Acid-Base Speciation as a Function of pH (Fractional composition : α notation)

HOCl is a weak acid (chlorination)

$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^-$

$HOCl \rightleftharpoons H^+ + OCl^-$ $K_a = 10^{-7.60}$

$pK_a = -\log K_a = 7.60$

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]} = 10^{-7.60}$$

HOCl is a better disinfectant than OCl^-.

When pH is low, $[H^+]$ is high, HOCl is the dominant form.

When pH is high, $[H^+]$ is low, OCl^- is the dominant form.

pH is the main parameter that defines the dominant forms.

- How do the concentrations of HOCl and OCl^- change with pH?

Acid-Base Speciation as a Function of pH (Fractional composition : α notation)

The presence of ammonia in wastewater is due in most part to the hydrolysis of urea to the ammonium ion. The ionization reaction for the ammonium ion is:

$$NH_{3(gas)} + H^+ \rightleftarrows NH_4^+ \qquad pK_b = -\log K_b = 9.40$$

$$K_b = \frac{[NH_4{}^+]}{[NH_3][H]^+} = 10^{-9.40}$$

At typical pH values of domestic ww. (pH=7-7.5), dominant form of ammonia is NH_4^+ .
If ammonia is to be removed by stripping it has to be converted to NH_3 form, which is a gas.

When pH is low, NH_4^+ is the dominant form.

When pH is high, NH_3 is the dominant form.

pH is the main parameter that defines the dominant forms.

- How do the concentrations of NH_3 and NH_4^+ change with pH?

α (alpha) notation

TOTA = sum of the concentrations of all the species in solution that contain a chemical group A.

$TOTOCl = [HOCl] + [OCl^-]$

$TOTCO_3 = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

$TOTPO_4 = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$

α (alpha) notation

TOTA = sum of the concentrations of all the species in solution that contain a chemical group A.

α_0 = fraction of TOTA that is in the most protonated form.

α_i = fraction of TOTA that is in a form that has lost i protons.

$$\alpha_0 = \frac{[H_3PO_4]}{TOTPO_4} \quad \alpha_1 = \frac{[H_2PO_4^-]}{TOTPO_4} \quad \alpha_2 = \frac{[HPO_4^{=}]}{TOTPO_4} \quad \alpha_3 = \frac{[PO_4^{-3}]}{TOTPO_4}$$

$$\Sigma \alpha_i = 1$$

α values of acid/base species depend only on the pH of the solution.

$[A^-] = \alpha_1 (TOTA)$ → **depends on TOTA, independent of pH**

↓ (α_1)

Depends on pH, independent of TOTA

α (alpha) notation for monoprotic acids

For a monoprotic acid, HA, having a value of pKa

$$HA \rightleftharpoons H^+ + A^-$$

Rearrange the Ka expression

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$$

By adding a value of 1.0 to each side

$$\frac{[HA]}{[HA]} + \frac{[A^-]}{[HA]} = \frac{Ka}{[H^+]} + \frac{[H^+]}{[H^+]}$$

$$[A^-] + [HA] = TOTA$$

$$\frac{1}{\alpha_0} = \frac{TOTA}{[HA]} = \frac{K_a + [H^+]}{[H^+]}$$

$$\alpha_0 = \frac{[H^+]}{[H^+] + K_a}$$ or $$\alpha_0 = \frac{1}{1 + \left({}^{K_a}/_{[H^+]}\right)}$$

Do the same thing to get an expression for α_1:

$$\frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$$

Take its reciprocal ===>

$$\frac{[HA]}{[A^-]} = \frac{[H^+]}{K_a}$$

Add 1.0 to each side

$$\frac{[HA]}{[A^-]} + \frac{[A^-]}{[A^-]} = \frac{[H^+]}{K_a} + \frac{K_a}{K_a}$$

$$\frac{TOTA}{[A^-]} = \frac{[H^+]+K_a}{K_a}$$

$$\frac{[A^-]}{TOTA} = \alpha_1 = \frac{K_a}{[H^+]+K_a} \quad \text{or} \quad \frac{1}{1+\left({[H^+]}/{K_a}\right)}$$

$$\alpha_0 = \frac{[H^+]}{[H^+]+K_a}$$

$$\alpha_1 = \frac{K_a}{[H^+]+K_a}$$

At pH = pKa

pH = 5 pKa = 10^{-5}

$$\alpha_0 = \frac{10^{-5}}{10^{-5} + 10^{-5}} = \frac{1}{2} = 0.5 = \frac{[HA]}{[A^-] + [HA]}$$

