

CO₂ chemistry in sea water: an overview

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In your course syllabus is a section prepared for the *EPOCA Guide to Best Practices* ...

The carbon dioxide system in sea water: equilibrium chemistry and measurements

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5 **1 Introduction**

10 The world's oceans can be thought of as a dilute solution (with a few acid-base species at still lower concentrations) in a sea of water. In the case of the North Atlantic, for example, the concentration of the concentrations of the three coexisting species (unionized dissolved carbon dioxide) is only about 2 μM . Bicarbonate ion, the proportion of carbonate ion is about 10% of unionized carbon dioxide yet another factor of 10 between these various species (see below), sea water is acidic in hydrogen ion (present at much lower concentration



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changes

So, where should we begin?

1. Thermodynamics
2. Measurements
3. Calculations

‘Thermodynamics is an experimental science, and not a branch of metaphysics. It consists of a collection of equations and also some inequalities, which interrelate certain kinds of measurable physical quantities. In any thermodynamic equation every quantity is independently measurable. What can such an equation “tell one” about ones system or process? Or, in other words, what can we learn from such an equation about the microscopic explanation of a macroscopic change? Nothing whatsoever. What then is the use of thermodynamic equations? They are useful because some quantities are easier to measure than others.’

M. L. McGlashan (1979)

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M. L. McGlashan (1979)

When is a chemical system at equilibrium?

Simple conceptual test

- Allow reaction to proceed in the forward direction until nothing more seems to happen, and determine the chemical composition of the system.
- Then allow the same reaction to proceed in the reverse direction until nothing more seems to happen.

If the composition of the system is the same regardless of the direction from which it was approached, then a true equilibrium exists.

You can think of equilibrium as a balance of opposing reactions

Dissociation of acetic acid into its ions



hydrated
hydrogen ion



Acetate ion and hydrogen ions recombining



At equilibrium these reactions balance each other, and the concentrations of acetic acid, acetate ion, and hydrogen ion are independent of time.



A. Mix 100 μmol of acetic acid with water to make 1 kg of solution

B. Mix 100 μmol of sodium acetate with 100 μmol of hydrochloric acid and with water (again to make 1 kg of solution)

1. The final composition is the same whether resulting from the forward or the backward reaction.

(This final composition will not change unless some substance is added or the temperature is changed.)

2. The system reaches equilibrium very quickly.

(This is typical of acid-base reactions.)

3. The total concentration of the acetate group remains constant throughout

If the system is at equilibrium

- It is possible to reduce the laws governing the concentrations of all the various ions and molecules in an equilibrium mixture to simple mathematical statements.
- You can then calculate the concentrations of all the species present in solution, provided you have sufficient information about the system.

The equilibrium constant

The equilibrium constant

- The quantitative study of chemical equilibria is based upon the existence of an **equilibrium constant** and its specific algebraic form.
- These can be derived as a consequence of the laws of thermodynamics.
- Here the existence of an equilibrium constant and its algebraic form will be presented as an empirical result.

General form for an equilibrium constant

For the general reaction,



the equilibrium constant

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Note: water will usually be ignored as a reactant

Examples

Chemical equilibrium



Equilibrium constant

$$K = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]}$$

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

$$K = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_2][\text{CO}_3^{2-}]}$$

$$K = \frac{[\text{H}^+][\text{B(OH)}_4^-]}{[\text{B(OH)}_3]}$$

Strictly,

it is the *thermodynamic equilibrium constant*,

$$K^\circ(T, p) = \frac{\gamma_{\text{H}}[\text{H}^+] \gamma_{\text{Ac}}[\text{Ac}^-]}{\gamma_{\text{HAc}}[\text{HAc}]}$$

that is constant at a particular T and p .

The various γ_x are known as *activity coefficients*, the various products, $\gamma_x[X]$, are called *activities*.

Note: The thermodynamic equilibrium constant is a function of temperature and pressure alone, not of the solution composition. The activity coefficients, however, are a function of temperature, pressure, and solution composition.

Thus contrast,

the *thermodynamic equilibrium constant*:

$$K^\circ(T, p) = \frac{\gamma_{\text{H}}[\text{H}^+] \gamma_{\text{Ac}}[\text{Ac}^-]}{\gamma_{\text{HAc}}[\text{HAc}]} ;$$

with the *concentration equilibrium constant*

$$K = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = K^\circ \left(\frac{\gamma_{\text{HAc}}}{\gamma_{\text{H}} \gamma_{\text{Ac}}} \right) .$$

The concentration equilibrium constant is only a constant if the activity coefficient term is constant.

The concentration equilibrium constant is a function of temperature, pressure, and solution composition.

For the rest of this course we will use (concentration) equilibrium constants

This is appropriate to the study of equilibria in a sea water background, where the constants will be functions of T , p , and S .

Note: In this course, square brackets imply *total* concentrations in moles per kilogram of solution. (In many texts however they mean moles per liter, be sure to check!)



Acid-base equilibria

pH and pK notation

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

$\lg x$ is $\log_{10} x$

and by analogy $\text{p}K = -\lg K$

for the acid-base reaction $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

$$K(\text{HA}) = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{p}K(\text{HA}) = \text{pH} - \lg\left([\text{A}^-]/[\text{HA}]\right)$$

$$\text{pH} = \text{p}K(\text{HA}) + \lg\left([\text{A}^-]/[\text{HA}]\right)$$

pH can thus be thought of as a measure of the ratio $[\text{A}^-]/[\text{HA}]$

Ion product of water



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

In pure water ($t = 25 \text{ }^\circ\text{C}$), $K_w = 10^{-14.00}$.

