Gas-Liquid Equilibrium

- *Alkalinity contributions by acidic or basic gases*
  - *Adding a weak base via gas dissolution is no different from adding it in some other way*
  - *H_2CO_3 addition or removal from solution has no effect on Alk, so dissolution or evolution of CO_2 also has no effect on Alk. Note that this result is independent of the solution pH. (The contribution of a species to pH always depends on the composition of what is added and the composition at the Alk endpoint, not on the speciation at intermediate times.)*

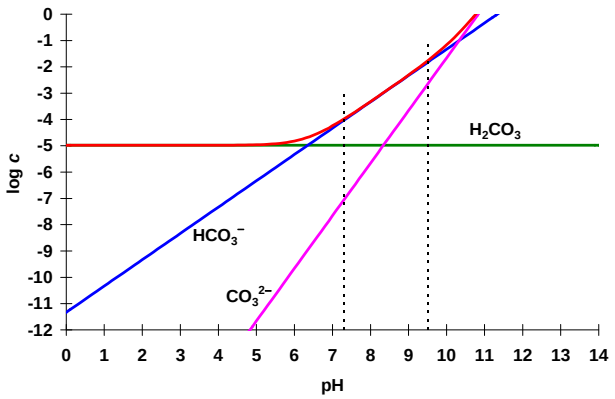
Example: Waters A (pH 9.50) and B (pH 7.30) are both in equilibrium with the atmosphere and are then mixed 1:1 without gas exchange. CO_3 species control pH.

(a) What are TOTCO_3, Alk, and TOTH of each solution and of the mixture? Use CO_3^{2-} as a component for computing TOTH.

(b) What are the pH and the composition of the mixture?

(c) How much and in what direction is CO_2 exchange as the mixture equilibrates with the atmosphere?

(a) What are TOTCO_3, Alk, and TOTH of each solution and of the mixture? Use CO_3^{2-} as a component for computing TOTH.



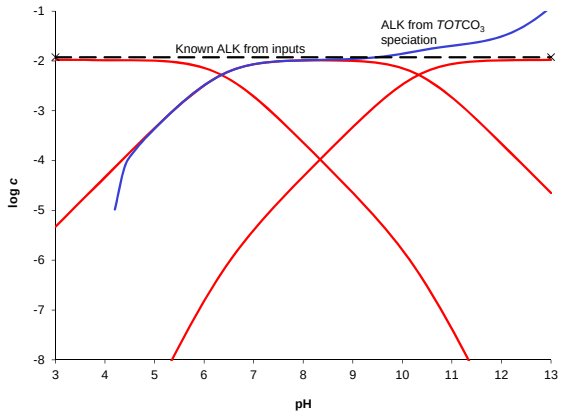
(a) What are TOTCO_3, Alk, and TOTH of each solution and of the mixture? Use CO_3^{2-} as a component for computing TOTH.

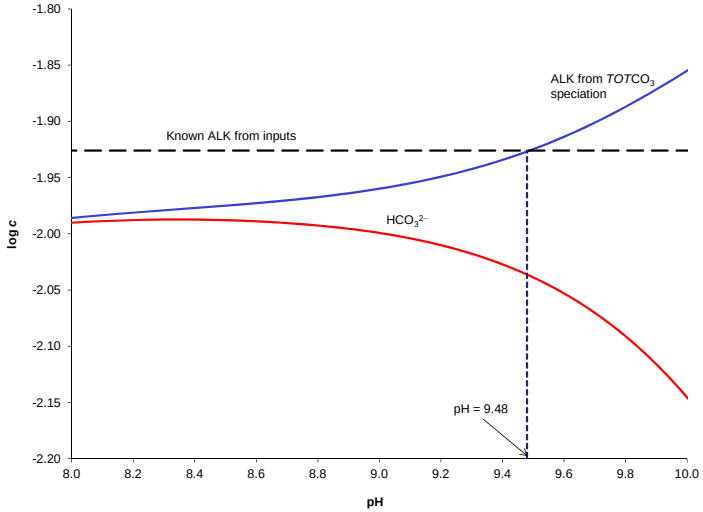
	(H^+)	(OH^-)	(H_2CO_3)	(HCO_3^-)	(CO_3^{2-})
A	$10^{-9.50}$	$10^{-4.50}$	1.29×10^{-5}	1.82×10^{-2}	2.70×10^{-3}
B	$10^{-7.30}$	$10^{-6.70}$	1.29×10^{-5}	1.15×10^{-4}	1.07×10^{-7}

TOTCO_3, Alk, and TOTH are all conservative quantities, so their values in the mixture are just weighted averages of their values in the two solutions.

