



ENV-200

Acid-base

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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.

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

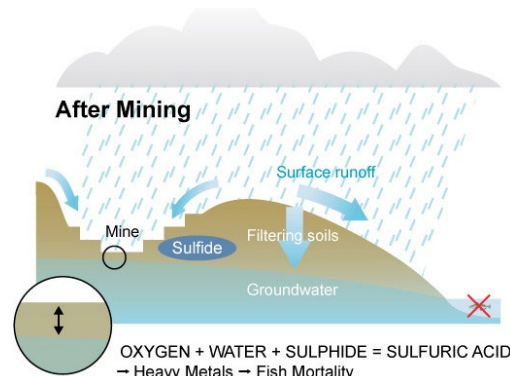
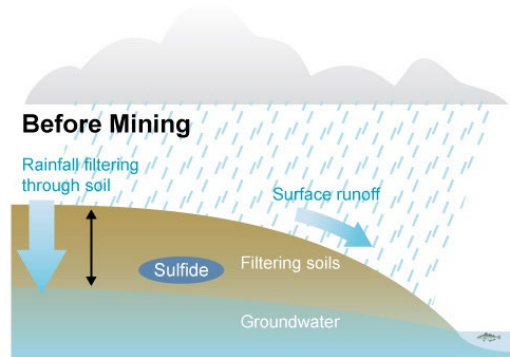
Engineering application: treatment of acid mine drainage

What is acid mine drainage?

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



- 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

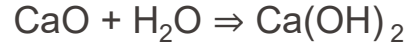


Treatment:

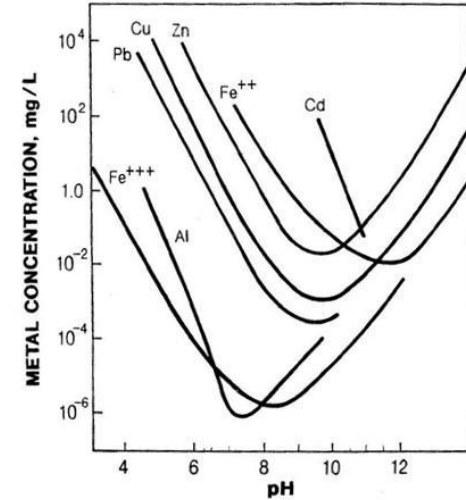
Physical: prevent oxidation e.g., by capping mine.

Biological: reduce sulfate, immobilize heavy metals.

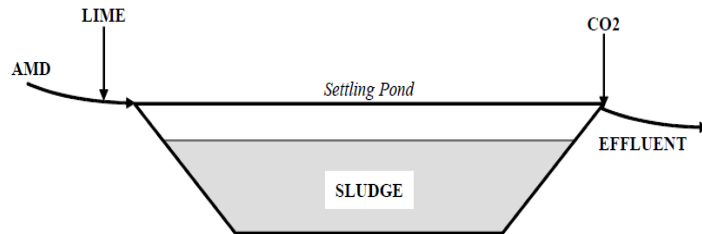
Chemical: neutralize pH, e.g., by addition of lime, to precipitate heavy metals.



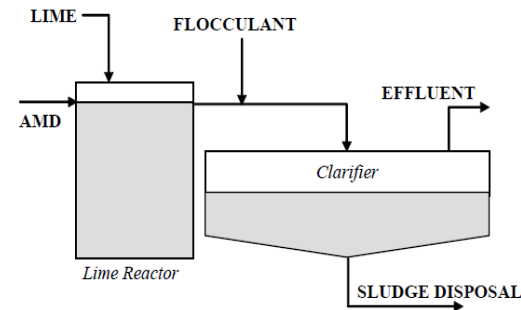
Many different configurations for lime treatment:



Pond treatment



Conventional treatment plant



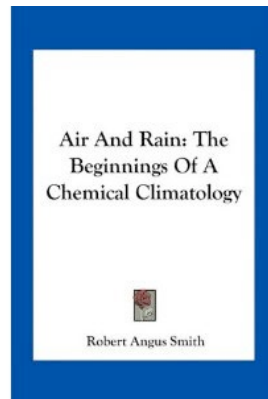
Famous environmental problem: acid rain

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 Institution¹

GUNNAR BRODIN, Royal Agricultural College, Uppsala

(Manuscript received March 3, 1955.)