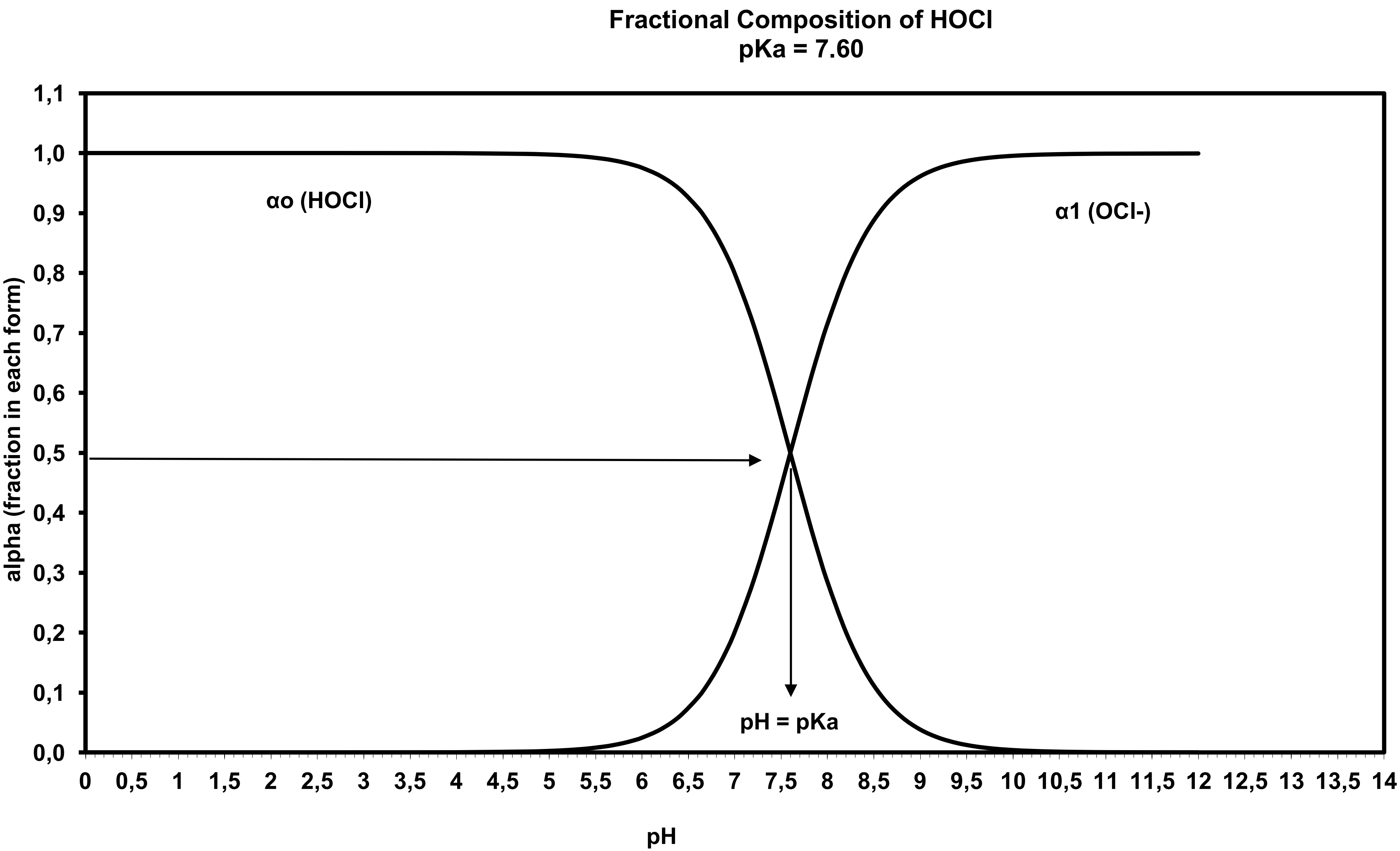
When pKa = pH => [HA] = [A$^-$]

$$\alpha_1 = \frac{10^{-5}}{10^{-5} + 10^{-5}} = \frac{1}{2} = 0.5 = \frac{[A^-]}{[A^-] + [HA]}$$