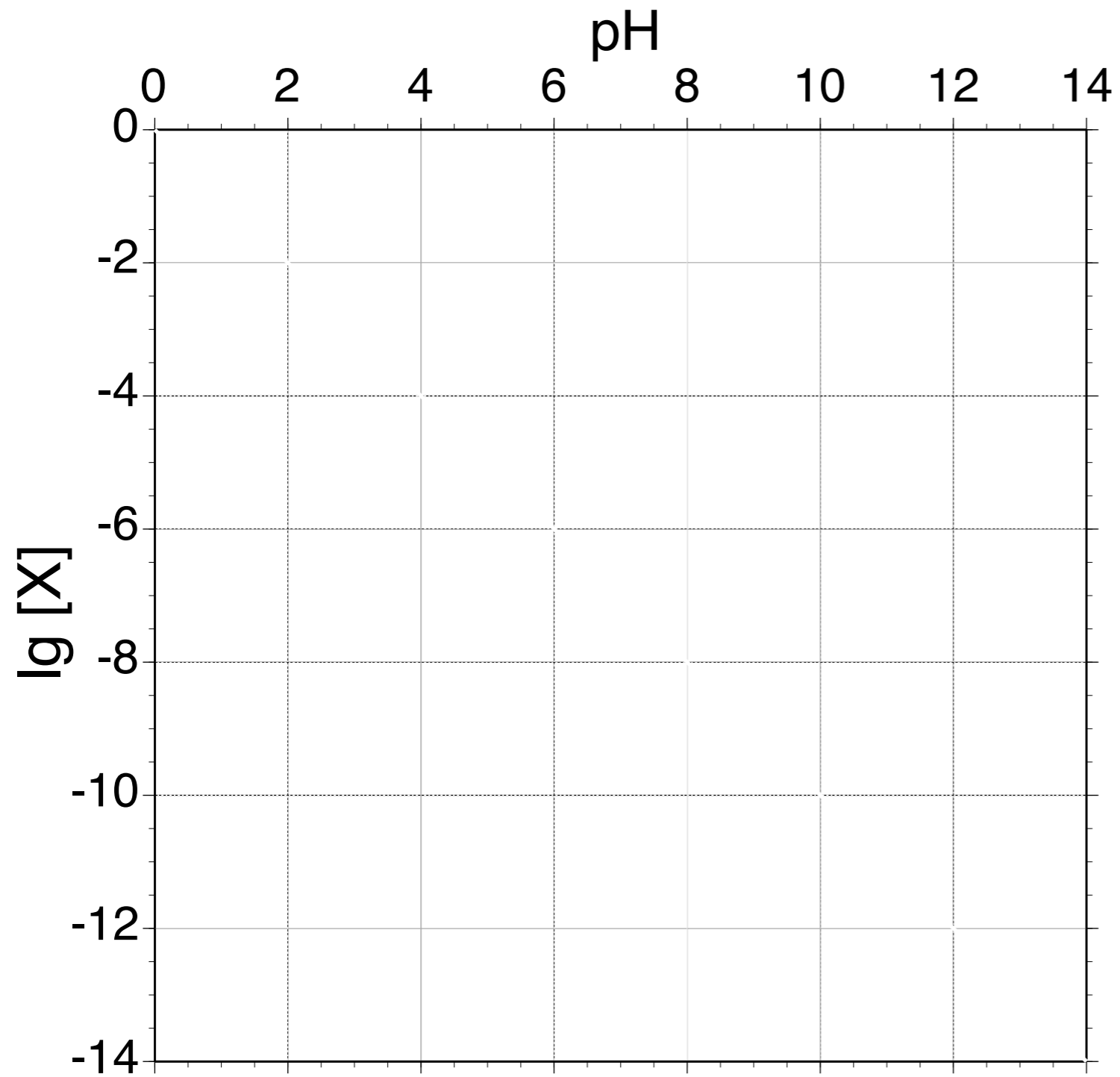
In 0.7 M sodium chloride ($t = 25 \text{ }^\circ\text{C}$), $K_w = 10^{-13.77}$.

In sea water ($t = 25 \text{ }^\circ\text{C}$; $S = 35$), $K_w = 10^{-13.22}$.

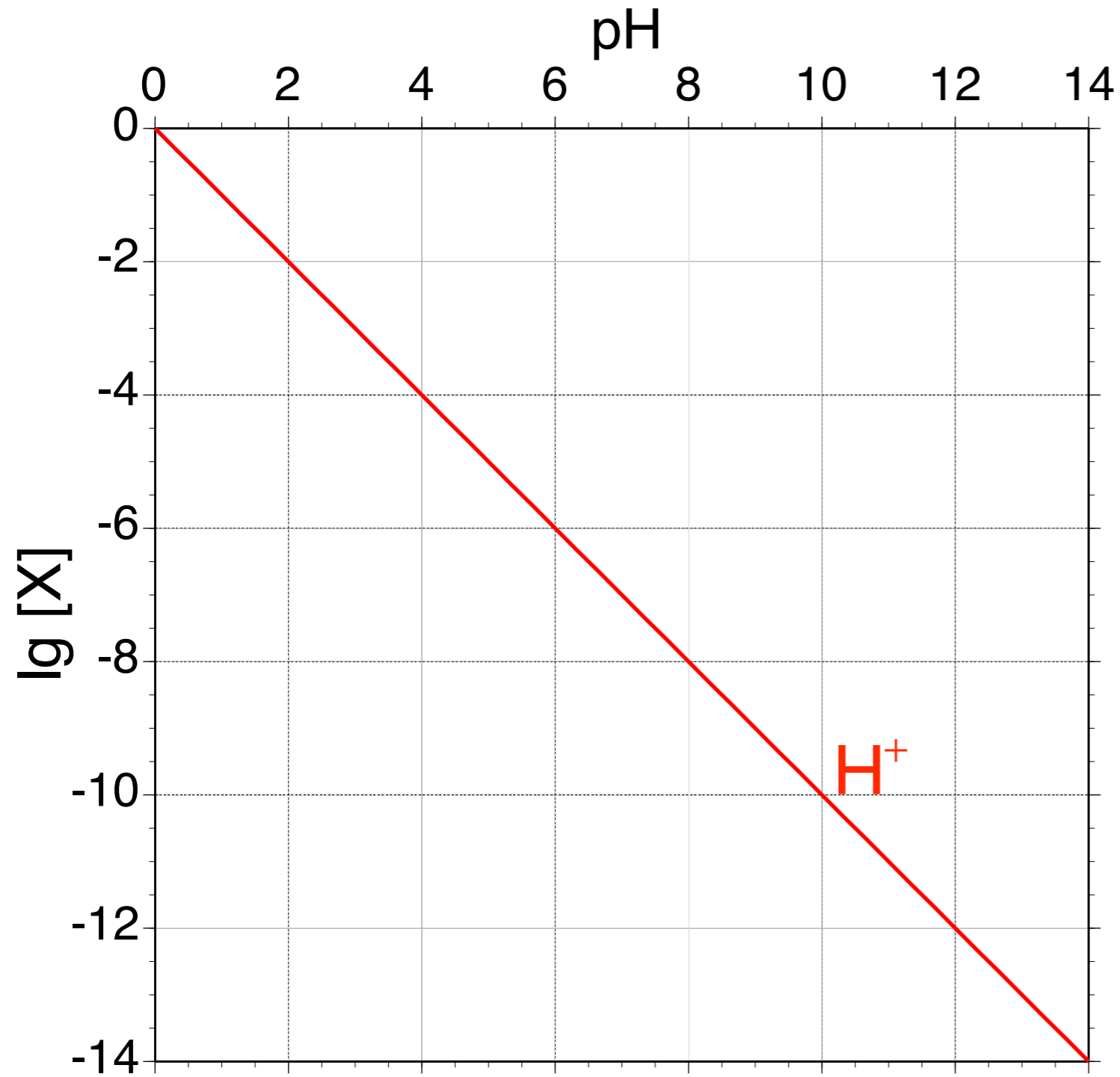
(at 1 atmosphere pressure)