pH contour plot of Scandinavia

Average precipitation pH

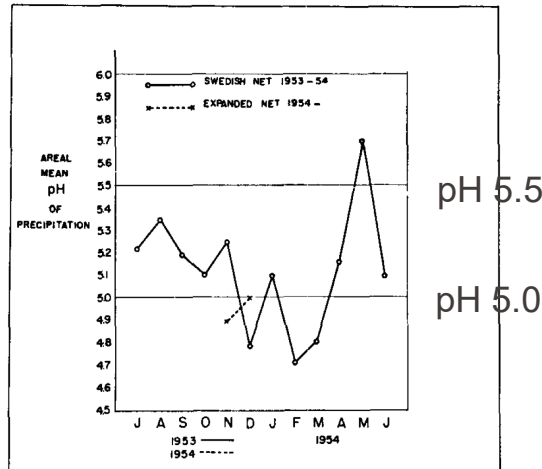


Fig. 4. Areal Mean of Precipitation pH vs. Time July 1953—June 1954 and Nov.—Dec. 1954.

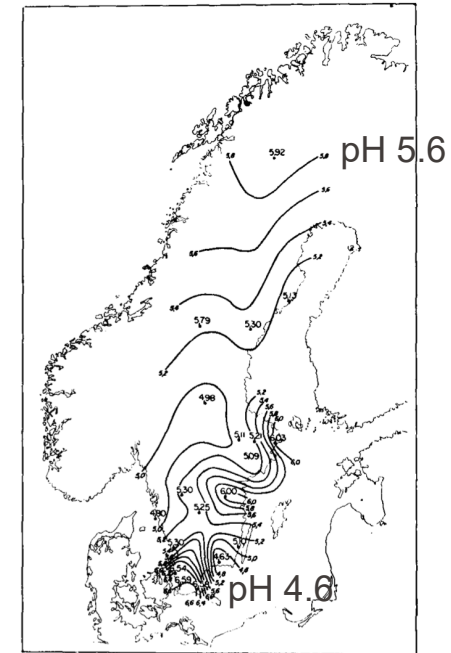


Fig. 2. pH of Precipitation, Sept. 1953.

Tellus VII (1955), 2

Famous environmental problem: acid rain

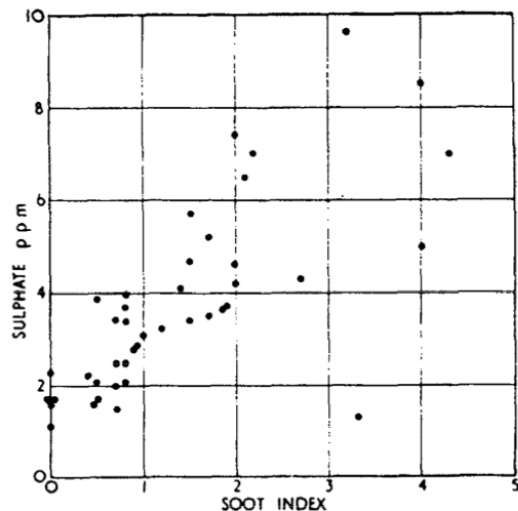
1950's: link made between rain and pollution (soot and/or sulfate)