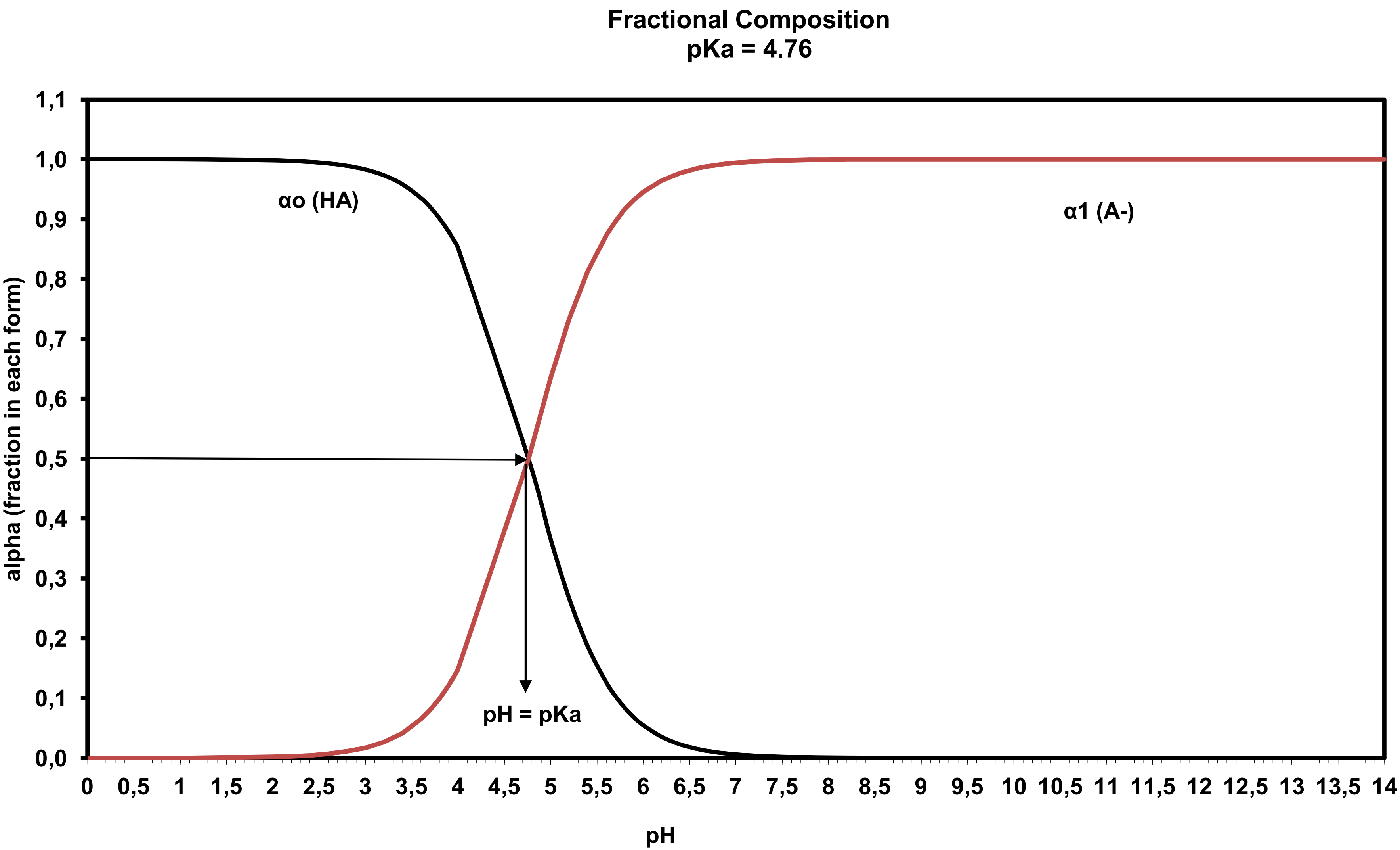
Using the appropriate Ka, we can plot α_i versus pH.

