ENV-200
Acid-base

Tamar Kohn
tamar.kohn@epfl.ch

Learning objectives

You should be able to:

1. Understand the importance of pH in natural systems.
2. Formulate acid and base equilibrium equations, mass balances and proton balances.
3. Draw pC – pH diagrams for acids or bases.
4. Determine the equilibrium pH and/or concentrations of acids and bases in a given system.

Resources

Sigg, Behra, Stumm, Chimie des milieux aquatiques, Chapter 2

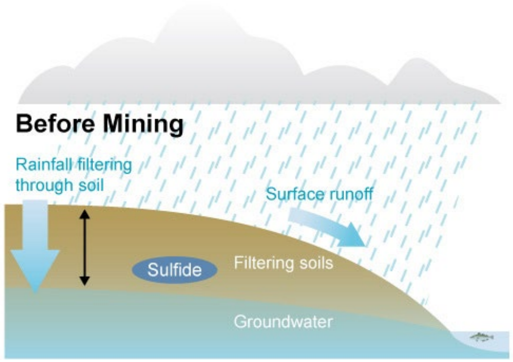
Engineering application: treatment of acid mine drainage

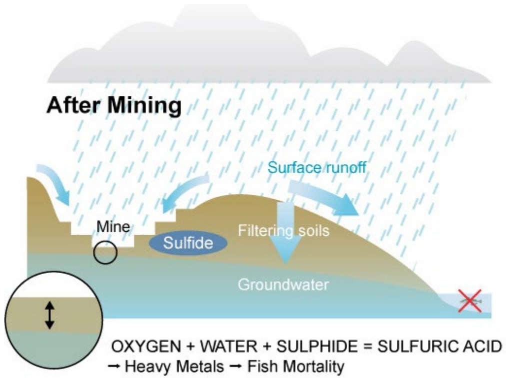
What is acid mine drainage?

- Common mining activites (e.g., coal) lead to exposure of pyrite (FeS_2).
- Pyrite reacts with oxygen in air to form a metal-rich, acidic runoff:

$$FeS_2 + O_2 + H_2O \rightleftharpoons Fe(OH)_3 + \mathbf{SO_4^{2-} + H^+}$$

- The acidic runoff dissolved heavy metals (Cu, Hg) and transports them to surface and groundwater. The receiving water will turn red-yellow from iron precipitation.
- Effects:
  - acid and heavy metals are toxic to wildlife
  - can contaminate surface, ground and drinking water
  - can corrode pipes, bridges, etc.





Source:http://maps.grida.no/go/graphic/mining_effects_on_rainfall_drainage

Engineering application: treatment of acid mine drainage

British Columbia,CA
http://dwb4.unl.edu

« yellow boy », West Virginia, USA
http://news.bbc.co.uk/2/hi/in_pictures/7789330.stm

Rio Tinto, Spain

South Africa
http://www.watersense.co.za/2010/05/24/sa-running-on-empty/

Engineering application: treatment of acid mine drainage

Treatment:

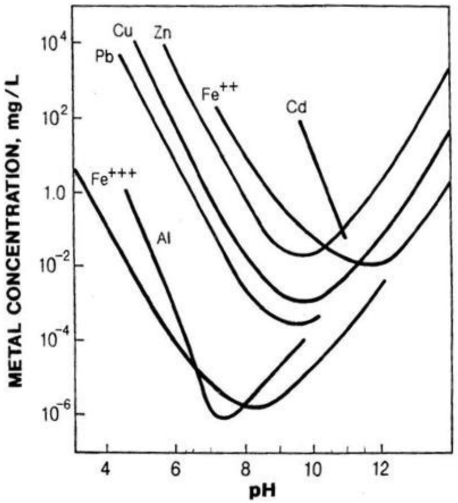
Physical: prevent oxidation e.g., by capping mine.

Biological: reduce sulfate, immobilize heavy metals.

Chemical: neutralize pH, e.g., by addition of lime, to precipitate heavy metals.

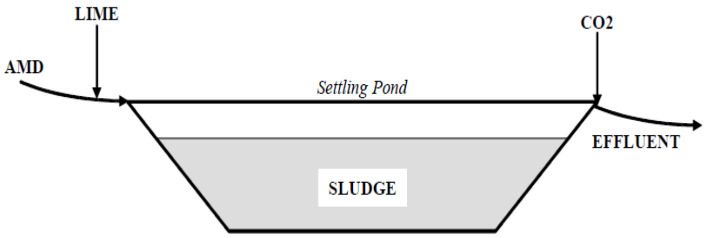
$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

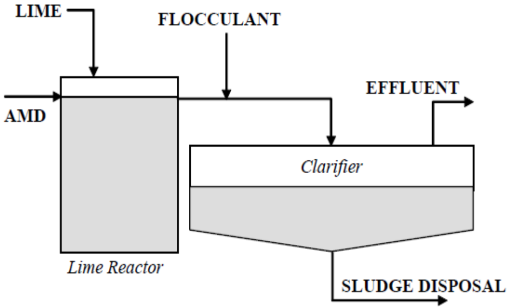


Many different configurations for lime treatment:

Pond treatment



Conventional treatment plant



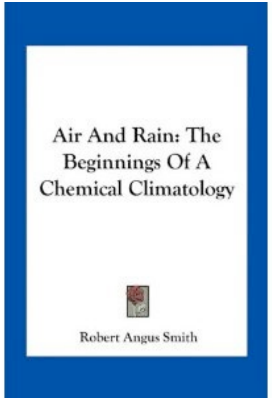
Famous environmental problem: acid rain

Definition:

- “a broad term referring to a mixture of wet and dry deposition from the atmosphere containing higher than normal amounts of **nitric and sulfuric acids**” (US EPA)
- rain with pH <5 or 5.5 (different definitions from different sources)

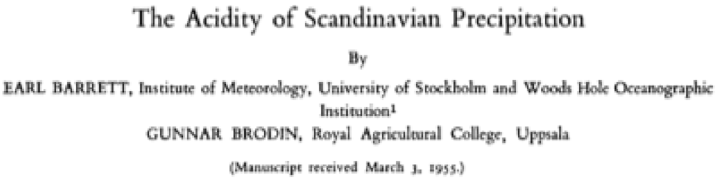
First reported in mid-1800’s

- Robert Angus Smith (1852): “Relationship of **Sooty Skies** and **Acid Precipitation** in Manchester, England”
- 1872: Smith coined the term “**acid rain**”