On the acidity and salinity of rain

EVILLE GORHAM

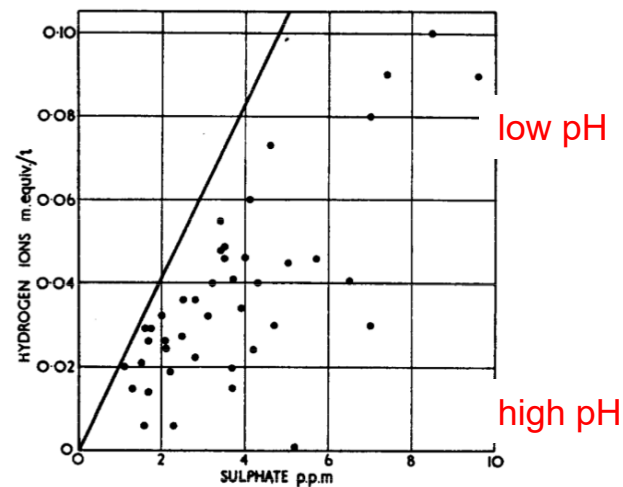
Geochimica et Cosmochimica Acta, 1955, Vol. 7, pp. 231 to 239. Pergamon Press Ltd. London

Rain samples in England
 SO_4^{2-} vs. Soot Index



$$\text{pH} = -\log [\text{H}^+]$$

H^+ vs. SO_4^{2-}



Famous environmental problem: acid rain

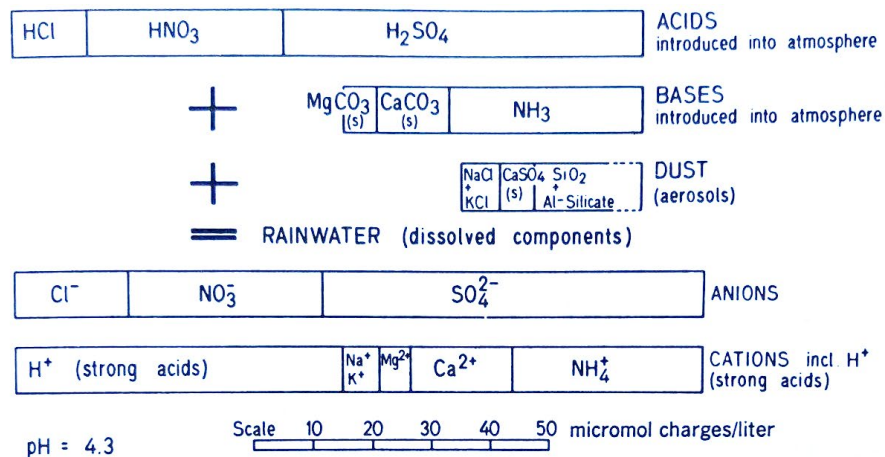
What makes rain acidic?

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

HCl: combustion of Cl-bearing polymers

HNO₃: from NO, NO₂ from combustion

H₂SO₄: from S in fossil fuels



NH₃: soils, manure

Carbonate minerals

Dust: NaCl, KCl, CaSO₄, SiO₂, Al-silicate

Acid rain pH is 3-5

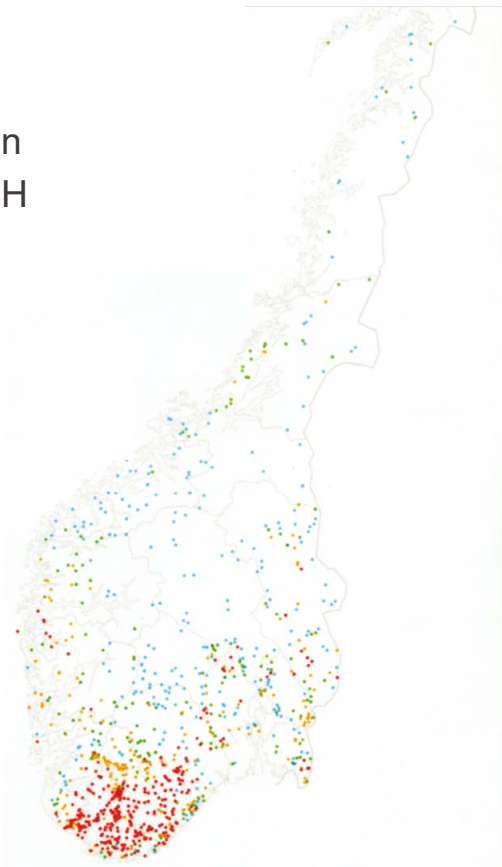
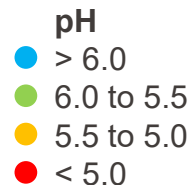
Fig. 3.1 Stumm & Morgan