	TOTCO_3	Alk (meq/L)	*TOT*H
A	2.09×10^{-2}	23.6	1.82×10^{-2}
B	1.28×10^{-4}	0.115	1.40×10^{-4}
Mix	1.05×10^{-2}	1.19×10^{-2}	9.16×10^{-3}

Value of $TOTCO_3$ is embedded in the log c – pH diagram. Satisfying the Alk equation is an alternative (to satisfying the CB, TOTH, or PC equation) for finding the equilibrium pH of a solution, e.g., for the mixture of A and B:





Equilibrium composition of the original solutions and the mixture before any CO_2 exchange

	$TOTCO_3$	Alk (meq/L)	TOTH
A	2.09×10^{-2}	23.6	1.82×10^{-2}
B	1.28×10^{-4}	0.115	1.40×10^{-4}
Mix	1.05×10^{-2}	1.19×10^{-2}	9.16×10^{-3}

	(H^+)	(OH^-)	(H_2CO_3)	(HCO_3^-)	(CO_3^{2-})
A	$10^{-9.50}$	$10^{-4.50}$	1.29×10^{-5}	1.82×10^{-2}	2.70×10^{-3}
B	$10^{-7.30}$	$10^{-6.70}$	1.29×10^{-5}	1.15×10^{-4}	1.07×10^{-7}
Mix	$10^{-9.49}$	$10^{-4.51}$	6.71×10^{-6}	9.18×10^{-3}	1.32×10^{-3}

(c) How much and in what direction is CO_2 exchange as the mixture equilibrates with the atmosphere?

We know the 'initial' solution composition (after mixing, but before equilibration with the atmosphere).

We don't know how much CO_2 exchange occurs, so we analyze the system using H_2CO_3 as a component. In that case, CO_2 exchange does not affect TOTH. We can therefore compute $TOTH_{in}$ and assign that value to $TOTH_{eq}$.

Tableau using H_2CO_3 a component and initial solution composition as 'Inputs'

	H_2O	H^+	H_2CO_3	Conc'n
H_2O	1	0	0	
H^+	0	1	0	
H_2CO_3	0	0	1	1.29×10^{-5}
OH^-	1	–1	0	
HCO_3^-	0	–1	1	
CO_3^{2-}	0	–2	1	
Inputs				
H^+	0	1	0	$10^{-9.49}$
OH^-	1	–1	0	$10^{-4.51}$
H_2CO_3	0	0	1	6.71×10^{-6}
HCO_3^-	0	–1	1	9.18×10^{-3}
CO_3^{2-}	0	–2	1	1.32×10^{-3}

$TOTH_{in} = (1)(10^{-9.49}) + (-1)(10^{-4.51}) + (-1)(9.18\times10^{-3}) + (-2)(1.32\times10^{-3})$

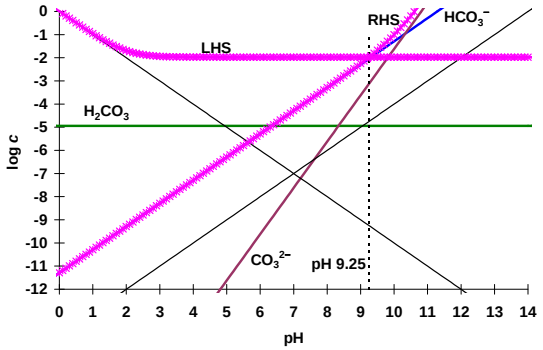
$= -1.19\times10^{-2}$

$TOTH_{eq} = (H^+) - (OH^-) - (HCO_3^-) - 2(CO_3^{2-}) = -1.19\times10^{-2}$

$TOTH_{in} = TOTH_{eq}$

$-1.19\times10^{-2} = (H^+) - (OH^-) - (HCO_3^-) - 2(CO_3^{2-})$

$(H^+) + 1.19\times10^{-2} = (OH^-) + (HCO_3^-) + 2(CO_3^{2-})$



$\underline{TOTCO_3}$

Final: 1.10×10^{-2}
Init: 1.05×10^{-2}
Δ: $+5.00\times10^{-4}$

Input Parameters for Gases in Visual Minteq

- *Like other species, input parameters for gaseous species are stoichiometry and log K for forming the species from components*

