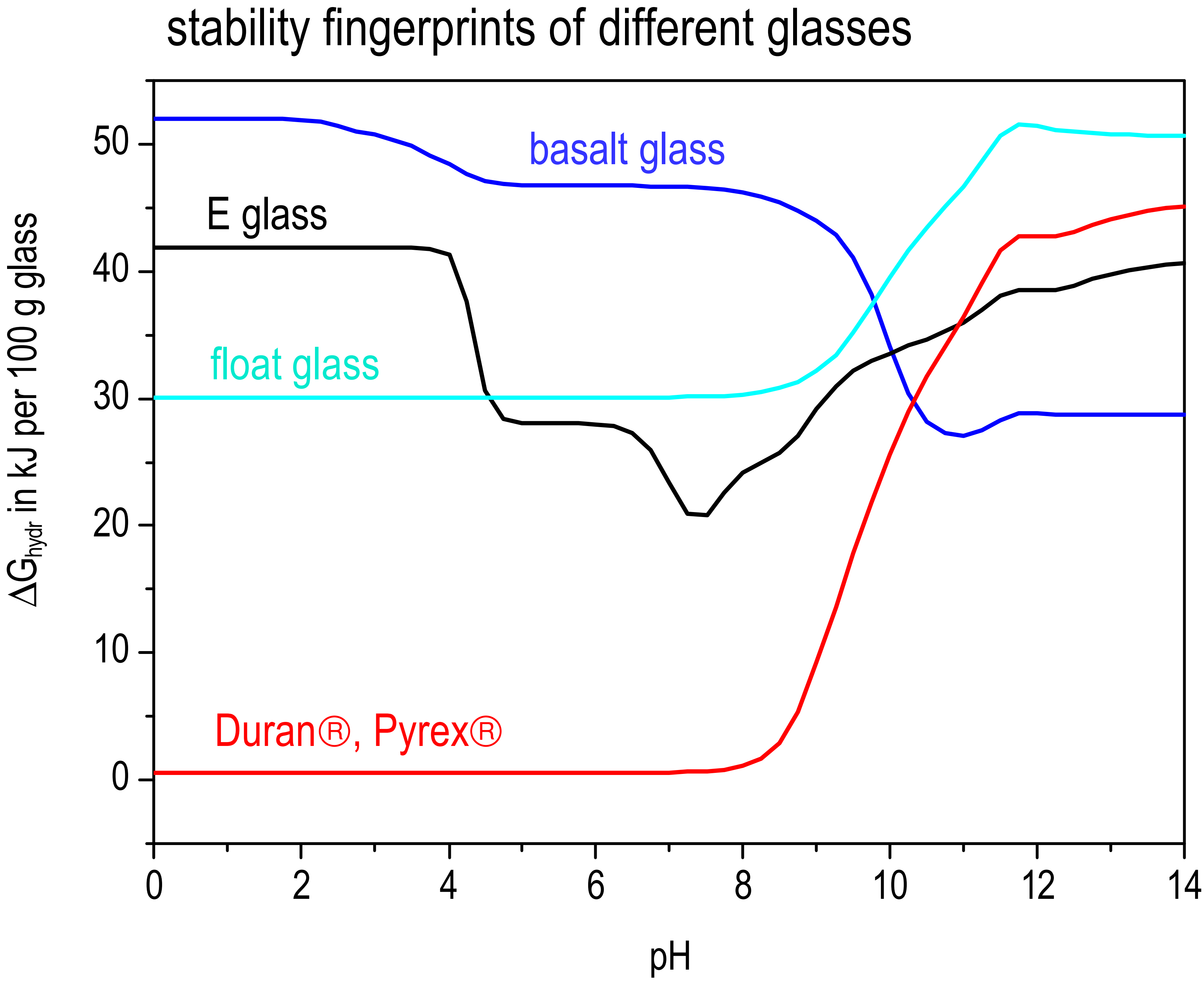
oxides $\rightarrow$ aqueous species − aqueous solution $\Rightarrow$? G_{aq}

(2) equilibrium compounds $\rightarrow$ oxides $\Rightarrow$ −? G_s

(3) glass $\rightarrow$ equilibrium compounds $\Rightarrow$ $-G^{vit}$

---

(4) glass + aqueous solution $\rightarrow$ aqueous species $\Rightarrow$? G_{hydr}

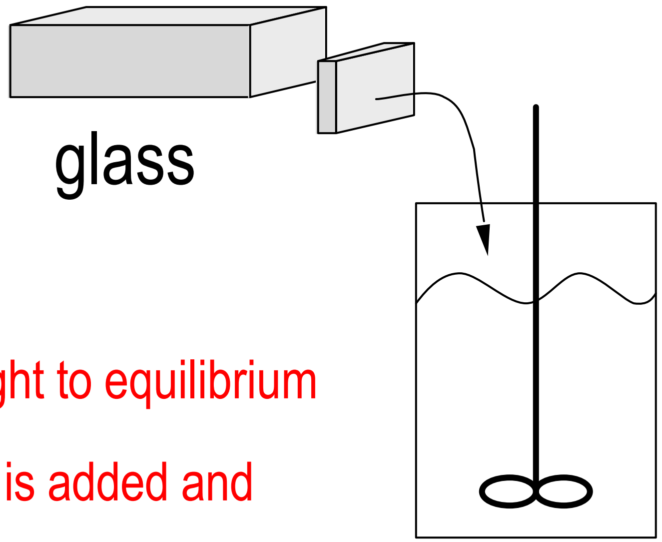


stability fingerprints of different glasses
basalt glass
E glass
float glass
Duran®, Pyrex®
ΔG_hydr in kJ per 100 g glass
pH
0
10
20
30
40
50
0
2
4
6
8
10
12
14

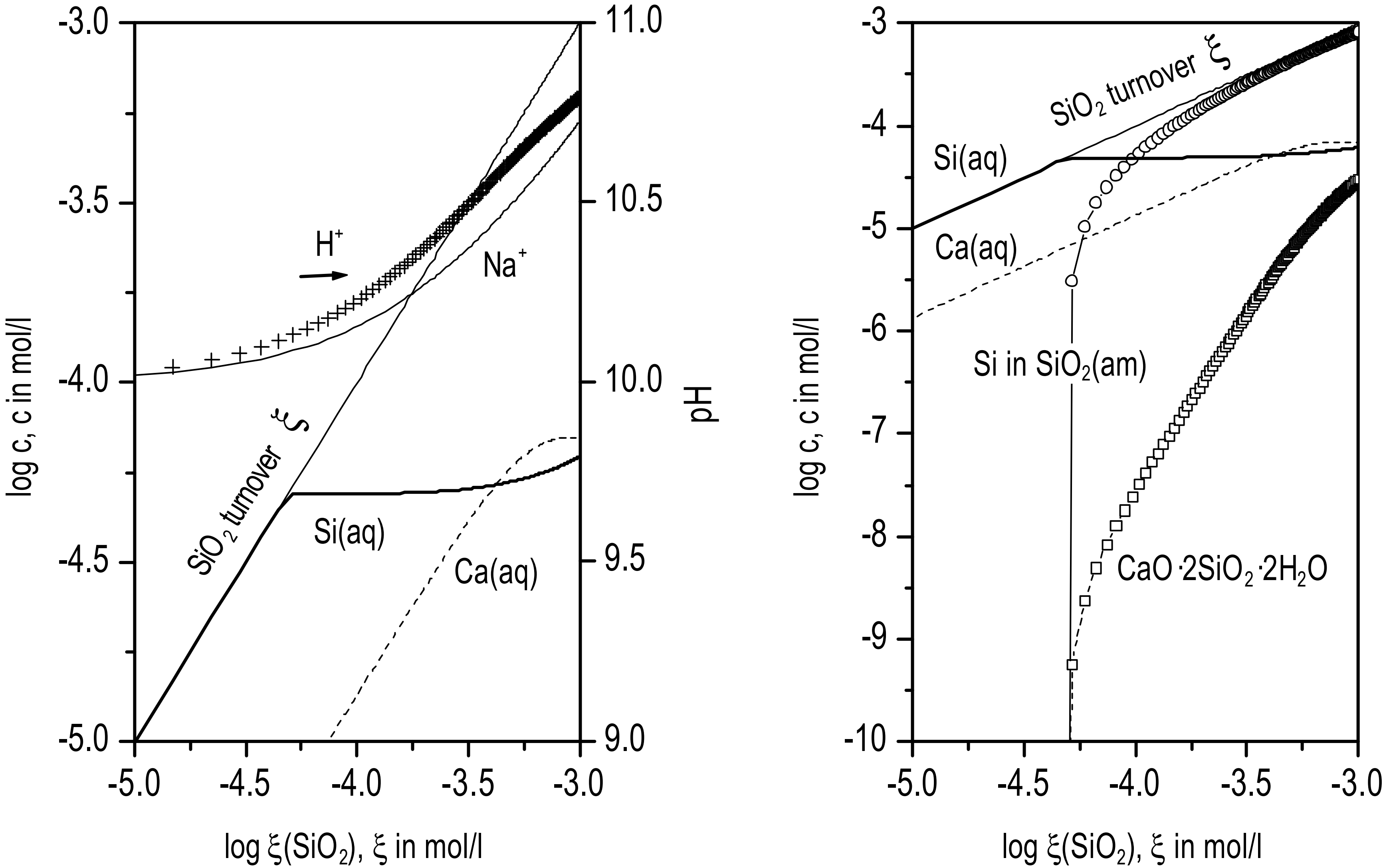
reaction path modeling

How to model the reaction path

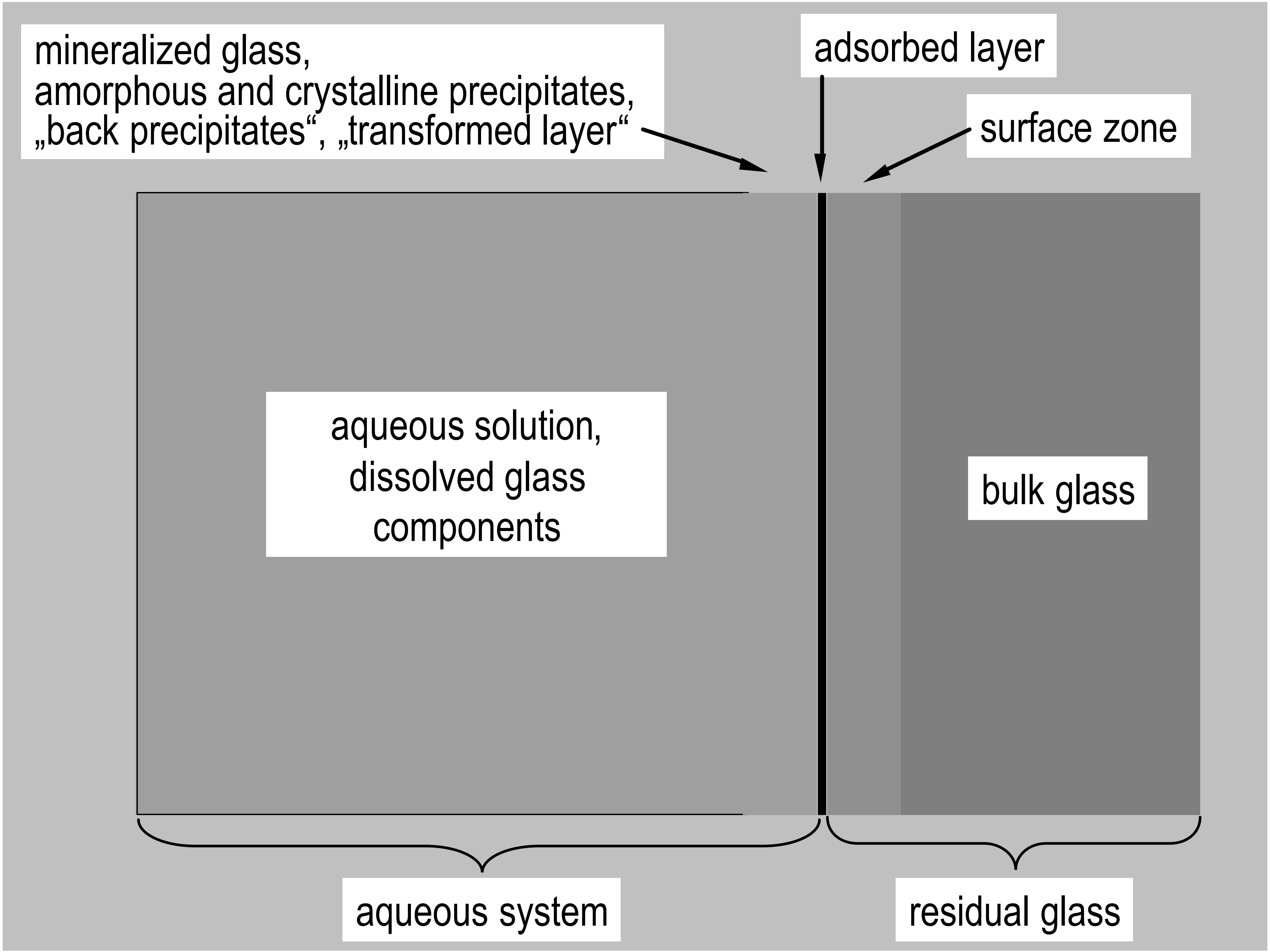
[composition](gl) ® [composition](aq) ?



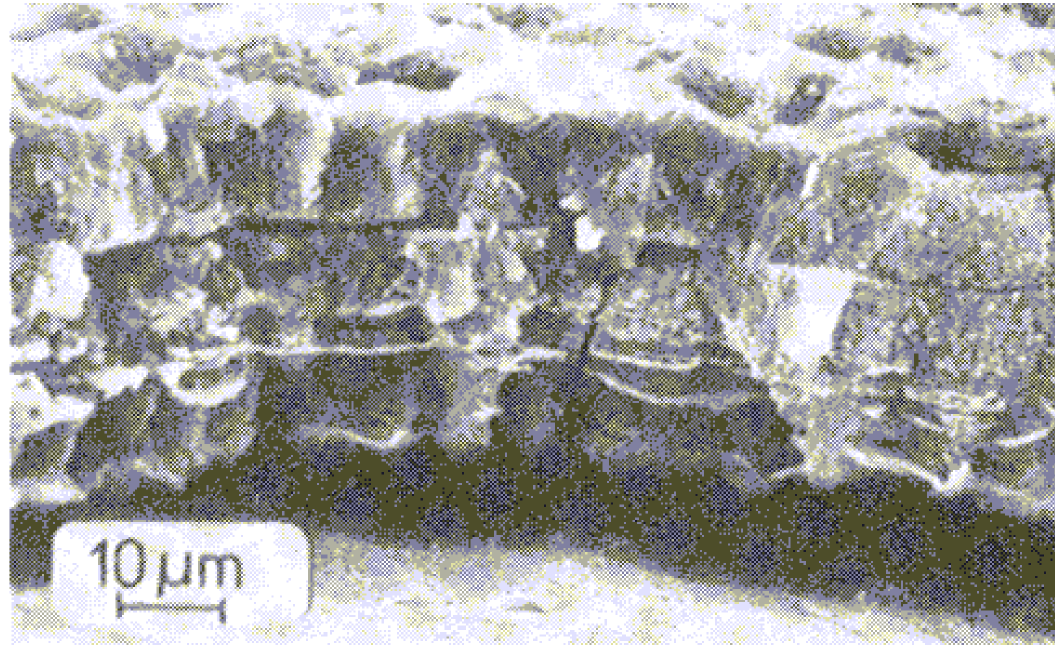
- A slice of glass is brought to equilibrium with the solution.
- The the next glass slice is added and brought to equilibrium.
- The time scale is replaced by a sequence of glass slices.
- We learn towards what state the corrosin process moves.



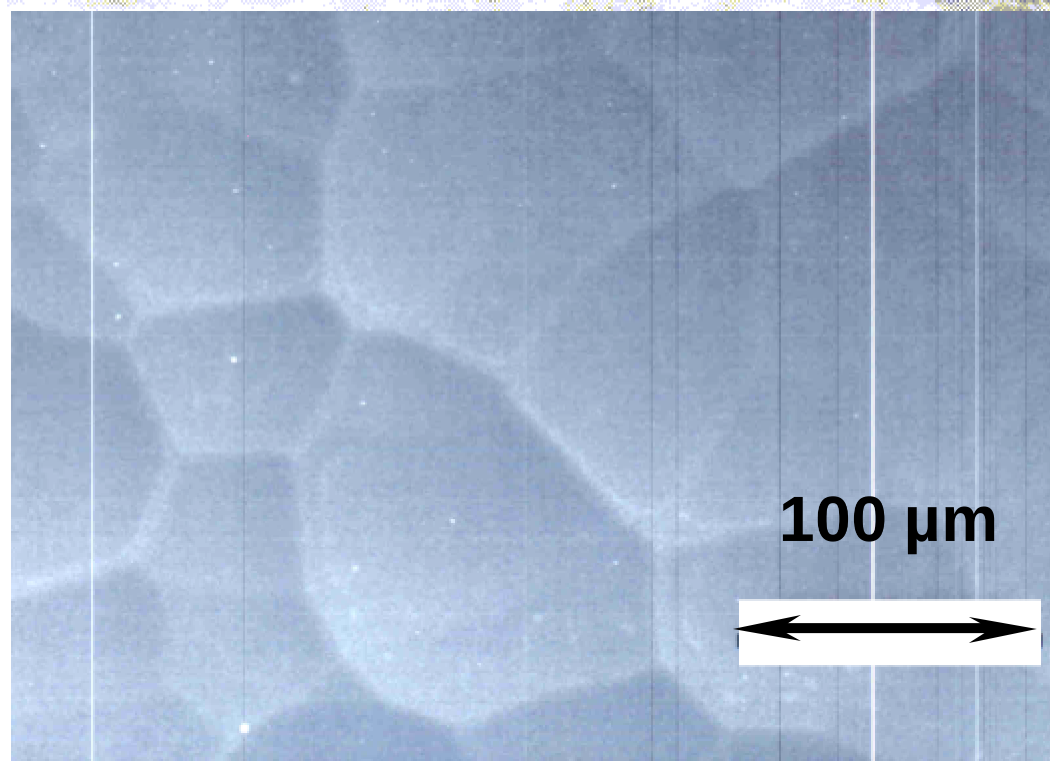
-3.0
-3.5
-4.0
-4.5
-5.0
11.0
10.5
10.0
9.5
9.0
pH
log c, c in mol/l
H+
Na+
SiO2 turnover ξ
Si(aq)
Ca(aq)
-5.0
-4.5
-4.0
-3.5
-3.0
log ξ(SiO2), ξ in mol/l
-3
-4
-5
-6
-7
-8
-9
-10
log c, c in mol/l
SiO2 turnover ξ
Si(aq)
Ca(aq)
Si in SiO2(am)
CaO·2SiO2·2H2O
-5.0
-4.5
-4.0
-3.5
-3.0
log ξ(SiO2), ξ in mol/l

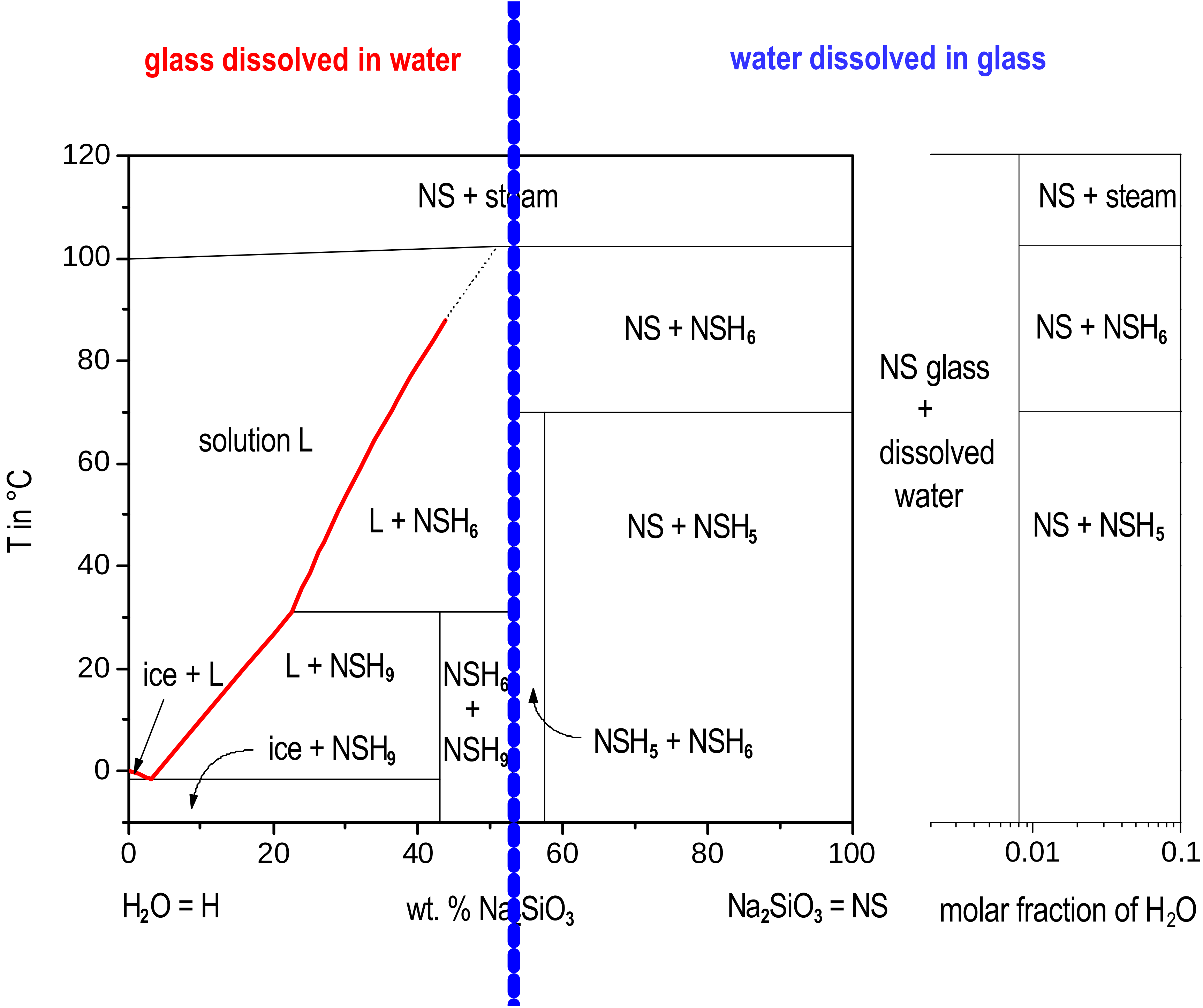

mineralized glass,
amorphous and crystalline precipitates,
„back precipitates“, „transformed layer“
adsorbed layer
surface zone
aqueous solution,
dissolved glass
components
bulk glass
aqueous system
residual glass

reaction product layer
(vertical section);

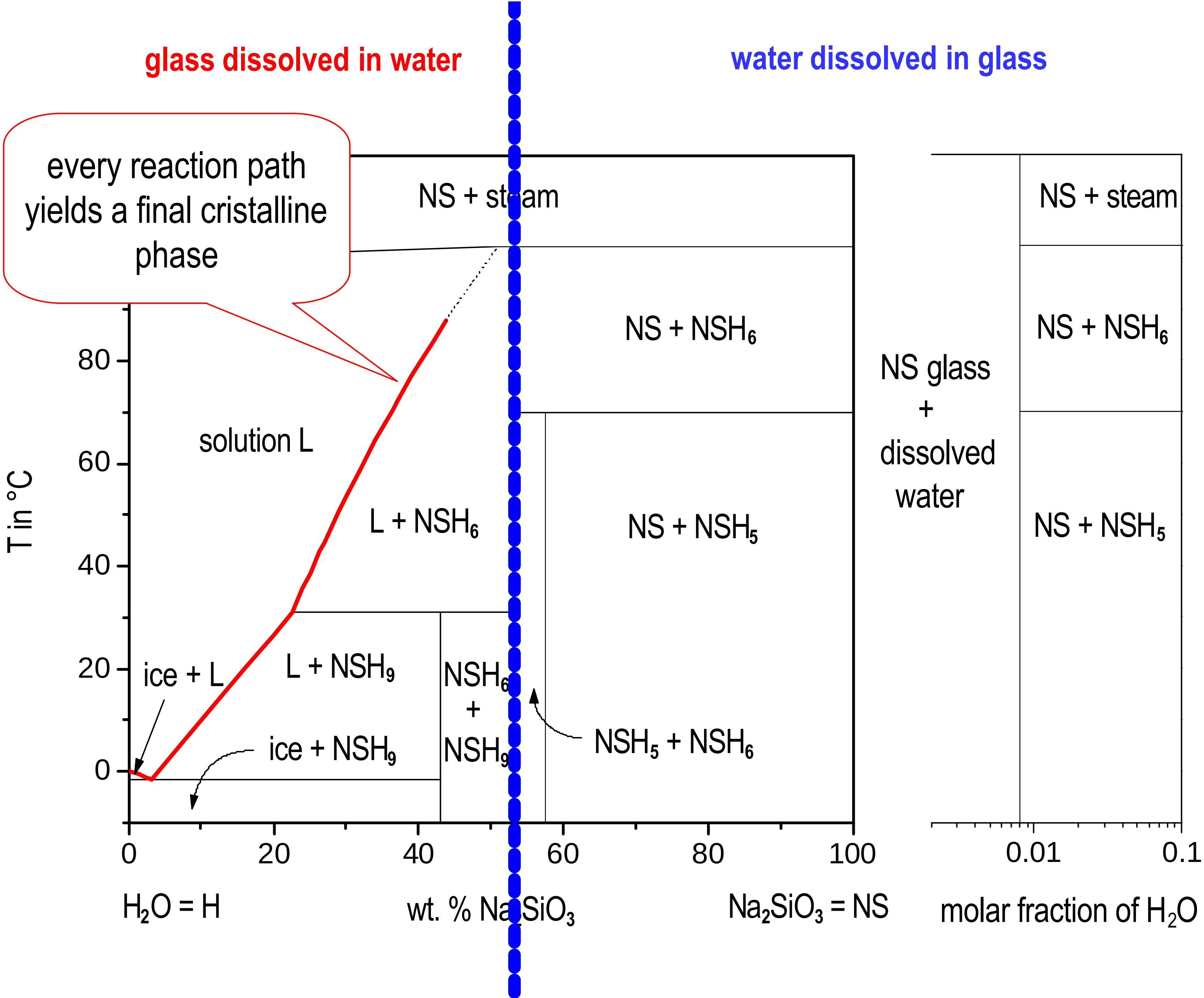


surface of the residual glass after removal of the reaction product layer
(top view)

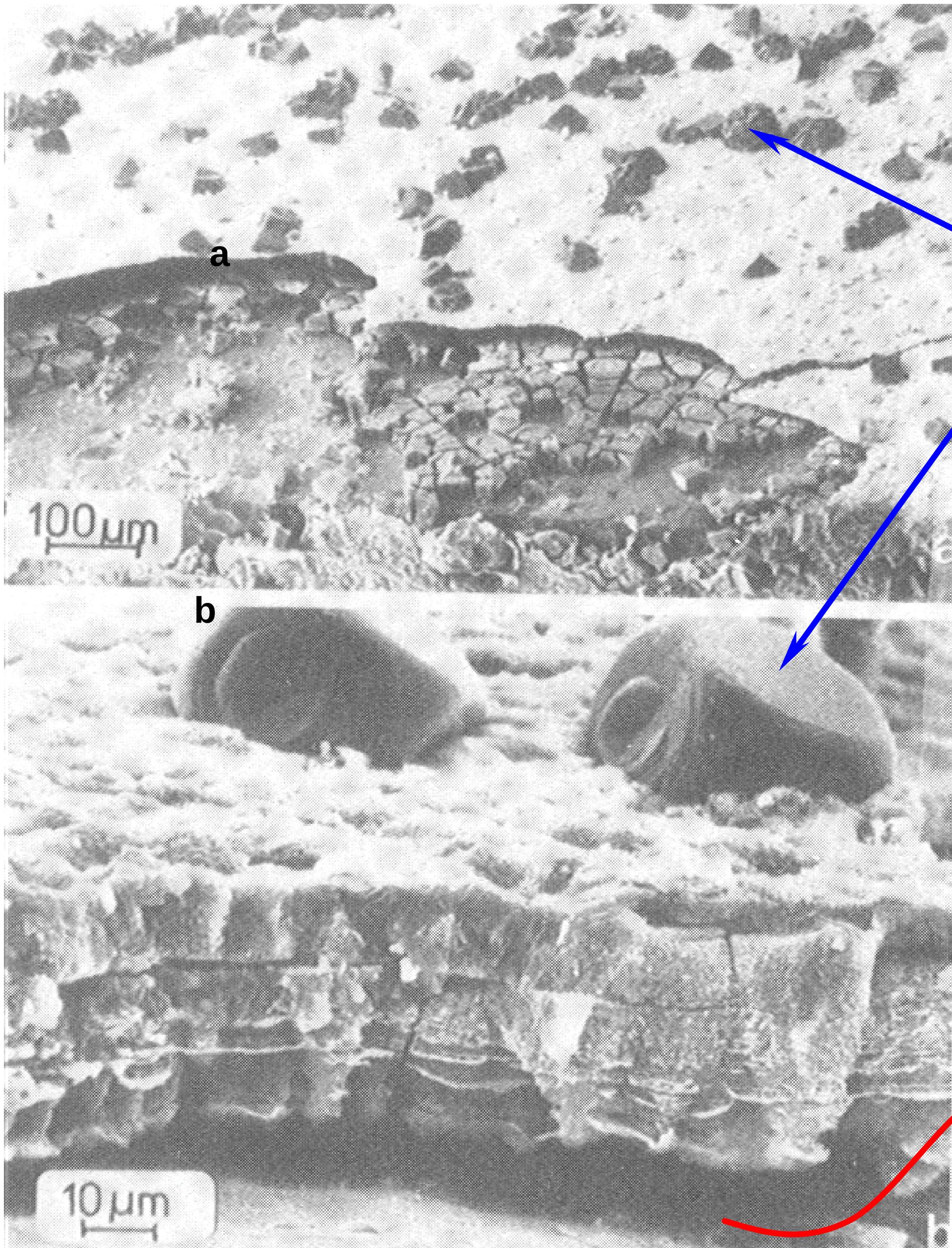




glass dissolved in water
water dissolved in glass
T in °C
NS + steam
NS + NSH_6
solution L
L + NSH_6
NS + NSH_5
ice + L
L + NSH_9
NSH_6 + NSH_9
ice + NSH_9
NSH_5 + NSH_6
NS glass + dissolved water
H_2O = H
wt. % Na_2SiO_3
Na_2SiO_3 = NS
molar fraction of H_2O


glass dissolved in water
water dissolved in glass
every reaction path yields a final cristalline phase
NS + steam
NS + NSH$_6$
NS + NSH$_5$
NS glass + dissolved water
solution L
L + NSH$_6$
L + NSH$_9$
ice + L
ice + NSH$_9$
NSH$_6$ + NSH$_9$
NSH$_5$ + NSH$_6$
T in °C
80
60
40
20
0
0
20
40
60
80
100
0.01
0.1
H$_2$O = H
wt. % Na$_2$SiO$_3$
Na$_2$SiO$_3$ = NS
molar fraction of H$_2$O

partially crystalline, partially amorphous layer of reaction products on top of the residual glass



G. Malow, W. Lutze, R.C. Ewing;
Stracchan; Chick & Pederson

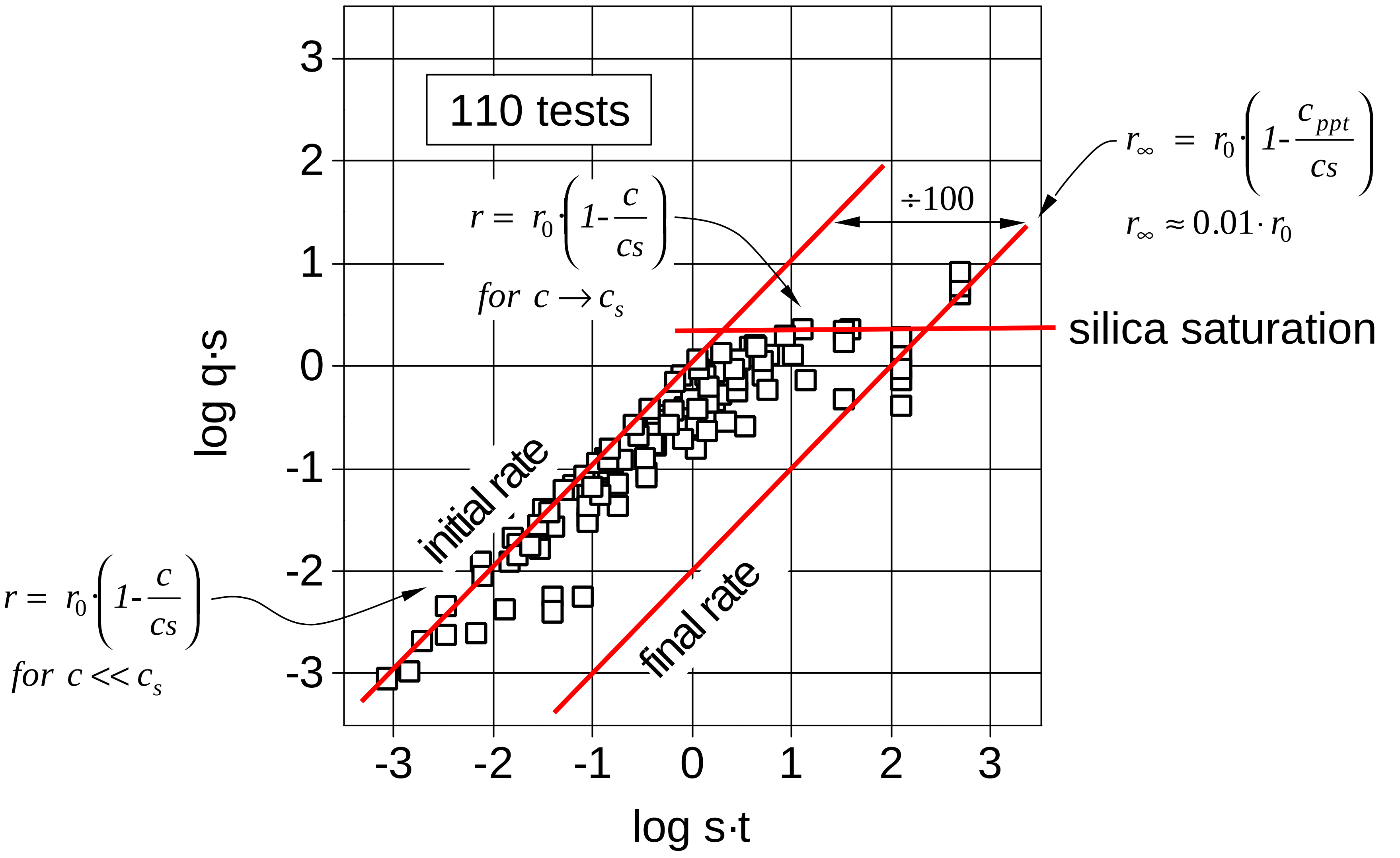
analcime crystals:
$Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H2O$

corrosion rate $r \rightarrow r_0 \cdot \left(1 - \frac{c_{ppt}}{cs}\right)$

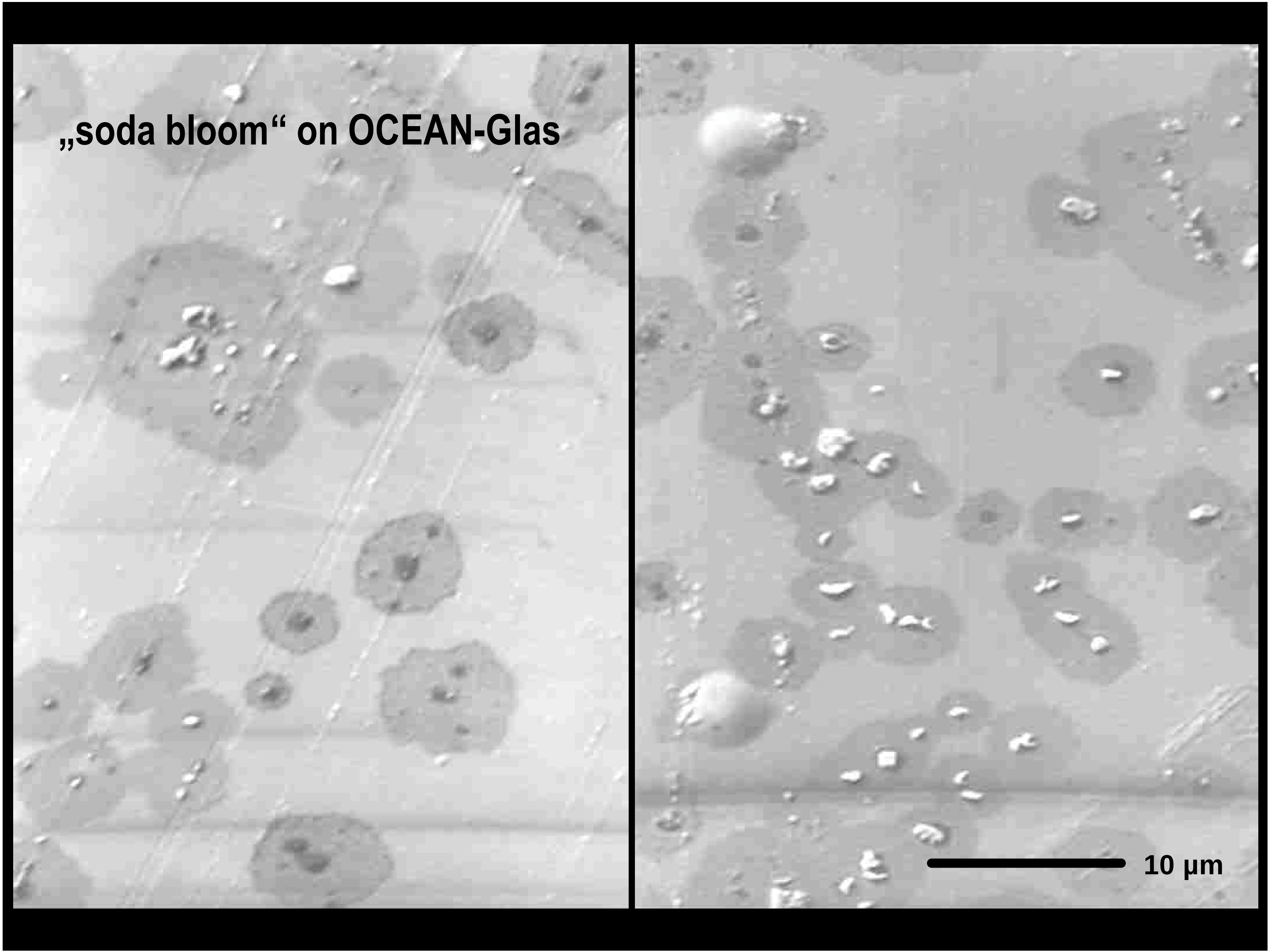
c_s = metastable solubility limit of the glass;
c_{ppt} = solubility limit of the final crystal formed along the reaction path
$c_s > c_{ppt} \Rightarrow$ r cannot reach zero

in many cases, the layer can be removed easily (like ice from a car windshield)

saturation with respect to the glass is a transient stage in most cases

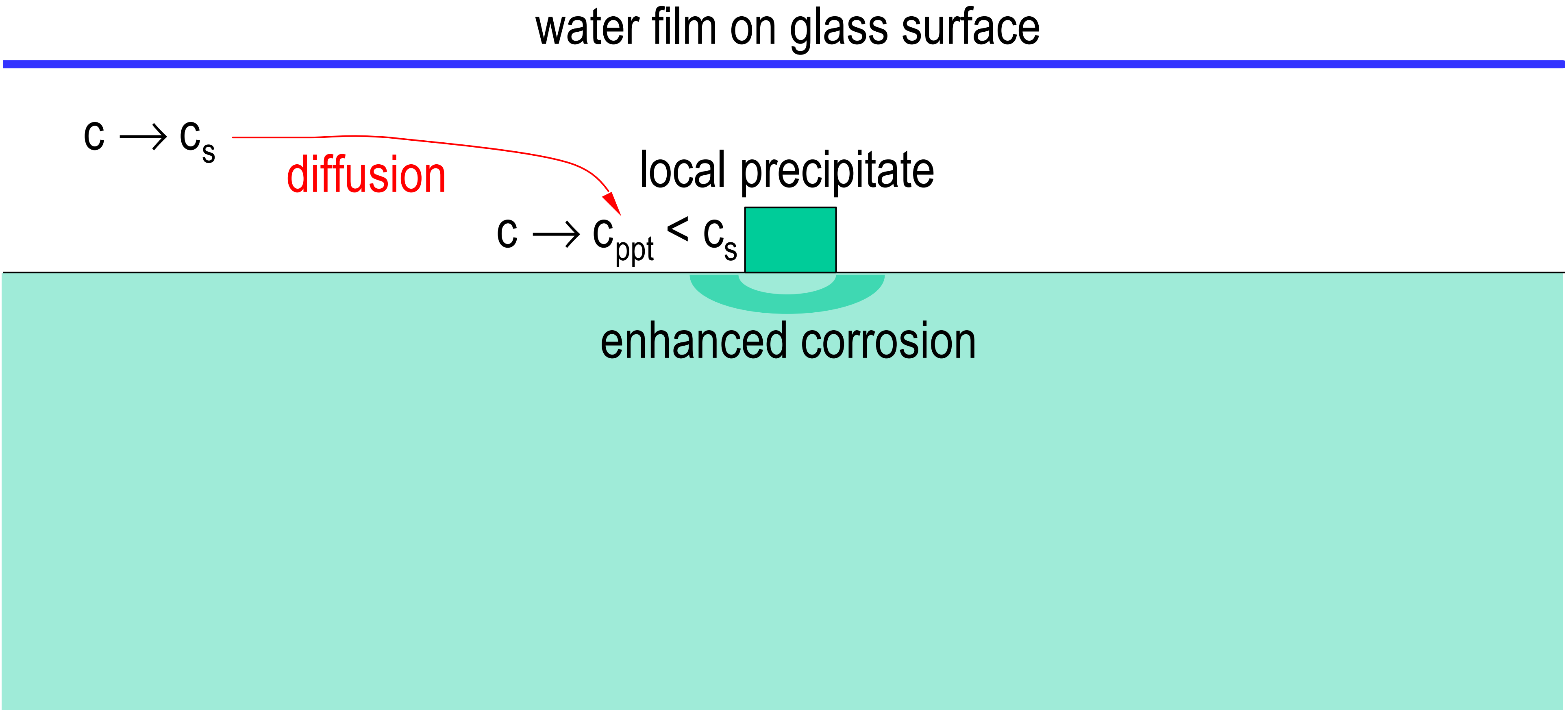


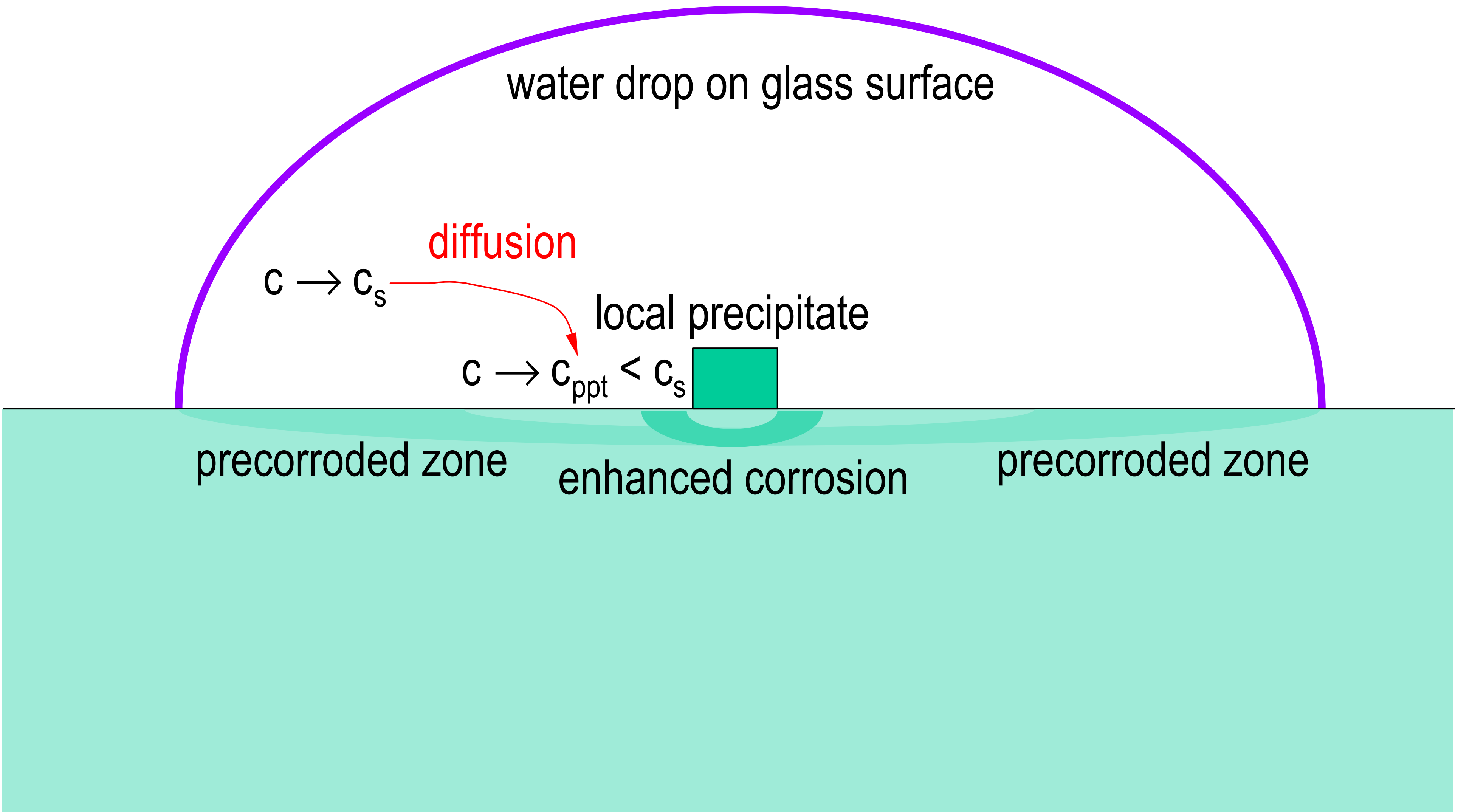
own work


„soda bloom“ on OCEAN-Glas
10 µm

stage 1: due to large SA/V, pH $\rightarrow$ pH_s and c $\rightarrow$ c_s; $r_s = r_0 \cdot (1 - c / cs) \rightarrow 0$

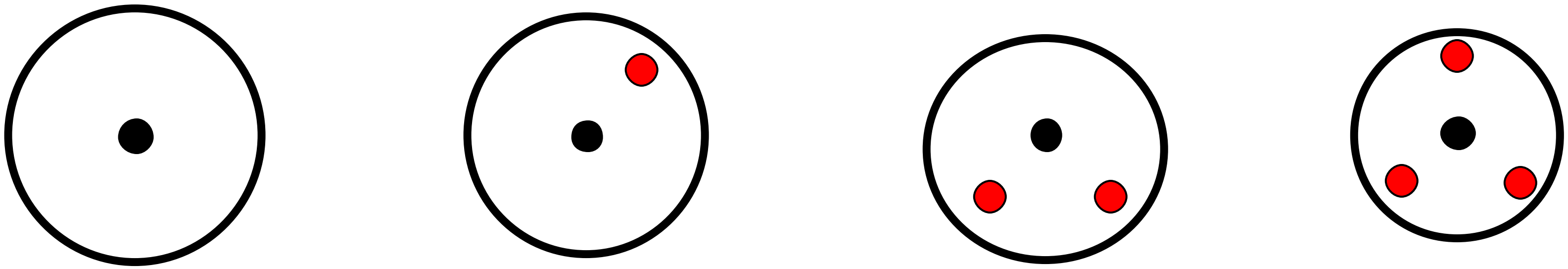
stage 2: eventually, a local ppt forms with solubility $c_{ppt} < c_s$; the rate in the vicinity of ppt is $r = r_0 \cdot (1 - c_{ppt} / cs) > 0$. Thus, a „local element" is generated.




water drop on glass surface
diffusion
c → c_s
local precipitate
c → c_ppt < c_s
precorroded zone
enhanced corrosion
precorroded zone

the nature of the sub-surface zone and the rate determining step

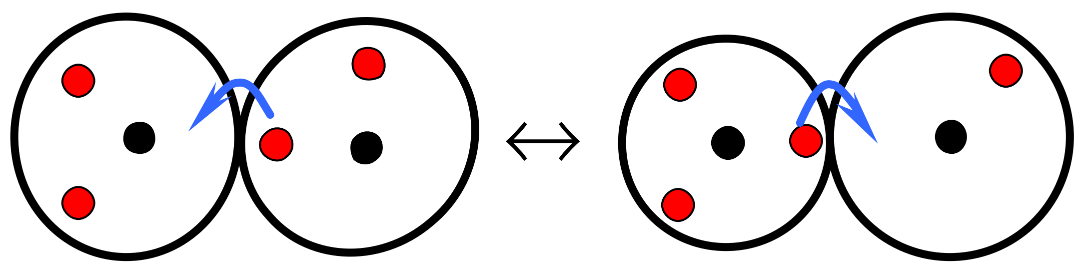
O^{2-}	OH^{-}	H_2O	H_3O^{+}



„radius“	0.140 nm	0.138 nm	0.137	0.136
d(O-H)	-.-	0.096 nm	0.0958	0.095
φ(H-O-H)	---	---	104.45°	120°

$$2\,H_2O \leftrightarrow H_3O^{+} + OH^{-}$$

$$K_W = 10^{-14}$$

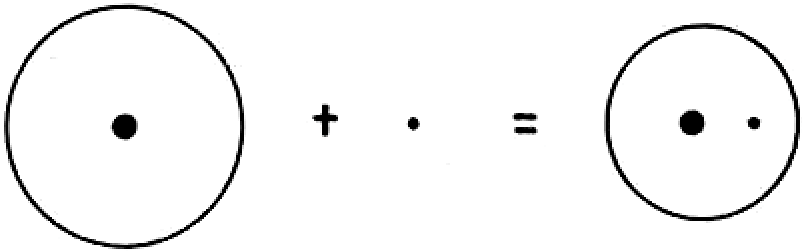


proton transfer!

H^{+} is not an ion, but an elementary particle

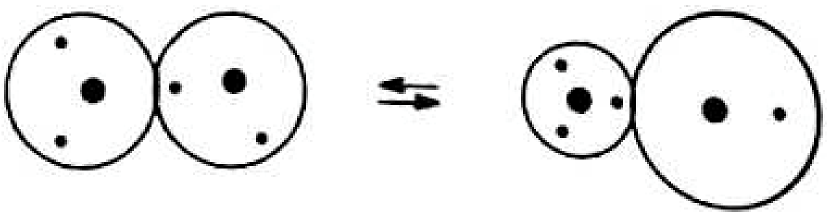
adsorption of proton by hydrogen:

$$O^{=} + H^{+} = OH^{-}$$



ionization (dissociation) of water:

$$H_2O + H_2O \rightleftarrows H_3O^{+} + OH^{-}$$



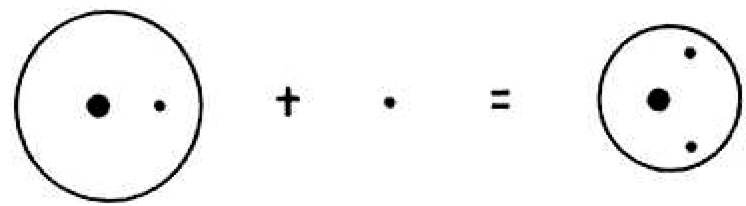
F.M.Ersnberger:
The Nonconformist Ion.
J. Am. Ceram. Soc. 66(1983)747-750.

adsorption of proton by water molecule:

$$H_2O + H^{+} = H_3O^{+}$$

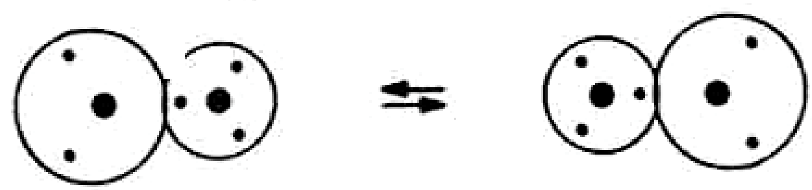
adsorption of proton by hydroxyl ion:

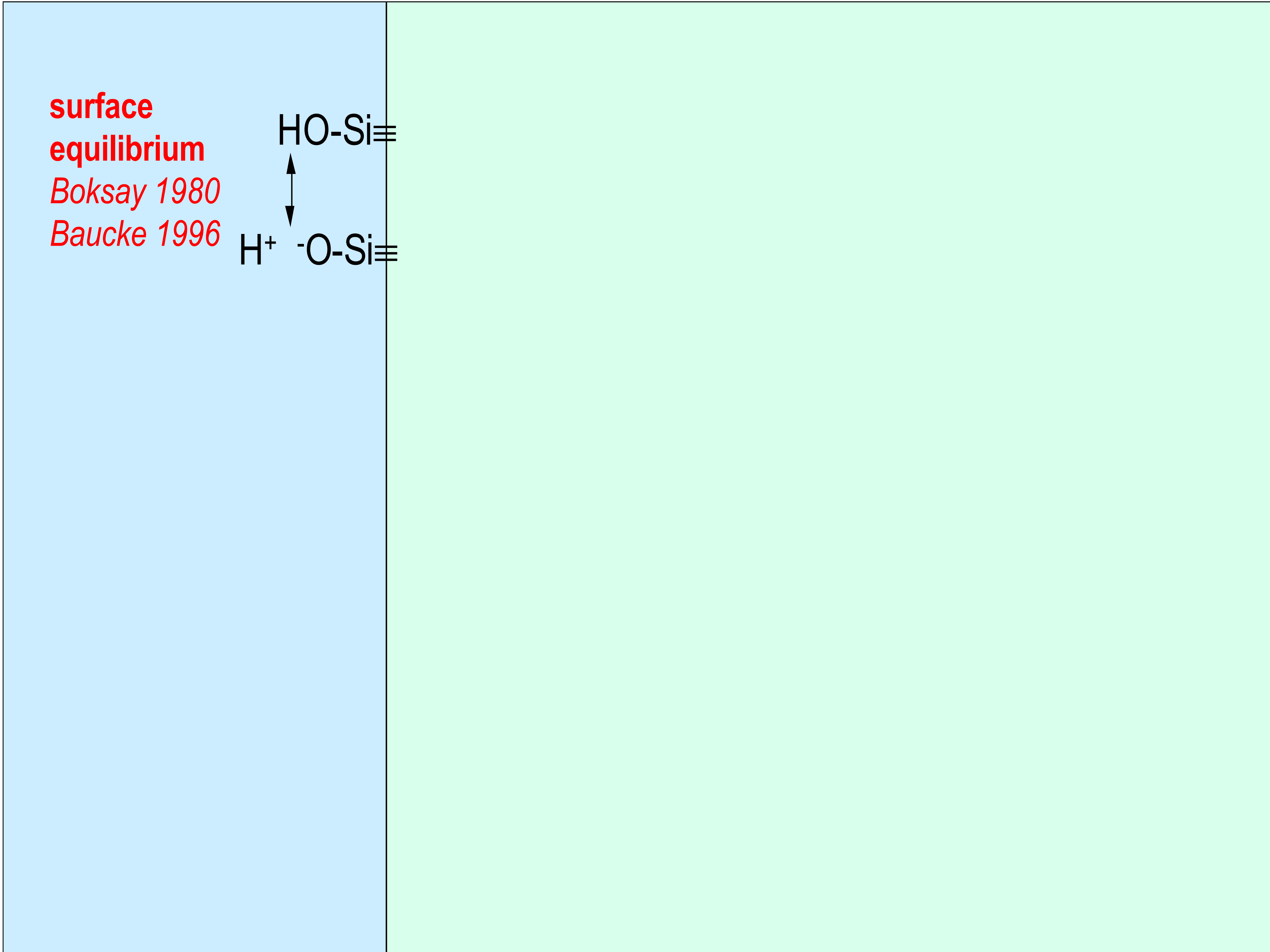
$$OH^{-} + H^{+} = H_2O$$



Grotthuss proton transfer:

$$H_2O + H_3O^{+} \rightleftarrows H_3O^{+} + H_2O$$




surface equilibrium
Boksay 1980
Baucke 1996
HO-Si≡
H+ -O-Si≡

surface equilibrium

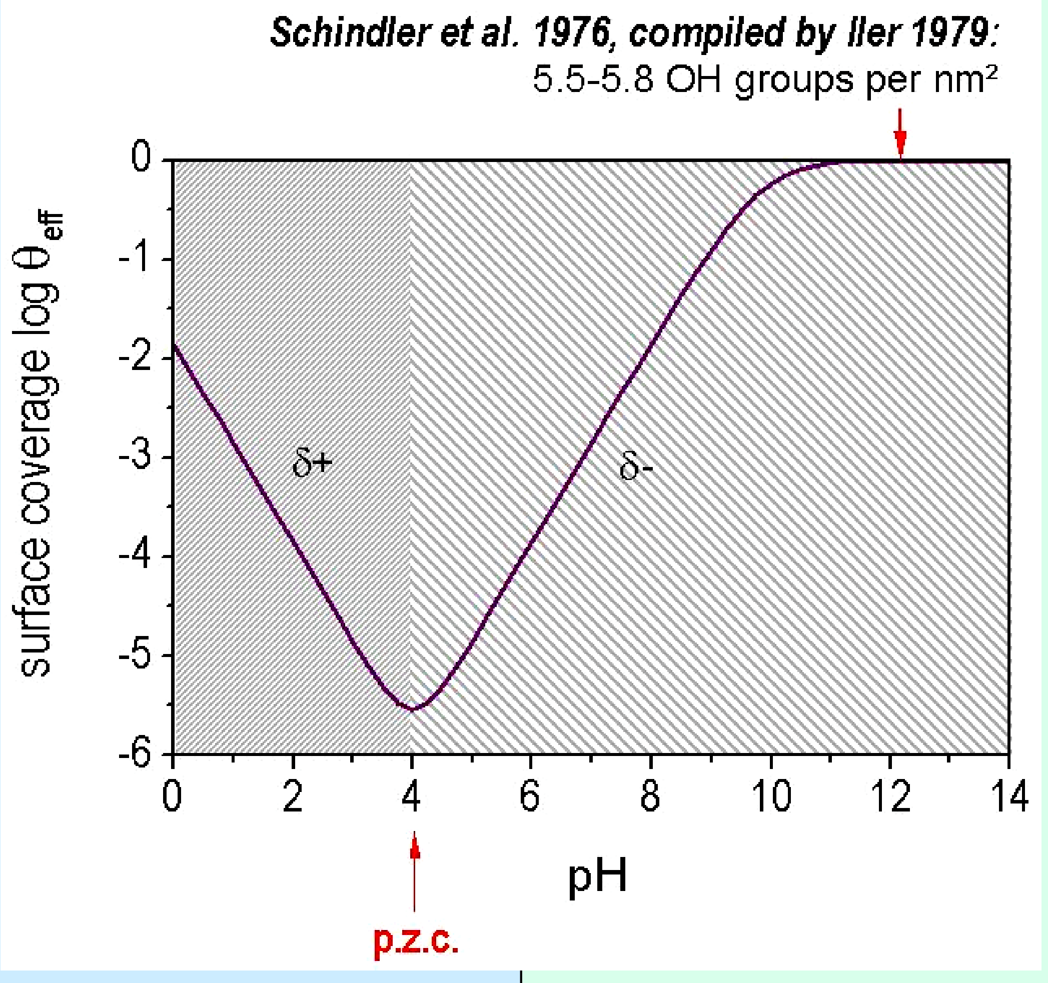
Boksay 1980

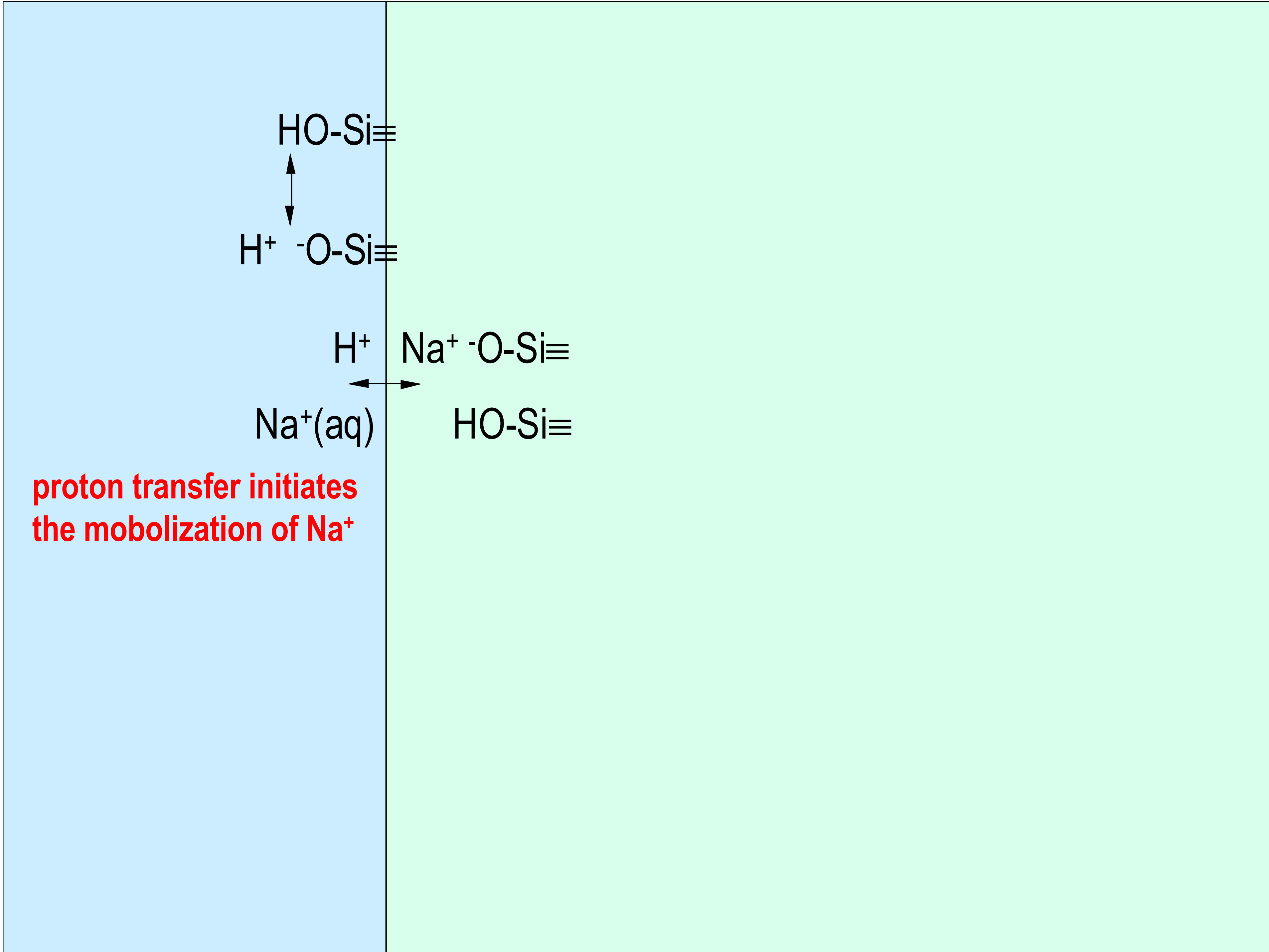
Baucke 1996

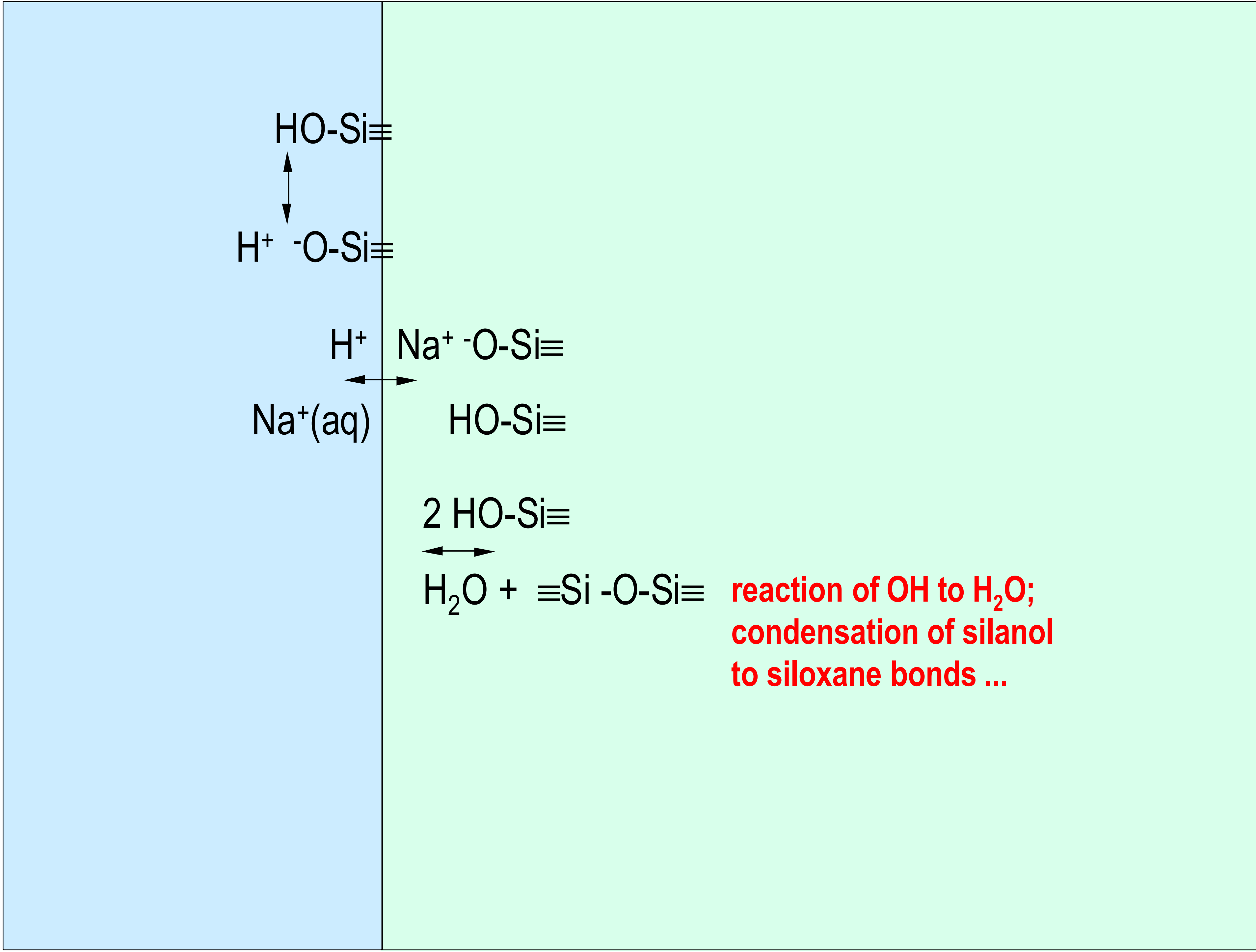
$HO\text{-}Si\equiv$

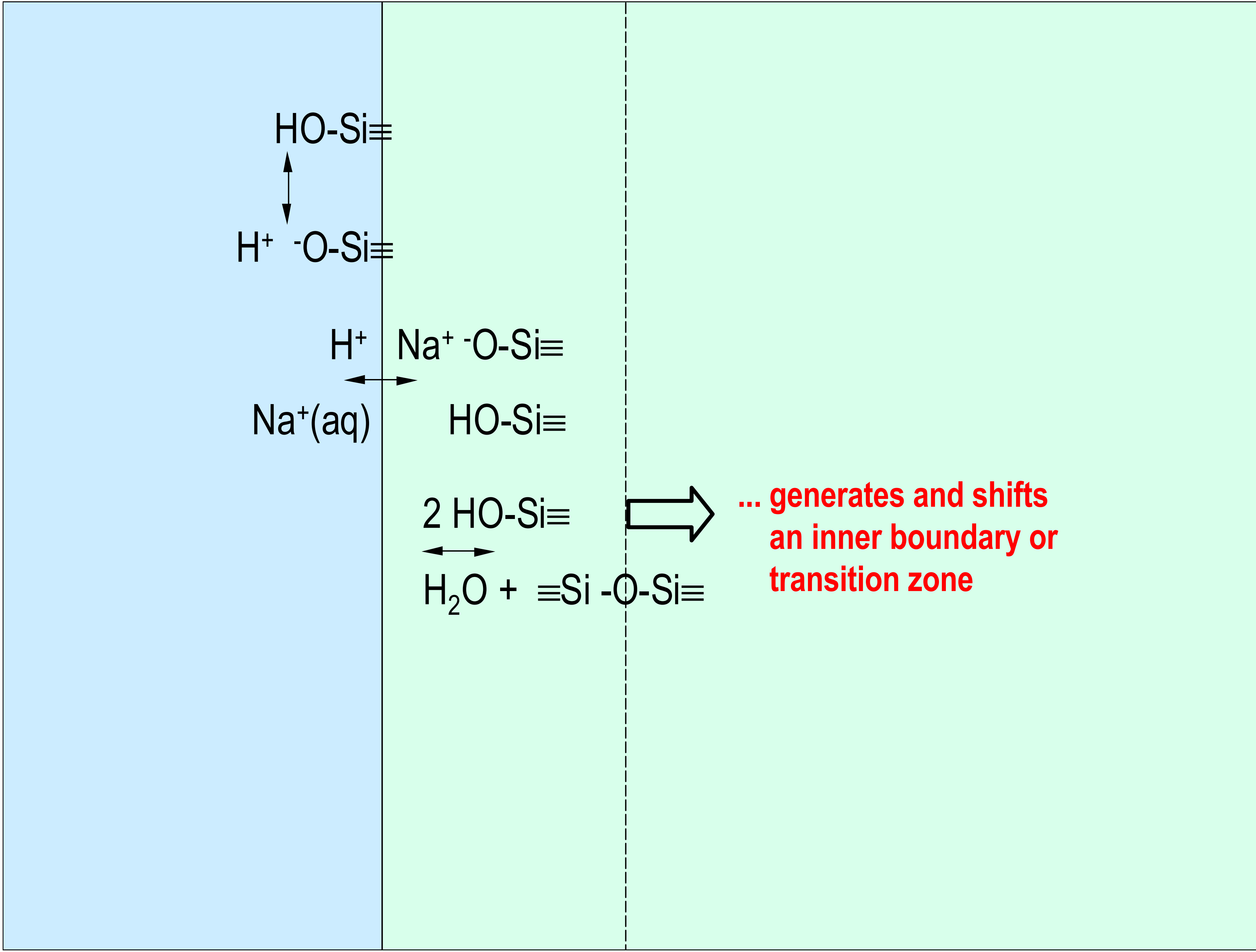
$\updownarrow$

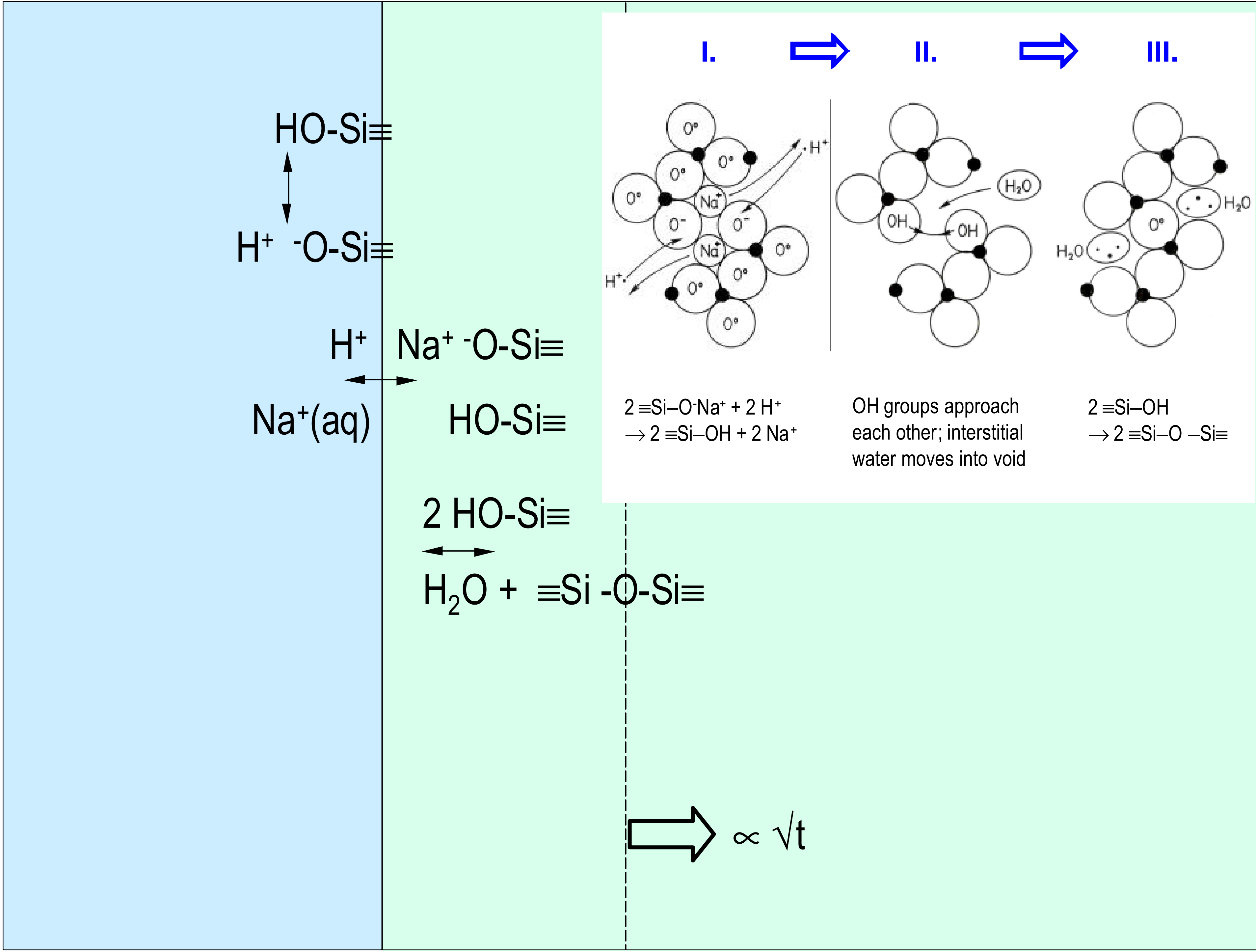
$H^+ \; {}^-O\text{-}Si\equiv$

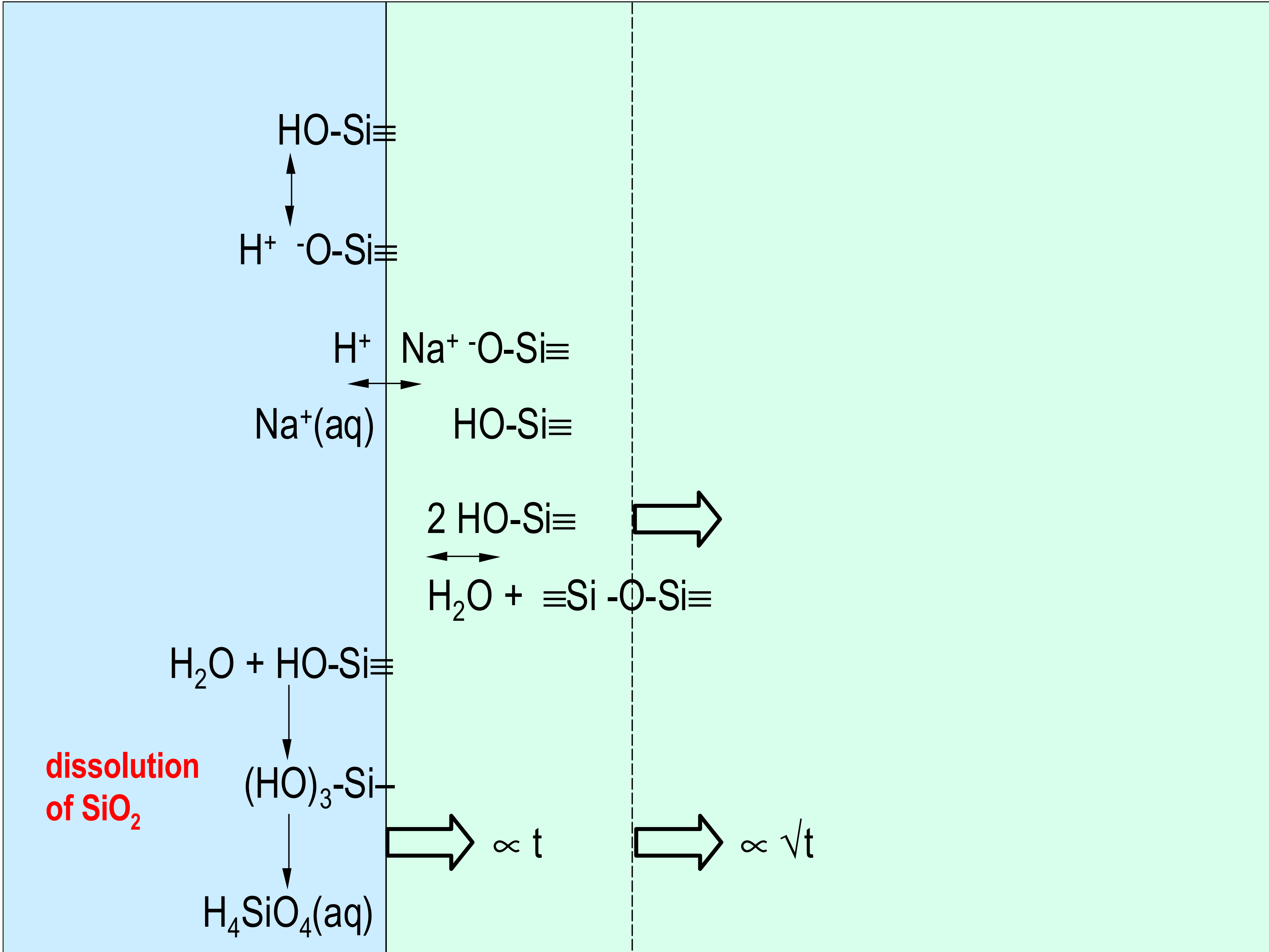


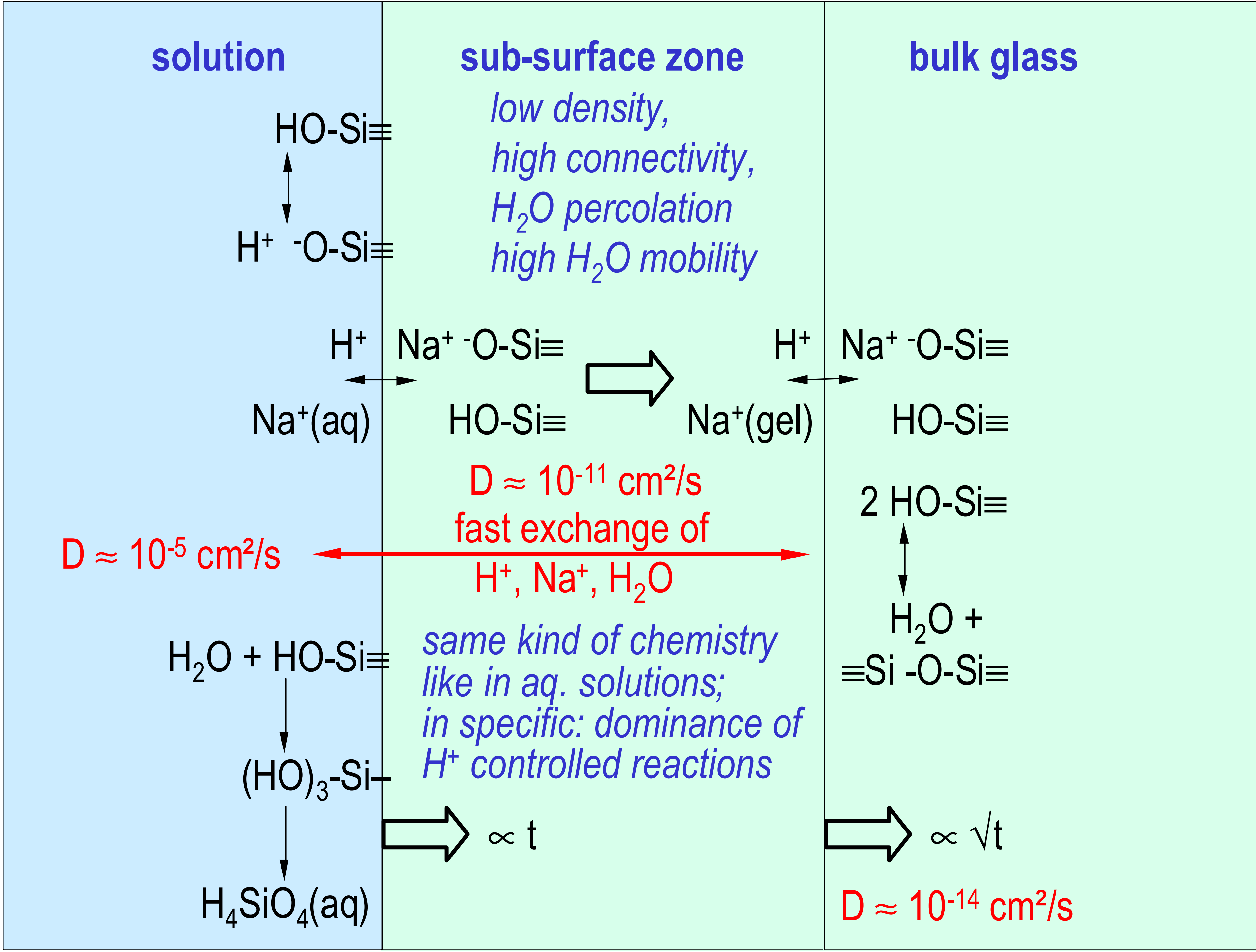

HO-Si≡
H+ -O-Si≡
H+ Na+ -O-Si≡
Na+(aq) HO-Si≡
proton transfer initiates
the mobolization of Na+


HO-Si≡
H+ -O-Si≡
H+
Na+ -O-Si≡
Na+(aq)
HO-Si≡
2 HO-Si≡
H2O + ≡Si -O-Si≡
reaction of OH to H2O;
condensation of silanol
to siloxane bonds ...

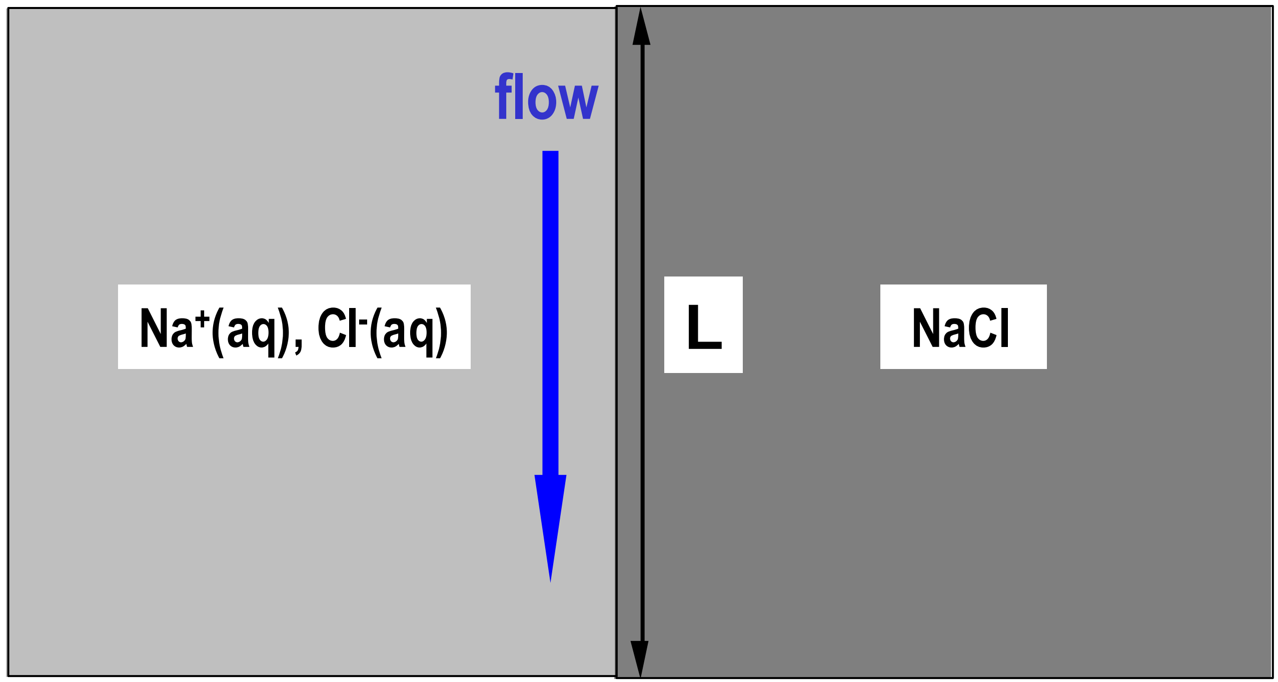

HO-Si≡
H+ -O-Si≡
H+ Na+ -O-Si≡
Na+(aq) HO-Si≡
2 HO-Si≡
H2O + ≡Si -O-Si≡
... generates and shifts an inner boundary or transition zone


HO-Si≡
H+ -O-Si≡
H+
Na+ -O-Si≡
Na+(aq)
HO-Si≡
2 HO-Si≡
H2O + ≡Si -O-Si≡
∝ √t
I.
II.
III.
2 ≡Si–O-Na+ + 2 H+
→ 2 ≡Si–OH + 2 Na+
OH groups approach
each other; interstitial
water moves into void
2 ≡Si–OH
→ 2 ≡Si–O –Si≡
H2O
OH
Na+
O-
H+


HO-Si≡
H+ -O-Si≡
H+
Na+ -O-Si≡
Na+(aq)
HO-Si≡
2 HO-Si≡
H2O + ≡Si -O-Si≡
H2O + HO-Si≡
dissolution of SiO2
(HO)3-Si–
∝ t
∝ √t
H4SiO4(aq)


solution
sub-surface zone
bulk glass
low density,
high connectivity,
H_2O percolation
high H_2O mobility
HO-Si≡
H^+ $^-$O-Si≡
H^+ Na^+ $^-$O-Si≡
Na^+(aq) HO-Si≡
H^+ Na^+ $^-$O-Si≡
Na^+(gel) HO-Si≡
$D \approx 10^{-11}$ cm²/s
fast exchange of
H^+, Na^+, H_2O
$D \approx 10^{-5}$ cm²/s
2 HO-Si≡
H_2O +
≡Si -O-Si≡
H_2O + HO-Si≡
$(HO)_3$-Si–
H_4SiO_4(aq)
same kind of chemistry
like in aq. solutions;
in specific: dominance of
H^+ controlled reactions
∝ t
∝ √t
$D \approx 10^{-14}$ cm²/s

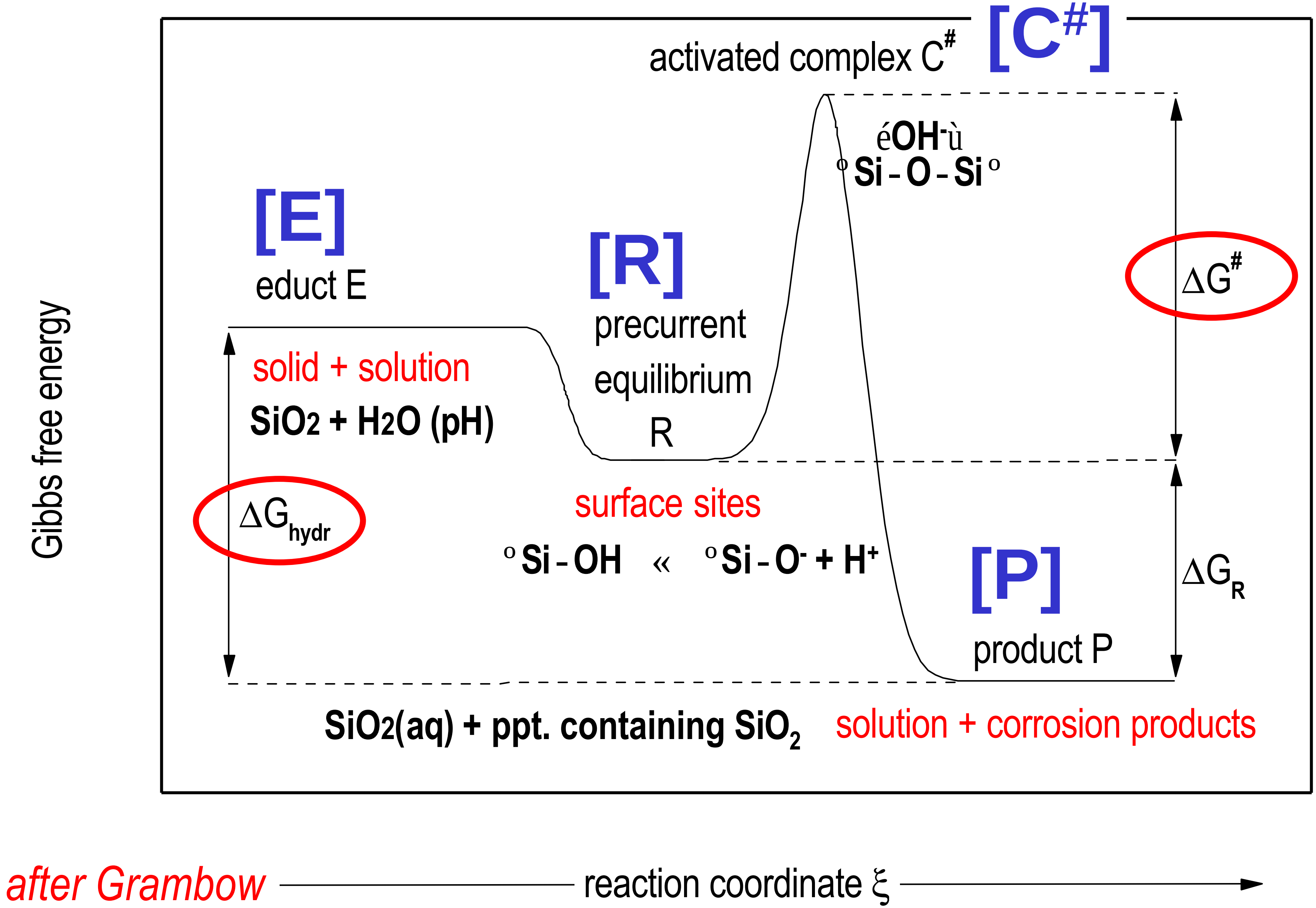
rate control by fluid film diffusion: $E_A \approx 20$ kJ/mol



$$r = \underbrace{b \cdot (c_s - 0)}_{r_0} \cdot \left(1 - \frac{c}{cs}\right), \quad b = f(\mathrm{v}, r, h, L)_{FLUID}$$

rate control by activated surface complex:

$E_A \approx$ 70-80 kJ/mol



reaction velocity:

$$r = r_+ - r_- \propto exp\left(\frac{-?G^\#}{RT}\right) - exp\left(\frac{-?G^\# - ?Ghydr}{RT}\right)$$

$$\propto exp\left(\frac{-?G^\#}{RT}\right) \cdot \left[1 - exp\left(\frac{-?Ghydr}{RT}\right)\right] \approx exp\left(\frac{-?G^\#}{RT}\right) \cdot \left[1 - \frac{c}{c_s}\right]$$

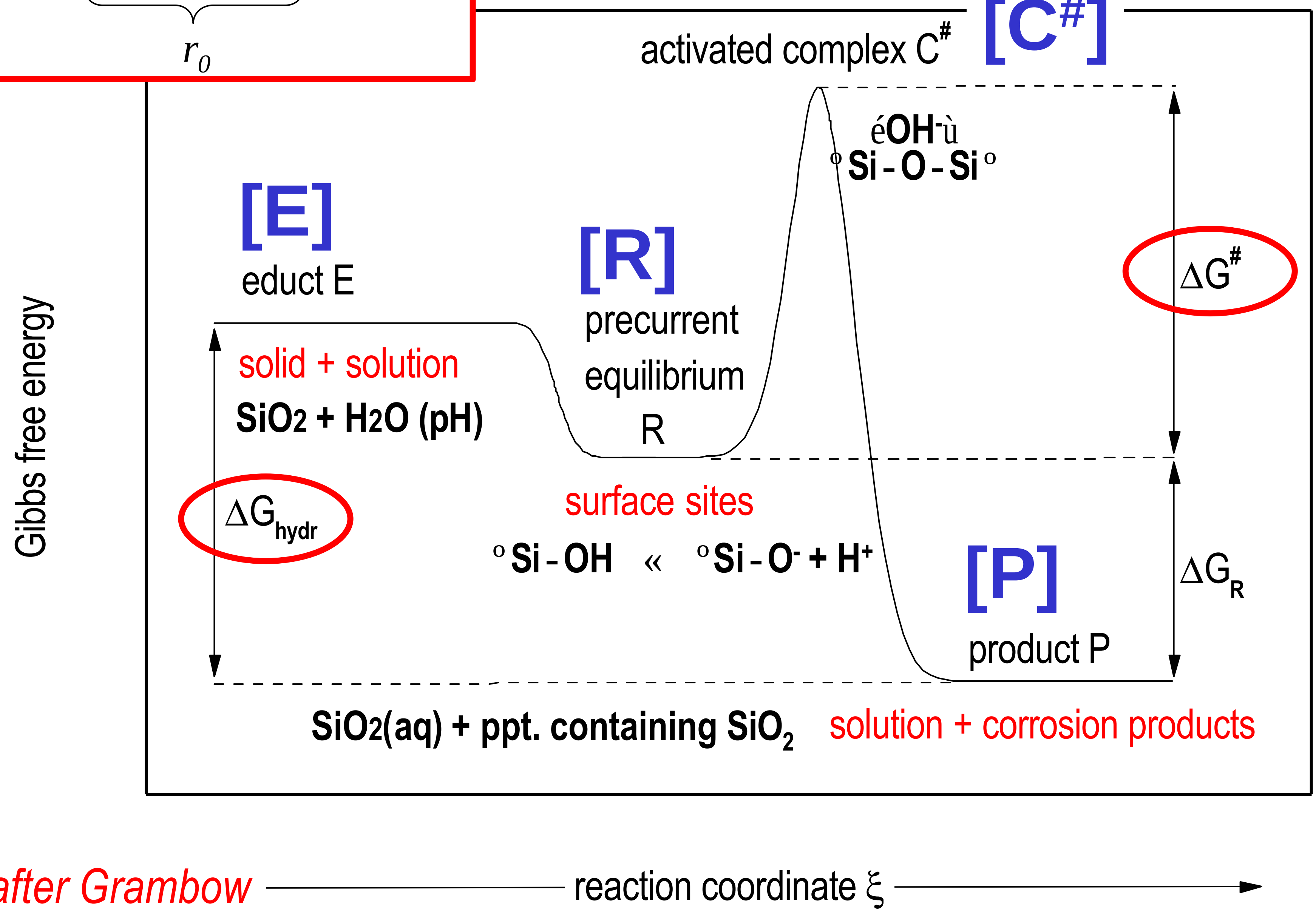
linear free energy relationship (LFER):

$$?G^\# \propto ?Ghydr$$

$$r = \underbrace{b \cdot \frac{kT}{h} \cdot [C^{\#}]}_{r_0} \cdot \left(1 - \frac{c}{cs}\right)$$

rate control by activated surface complex:

$E_A \approx$ 70-80 kJ/mol



thermochemical rate equation

LFER

$$\log r = \log r_X - \frac{E_A}{RT} - b \cdot \log q - \frac{e \cdot ?G_{hydr}(x)}{RT} + \log\left(1 - \frac{c(x)}{c_s}\right)$$

molecular dynamics

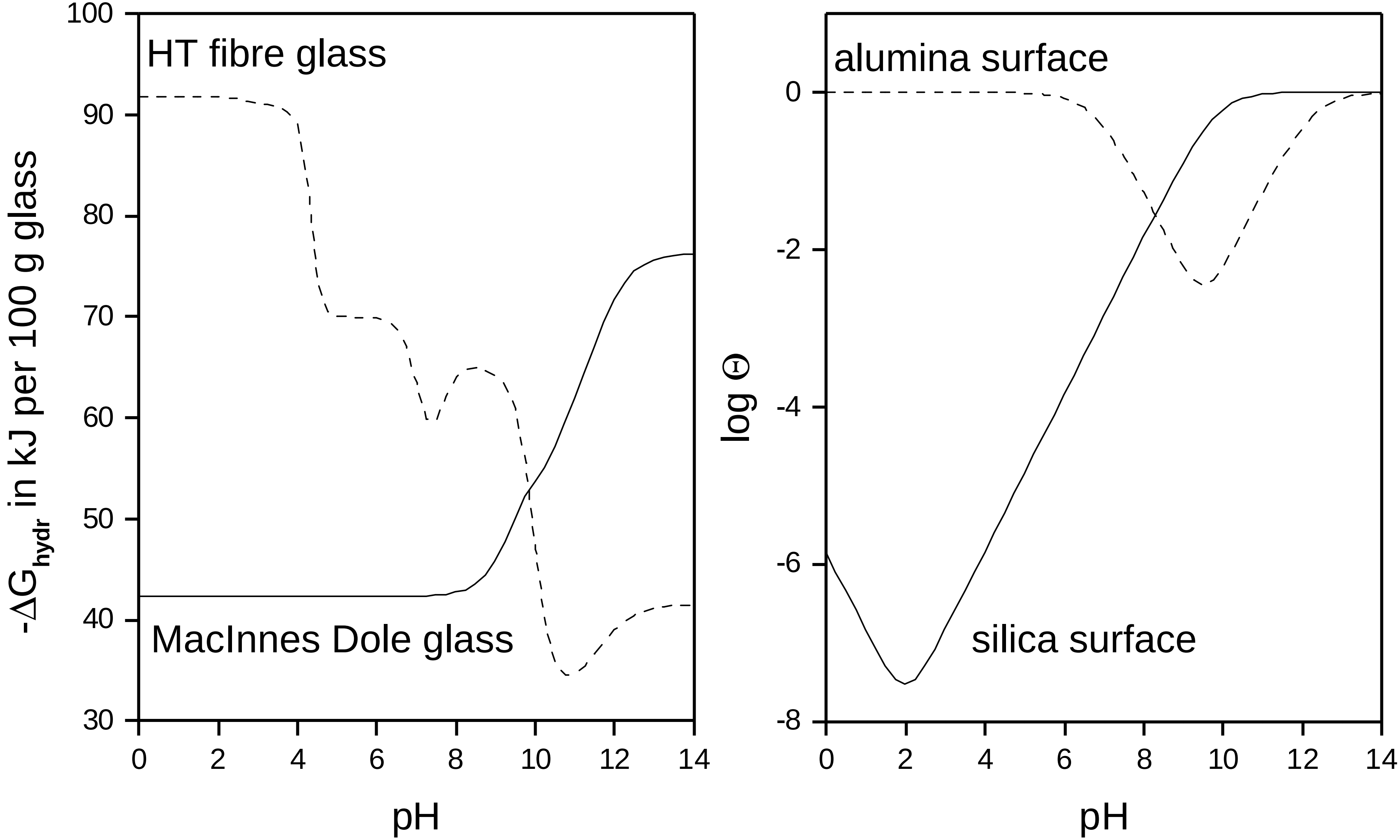
surface equilibrium

glass chemistry

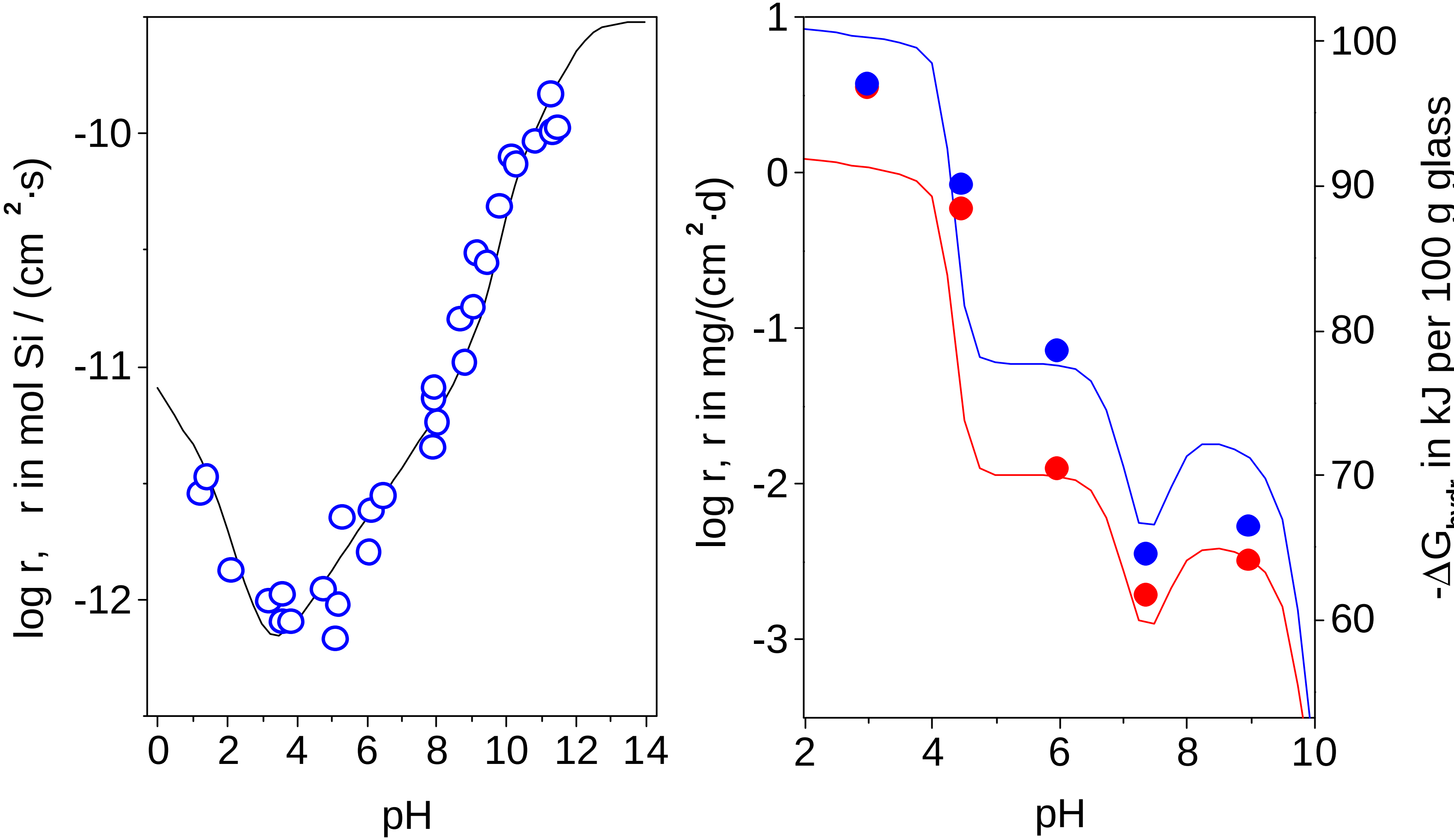
saturation; long term exposure

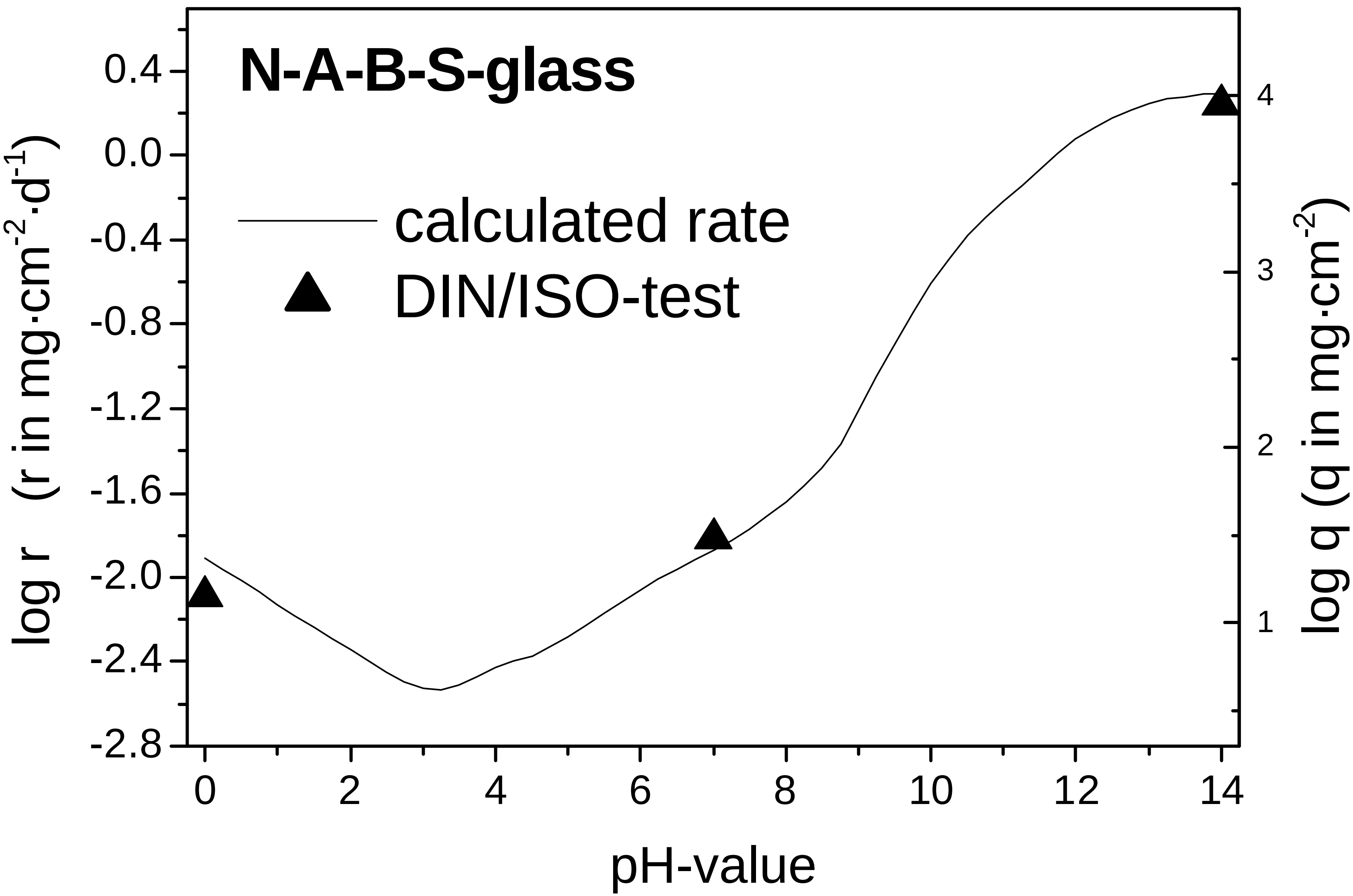
Corrosion rates at high water excess (low s parameter) :

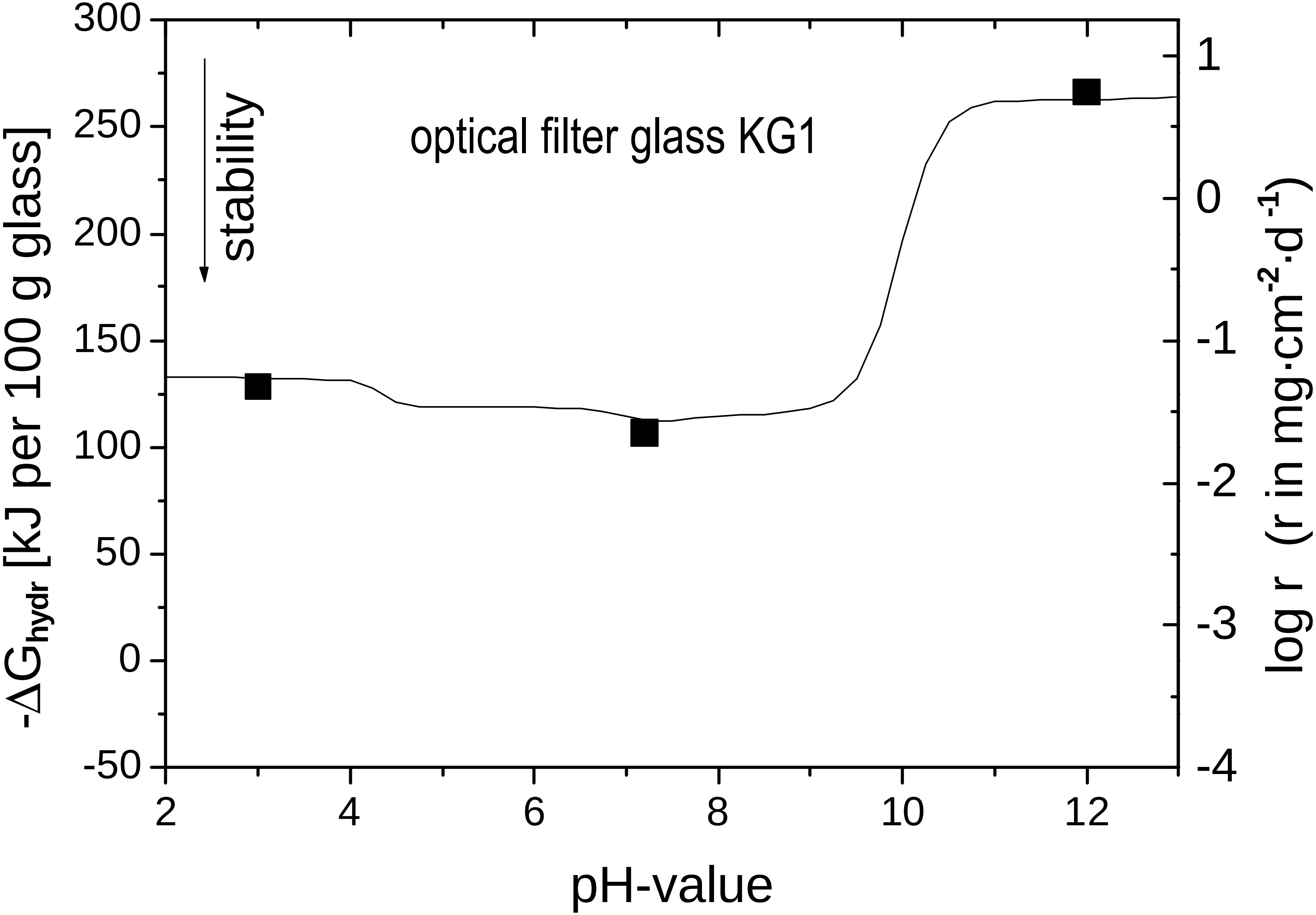
„Multiply“ the stability fingerprint or solubility (left graph) with the surface coverage (right graph) ...



... and obtain a prediction of the dissolution rate as f(pH).




N-A-B-S-glass
calculated rate
DIN/ISO-test
log r (r in mg·cm-2·d-1)
log q (q in mg·cm-2)
pH-value
0.4
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
-2.4
-2.8
0
2
4
6
8
10
12
14
1
2
3
4

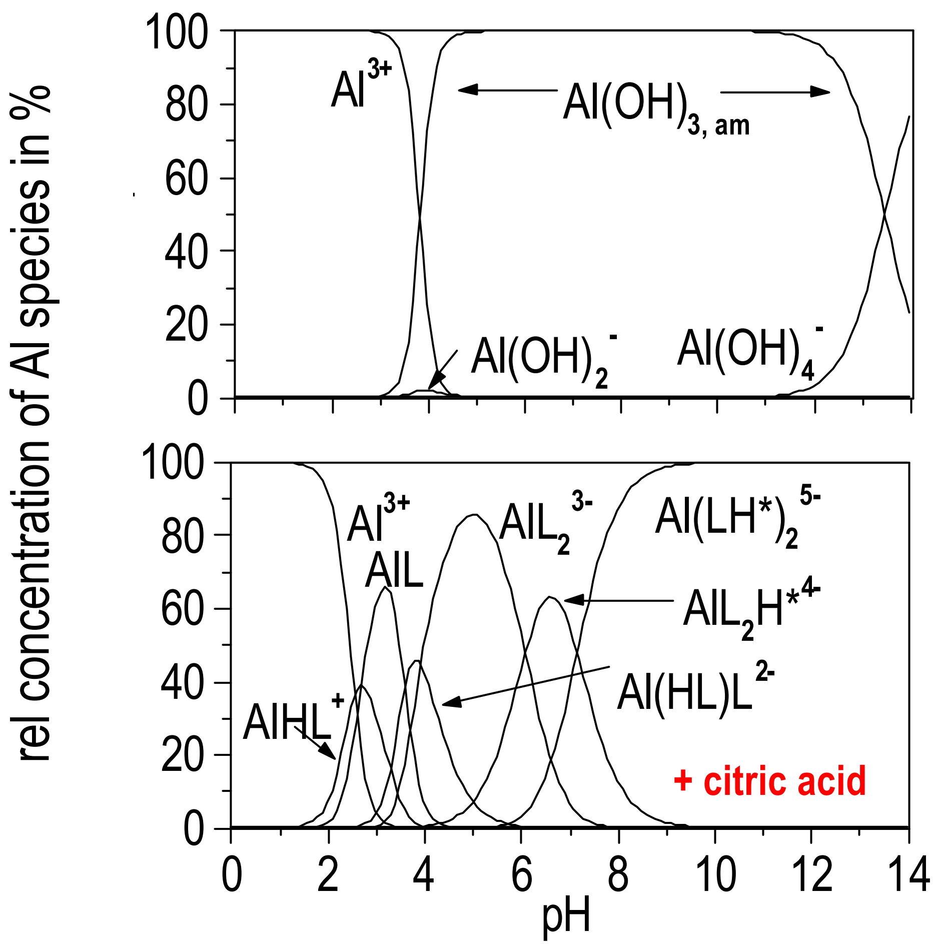


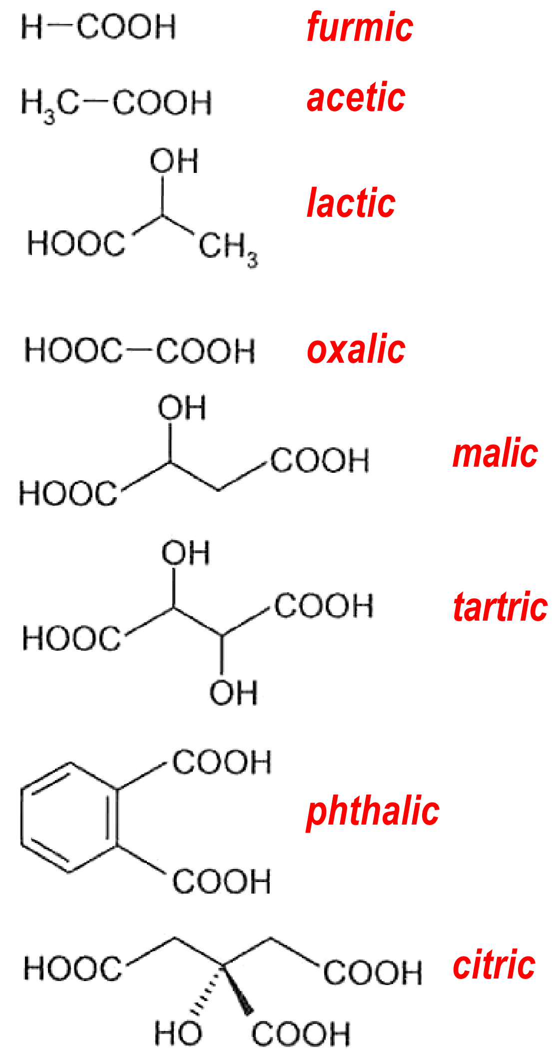
optical filter glass KG1
stability
-ΔG_hydr [kJ per 100 g glass]
log r (r in mg·cm-2·d-1)
pH-value
300
250
200
150
100
50
0
-50
1
0
-1
-2
-3
-4
2
4
6
8
10
12

Interaction between organic components and glass – a key to applications in medicine and biotechnology

two key mechanisms:

- influence on the solubility,
- influence on the surface equilibrium.





Ganor & Lasaga 1998, Gross & Dahlmann 2003

Thank you for your kind attention!