Fractional Composition of HOCl
pKa = 7.60

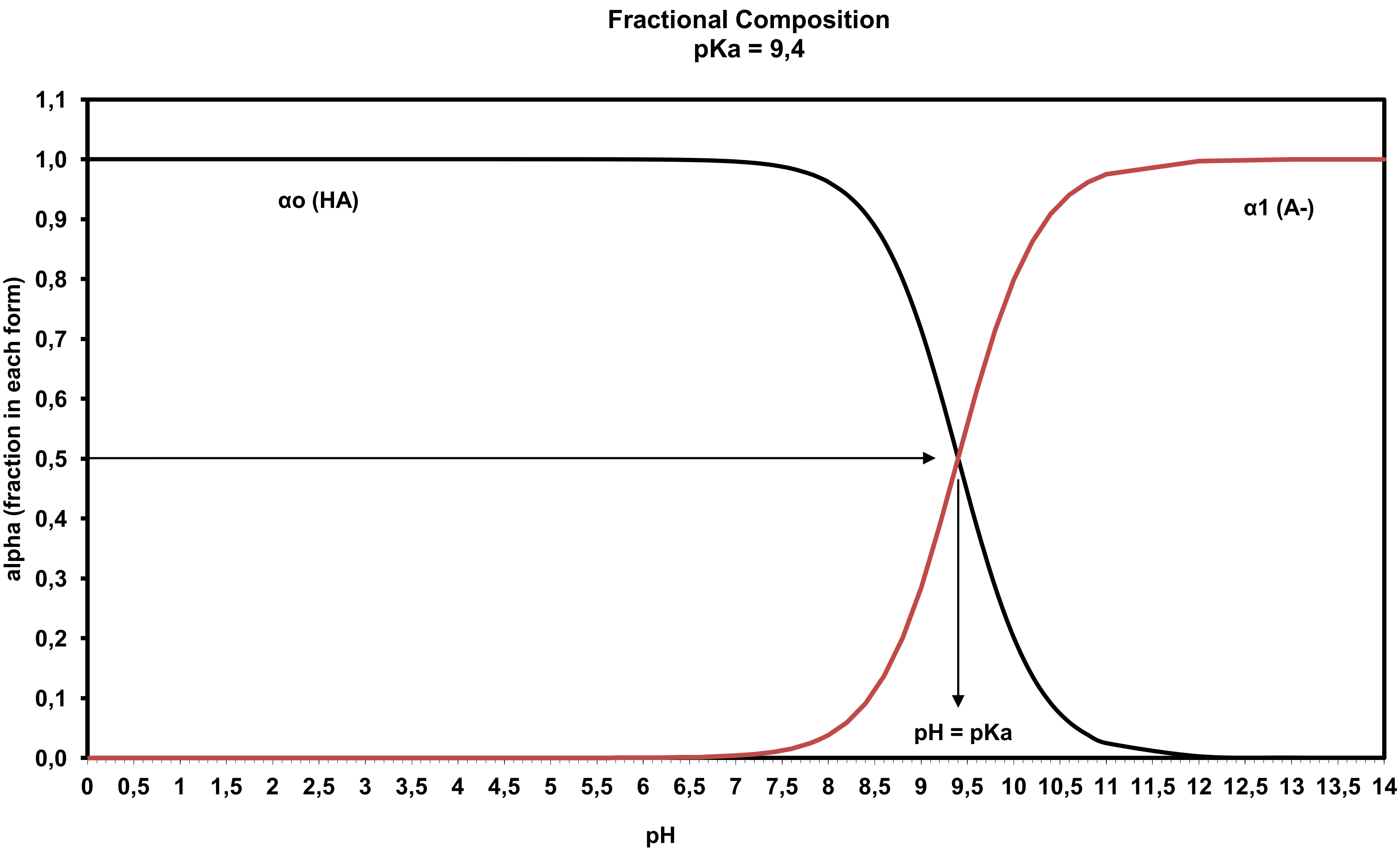
pH	[H+]	α0 (HOCl)	α1 (OCl-)
		[H+]/([H+]+Ka)	[Ka]/([H+]+Ka)
0	1	1,0000000	0,0000000
1	0,1	0,9999997	0,0000003
2	0,01	0,9999975	0,0000025
3	1,0E-03	0,9999749	0,0000251
4	1,0E-04	0,9997489	0,0002511
5	1,0E-05	0,9974944	0,0025056
6	1,0E-06	0,9754966	0,0245034
7	1,0E-07	0,7992400	0,2007600
7,6	2,5E-08	0,5000000	0,5000000
8	1,0E-08	0,2847472	0,7152528
9	1,0E-09	0,0382865	0,9617135
10	1,0E-10	0,0039653	0,9960347
11	1,0E-11	0,0003979	0,9996021
12	1,0E-12	0,0000398	0,9999602
13	1,0E-13	0,0000040	0,9999960
14	1,0E-14	0,0000004	0,9999996



Fractional Composition of HOCl
pKa = 7.60
1,1
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
alpha (fraction in each form)
αo (HOCl)
α1 (OCl-)
pH = pKa
0
0,5
1
1,5
2
2,5
3
3,5
4
4,5
5
5,5
6
6,5
7
7,5
8
8,5
9
9,5
10
10,5
11
11,5
12
12,5
13
13,5
14
pH



Fractional Composition
pKa = 4.76
1,1
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
alpha (fraction in each form)
αo (HA)
α1 (A-)
pH = pKa
0
0,5
1
1,5
2
2,5
3
3,5
4
4,5
5
5,5
6
6,5
7
7,5
8
8,5
9
9,5
10
10,5
11
11,5
12
12,5
13
13,5
14
pH