- Emissions of SO₂ and NO_x from combustion are the major drivers
- SO₂ and NO_x are converted in the atmosphere to H₂SO₄ and HNO₃ (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):
 $\text{CaCO}_3(\text{s}) = \text{Ca}^{2+} + \text{CO}_3^{2-}$
- 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: $T = 25\text{ }^{\circ}\text{C}$

$P = 1\text{ atm}$

Ionic strength = 0 M $\rightarrow$ most common source for non-ideal behavior

Now on to the acid-base lecture...

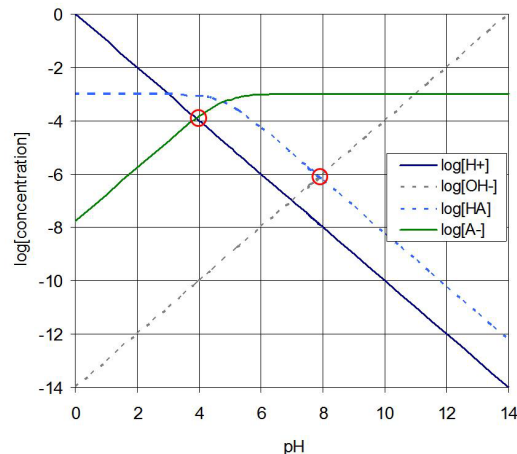
In this part of the course, we are interested in the pH of water of different composition. It is always helpful to know the pH, because it is an extremely important variable that can determine speciation, precipitation-dissolution, redox conditions, ecotoxicology, buffering capacity, etc.

Specifically, we want to know:

1. If we add ... M of total acid ($C_T = \text{HA} + \text{A}^-$) to water, what is the pH and what are the concentrations of HA and A^- at equilibrium?
2. If $[\text{HA}] = \dots$ M and $C_T = \dots$ M, what is $[\text{A}^-]$ and the pH?
3. If the pH is ..., what is $[\text{A}^-]$, $[\text{HA}]$?
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 ₂ SO ₄	Sulfuric acid	~ –3
HNO ₃	Nitric acid	–1
H ₃ O ⁺	Hydronium ion	–1.74
HSO ₄ [–]	Bisulfate	1.9
H ₃ PO ₄	Phosphoric acid	2.1
[Fe(H ₂ O) ₆] ³⁺	Aquo ferric ion	2.2
CH ₃ COOH	Acetic acid	4.7
[Al(H ₂ O) ₆] ³⁺	Aquo aluminum ion	4.9
H ₂ CO ₃ [*]	Carbon dioxide ^c	6.3
H ₂ S	Hydrogen sulfide	7.1
H ₂ PO ₄ [–]	Dihydrogen phosphate	7.2
HOCl	Hypochlorous acid	7.6
HCN	Hydrogen cyanide	9.2
H ₃ CO 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 ₂ O ₂	Hydrogen peroxide	11.7
SiO(OH) ₃ [–]	Silicate	12.6
HS [–]	Bisulfide	~ 17 ^d
H ₂ O	Water ^e	15.74
NH ₃	Ammonia	~ 23
OH [–]	Hydroxide ion	~ 24
CH ₄	Methane	~ 34

^aIn 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.

Acid can donate only one proton: $\text{HA} \leftrightarrow \text{H}^+ + \text{A}^-$ $K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]}$

Recall :

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

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

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

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) $\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$ K_w (always present!)
- B) $\text{HA} \leftrightarrow \text{H}^+ + \text{A}^-$ K_a
- C) none, fully dissociated

3. List mass balance equations:

- A) None (concentration of water is always 55.4 M)
- B) $C_T = \text{HA} + \text{A}^-$ One for each acid
- C) One per component e.g., $\text{Na}_T = [\text{Na}^+]_{\text{from NaCl}} + [\text{Na}^+]_{\text{from H}_3\text{CCOONa}}$

4. List proton balance equation (see next slide):

- $[\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$ if added as HA
- $[\text{HA}] + [\text{H}^+] = [\text{OH}^-]$ 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 H₂O (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 ₂ O	OH ⁻	H ₂ O	H ₃ O ⁺
HA	A ⁻	HA	-

Added as A⁻ (e.g., NaA)

Ref.	- 1 H ⁺	0	+1 H ⁺
H ₂ O			
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:

$$[\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$$

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 $\log[\text{concentration}]$ 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

$$\log[OH^-] = \log K_w + pH$$

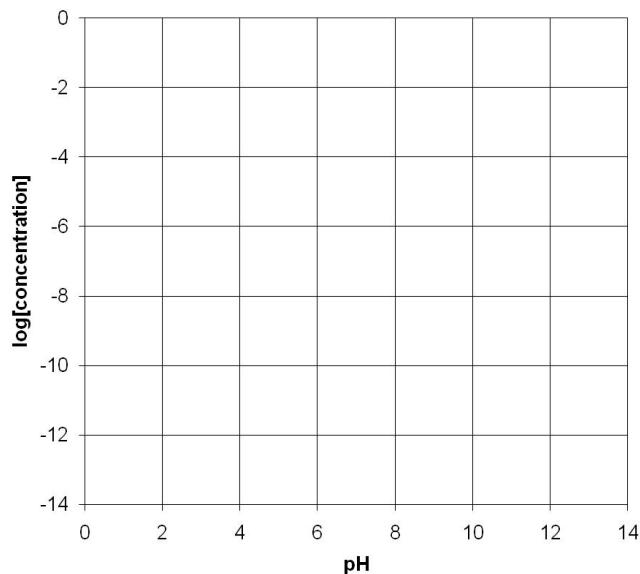
graph line with slope 1 and intercept of -14 (at 25 °C)

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

- Express all species as a function of C_T and/or pH
- 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 °C)

Recall:

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

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

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

$\log[HA]$ and $\log[A^-]$: Consider $[HA]$ and $[A^-]$ for separate pH regions. In the case of a monoprotic acid:

- $pH < pK_a$ (or $[H^+] \gg K_a$)
 $\log [A^-] = \log C_T - pK_a + pH$
 $\log [HA] = \log C_T$
- $pH > pK_a$ (or $[H^+] \ll K_a$)
 $\log [A^-] = \log C_T$
 $\log [HA] = \log C_T + pK_a - pH$
- $pH = pK_a$
 $\log [A^-] = \log [HA] = \log C_T - \log 2 = \log C_T - 0.3$

- Use proton balance to find equilibrium conditions:

$$[H^+] = [A^-] + [OH^-] \quad \text{if added as HA}$$

$$[HA] + [H^+] = [OH^-] \quad \text{if added as NaA}$$

Exercise 1

Addition of acetic acid / acetate ($\text{HA}=\text{H}_3\text{CCOOH}$) 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; $T = 25^\circ\text{C}$; $\text{p}K_a = 4.76$; $\text{p}K_w = 14$

Species:

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

Equilibrium equations:



Mass balance equation:

$$C_T = \text{HA} + \text{A}^- = 10^{-3} \text{ M}$$

Proton balance equation:

$$\begin{array}{ll} [\text{H}^+] = [\text{A}^-] + [\text{OH}^-] & \text{(if added as HA)} \\ [\text{HA}] + [\text{H}^+] = [\text{OH}^-] & \text{(if added as NaA)} \end{array}$$

Graphical solution: next slides

Exercise 1, continued

Graphical solution:

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

$$\log[H^+] = -\text{pH}$$

$$\log[OH^-] = \log K_w + \text{pH} = -14 + \text{pH}$$

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

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

i) $\text{pH} < 4.76$ (or $[H^+] \gg K_a$)

$$\log[A^-] = \log C_T - \text{p}K_a + \text{pH} = -7.76 + \text{pH}$$

$$\log[HA] = \log C_T = -3$$

ii) $\text{pH} > 4.76$ (or $[H^+] \ll K_a$)

$$\log[A^-] = \log C_T = -3$$

$$\log[HA] = \log C_T + \text{p}K_a - \text{pH} = 1.76 - \text{pH}$$

iii) $\text{pH} = 4.76$

$$\log[A^-] = \log[HA] = \log C_T - \log 2 = -3.3$$

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

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

2. Plot $\log[\text{concentration}]$ of all species vs. pH

3. Use proton balances to find equilibrium pH

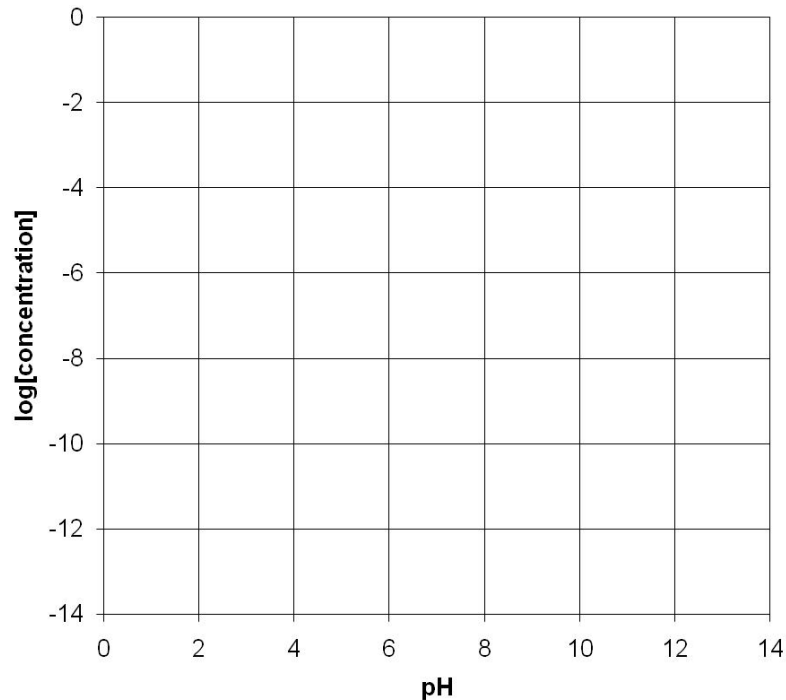
4. Find: equilibrium pH if added as HA: 3.9 (point x on graph)

equilibrium pH if added as NaA: 7.9 (point y on graph)

Exercise 1, continued

Conditions: $C_T = 10^{-3} \text{ M}$; $T = 25 \text{ }^\circ\text{C}$; $\text{pK}_a = 4.76$; $\text{pK}_w = 14$

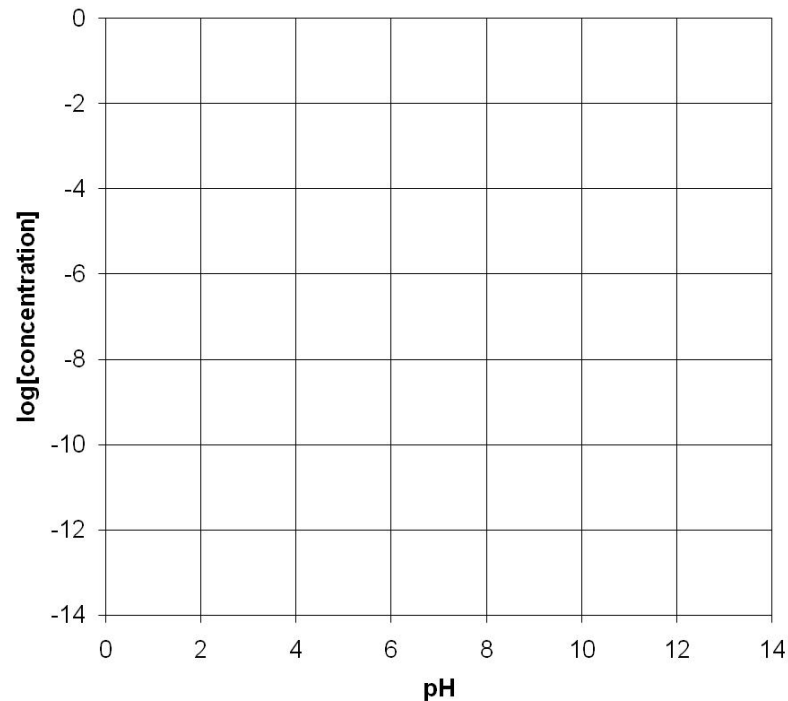
- i) $\text{pH} < 4.76$ (or $[\text{H}^+] \gg K_a$)
 $\log [\text{A}^-] = \log C_T - \text{pK}_a + \text{pH} = -7.76 + \text{pH}$
 $\log [\text{HA}] = \log C_T = -3$
- ii) $\text{pH} > 4.76$ (or $[\text{H}^+] \ll K_a$)
 $\log [\text{A}^-] = \log C_T = -3$
 $\log [\text{HA}] = \log C_T + \text{pK}_a - \text{pH} = 1.76 - \text{pH}$
- iii) $\text{pH} = 4.76$
 $\log [\text{A}^-] = \log [\text{HA}] = \log C_T - \log 2 = -3.3$