Famous environmental problem: acid rain

1950's: first systematic, large scale rain pH measurements in Scandinavia



The Acidity of Scandinavian Precipitation

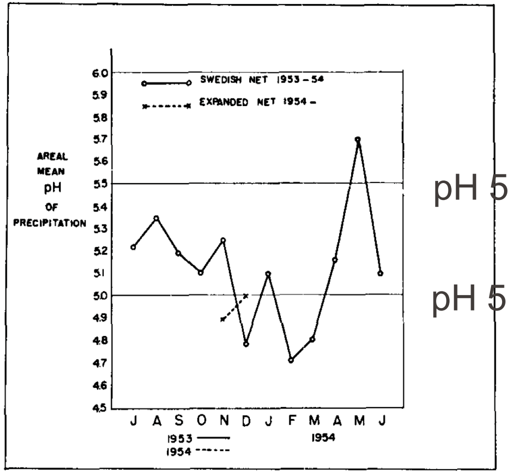
By

EARL BARRETT, Institute of Meteorology, University of Stockholm and Woods Hole Oceanographic Institution[1]

GUNNAR BRODIN, Royal Agricultural College, Uppsala

(Manuscript received March 3, 1955.)

Average precipitation pH

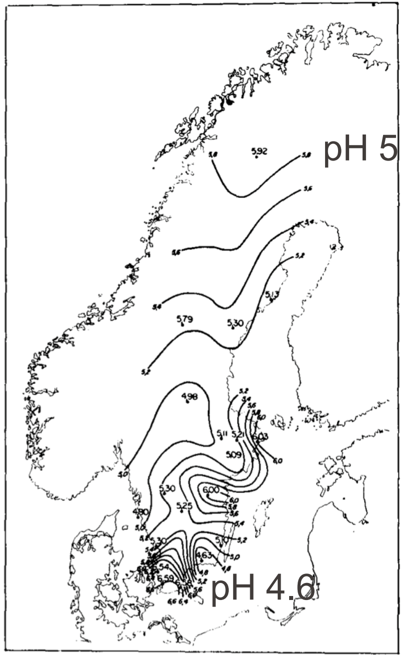


pH 5.5

pH 5.0

Fig. 4. Areal Mean of Precipitation pH vs. Time July 1953—June 1954 and Nov.—Dec. 1954.

pH contour plot of Scandanavia



pH 5.6

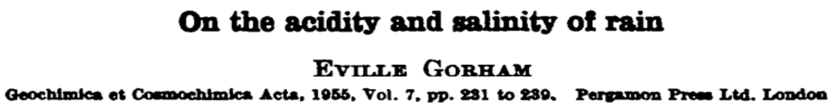
pH 4.6

Fig. 2. pH of Precipitation, Sept. 1953.

Tellus VII (1955), 2

Famous environmental problem: acid rain

1950’s: link made between rain and pollution (soot and/or sulfate)



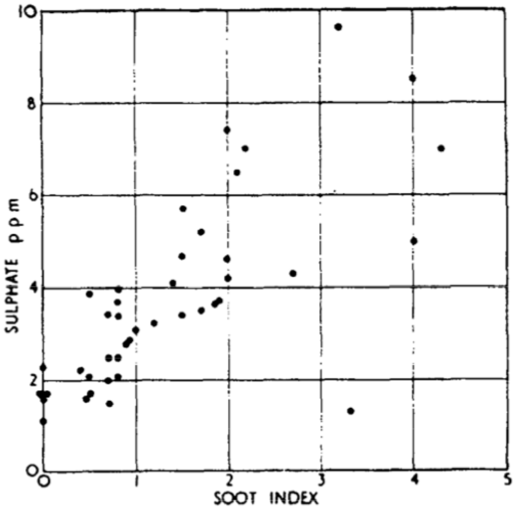
On the acidity and salinity of rain

EVILLE GORHAM

Geochimica et Cosmochimica Acta, 1955, Vol. 7, pp. 231 to 239. Pergamon Press Ltd. London

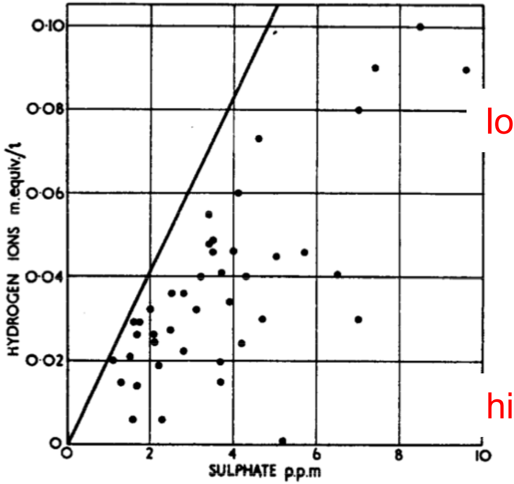
Rain samples in England

SO_4^{2-} vs. Soot Index



H^+ vs. SO_4^{2-}

pH = -log [H^+]



low pH

high pH

Famous environmental problem: acid rain

What makes rain acidic?

strong **acids** from atmospheric pollutants interact in the atmosphere with **bases**