Neutral defined as $[\text{H}^+] = [\text{OH}^-] = (K_w)^{0.5}$

Plot of logarithm of species concentration against pH

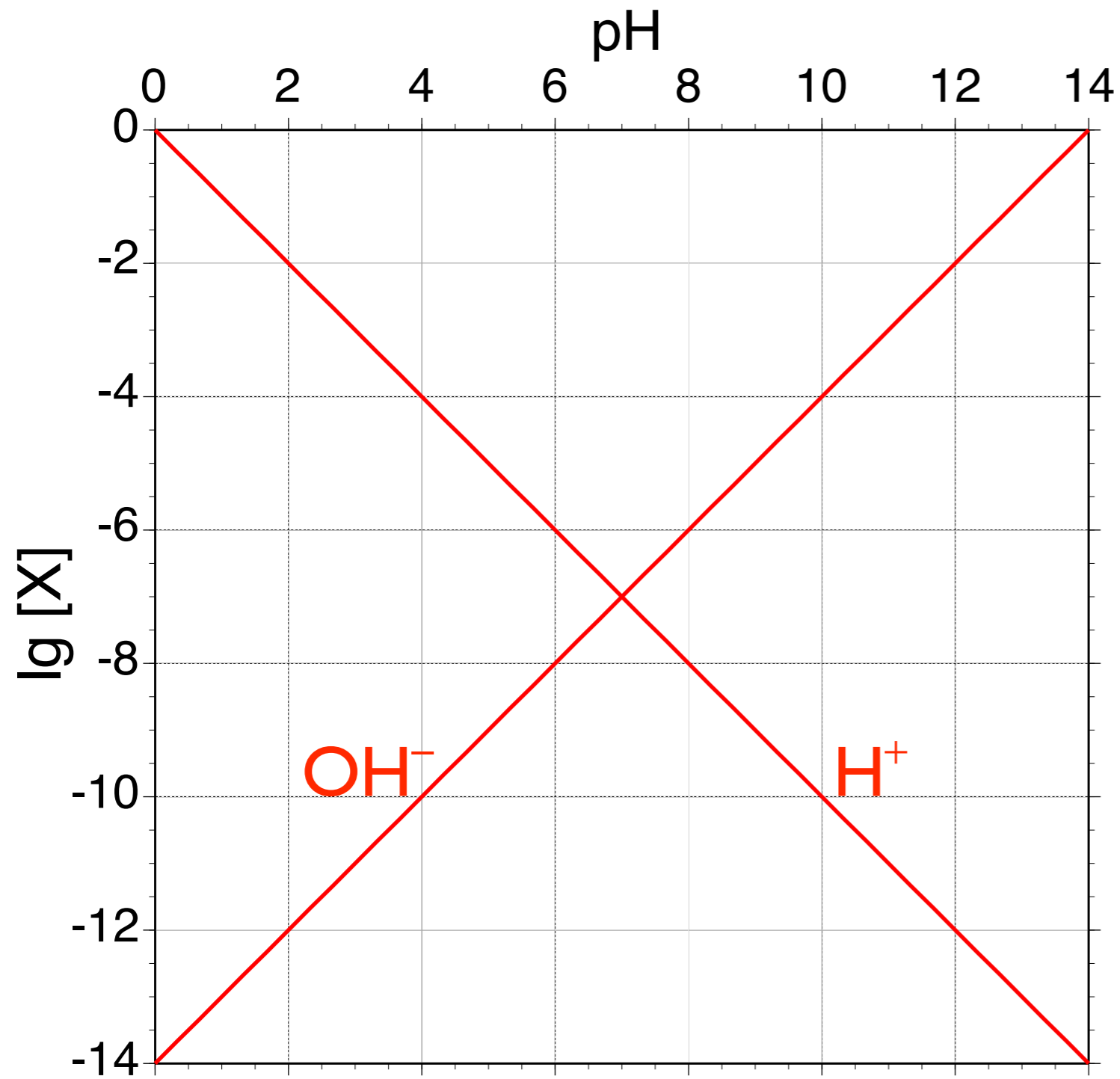


Plot of logarithm of species concentration against pH



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