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; $T = 25^\circ\text{C}$; $\text{p}K_a = 9.2$; $\text{p}K_w = 14$



Acid can donate two protons: $\text{H}_2\text{A} \leftrightarrow \text{H}^+ + \text{HA}^- \leftrightarrow \text{H}^+ + \text{A}^{2-}$ $K_{a1} = \frac{[\text{HA}^-][\text{H}^+]}{[\text{H}_2\text{A}]}$ $K_{a2} = \frac{[\text{A}^{2-}][\text{H}^+]}{[\text{HA}^-]}$

$$C_T = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]$$

$$[\text{H}_2\text{A}] = C_T \left(\frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \right) = C_T \cdot \alpha_0$$

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

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

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

1. Identify species present at equilibrium:



2. Write out equilibrium equations:



K_w (always present!)



K_{a1}

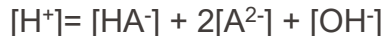


K_{a2}

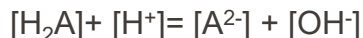
3. List mass balance equations:



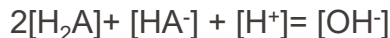
4. List proton balance equation (see next slide):



if added as H_2A



if added as HA^-



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-} :

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 $\log[\text{concentration}]$ vs. pH: for each species, simplify equations according to pH regions

	<u>H_2A</u>	<u>HA^-</u>	<u>A^{2-}</u>
pH < pK ₁ :	$\log[H_2A] = \log C_T$	$\log[HA^-] = \log C_T - pK_{a1} + \text{pH}$	$\log[A^{2-}] = \log C_T - pK_{a1} - pK_{a2} + 2\text{pH}$
pK ₁ < pH < pK ₂ :	$\log[H_2A] = \log C_T + pK_{a1} - \text{pH}$	$\log[HA^-] = \log C_T$	$\log[A^{2-}] = \log C_T - pK_{a2} + \text{pH}$
pH > pK ₂ :	$\log[H_2A] = \log C_T + pK_{a1} + pK_{a2} - 2\text{pH}$	$\log[HA^-] = \log C_T + pK_{a2} - \text{pH}$	$\log[A^{2-}] = \log C_T$