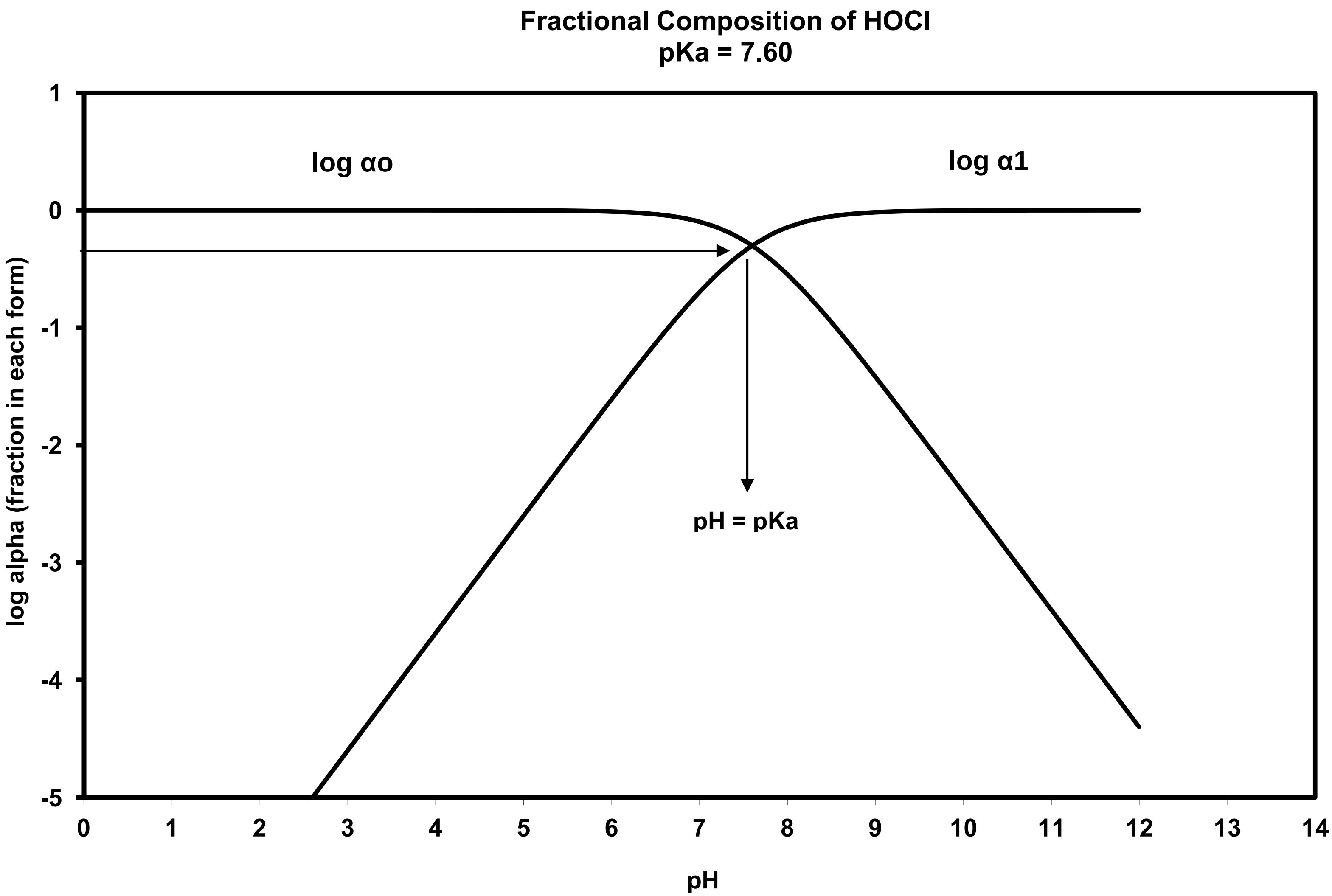

Fractional Composition
pKa = 9,4
alpha (fraction in each form)
αo (HA)
α1 (A-)
pH = pKa
pH
1,1
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
0 0,5 1 1,5 2 2,5 3 3,5 4 4,5 5 5,5 6 6,5 7 7,5 8 8,5 9 9,5 10 10,5 11 11,5 12 12,5 13 13,5 14

We can also plot log α_i versus pH.