$$2\,H^+ + CO_3^{2-} \rightleftharpoons CO_2(g) + H_2O \qquad K = ??$$

$$2\,H^+ + CO_3^{2-} \rightleftharpoons H_2CO_3 \qquad K = 10^{+16.68}$$

$$H_2CO_3 \rightleftharpoons CO_2(g) + H_2O \qquad \underline{K = H = 10^{+1.47}}$$

$$2\,H^+ + CO_3^{2-} \rightleftharpoons CO_2(g) + H_2O \qquad K = 10^{+16.68}10^{+1.47} = 10^{18.15}$$

Using Visual Minteq to Determine Composition of Solutions Equilibrated with Gases

Example: Waters A (pH 9.5) and B (pH 7.3) are both in equilibrium with the atmosphere and are then mixed 1:1 without gas exchange. CO_3 species control pH.

(a) What are $TOTCO_3$ and Alk of each solution and of the mixture?

(b) What are the pH and the composition of the mixture?

(c) How much and in what direction is CO_2 exchange as the mixture equilibrates with the atmosphere?

- *pH specified by user (7.3 or 9.5)*
- *Gases/ Specify fixed CO2 partial pressure (0.00038 atm x 1.0)*

Output: Equilibrium Species at pH 7.3 (all calculations at I =0)

pH	7.300	Sum of cations (eq/kg)	5.0119E-08
Ionic strength	0.00e+00	Sum of anions (eq/kg)	1.1517E-04
		Charge difference (%)	99.913006

Concentrations and activities of aqueous inorganic species (mol / l) — Print to Excel — Gases

	Concentration	Activity	Log activity
Cl-1	1.0000E-16	1.0000E-16	-16.000
CO3-2	1.0735E-07	1.0735E-07	-6.969
H+1	5.0119E-08	5.0119E-08	-7.300
H2CO3* (aq)	1.2936E-05	1.2936E-05	-4.888
HCO3-	1.1476E-04	1.1476E-04	-3.940
OH-	2.0091E-07	2.0091E-07	-6.697

Component	Total dissolved
Cl-1	1.0000E-16
CO3-2	1.2780E-04
H+1	1.4048E-04

Output: Equilibrium Species at pH 9.5 (all calculations at I =0)

pH	9.500	Sum of cations (eq/kg)	3.1623E-10
Ionic strength	0.00e+00	Sum of anions (eq/kg)	2.3613E-02
		Charge difference (%)	99.999997

Concentrations and activities of aqueous inorganic species (mol / l) — Print to Excel — Gases

	Concentration	Activity	Log activity
Cl-1	1.0000E-16	1.0000E-16	-16.000
CO3-2	2.6964E-03	2.6964E-03	-2.569
H+1	3.1623E-10	3.1623E-10	-9.500
H2CO3* (aq)	1.2936E-05	1.2936E-05	-4.888
HCO3-	1.8188E-02	1.8188E-02	-1.740
OH-	3.1842E-05	3.1842E-05	-4.497

Component	Total dissolved
Cl-1	1.0000E-16
CO3-2	2.0897E-02
H+1	1.8182E-02

Visual Minteq Input and Output for Mixture Prior to Equilibration with Atmospheric CO_2

Input

pH calculated by mass balance, no Fixed species

TOTAL CO3(2-) (1.278e-4 + 2.090e-2)/2 = 1.0511e-2

TOTAL H(+) (1.4048e-4 + 1.8182e-2)/2 = 9.1612e-3

Output

pH 9.495

H_2CO_3 6.71e-6 (undersaturated, CO_2 will dissolve)

Visual Minteq Input and Output for Mixture after Equilibration with Atmosphere

Input

pH calculated by mass balance

CO2 as Fixed species, log P(CO2) = –3.48

*TOT*CO3 1.0511e-2

*TOT*H 9.1612e-3

Output

pH 9.247

*TOT*CO3: 1.1014e-2

*TOT*H: 1.0168e-2

Offline calculations

pH 9.247

$\Delta TOTCO_3$ +5.00e-4

$\Delta TOTH$ +1.07e-3

Aqueous Chemistry of Metals

What are metals?

How do metal ions interact with water molecules?

How do metal ions interact with other solutes?

What causes metals to precipitate or dissolve, and what solids are most stable in various conditions?

Aqueous Chemistry of Metals

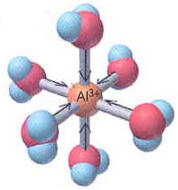
What are metals?

When considering the solid state, metals are defined by the presence of highly mobile electrons, which make the metals electrically conductive

In aqueous systems, metals are cations that have a significant attraction for unshared electrons (e.g., those at two of the corners of the water tetrahedron)

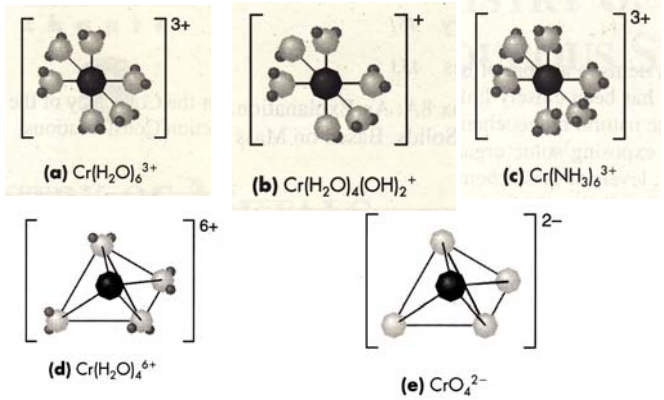
Oxidation number or state

("di-, tri-, hexa-valent," etc.)



Aqueous Chemistry of Metals

Oxidation number or state ("di-, tri-, hexa-valent," etc.)

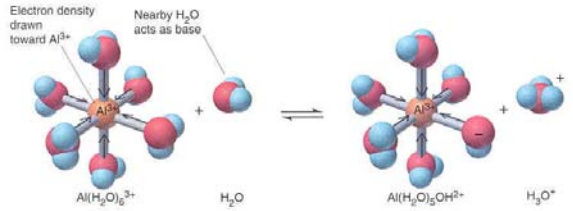


Aqueous Chemistry of Metals

How do metal ions interact with water?

Inner and out hydration spheres
Hydrolysis, acidity, etc.
Coordination number
Stability constant

Free metal ions
Ligands
Complexation
Chelate



Aqueous Chemistry of Metals

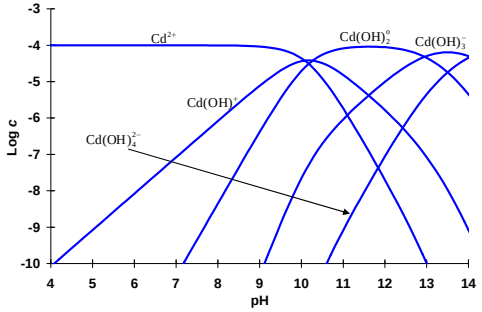
How do metal ions interact with water and/or OH^-?

Stability constants for Hydrolysis

$Cd^{2+} + OH^- \leftrightarrow CdOH^+$ K_1

$Cd^{2+} + H_2O \leftrightarrow CdOH^+ + H^+$ $^*K_1$ ($=K_a$)

$Cd^{2+} + 2\ OH^- \leftrightarrow Cd(OH)_2^o$ β_2



Aqueous Chemistry of Metals

How do metal ions interact with other solutes?

Stability constants for complexation with Chloride

$Cd^{2+} + Cl^- \leftrightarrow CdCl^+$ K_1

$Cd^{2+} + 2\ Cl^- \leftrightarrow CdCl_2^o$ β_2