HCl: combustion of Cl-bearing polymers

HNO_3: from NO, NO_2 from combustion

H_2SO_4: from S in fossil fuels

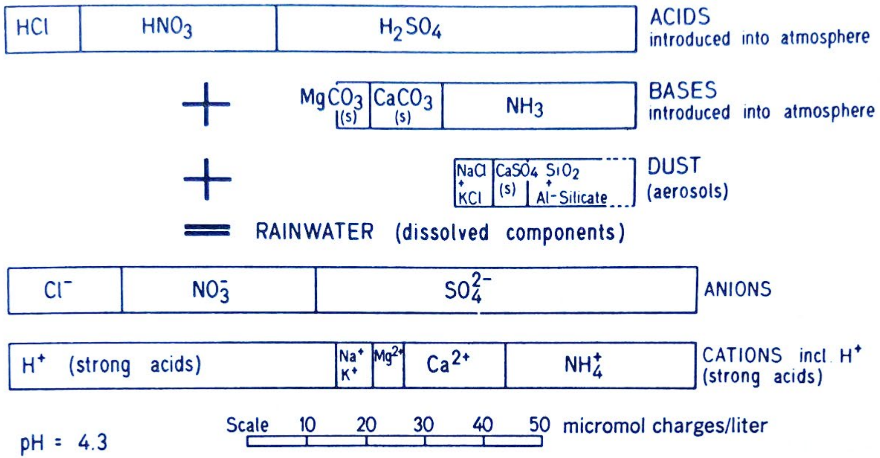


Fig. 3.1 Stumm & Morgan

NH_3: soils, manure

Carbonate minerals

Dust: NaCl, KCl, $CaSO_4$, SiO_2, Al-silicate

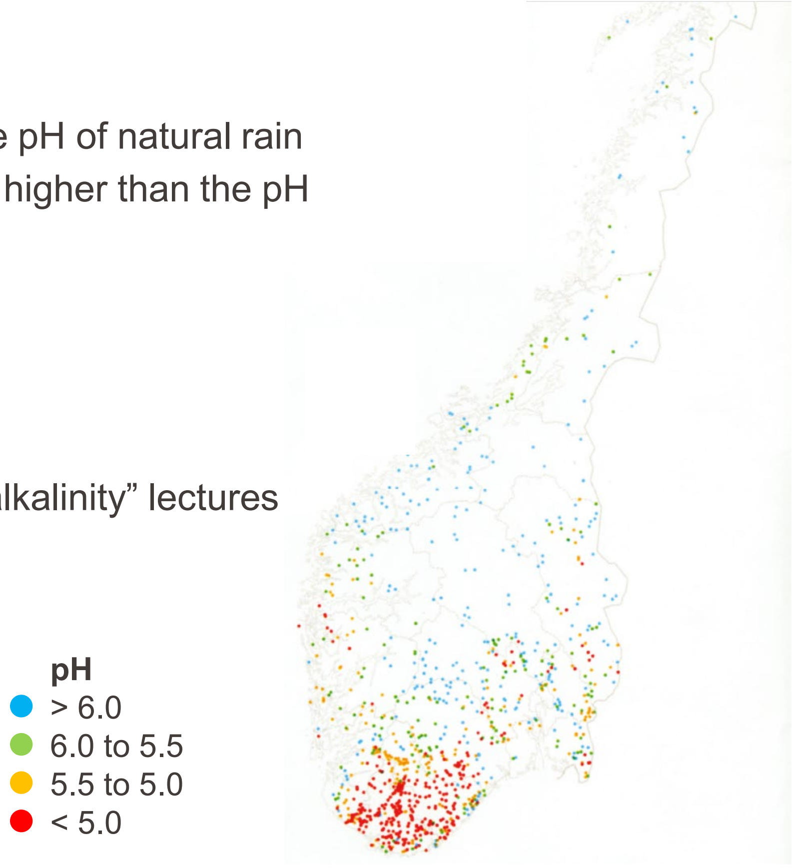
Acid rain pH is 3-5

- Emissions of SO_2 and NO_x from combustion are the major drivers
- SO_2 and NO_x are converted in the atmosphere to H_2SO_4 and HNO_3 (strong acids)

Famous environmental problem: acid rain

Effect on pH of lakes and rivers

- Natural lakes have a pH of 6.5-9 → higher than the pH of natural rain
- Lakes impacted by acid rain have a pH of 4.5-6 → higher than the pH of acid rain (but still problematically low)
- Why do rivers and lakes have a higher pH?
- Natural waters can buffer acid
- A good source of buffering capacity (= alkalinity):
  $CaCO_3(s) = Ca^{2+} + CO_3^-$
- We will discuss all this during the “carbonate and alkalinity” lectures



pH of acid-sensitive lakes in Norway, 1986

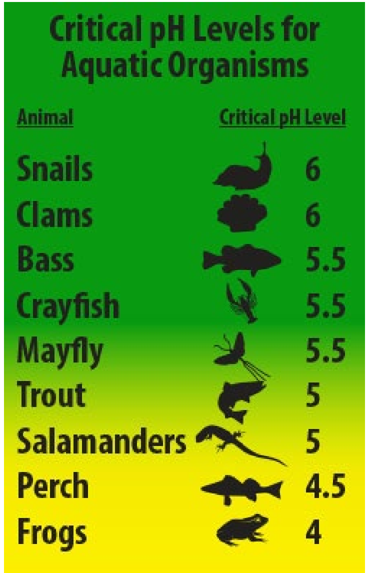
Source: Ambio , 1988, Vol. 17, No. 4

Famous environmental problem: acid rain

Effect on biota

- Acid rain causes a cascade of effects that harm or kill **individual fish**, reduce fish **population** numbers, completely eliminate fish **species** from a water body, and decrease **biodiversity**.

- Some species can tolerate more acidic conditions.
  - **pH = 6.0**: insects, and some plankton species begin to disappear
  - **pH = 5.0**: major changes in the makeup of the plankton community occur, less desirable species of mosses and plankton may begin to invade, and the progressive loss of some fish populations is likely
  - **pH < 5.0**: the water is largely devoid of fish



Critical pH Levels for Aquatic Organisms

Animal	Critical pH Level
Snails	6
Clams	6
Bass	5.5
Crayfish	5.5
Mayfly	5.5
Trout	5
Salamanders	5
Perch	4.5
Frogs	4

Source: https://www.epa.gov/acidrain/effects-acid-rain

Famous environmental problem: acid rain

Other effects

- Vegetation:
  - direct deposition of acids causes burning of leaves; alters the protective waxy surface of leaves, lowering disease resistance, germination and reproduction.
  - acids can alter soil properties:
    - react with minerals to leach out metals (e.g., Al)
    - change nutrients available to plants – generally making them more mobile
    - affect decomposition of humus and subsequent organic material, which are necessary for normal plant development.
- Materials: deterioration of metals (such as bronze), paint and stone (such as marble and limestone)

Tree branches from Black Forest, Germany

1908

1968

Now on to the acid-base lecture…

A quick note on ion activity

The measure « concentration » is, strictly speaking, only applicable to ideal solutions under standard conditions*. The theory of ideal solutions assumes that no interactions exist between the individual dissolved species (= infinite dilution of all species). In electrolyte solutions (solutions with $I \neq 0$) this is not the case! Various interactions between species can occur, most importantly electrostatic effects (attraction between ions with opposite charge). These interactions influence the behavior of the ions and don't allow to treat every ion in the solution independently. To accurately do equilibrium calculations in electrolyte solutions, we use « ion activity » instead of «ion concentration » to account for this non-ideal behavior.

Activity of compound i is indicated by { i }
concentration of compound i is indicated by [i]

In this part of the course, we deal with mass balances a lot, and we therefore only use the concept of «concentration». But keep in mind that for equilibria, reactions, etc., we often deal with activities. You will use activities later in the course (metal ions).

*Standard conditions: T = 25 °C
P = 1 atm
Ionic strength = 0 M → most common source for non-ideal behavior

Now on to the acid-base lecture…

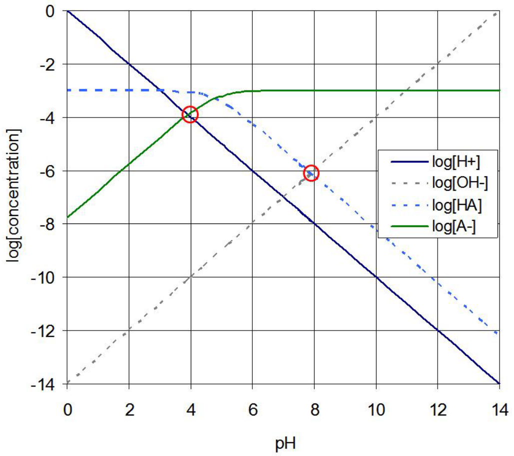
In this part of the course, we are interested in the pH of water of different composition. It is always helpful to know the pH, because it is an extremely important variable that can determine speciation, precipiation-dissolution, redox conditions, ecotoxicology, buffering capacity, etc.

Specifically, we want to know:

1. If we add … M of total acid (C_T = HA + A^-) to water, what is the pH and what are the concentrations of HA and A^- at equilibrium?
2. If [HA] = … M and C_T = … M, what is [A^-] and the pH?
3. If the pH is …, what is [A^-], [HA]?
4. etc.

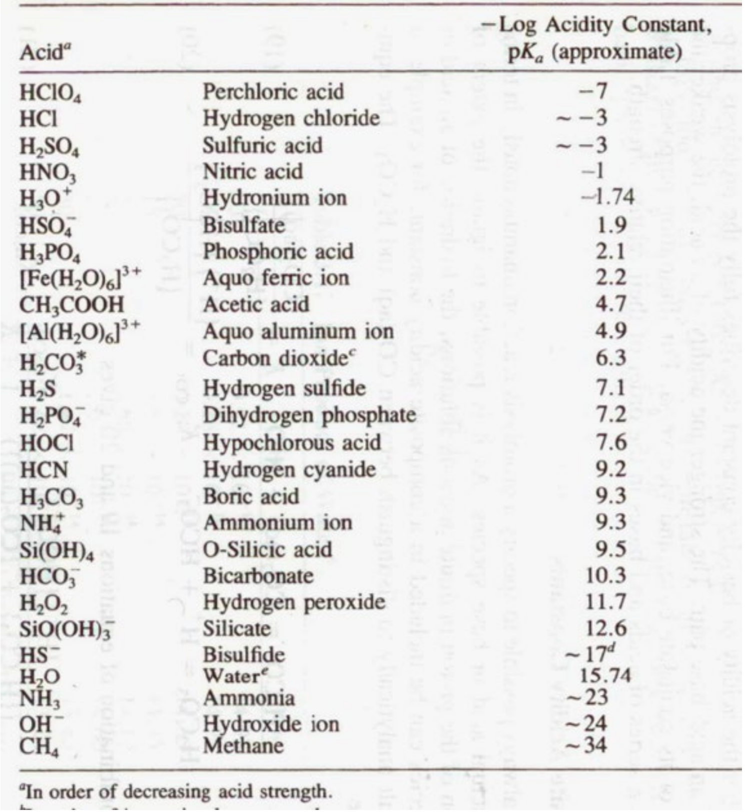
We will learn to use a **graphical approach** to answer these Questions rapidly and intuitively. We will create a lot of plots of C vs. pH for the species of interest.

Note: for this part of the course, we always assume **equilibrium conditions!**



Some important tables

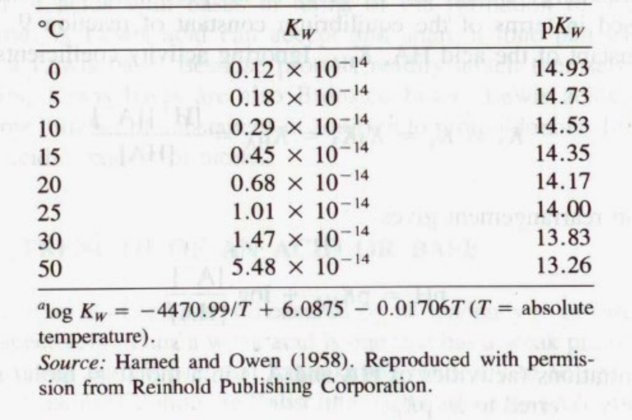
pK_a of various environmentally relevant acids



Acid[a]		−Log Acidity Constant, pK_a (approximate)
$HClO_4$	Perchloric acid	−7
HCl	Hydrogen chloride	∼ −3
H_2SO_4	Sulfuric acid	∼ −3
HNO_3	Nitric acid	−1
H_3O^+	Hydronium ion	−1.74
HSO_4^-	Bisulfate	1.9
H_3PO_4	Phosphoric acid	2.1
$[Fe(H_2O)_6]^{3+}$	Aquo ferric ion	2.2
CH_3COOH	Acetic acid	4.7
$[Al(H_2O)_6]^{3+}$	Aquo aluminum ion	4.9
$H_2CO_3^*$	Carbon dioxide[c]	6.3
H_2S	Hydrogen sulfide	7.1
$H_2PO_4^-$	Dihydrogen phosphate	7.2
$HOCl$	Hypochlorous acid	7.6
HCN	Hydrogen cyanide	9.2
H_3CO_3	Boric acid	9.3
NH_4^+	Ammonium ion	9.3
$Si(OH)_4$	O-Silicic acid	9.5
HCO_3^-	Bicarbonate	10.3
H_2O_2	Hydrogen peroxide	11.7
$SiO(OH)_3^-$	Silicate	12.6
HS^-	Bisulfide	∼17[d]
H_2O	Water[e]	15.74
NH_3	Ammonia	∼23
OH^-	Hydroxide ion	∼24
CH_4	Methane	∼34

[a] In order of decreasing acid strength.

K_w at different temperatures



°C	K_W	pK_W
0	0.12×10^{-14}	14.93
5	0.18×10^{-14}	14.73
10	0.29×10^{-14}	14.53
15	0.45×10^{-14}	14.35
20	0.68×10^{-14}	14.17
25	1.01×10^{-14}	14.00
30	1.47×10^{-14}	13.83
50	5.48×10^{-14}	13.26

[a] $\log K_W = -4470.99/T + 6.0875 - 0.01706T$ (T = absolute temperature).

Source: Harned and Owen (1958). Reproduced with permission from Reinhold Publishing Corporation.

Monoprotic acids

Acid can donate only one proton: $HA \rightleftharpoons H^+ + A^-$

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

Recall :

$$C_T = [HA] + [A^-] = [HA](1 + \frac{K_a}{[H^+]})$$

$$[HA] = C_T(\frac{[H^+]}{K_a + [H^+]}) = C_T\alpha_0$$

$$[A^-] = C_T(\frac{K_a}{K_a + [H^+]}) = C_T\alpha_1$$

These α values are only valid for monoprotic acids. They need to be adjusted for polyprotic acids. They only depend on pH and K_a

Equilibrium calculations: formal approach

1. Identify species present at equilibrium:
    - A) H^+, OH^-, H_2O
    - B) Acids, bases (HA / A^-) — e.g., acetic acid H_3CCOOH / H_3CCOO^-
    - C) Salts (NaA, HCl) — if acids/bases are added as salts, e.g., $H_3CCOONa$

2. Write out equilibrium equations:
    - A) $H_2O \rightleftharpoons H^+ + OH^-$ — K_w (always present!)
    - B) $HA \rightleftharpoons H^+ + A^-$ — K_a
    - C) none, fully dissociated

3. List mass balance equations:
    - A) None — (concentration of water is always 55.4 M)
    - B) $C_T = HA + A^-$ — One for each acid
    - C) One per component — e.g., $Na_T = [Na^+]_{\text{from NaCl}} + [Na^+]_{\text{from H3CCOONa}}$

4. List proton balance equation (see next slide):
    - $[H^+] = [A^-] + [OH^-]$ — if added as HA
    - $[HA] + [H^+] = [OH^-]$ — if added as NaA

5. Solve equations (x unknowns require x equations)
    - analytically (see Sigg, Behra Stumm, table p. 39)
    - numerically
    - **graphical approach** (often simplest, and helps gaining some intuition about equilibria!)

Equilibrium calculations: proton (or charge) balance

- Define the reference states of each species added to the system:
  For each HA/A- pair, define if it is added as the acid (HA) or the conjugated base (A-):

  Water: the reference species is usually H_2O (not H^+ or OH^-).
  HA/A-: If the substance is added in the acid form (e.g., acetic acid), HA is the reference state. If it is added as the conjugated base (e.g., Na acetate), A- is the reference state.

- Define how many protons can be added or subtracted from the reference states.
  It's easiest to make a table with a row for each reference species, and columns for adding and subtracting protons

Added as HA:

Ref.	**- 1 H^+**	**0**	**+1 H^+**
H_2O	OH^-	H_2O	H_3O^+
HA	A^-	HA	-

Added as A^- (e.g., NaA)

Ref.	**- 1 H^+**	**0**	**+1 H^+**
H_2O			
A-			

- Make a proton balance: the concentration of protons removed from the reference states must equal the ones added to the reference states:

  Proton balance if added as HA:
  $[H^+]= [A^-] + [OH^-]$

  Proton balance if added as A^-:

Equilibrium calculations: graphical approach

1. Express all species as a function of C_T and/or pH
2. Plot log[concentration] of all species (H^+, OH^-, HA, A^-) vs. pH.

   General rule for log[H^+] and log[OH^-]:

   log[H^+] = -pH, graph line with slope -1 and an intercept of 0

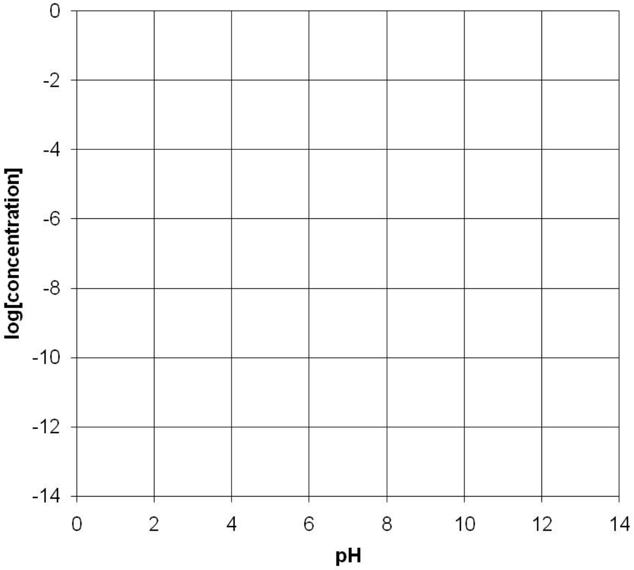
   log[OH^-] = log K_W + pH graph line with slope 1 and intercept of -14 (at 25 ºC)

Recall:

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

$$[HA] = C_T\left(\frac{[H^+]}{K_a + [H^+]}\right)$$

$$[A^-] = C_T\left(\frac{K_a}{K_a + [H^+]}\right)$$



Equilibrium calculations: graphical approach

Recall:

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

$[HA] = C_T\left(\frac{[H^+]}{K_a + [H^+]}\right)$

$[A^-] = C_T\left(\frac{K_a}{K_a + [H^+]}\right)$

1. Express all species as a function of C_T and/or pH
2. Plot log[concentration] of all species (H^+, OH^-, HA, A^-) vs. pH.