3) Use proton balances to find equilibrium pH

$$[H^+] = [HA^-] + 2[A^{2-}] + [OH^-]$$

$$[H_2A] + [H^+] = [A^{2-}] + [OH^-]$$

$$2[H_2A] + [HA^-] + [H^+] = [OH^-]$$

if added as H_2A

if added as HA^-

if added as A^{2-}

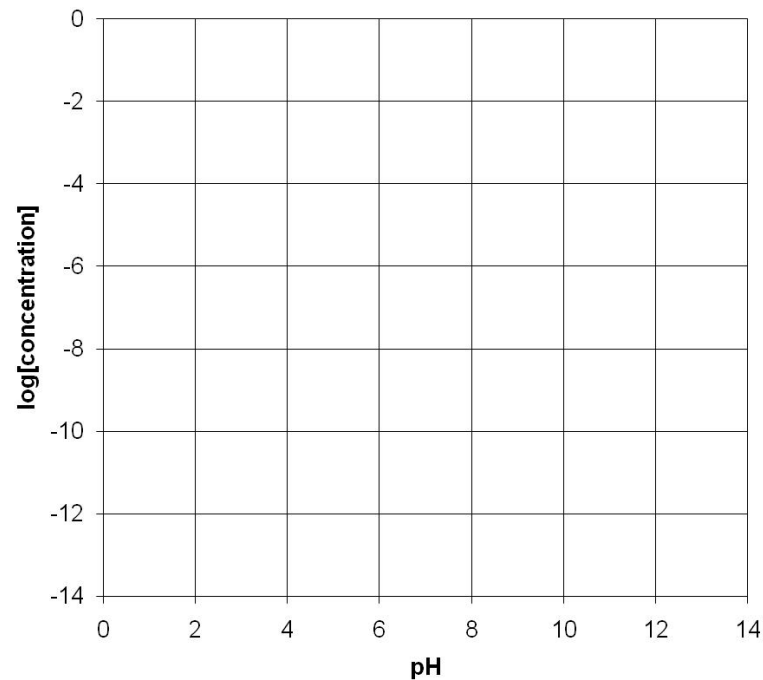
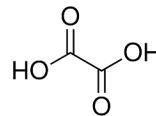
Exercise 3

Addition of oxalic acid ($\text{H}_2\text{A}=\text{H}_2\text{C}_2\text{O}_4$) 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; $T = 25^\circ\text{C}$; $\text{pK}_{a1}=1.27$; $\text{pK}_{a2} = 4.27$; $\text{pK}_W = 14$



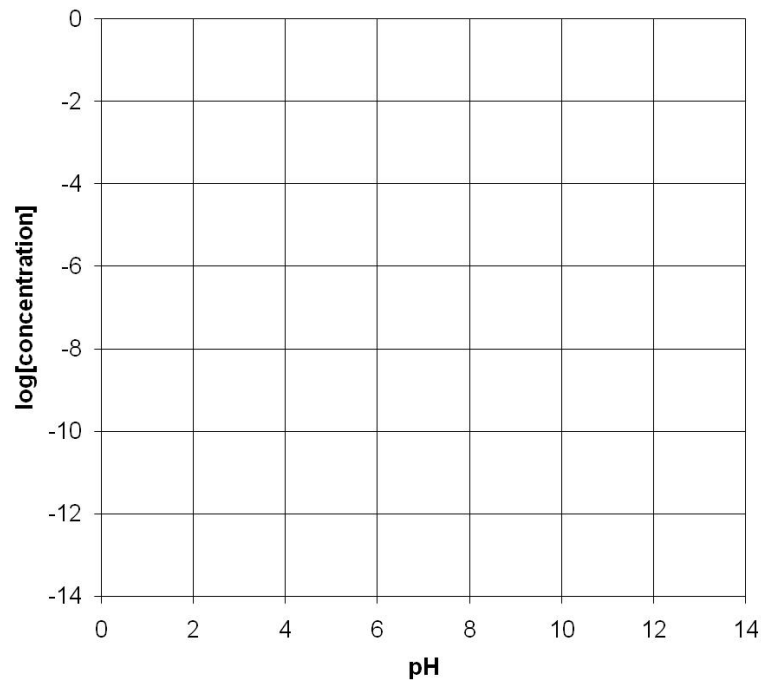
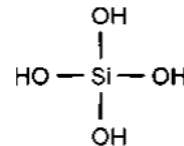
Exercise 4

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

- 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; $T = 25^\circ\text{C}$; $\text{pK}_{a1} = 9.5$; $\text{pK}_{a2} = 12.6$; $\text{pK}_W = 14$



- 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 $\log C = -7$!
 - 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 $\frac{1}{2}$ of the total acid concentration ($\log C - 0.3$ on a log-scale)