Plot of logarithm of species concentration against pH



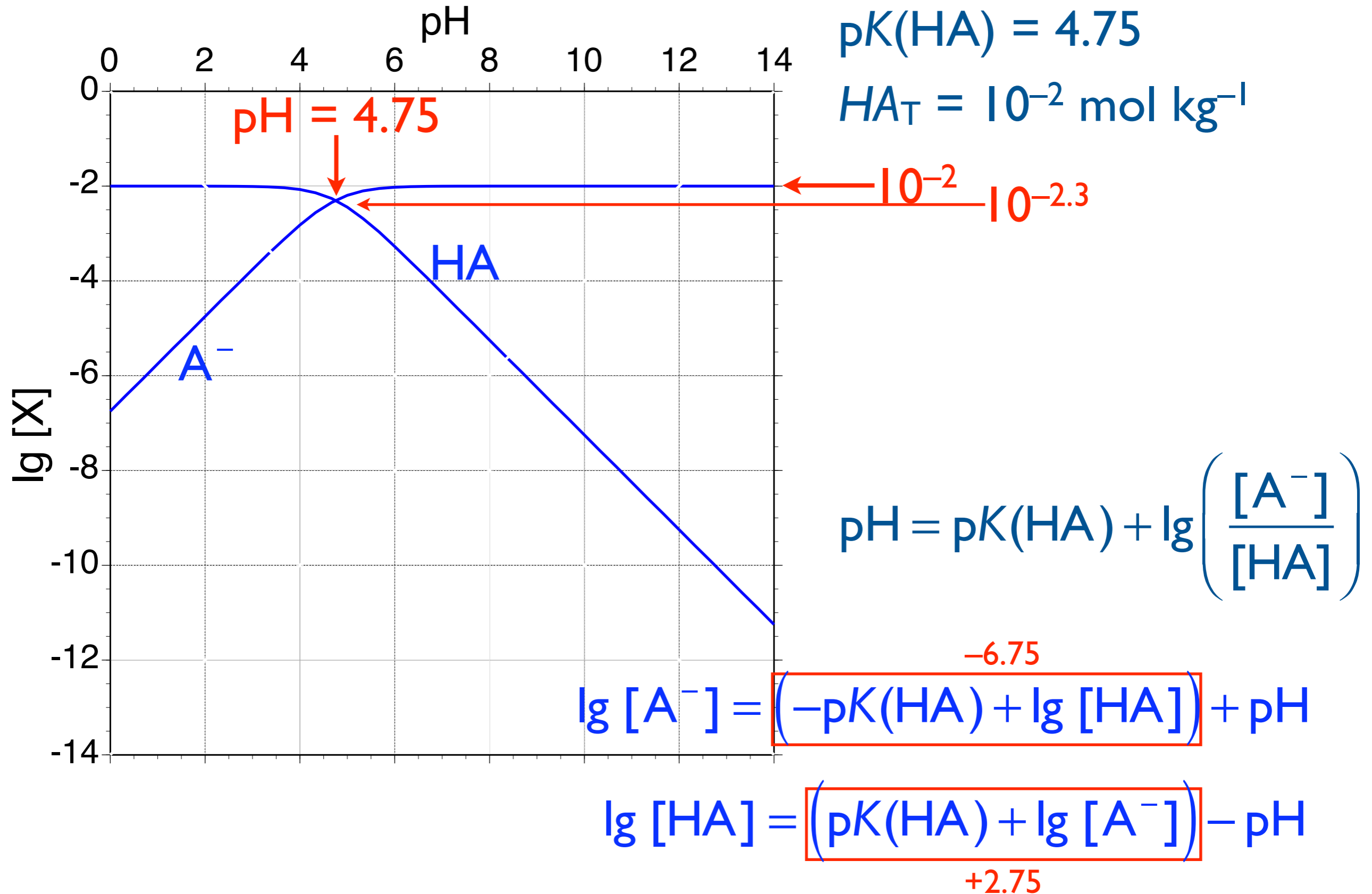
$$\lg [H^+] = -\text{pH}$$

$$[OH^-] = K_w / [H^+]$$

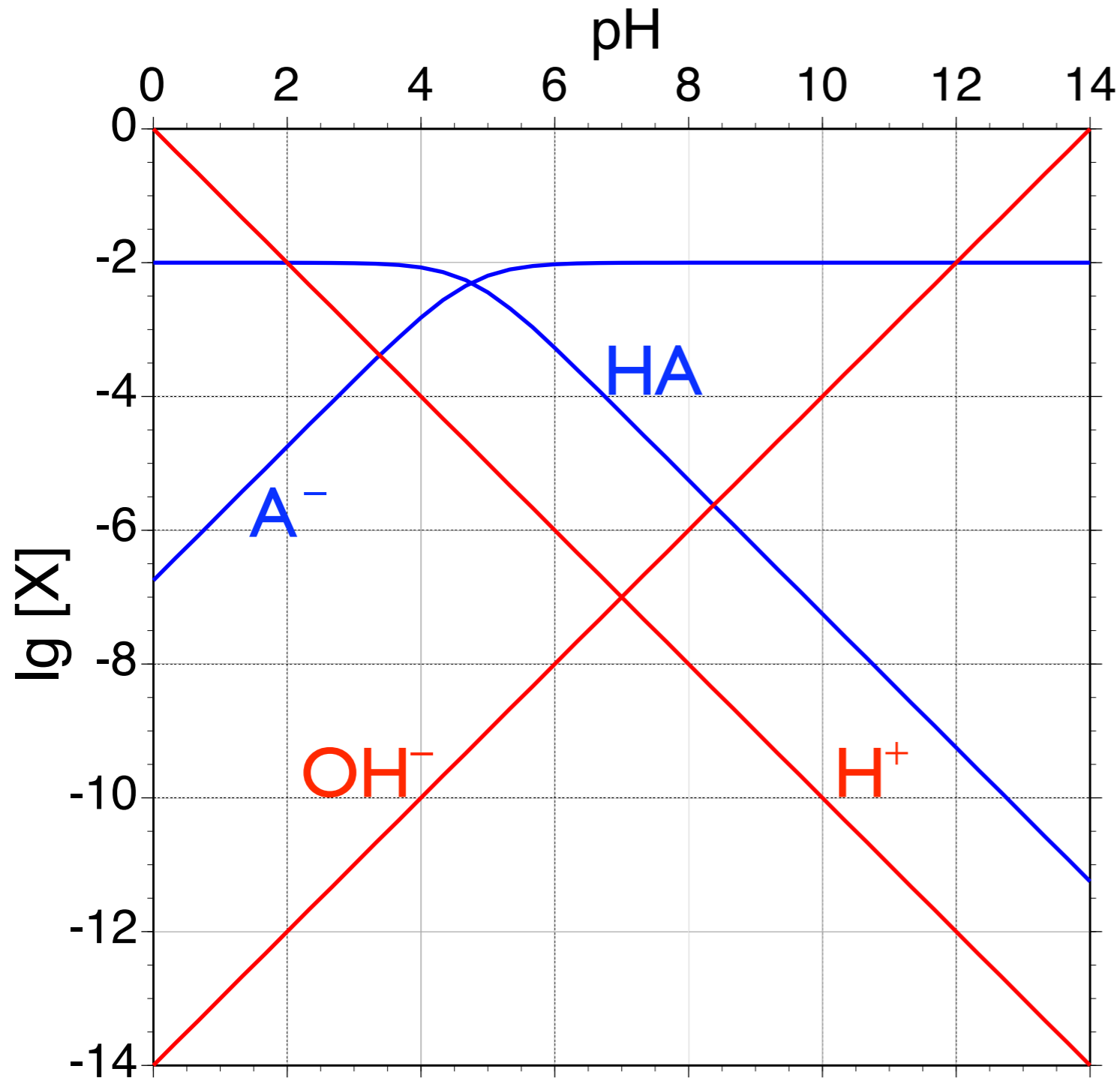
$$\lg [OH^-] = \text{pH} - \text{p}K_w$$

$$(\text{p}K_w = 14)$$

Plot of logarithm of species concentration against pH



Plot of logarithm of species concentration against pH



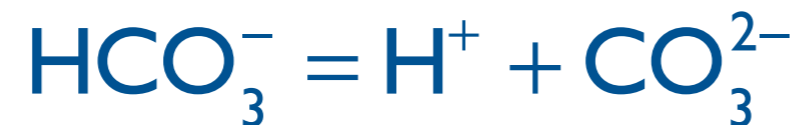
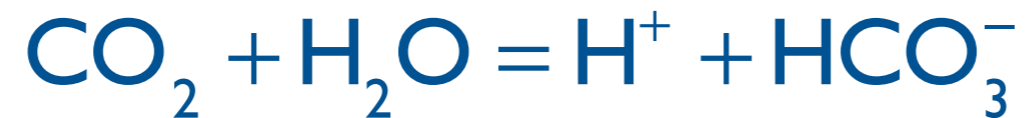
Note: can add additional acid-base systems to this diagram. They are independent, with pH simply indicating the ratio of the base to the acid form.

$$pH = pK(HA) + \lg \left(\frac{[A^-]}{[HA]} \right)$$

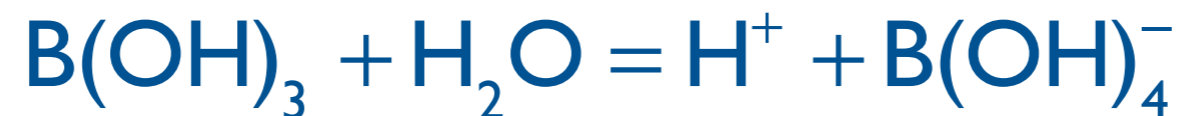
Acid-base equilibria in sea water

Acid-base chemistry in sea water

- Carbon dioxide equilibria



- Boric acid equilibrium



- Water dissociation



Acid-base chemistry in sea water

- Carbon dioxide equilibria

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

- Boric acid equilibrium

$$K_B = \frac{[\text{H}^+][\text{B}(\text{OH})_4^-]}{[\text{B}(\text{OH})_3]}$$

- Water dissociation

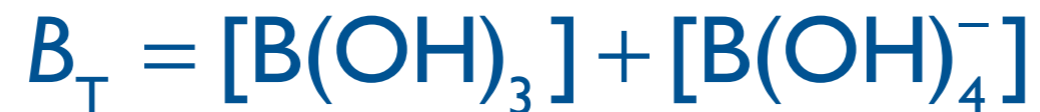
$$K_w = [\text{H}^+][\text{OH}^-]$$

Acid-base chemistry in sea water

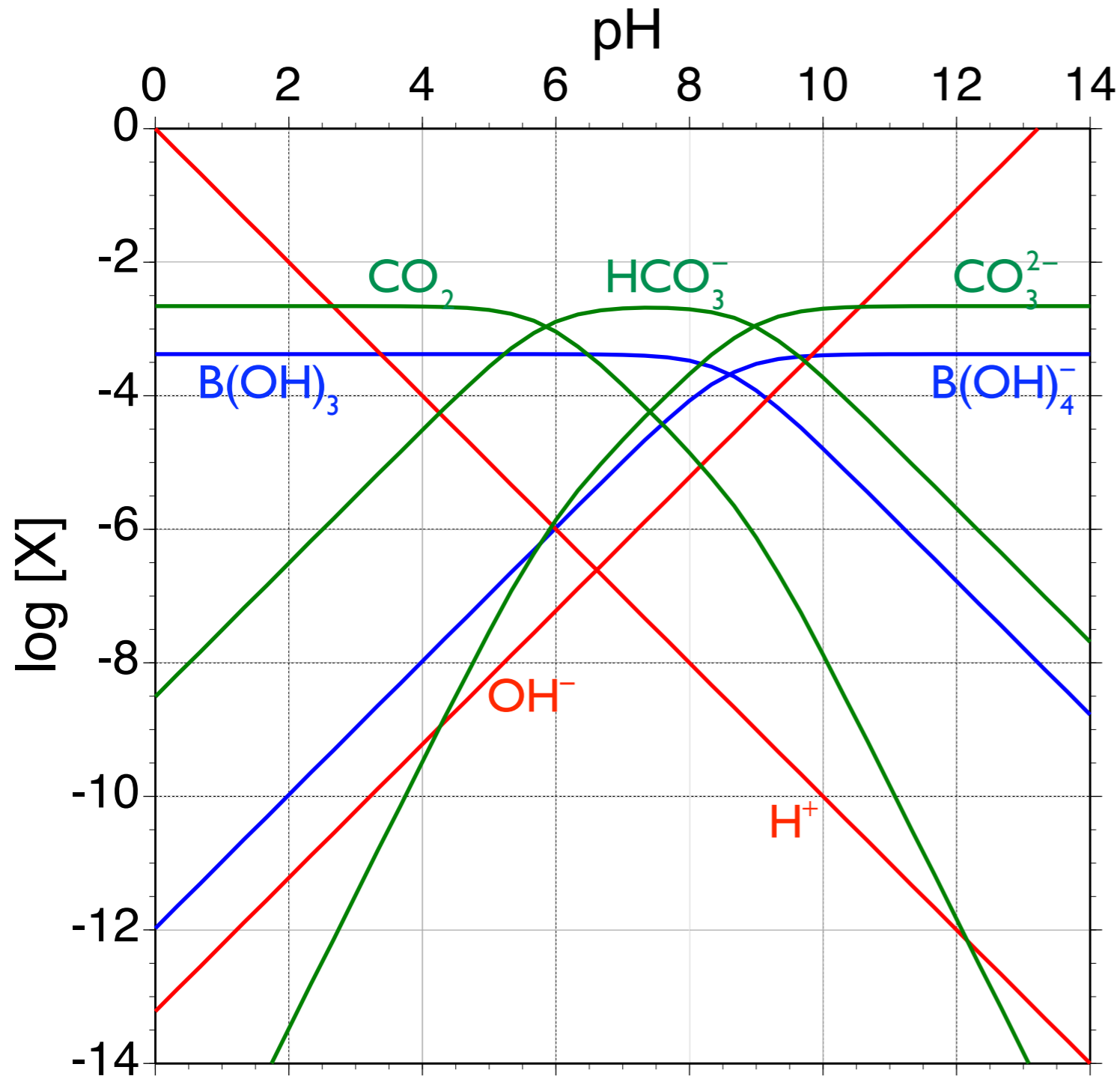
- Carbon dioxide mass-balance



- Boric acid mass-balance



Logarithmic diagram for sea water



$$pK_W = 13.22$$

$$pK_B = 8.6$$

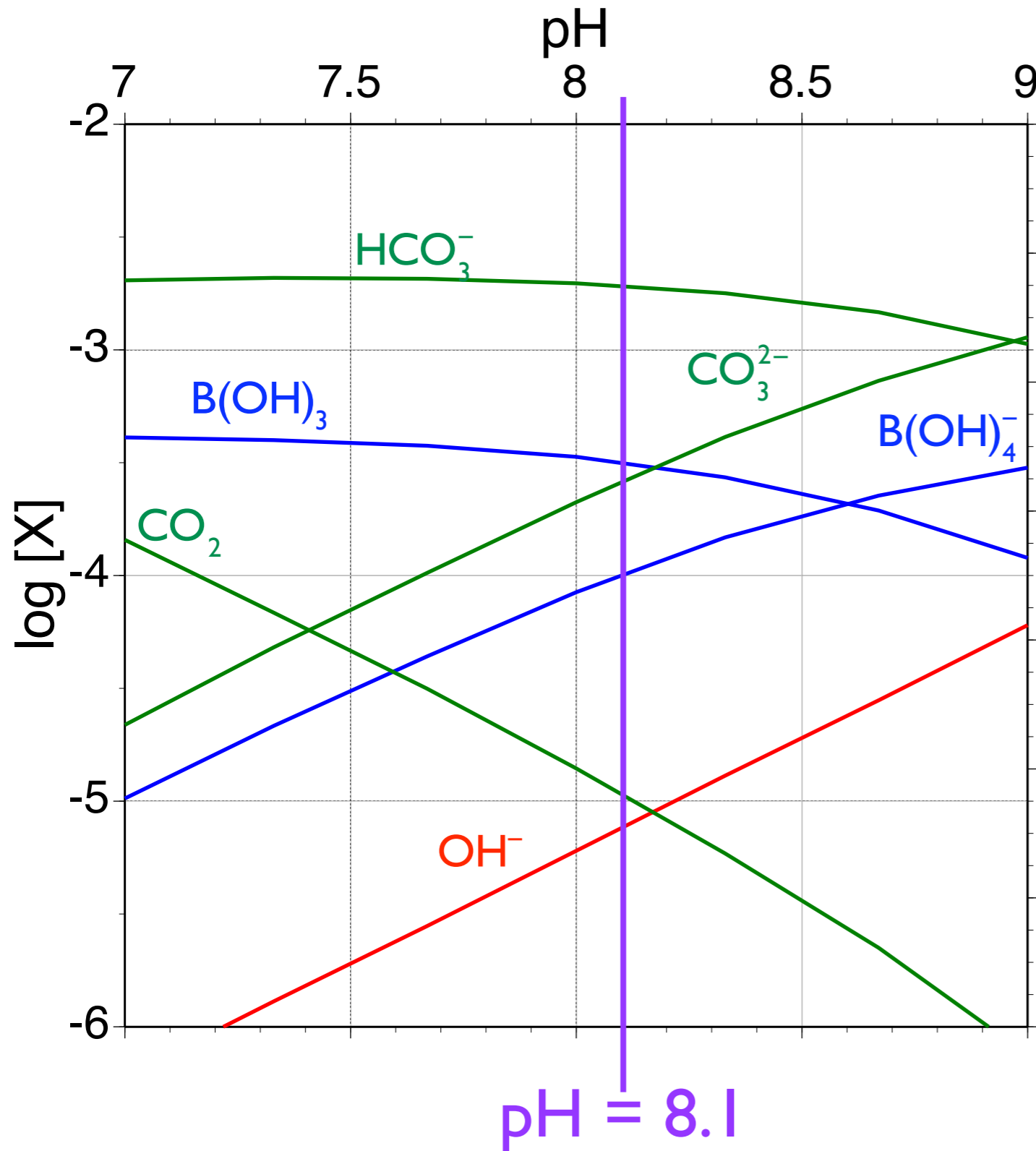
$$pK_1 = 5.85$$

$$pK_2 = 8.97$$

$$B_T = 0.00042 \text{ mol kg}^{-1}$$

$$C_T = 0.0022 \text{ mol kg}^{-1}$$

Logarithmic diagram for sea water (expanded scale)



At pH = 8.1

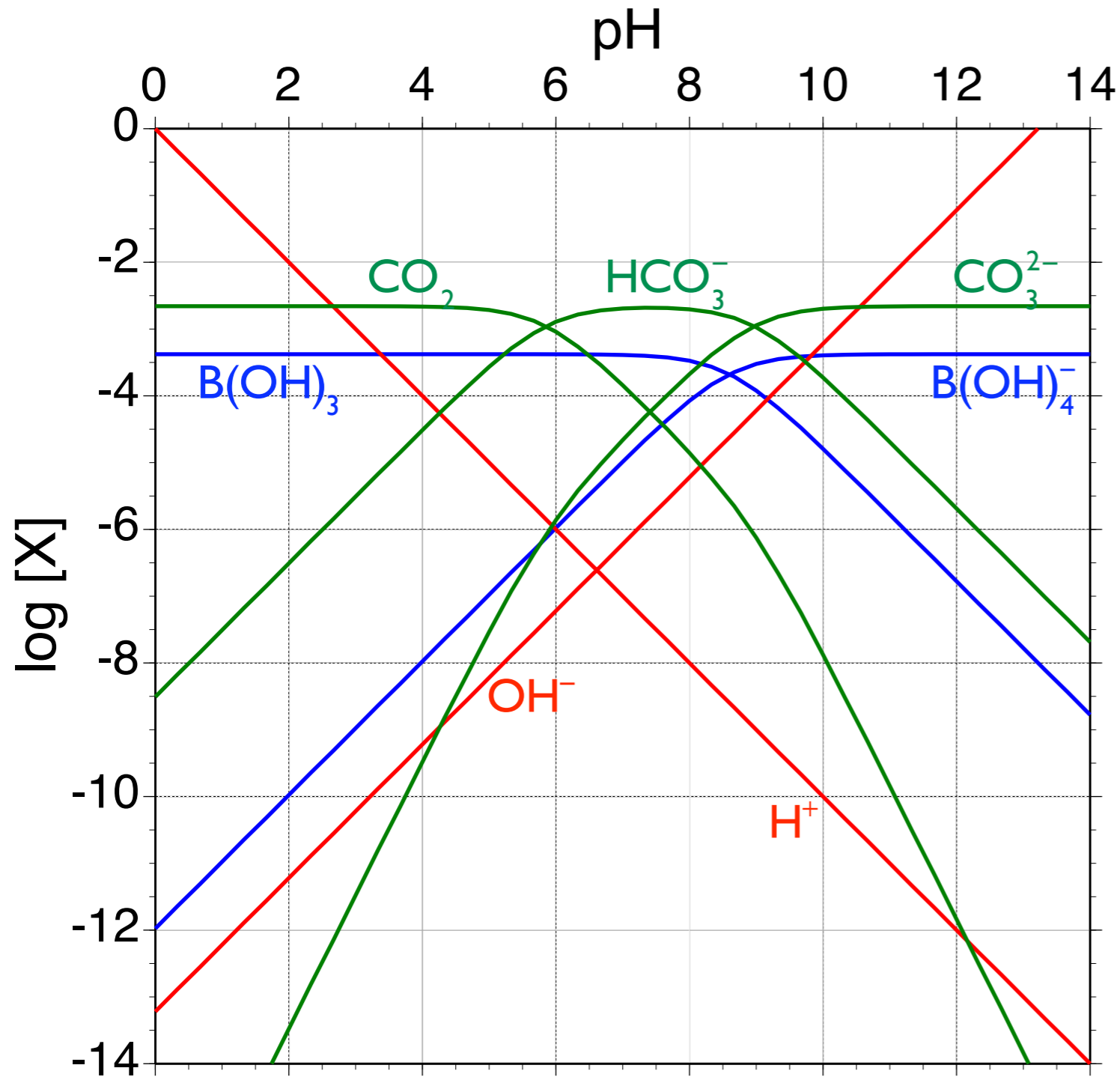
$$\frac{[\text{HCO}_3^-]}{[\text{CO}_2]} = 10^{\text{pH} - \text{p}K_1} = 178$$

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{\text{pH} - \text{p}K_2} = 0.135$$

$$\frac{[\text{B(OH)}_4^-]}{[\text{B(OH)}_3]} = 10^{\text{pH} - \text{p}K_B} = 0.316$$

$$[\text{OH}^-] = 10^{\text{pH} - \text{p}K_W} = 7.6 \times 10^{-6}$$

Logarithmic diagram for sea water



7 species (H_2O implicit in concentration)

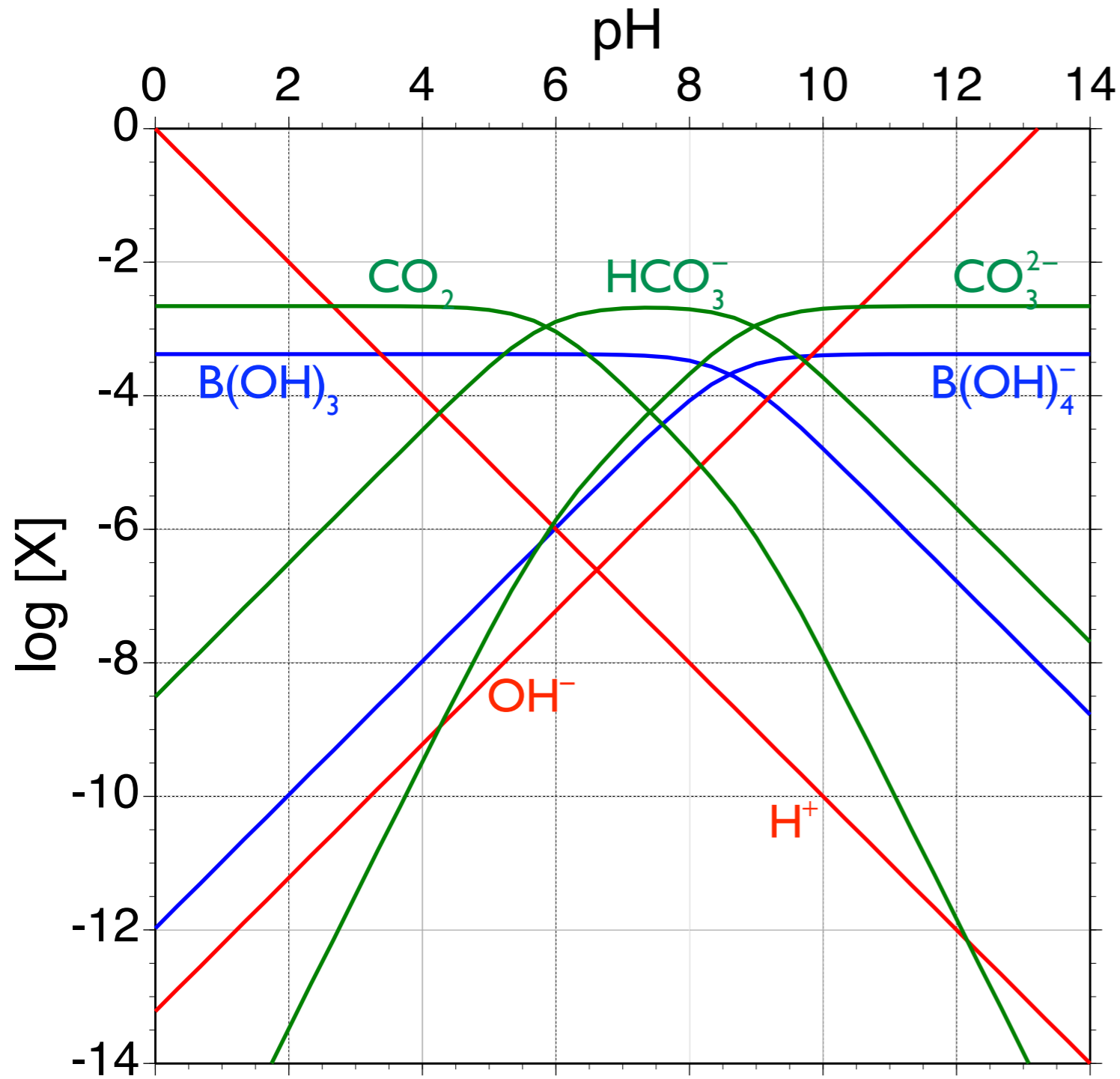
4 equilibrium constants K_1, K_2, K_B, K_W are $f(T, p, S)$

total borate B_T is $f(S)$

need 2 more pieces of information

Analytical parameters of the CO₂ system

Logarithmic diagram for sea water



7 species (H_2O implicit in concentration)

4 equilibrium constants K_1, K_2, K_B, K_W are $f(T, p, S)$

total borate B_T is $f(S)$

need 2 more pieces of information

Analytical parameters of the CO₂ system

1. Total dissolved inorganic carbon

$$C_T = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

mass-balance equation
T, p independent

2. Hydrogen ion concentration (pH)

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

species concentrations
f(T, p)

3. Partial pressure of CO₂

(in solubility equilibrium with water sample)

$$\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq}) \quad K_0(T, p, S) = \frac{[\text{CO}_2]}{p(\text{CO}_2)}$$

$$p(\text{CO}_2) = [\text{CO}_2] / K_0 \quad p(\text{CO}_2) = x(\text{CO}_2) p$$

Analytical parameters of the CO₂ system

4. Total alkalinity

$$A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+]$$

T, p independent

Why is this particular sum of species concentrations independent of temperature and pressure though each of the individual species contributions is itself a function of T and p ?



Guide to Best Practices for Ocean CO₂ Measurements

PICES SPECIAL PUBLICATION 3
IOCCP REPORT No. 8



http://cdiac.ornl.gov/oceans/Handbook_2007.html

Analytical parameters of the CO₂ system

I. Total dissolved inorganic carbon



mass-balance equation
T, p independent

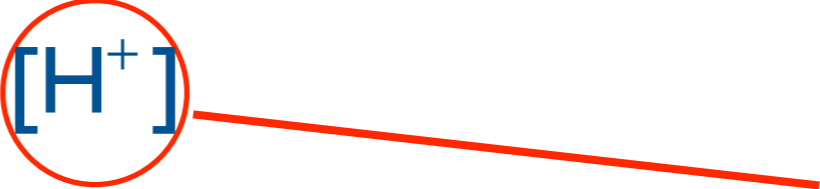
1. Acidify
2. Extract
3. Measure
 - a. Coulometry
 - b. Infra-red
 - c. other

Analytical parameters of the CO₂ system

2. Hydrogen ion concentration (pH)

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

species concentration
 $f(T, p)$



- A. pH electrodes
- B. Spectrophotometry

Analytical parameters of the CO₂ system

3. Partial pressure of CO₂ (in solubility equilibrium with water sample)

$$p(\text{CO}_2) = \frac{[\text{CO}_2]}{K_0}$$

species concentration
 $f(T, p)$

- A. Gas phase equilibration $p(\text{CO}_2) = x(\text{CO}_2) p$
- a. infra-red measure of $x(\text{CO}_2)$
 - b. gas chromatographic measure of $x(\text{CO}_2)$
- B. Membrane equilibration of CO₂(aq)
- a. measure of pH change in external solution

Analytical parameters of the CO₂ system

4. Total alkalinity

$$A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+]$$

T, p independent

A. Acidimetric titration

- a. closed-cell
- b. open-cell

- a. Can also add acid in one aliquot (single point method)
- b. Can use either pH cell or spectrophotometry to locate equivalence point

That's all!

for now



**Oceans are suffering from
second hand smoke...**