<u>General rule for log[H^+] and log[OH^-]:</u>

$\log[H^+] = -pH$, graph line with slope -1 and an intercept of 0

$\log[OH^-] = \log K_W + pH$ graph line with slope 1 and intercept of -14 (at 25 ºC)

<u>log[HA] and log[A^-]:</u> Consider [HA] and [A^-] for separate pH regions. In the case of a monoprotic acid:

i) $pH < pK_a$ (or $[H^+] >> K_a$)
$\log [A^-] = \log C_T - pK_a + pH$
$\log [HA] = \log C_T$

ii) $pH > pK_a$ (or $[H^+] << K_a$)
$\log [A^-] = \log C_T$
$\log [HA] = \log C_T + pK_a - pH$

iii) $pH = pK_a$
$\log [A^-] = \log[HA] = \log C_T - \log 2 = \log C_T - 0.3$

3. Use proton balance to find equilibrium conditions:

$[H^+] = [A^-] + [OH^-]$ if added as HA

$[HA] + [H^+] = [OH^-]$ if added as NaA

Exercise 1

Addition of acetic acid / acetate (HA=H_3CCOOH) to pure water

- What is the equilibrium pH if 10^{-3} M acidic acid (HA) is added?
- What is the equilibrium pH if 10^{-3} M sodium acetate (NaA) is added?

Conditions: $C_T = 10^{-3}$ M; T = 25 °C; $pK_a = 4.76$; $pK_W = 14$

Species:
H^+, HA, A^-, OH^- → need 4 equations

Equilibrium equations:
$H_2O \leftrightarrow H^+ + OH^-$ $K_w = 10^{-14}$
$HA \leftrightarrow H^+ + A^-$ $K_a = 10^{-4.76}$

Mass balance equation:
$C_T = HA + A^- = 10^{-3}$ M

Proton balance equation:

$[H^+] = [A^-] + [OH^-]$ (if added as HA)
$[HA] + [H^+] = [OH^-]$ (if added as NaA)

Graphical solution: next slides

Exercise 1, continued

Graphical solution:

1. Express all species as a function of C_T and/or pH:

$\log[H^+] = -pH$
$\log[OH^-] = \log K_W + pH = -14 + pH$

$\log[HA]$ and $\log[A^-]$:

Consider [HA] and $[A^-]$ at 3 pH regions:

i) $pH < 4.76$ (or $[H^+] >> K_a$)
$\log[A^-] = \log C_T - pK_a + pH = -7.76 + pH$
$\log[HA] = \log C_T = -3$

ii) $pH > 4.76$ (or $[H^+] << K_a$)
$\log[A^-] = \log C_T = -3$
$\log[HA] = \log C_T + pK_a - pH = 1.76 - pH$

iii) $pH = 4.76$
$\log[A^-] = \log[HA] = \log C_T - \log 2 = -3.3$

$$[HA] = C_T\left(\frac{[H^+]}{K_a + [H^+]}\right)$$

$$[A^-] = C_T\left(\frac{K_a}{K_a + [H^+]}\right)$$

2. Plot log[concentration] of all species vs. pH

3. Use proton balances to find equilibrium pH

4. Find: equilibrium pH if added as HA: 3.9 (point x on graph)
equilibrium pH if added as NaA: 7.9 (point y on graph)

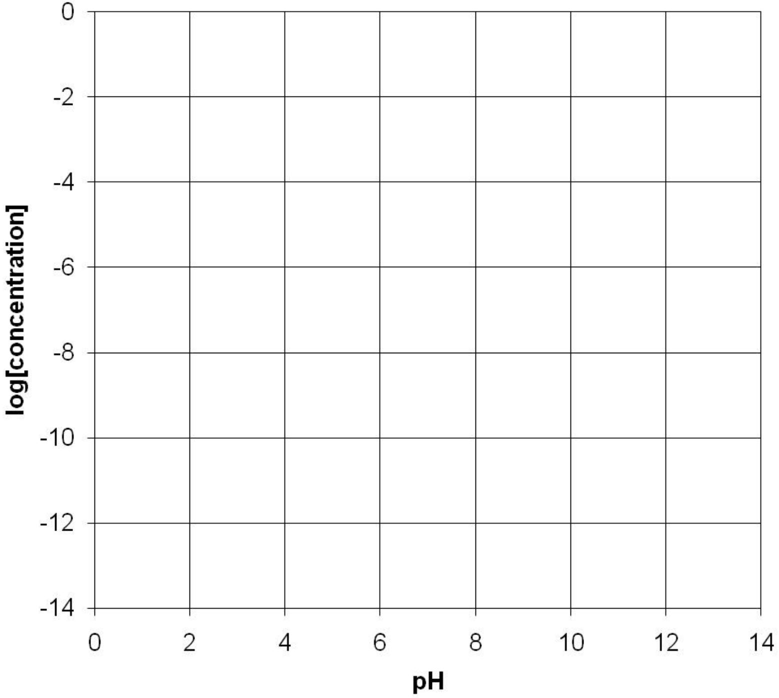
Exercise 1, continued

Conditions: $C_T = 10^{-3}$ M; T = 25 °C; $pK_a = 4.76$; $pK_W = 14$

i) $pH < 4.76$ (or $[H^+] >> K_a$)
   $\log [A^-] = \log C_T - pK_a + pH = -7.76 + pH$
   $\log [HA] = \log C_T = -3$

ii) $pH > 4.76$ (or $[H^+] << K_a$)
   $\log [A^-] = \log C_T = -3$
   $\log [HA] = \log C_T + pK_a - pH = 1.76 - pH$

iii) $pH = 4.76$
   $\log [A^-] = \log[HA] = \log C_T - \log 2 = -3.3$

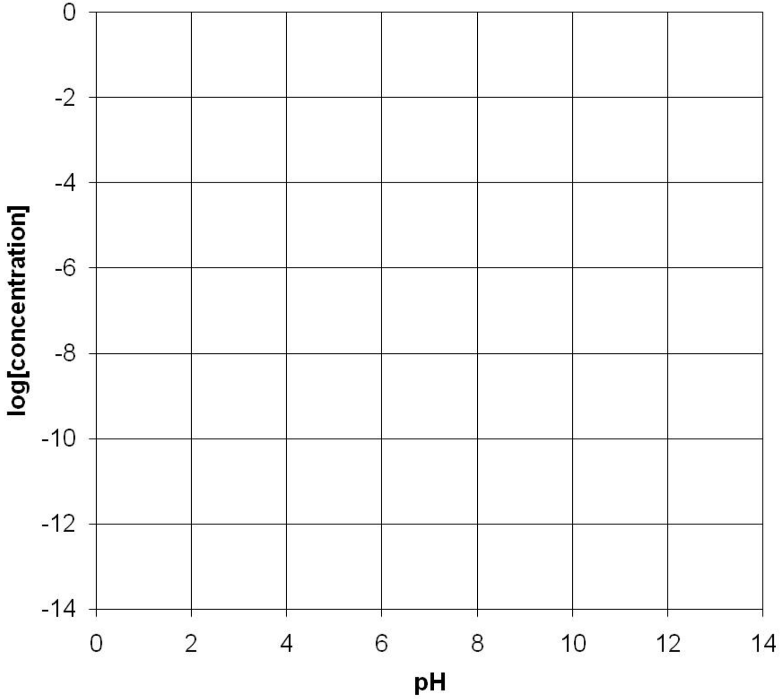


Exercise 2

Addition of hydrogen cyanide (HCN / CN^-) to pure water.

- What is the equilibrium pH if 10^{-2} M HCN is added?
- What is the equilibrium pH if 10^{-2} M CN^- is added?

Conditions: $C_T = 10^{-2}$ M; T = 25 °C; $pK_a = 9.2$; $pK_W = 14$



Diprotic acids

Acid can donate two protons: $H_2A \rightleftharpoons H^+ + HA^- \rightleftharpoons H^+ + A^{2-}$

$$K_{a1} = \frac{[HA^-][H^+]}{[H_2A]} \qquad K_{a2} = \frac{[A^{2-}][H^+]}{[HA^-]}$$

$$C_T = [H_2A] + [HA^-] + [A^{2-}]$$

$$[H_2A] = C_T\left(\frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}\right) = C_T \cdot \alpha_0$$

$$[HA^-] = C_T\left(\frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}\right) = C_T \cdot \alpha_1$$

$$[A^{2-}] = C_T\left(\frac{K_{a1}Ka_2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}\right) = C_T \cdot \alpha_2$$

Notice that these α values are different from those derived for monoprotic acids!

Diprotic acids

1. Identify species present at equilibrium:
   H_2A , HA^- , A^{2-}, H^+, OH^-

2. Write out equilibrium equations:
   $H_2O \rightleftharpoons H^+ + OH^-$ K_w (always present!)
   $H_2A \rightleftharpoons H^+ + HA^-$ K_{a1}
   $HA^- \rightleftharpoons H^+ + A^{2-}$ K_{a2}

3. List mass balance equations:
   $C_T = H_2A + HA^- + A^{2-}$

4. List proton balance equation (see next slide):
   $[H^+] = [HA^-] + 2[A^{2-}] + [OH^-]$ if added as H_2A
   $[H_2A] + [H^+] = [A^{2-}] + [OH^-]$ if added as HA^-
   $2[H_2A] + [HA^-] + [H^+] = [OH^-]$ if added as A^{2-}

5. Solve equations (5 unknowns require 5 equations)
   analytically (see Sigg, Behra Stumm, table p. 39)
   graphical approach (often simplest, and helps gaining some intuition about equilibria!)

Diprotic acids: proton (or charge) balances

- Define the reference states of each species added to the system: H_2A, HA^- or A^{2-}
- Define how many protons can be added or subtracted from the reference states.

Added as H_2A:

Ref.	$-2H^+$	$-1\ H^+$	0	$+1\ H^+$	$+2\ H^+$
H_2O		OH^-	H_2O	H_3O^+	
H_2A	A^{2-}	HA^-	H_2A		

Added as NaHA:
(fill in yourself)

Ref.	$-2H^+$	$-1\ H^+$	0	$+1\ H^+$	$+2\ H^+$
H_2O		OH^-	H_2O	H_3O^+	
HA^-					

Added as Na_2A:
(fill in yourself)

Ref.	$-2H^+$	$-1\ H^+$	0	$+1\ H^+$	$+2\ H^+$
H_2O		OH^-	H_2O	H_3O^+	
A^{2-}					

- Make a proton balance: the concentration protons removed from the reference states must equal the ones added to the reference states:

Proton balance if added as H_2A:

Proton balance if added as HA^-:

Proton balance if added as A^{2-}:

Diprotic acids: proton (or charge) balances

- Define the reference states of each species added to the system: H_2A, HA^- or A^{2-}
- Define how many protons can be added or subtracted from the reference states.

Added as H_2A:

Ref.	-2H⁺	- 1 H⁺	0	+1 H⁺	+2 H⁺
H_2O		OH^-	H_2O	H_3O^+	
H_2A	A^{2-}	HA^-	H_2A		

Added as NaHA:
(fill in yourself)

Ref.	-2H⁺	- 1 H⁺	0	+1 H⁺	+2 H⁺
H_2O		OH^-	H_2O	H_3O^+	
HA^-		A^{2-}	HA^-	H_2A	

Added as Na_2A:
(fill in yourself)

Ref.	-2H⁺	- 1 H⁺	0	+1 H⁺	+2 H⁺
H_2O		OH^-	H_2O	H_3O^+	
A^{2-}			A^{2-}	HA^-	H_2A

- Make a proton balance: the concentration protons removed from the reference states must equal the ones added to the reference states:

Proton balance if added as H_2A:
$[H^+]= [HA^-] + 2[A^{2-}] + [OH^-]$

Proton balance if added as HA^-:
$[H_2A]+ [H^+]= [A^{2-}] + [OH^-]$

Proton balance if added as A^{2-}:
$2[H_2A]+ [HA^-] + [H^+]= [OH^-]$

Equilibrium in a pure, closed system

*Equilibrium equations combined with mass balance equation for **graphical solution**:*

1) Express all species as a function of C_T and $[H^+]$

$$[H_2A] = C_T\left(\frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right) = C_T \cdot \alpha_0$$

$$[HA^-] = C_T\left(\frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2}\right) = C_T \cdot \alpha_1$$

$$[A^{2-}] = C_T\left(\frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right) = C_T \cdot \alpha_2$$

2) Plot in log[concentration] vs. pH: for each species, simplify equations according to pH regions

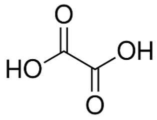
	H_2A	*HA^-*	*A^{2-}*
$pH < pK_1$:	$\log[H_2A]=\log C_T$	$\log[HA^-]=\log C_T-pK_{a1}+pH$	$\log[A^{2-}]=\log C_T -pK_{a1}-pK_{a2}+2pH$
$pK_1< pH < pK_2$:	$\log[H_2A]=\log C_T+pK_{a1}-pH$	$\log[HA^-]=\log C_T$	$\log[A^{2-}]=\log C_T-pK_{a2}+pH$
$pH > pK_2$:	$\log[H_2A]=\log C_T+pK_{a1}+pK_{a2}-2pH$	$\log[HA^-]=\log C_T+pK_{a2}-pH$	$\log[A^{2-}]=\log C_T$

3) Use proton balances to find equilibrium pH

$[H^+]= [HA^-] + 2[A^{2-}] + [OH^-]$ if added as H_2A
$[H_2A]+ [H^+]= [A^{2-}] + [OH^-]$ if added as HA^-
$2[H_2A]+ [HA^-] + [H^+]= [OH^-]$ if added as A^{2-}

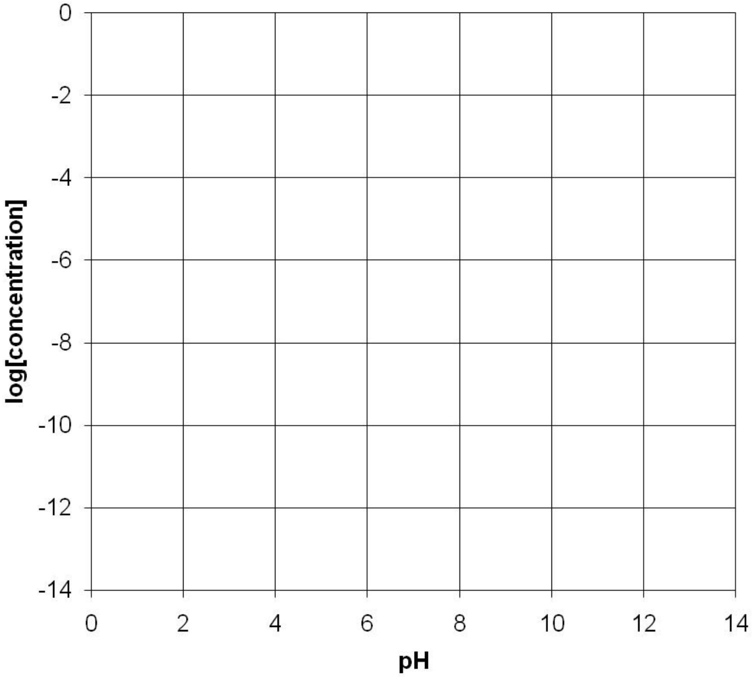
Exercise 3

Addition of oxalic acid ($H_2A=H_2C_2O_4$) to pure water.



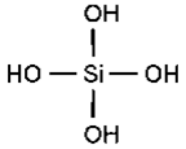
- What is the equilibrium pH if 10^{-2} M H_2A is added?
- What is the equilibrium pH if 10^{-2} M HA^- is added?
- What is the equilibrium pH if 10^{-2} M A^{2-} is added?

Conditions:
$C_T = 10^{-2}$ M; T = 25 °C; $pK_{a1}=1.27$; $pK_{a2} = 4.27$; $pK_W = 14$



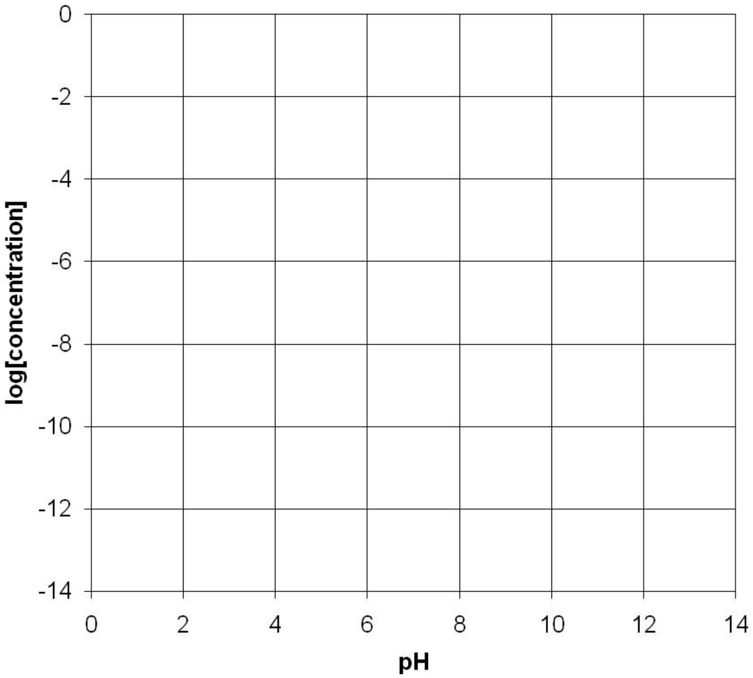
Exercise 4

Addition of silicic acid to pure water: $Si(OH)_4 \rightleftharpoons SiO(OH)_3^- \leftrightarrow SiO_2(OH)_2^{2-}$



- What is the equilibrium pH if 10^{-3} M H_2A is added?
- What is the equilibrium pH if 10^{-3} M HA^- is added?

Conditions:
$C_T = 10^{-3}$ M; T = 25 °C; $pK_{a1}=9.5$; $pK_{a2} = 12.6$; $pK_W = 14$



Summary

- Acids can release one (monoprotic) or several (e.g., diprotic) protons.
- We can use a graphical approach to determine the speciation of acids and basis as function of pH.
- We can then use graphical approaches to determine the equilibrium pH of the acid-base system under consideration.
- The equilibrium pH depends on the form in which the acid was added.
- At the equilibrium pH the (appropriate) proton balance is fulfilled and all charges are balanced.
- The approach is not 100% exact but very rapid and exact enough for our purposes
- Some important points to remember:
    - K_w is temperature-dependent, so the intersection of H^+ and OH^- is not always at logC = -7!
    - When pH = pK_a the concentrations of the acidic and conjugate basic species of a given acid are equal.
    - When pH = pK_a the concentration of the two dominant acid species corresponds to ½ of the total acid concentration (log C-0.3 on a log-scale)