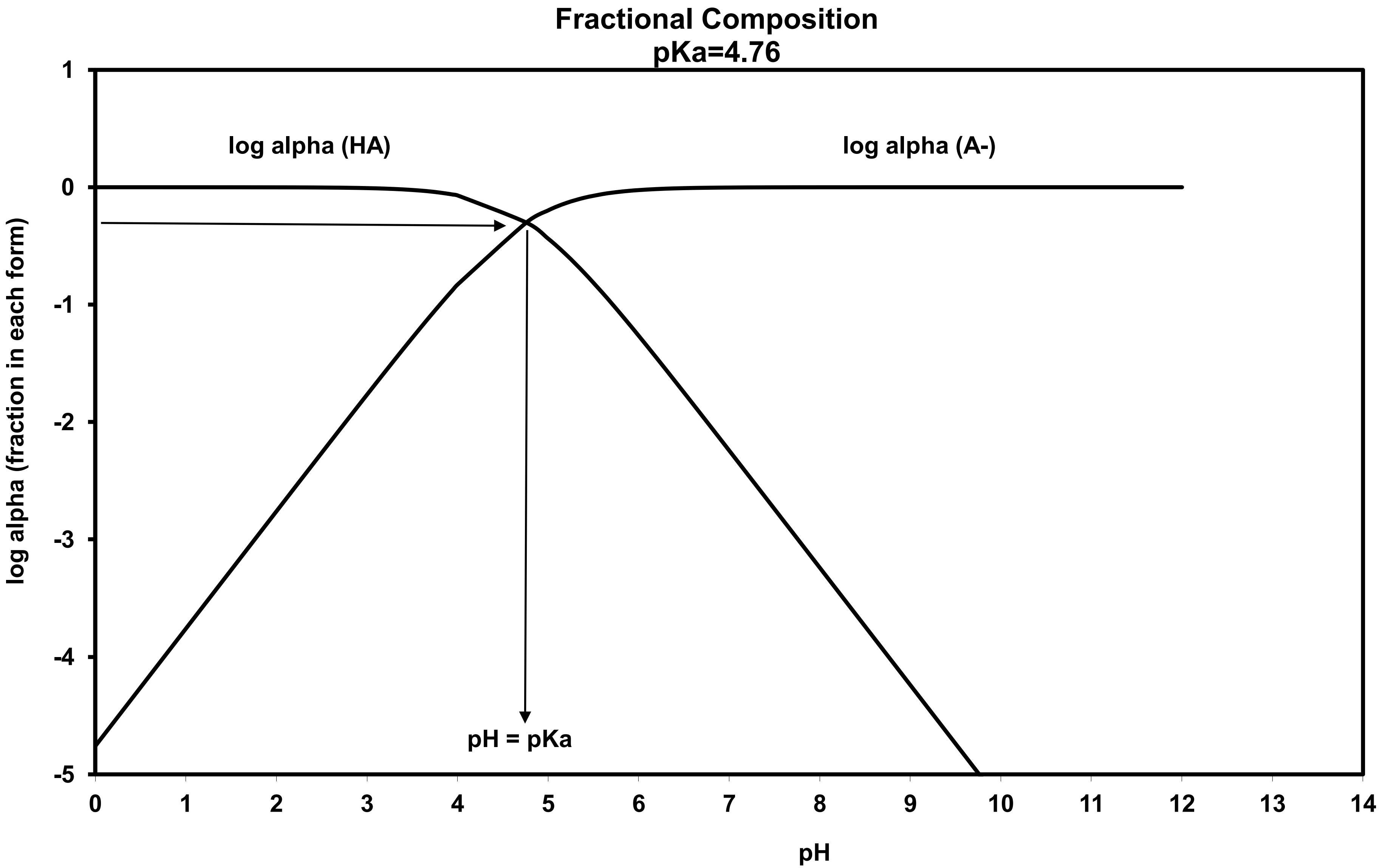
Fractional Composition of HOCl

pKa = 7.60

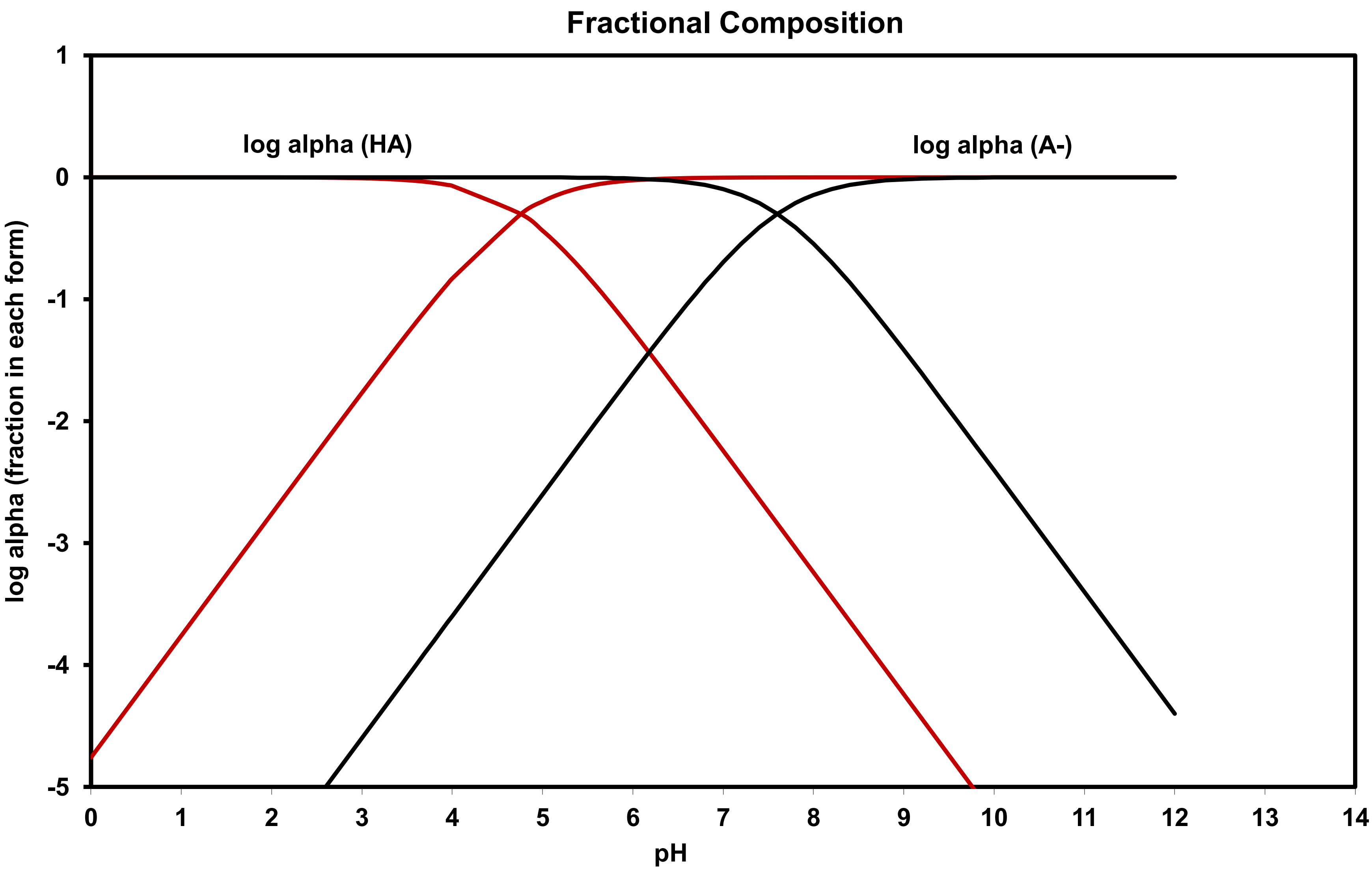
pH	[H+]	α0 (HOCl) [H+]/([H+]+Ka)	α1 (OCl-) [Ka]/([H+]+Ka)	Log α0	Log α1
0	1	1,0000000	0,0000000	-1,0909E-08	-7,600000011
1	0,1	0,9999997	0,0000003	-1,0909E-07	-6,600000109
2	0,01	0,9999975	0,0000025	-1,0909E-06	-5,600001091
3	1,0E-03	0,9999749	0,0000251	-1,09088E-05	-4,600010909
4	1,0E-04	0,9997489	0,0002511	-0,000109076	-3,600109076
5	1,0E-05	0,9974944	0,0025056	-0,001089531	-2,601089531
6	1,0E-06	0,9754966	0,0245034	-0,010774226	-1,610774226
7	1,0E-07	0,7992400	0,2007600	-0,097322794	-0,697322794
7,6	2,5E-08	0,5000000	0,5000000	-0,301029996	-0,301029996
8	1,0E-08	0,2847472	0,7152528	-0,545540463	-0,145540463
9	1,0E-09	0,0382865	0,9617135	-1,416954289	-0,016954289
10	1,0E-10	0,0039653	0,9960347	-2,401725525	-0,001725525
11	1,0E-11	0,0003979	0,9996021	-3,400172861	-0,000172861
12	1,0E-12	0,0000398	0,9999602	-4,400017289	-1,72892E-05
13	1,0E-13	0,0000040	0,9999960	-5,400001729	-1,72895E-06
14	1,0E-14	0,0000004	0,9999996	-6,400000173	-1,72896E-07



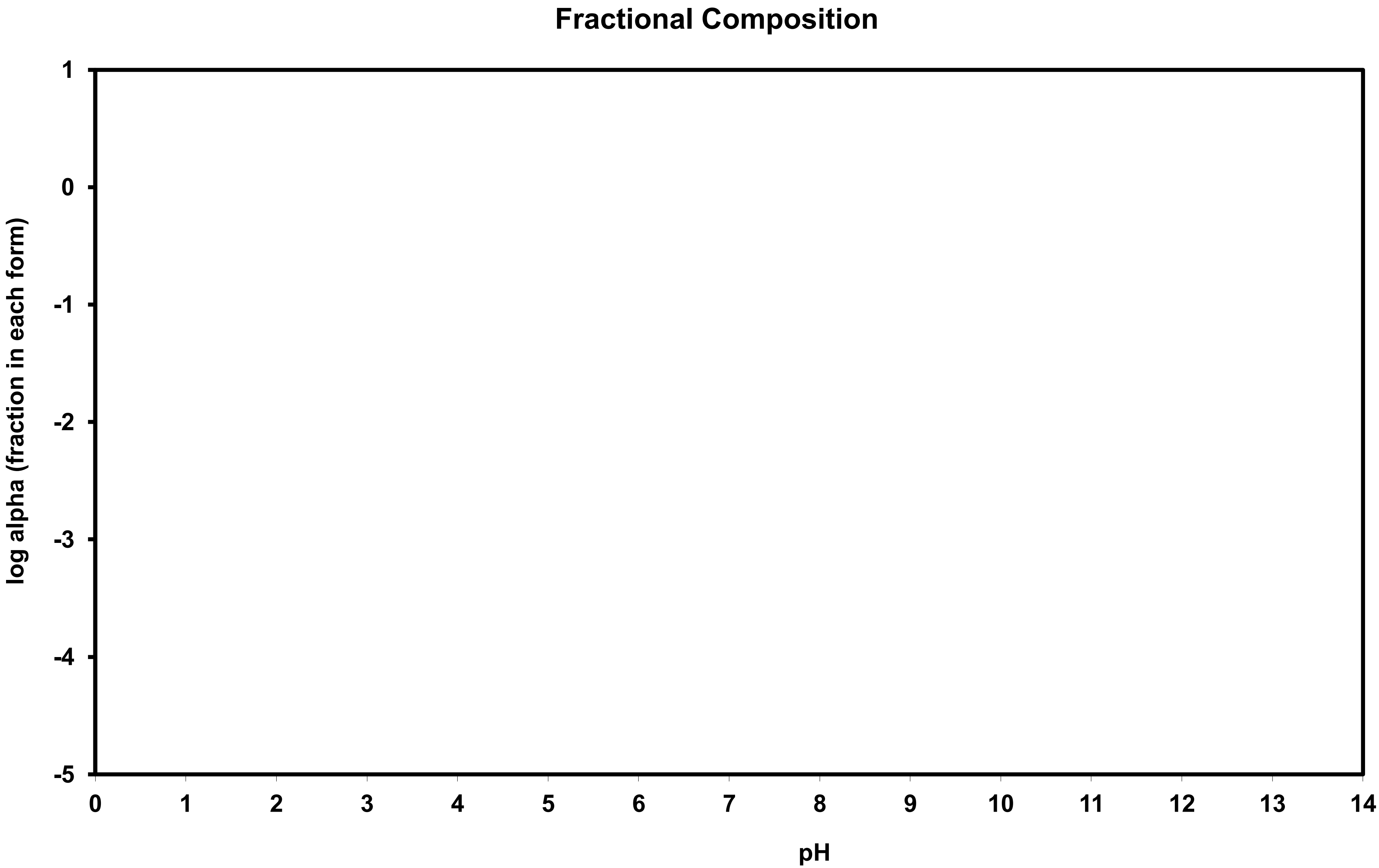
Fractional Composition of HOCl
pKa = 7.60
log αo
log α1
pH = pKa
log alpha (fraction in each form)
pH
1
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14



Fractional Composition
pKa=4.76
log alpha (HA)
log alpha (A-)
pH = pKa
log alpha (fraction in each form)
pH
1
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14



Fractional Composition
log alpha (HA)
log alpha (A-)
log alpha (fraction in each form)
1
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH


Fractional Composition
log alpha (fraction in each form)
1
0
-1
-2
-3
-4
-5
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH