

CO₂ chemistry in sea water: pH and alkalinity

Andrew G. Dickson

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 of bicarbonate (together with other acid-base species at still lower concentrations) in a salt-water background. In the surface waters of the North Atlantic, for example, the concentration of total dissolved inorganic carbon (the sum of the concentrations of the three coexisting species: bicarbonate ion, carbonate ion, and unionized dissolved carbon dioxide) is only about 2 mmol kg^{-1} . About 90% of this is present as bicarbonate ion, the proportion of carbonate ion is about a factor of 10 less (~10%), and that of unionized carbon dioxide yet another factor of 10 less (<1%). As a result of the equilibria between these various species (see below), sea water is buffered (weakly) with respect to changes in hydrogen ion (present at much lower concentrations: $<10^{-8} \text{ } \mu\text{mol kg}^{-1}$).

Guide to Best Practices for Ocean CO₂ Measurements

PICES SPECIAL PUBLICATION 3
IOCCP REPORT No. 8



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



275 3 The definition and measurement of pH in sea water

3.1 Introduction

Unfortunately, as noted by Dickson (1984), the field of pH scales and the study of acid-base reactions in sea water is one of the more confused areas of marine chemistry. The primary intent of measuring pH is to use it together with appropriated acid-dissociation constants (and other information – see part 2.5 above) to calculate the speciation of the various acid-base systems in sea water. For a particular acid-dissociation, *e.g.*,



the corresponding equilibrium expression can be written in the form

$$\text{pH} + \lg K(\text{HB}) = \lg \{[\text{B}^-] / [\text{HB}]\}. \quad (27)$$

285 If the pH scale is changed, changing the numerical value of pH, the corresponding value of the equilibrium constant must also change, and by the same amount, to ensure that the right hand side of this equation remains constant. It is thus essential that the pH be defined on the same pH scale as that of all acid-dissociation constants that are used with it.

Relationship between pH and lgK

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

lg x is $\log_{10} x$

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

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

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

For this to be true, pH and $\lg K(\text{HA})$ must be defined on the same pH scale

The total hydrogen ion concentration pH scale (I)

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

As mentioned yesterday, the brackets imply total concentration, that is the sum of the *free concentration* plus the concentrations of all complexes with the background ionic medium

(H_2O , Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Cl^- , SO_4^{2-})

For H^+ these include complexes with H_2O , and with SO_4^{2-} , i.e., HSO_4^- .

The total hydrogen ion concentration pH scale (2)



$$[\text{H}^+] = [\text{H}^+]_F + [\text{HSO}_4^-]$$

$$[\text{H}^+] = [\text{H}^+]_F \left(1 + [\text{SO}_4^{2-}] / K(\text{HSO}_4^-) \right)$$

At low pH the term in parentheses is not constant

$$\Rightarrow [\text{H}^+] = [\text{H}^+]_F \left(1 + S_T / K(\text{HSO}_4^-) \right)$$

S_T is a function of salinity



At pH > 5, these two equations are essentially equivalent.

The total hydrogen ion concentration pH scale (3)

$$[\text{H}^+] \stackrel{\text{def}}{=} [\text{H}^+]_{\text{F}} \left(1 + S_{\text{T}} / K(\text{HSO}_4^-) \right)$$

The advantage of this is that $[\text{H}^+]$ is directly proportional to $[\text{H}^+]_{\text{F}}$ at all pHs.



Measuring total hydrogen ion concentration using a pH cell



measured emfs in sample and standard

$$\text{pH}(X) = \text{pH}(S) - \frac{E_x - E_s}{RT \ln 10 / F}$$

pH of sample solution
pH of standard buffer
0.05916 V per pH unit

Measuring total hydrogen ion concentration using a pH cell

$$\text{pH}(X) = \text{pH}(S) - \frac{E_x - E_s}{RT \ln 10 / F}$$

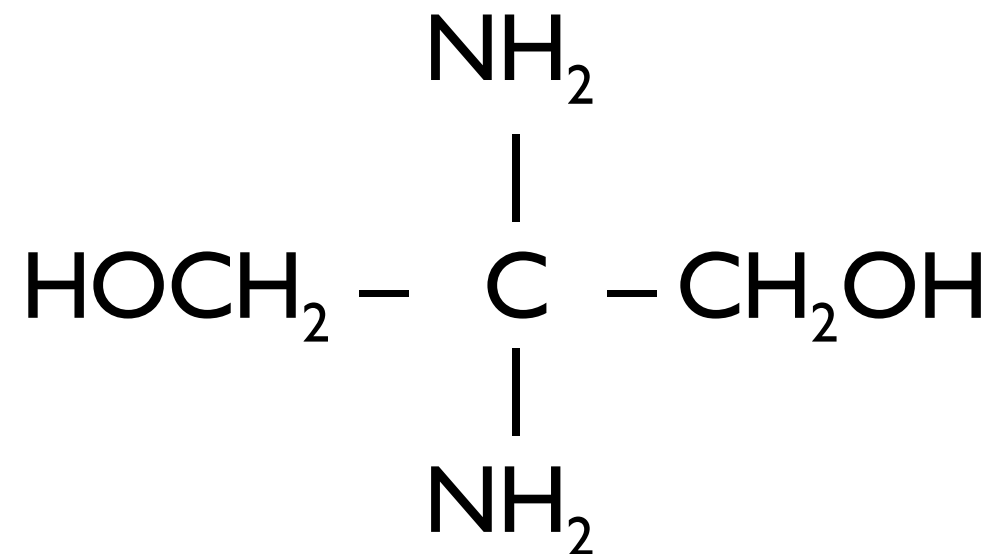
NEED

1. pH cell (glass / reference electrodes)
2. pH meter (high input impedance & ± 0.1 mV)
3. Standard buffer (“Tris” buffer in synthetic s/w)
4. Temperature control (± 0.1 °C)

Measuring total hydrogen ion concentration using a pH cell

What on earth is “Tris” buffer in synthetic sea water and where can I get it?

2-amino-2-hydroxymethyl-1,3-propanediol



pK ~ 8.1 in
sea water



Available online at www.sciencedirect.com

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Marine Chemistry 96 (2005) 237–242

MARINE
CHEMISTRY

www.elsevier.com/locate/marchem

The stability and reproducibility of Tris buffers in synthetic seawater

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Available online 21 April 2005

Table 1

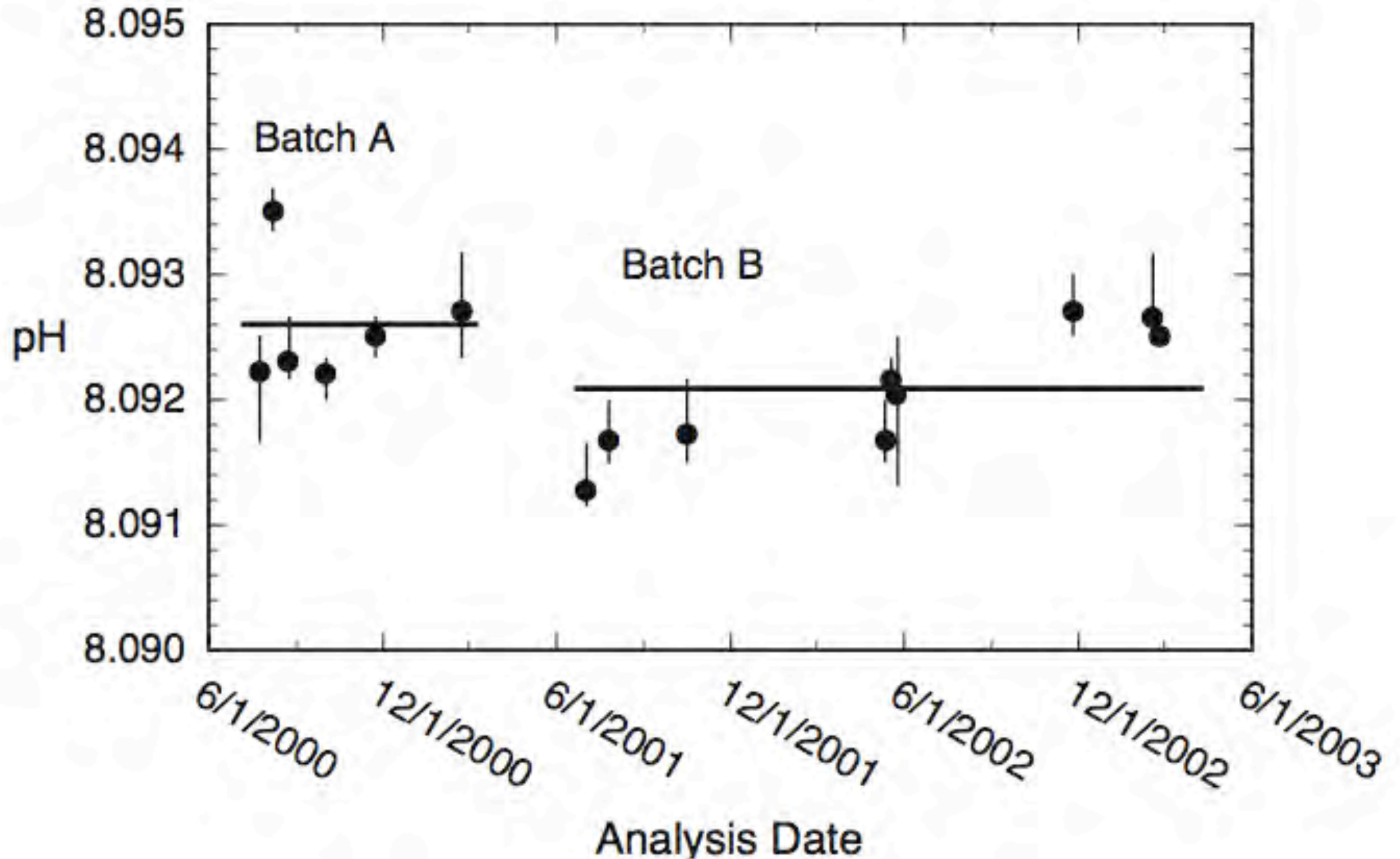
Nominal composition of equimolar (0.04 mol/kg-H₂O Tris+0.04 mol/kg-H₂O Tris-HCl) Tris buffer in synthetic seawater of salinity 35

Component	Concentration (mol/kg-H ₂ O)	Concentration (mol/kg-soln)	Weight (g) in 1 kg solution ^a
NaCl	0.38762 ^b	0.37087	21.6884
Na ₂ SO ₄	0.02927	0.02801	3.9808
KCl	0.01058	0.01012	0.7551
MgCl ₂	0.05474	0.05238	—
CaCl ₂	0.01075	0.01029	—
Tris	0.08000	0.07654	9.2748
HCl	0.04000	0.03827	—

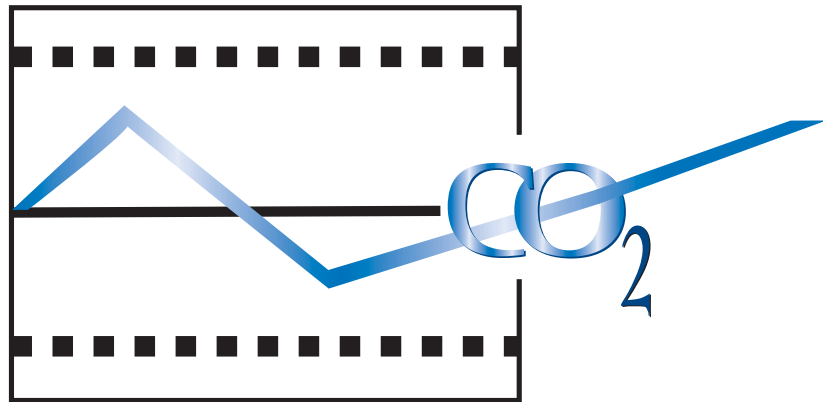
^a Weights in air at sea level (i.e., not corrected to mass). If a weight is not given, the component is added as the appropriate amount of a calibrated solution.

^b $m(\text{NaCl}) = 0.42762 - 0.04 \text{ mol/kg-H}_2\text{O}$, i.e. replacing NaCl with HCl.

Stability and reproducibility of buffer



Available from my lab (in small quantities)



Equimolal tris buffer in synthetic sea water
stored in 125 mL Schott Duran bottle
pH certified using hydrogen electrode system at 25 °C
stability ~1 year

Measuring total hydrogen ion concentration using a pH cell

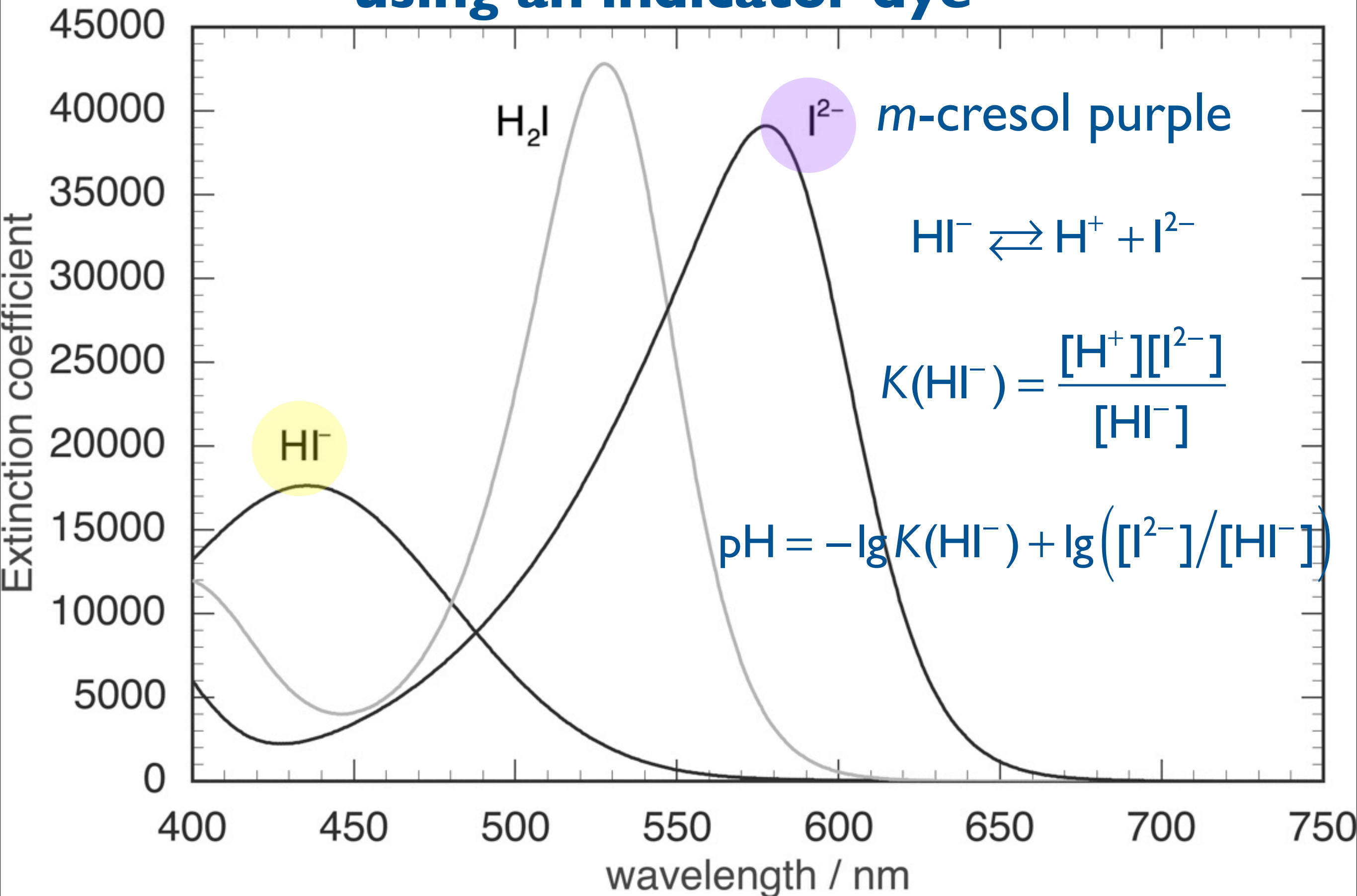
Sources of uncertainty:

1. Non-certified “tris” buffer (≥ 0.005)
2. Poor salinity match of buffer ($\Delta S < 5$, $\Delta \text{pH} < 0.01$)
3. Non-Nernstian electrode ($>99\%$, $\Delta \text{pH} < 0.02$)
4. Poor sample handling

Overall uncertainty ~ 0.02 pH units
even with good sample handling

$$\Delta C_T \sim 10 \mu\text{mol kg}^{-1} ; \Delta p(\text{CO}_2) \sim 5\%$$

Measuring total hydrogen ion concentration using an indicator dye



Measuring total hydrogen ion concentration using an indicator dye

The (normalized) absorbance at a particular wavelength, λ

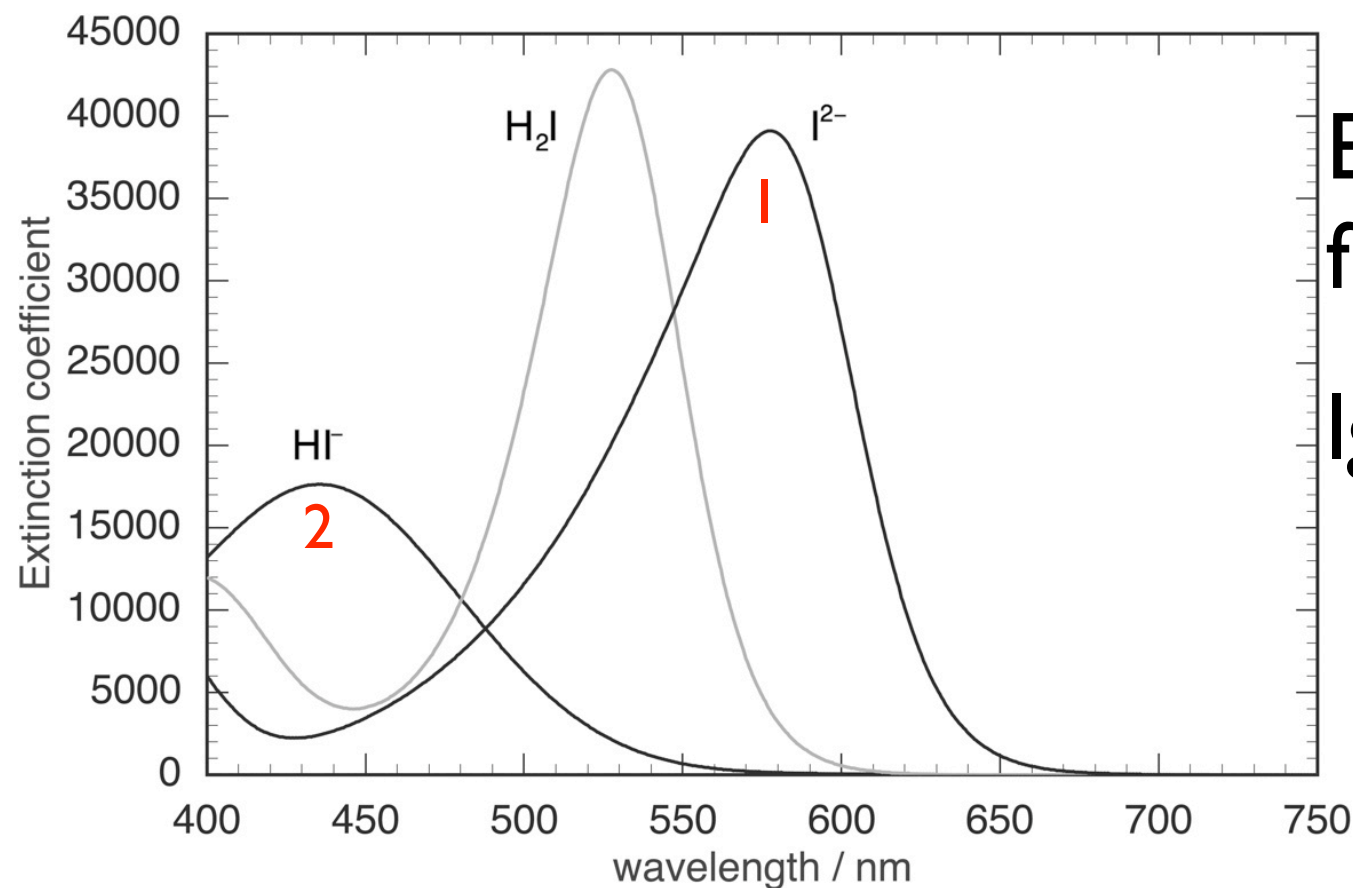
$$A_{\lambda} / \ell = \varepsilon_{\lambda}(\text{HI}^{-})[\text{HI}^{-}] + \varepsilon_{\lambda}(\text{I}^{2-})[\text{I}^{2-}]$$

Make measurements at 2 separate wavelengths, then

$$\text{pH} = -\lg K(\text{HI}^{-}) + \lg \left([\text{I}^{2-}] / [\text{HI}^{-}] \right)$$

$$\text{pH} = -\lg K(\text{HI}^{-}) + \lg \left(\frac{A_1 / A_2 - \varepsilon_1(\text{HI}^{-}) / \varepsilon_2(\text{HI}^{-})}{\varepsilon_1(\text{I}^{2-}) / \varepsilon_1(\text{HI}^{-}) - (A_1 / A) \varepsilon_2(\text{I}^{2-}) / \varepsilon_2(\text{HI}^{-})} \right)$$

Measuring total hydrogen ion concentration using an indicator dye



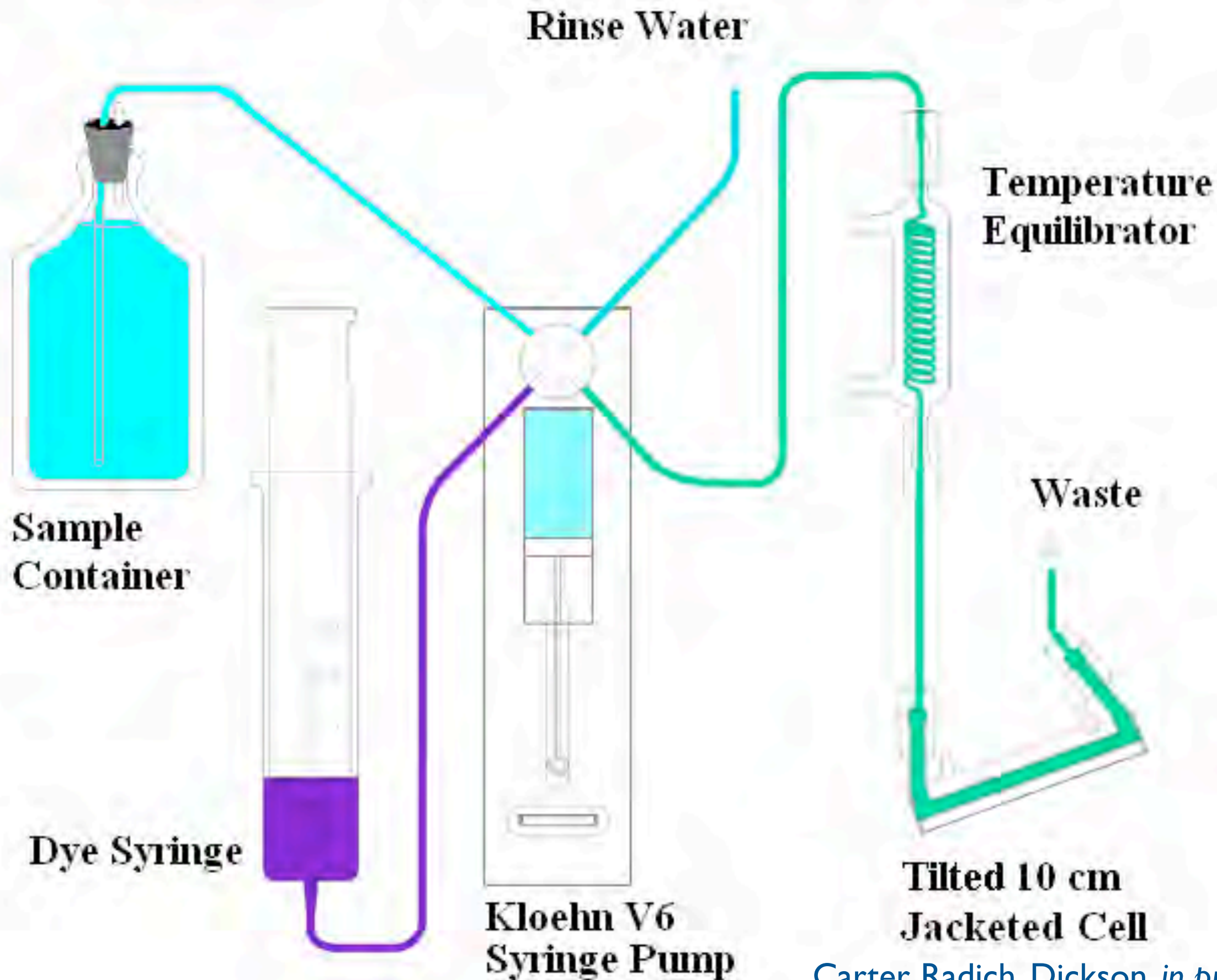
Extinction coefficients are weak functions of T

$\lg K(\text{HI}^-)$ is function of $T, S,$ (and p)

$$\text{pH} = -\lg K(\text{HI}^-) + \lg \left(\frac{A_1 / A_2 - \varepsilon_1(\text{HI}^-) / \varepsilon_2(\text{HI}^-)}{\varepsilon_1(\text{I}^{2-}) / \varepsilon_1(\text{HI}^-) - (A_1 / A) \varepsilon_2(\text{I}^{2-}) / \varepsilon_2(\text{HI}^-)} \right)$$

Again calibrated using a standard reference buffer

Automated pH measurement system setup



Carter, Radich, Dickson, *in preparation*

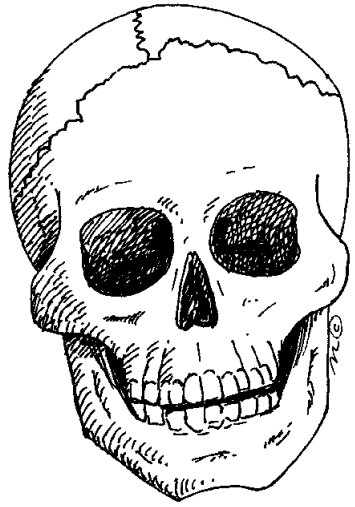
Measuring total hydrogen ion concentration using an indicator dye

Sources of uncertainty:

1. Error in pK of dye (≤ 0.005)
2. Extinction coefficients (up to 0.01 – dye impurities)
3. Change in solution pH on adding dye (0.005)
4. Poor sample handling

Overall uncertainty ~ 0.01 pH units

$$\Delta C_T \sim 5 \mu\text{mol kg}^{-1} ; \Delta p(\text{CO}_2) \sim 2.5\%$$



Other pH scales **NOT RECOMMENDED!!!**

Two other scales have been used:

1. NBS scale (IUPAC scale) **uncertainty ~ 0.05**
 - a. Uses low ionic strength (~0.1 M) buffers
 - b. Resulting liquid junction error in sea water solutions
 - c. Often takes a long time to get stable result
2. Sea water scale **uncertainty ~ 0.01–0.02**
 - a. Includes HF in definition (more complex medium)
 - b. Additional uncertainty in assigning pH to buffers

$$\text{pH} \approx \text{pH}(\text{NBS}) - 0.15 ; \quad \text{pH} \approx \text{pH}(\text{SWS}) + 0.01$$

Measuring total hydrogen ion concentration

	Equipment cost	Ease of use	Uncertainty
pH cell	Relatively cheap	Easy	0.02 (limited RMs)
spectrophotometry	Mid-range k\$10–20	Can be very easy	≤ 0.01



Questions?

Alkalinity and the CO₂ system in sea water

Total alkalinity

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

T, p independent

Q1. 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 ?

Total alkalinity

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

If you dissolve additional CO_2 gas into sea water:

1. C_T will increase
2. pH will decrease
3. $p(\text{CO}_2)$ will increase
4. but A_T stays the same

Q2. Why?



Development of alkalinity concept

Mixture of NaCl and NaOH

NaCl 0.700 moles
NaOH 0.002 moles } in 1 kilogram of solution

What species are present in the solution?

H^+ , OH^- , Na^+ , Cl^- , (H_2O)

mass balance information

$$[Na^+] = 0.702 \text{ mol kg}^{-1}$$

$$[Cl^-] = 0.700 \text{ mol kg}^{-1}$$

charge balance relation

$$[Na^+] + [H^+] = [Cl^-] + [OH^-]$$

Mixture of NaCl and NaOH

NaCl 0.700 moles
NaOH 0.002 moles } in 1 kilogram of solution

Can rearrange the charge balance relation:

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

Hence:

$$[\text{OH}^-] - [\text{H}^+] = 0.002 \text{ mol kg}^{-1} \quad T, p \text{ independent}$$

Mixture of NaCl + NaOH + CO₂

NaCl 0.700 moles
NaOH 0.002 moles
CO₂ 0.002 moles } in 1 kilogram of solution

What species are present in the solution?

H⁺, OH⁻, Na⁺, Cl⁻, CO₂, HCO₃⁻, CO₃²⁻, (H₂O)

mass balance information

$$[\text{Na}^+] = 0.702 \text{ mol kg}^{-1}$$

$$[\text{Cl}^-] = 0.700 \text{ mol kg}^{-1}$$

$$C_T = 0.002 \text{ mol kg}^{-1}$$

charge balance relation

$$[\text{Na}^+] + [\text{H}^+] = [\text{Cl}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

Mixture of NaCl + NaOH + CO₂



Can rearrange the charge balance relation:

$$[\text{Na}^+] - [\text{Cl}^-] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Hence:

$$[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] = 0.002 \text{ mol kg}^{-1}$$

T, p independent

Mixture of NaCl and NaHCO₃

NaCl 0.700 moles
NaHCO₃ 0.002 moles } in 1 kilogram of solution

What species are present in the solution?

H⁺, OH⁻, Na⁺, Cl⁻, CO₂, HCO₃⁻, CO₃²⁻, (H₂O)

mass balance information

$$[\text{Na}^+] = 0.702 \text{ mol kg}^{-1}$$

$$[\text{Cl}^-] = 0.700 \text{ mol kg}^{-1}$$

$$C_T = 0.002 \text{ mol kg}^{-1}$$

charge balance relation

$$[\text{Na}^+] + [\text{H}^+] = [\text{Cl}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

Mixture of NaCl and NaHCO₃

NaCl 0.700 moles
NaHCO₃ 0.002 moles } in 1 kilogram of solution

Can rearrange the charge balance relation:

$$[\text{Na}^+] - [\text{Cl}^-] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Thus:

$$[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] = 0.002 \text{ mol kg}^{-1}$$

T, p independent

Mixture of NaCl and Na₂CO₃



What species are present in the solution?



mass balance information

$$[\text{Na}^+] = 0.702 \text{ mol kg}^{-1}$$

$$[\text{Cl}^-] = 0.700 \text{ mol kg}^{-1}$$

$$C_T = 0.001 \text{ mol kg}^{-1}$$

charge balance relation

$$[\text{Na}^+] + [\text{H}^+] = [\text{Cl}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

Mixture of NaCl and Na₂CO₃



Can rearrange the charge balance relation:

$$[\text{Na}^+] - [\text{Cl}^-] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Thus:

$$[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] = 0.002 \text{ mol kg}^{-1}$$

T, p independent

What is the entity we are specifying “moles” for?

Strictly, the number of moles of hydrogen ion whose charge is equivalent to $[\text{Na}^+] - [\text{Cl}^-]$.

Mixture of NaCl + NaOH + CO₂ + B(OH)₃

NaCl	0.700	moles	} in 1 kilogram of solution
NaOH	0.002	moles	
CO ₂	0.002	moles	
B(OH) ₃	0.0004	moles	

What species are present in the solution?



mass balance information

$$[\text{Na}^+] = 0.702 \text{ mol kg}^{-1}$$

$$[\text{Cl}^-] = 0.700 \text{ mol kg}^{-1}$$

$$C_T = 0.002 \text{ mol kg}^{-1}$$

$$B_T = 0.0004 \text{ mol kg}^{-1}$$

charge balance relation

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

Mixture of NaCl + NaOH + CO₂ + B(OH)₃

NaCl	0.700	moles	} in 1 kilogram of solution
NaOH	0.002	moles	
CO ₂	0.002	moles	
B(OH) ₃	0.0004	moles	

Rearrange the charge balance expression:

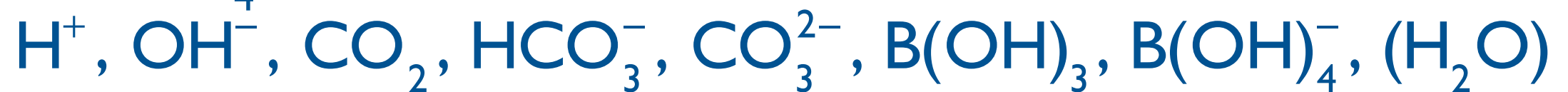
$$\begin{aligned} [\text{Na}^+] - [\text{Cl}^-] &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] \\ &= 0.002 \text{ mol kg}^{-1} \end{aligned} \quad T, p \text{ independent}$$

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 ?

It is a linear combination of mass balance terms, each of which is independent of T & p .

For a simple sea water

The species present are:



Can therefore define **total alkalinity**

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

$$= [\text{Na}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{K}^+] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}]$$

What happens to A_T when we add CO_2 ?

What happens to A_T when we remove CaCO_3 ?

Measurement of alkalinity by acidimetric titration

Titrate sea water sample with acid (HCl) to find equivalence point where $A_T = 0$

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

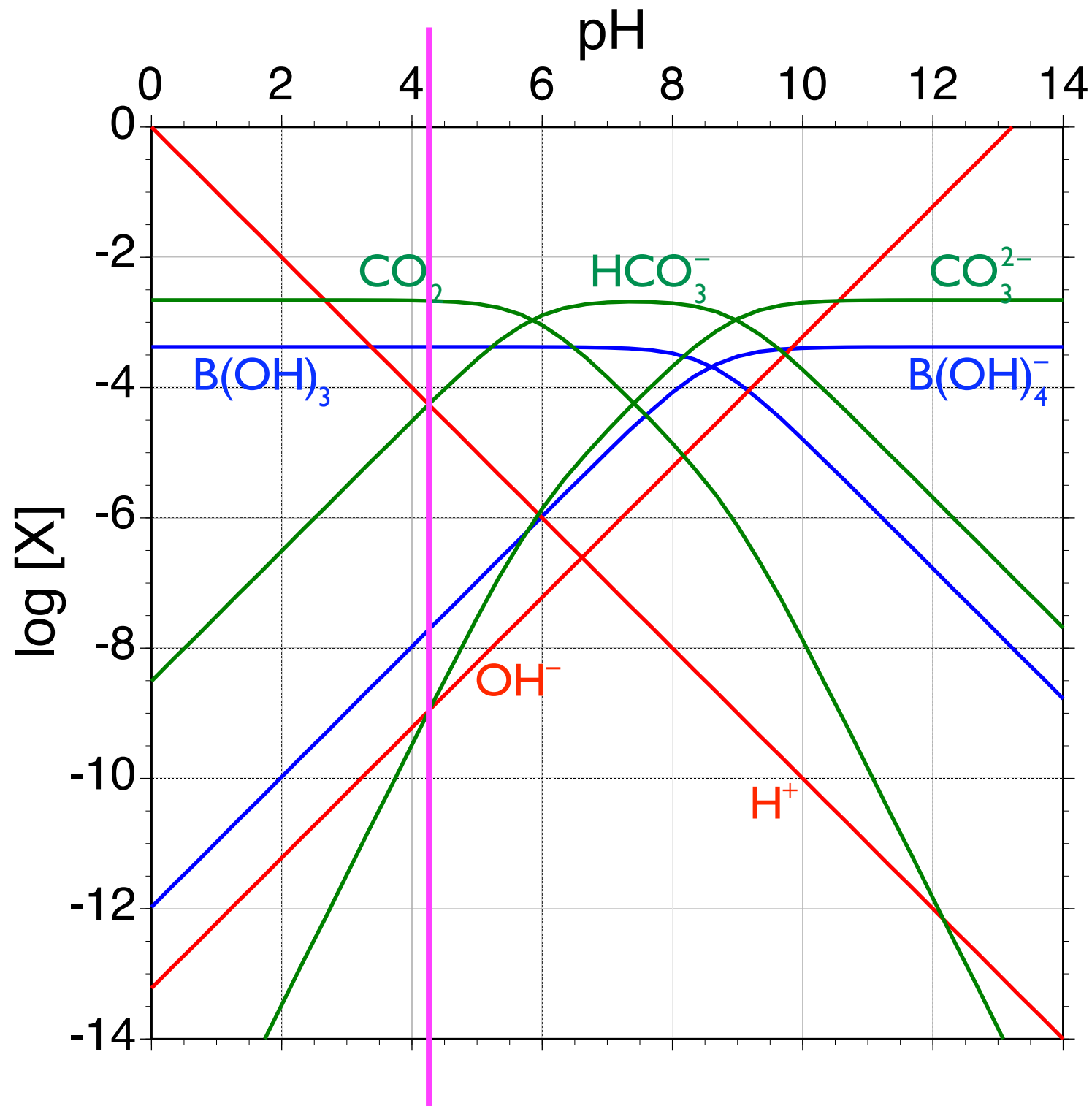
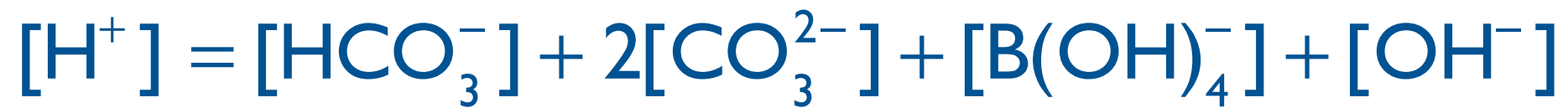
If $A_T = 0$:

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

This type of expression is known as a *proton condition*, it can be seen to represent a type of mass-balance in protons relative to a zero of H_2O , CO_2 , and $\text{B}(\text{OH})_3$.

The equivalence point is thus the composition corresponding to this *zero point*.

Alkalinity equivalence point



Can be found approximately at the pH where $[\text{H}^+] = [\text{HCO}_3^-]$

Approach

Titration of seawater with HCl, using a glass electrode cell to measure $[\text{H}^+]$, and a non-linear least-squares approach to determine the equivalence point.

See SOP 3b



Guide to Best Practices for Ocean CO₂ Measurements

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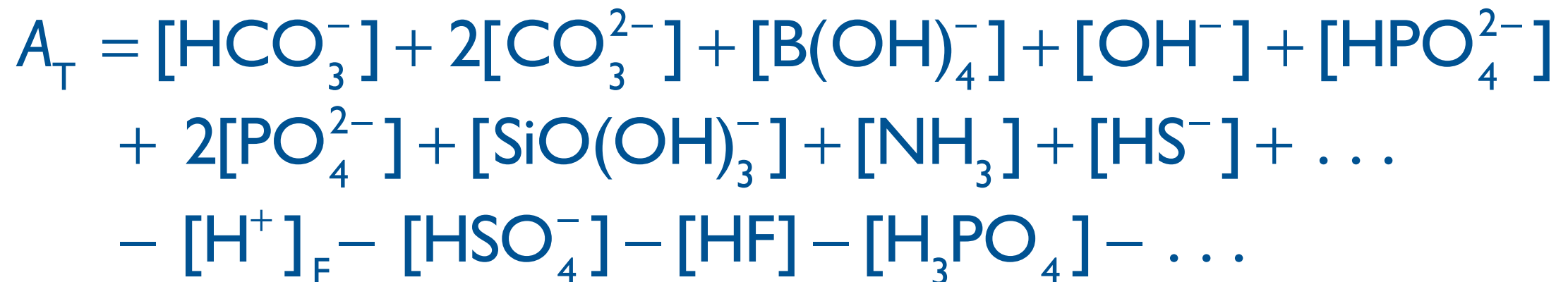


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Formal definition of alkalinity

The total alkalinity of a sample of sea water is a form of mass-conservation relationship for hydrogen ion. It is rigorously defined (Dickson, 1981) as

“... the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at 25°C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in 1 kilogram of sample.”



Formal definition of alkalinity

If we choose to omit species typically present at low concentration, we then get the version we have used so far.

$$\begin{aligned} A_T = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] \\ & + 2[\text{PO}_4^{2-}] + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] + [\text{HS}^-] + \dots \\ & - \underbrace{[\text{H}^+]_F + [\text{HSO}_4^-] + [\text{HF}] + [\text{H}_3\text{PO}_4] + \dots}_{- [\text{H}^+]} \end{aligned}$$

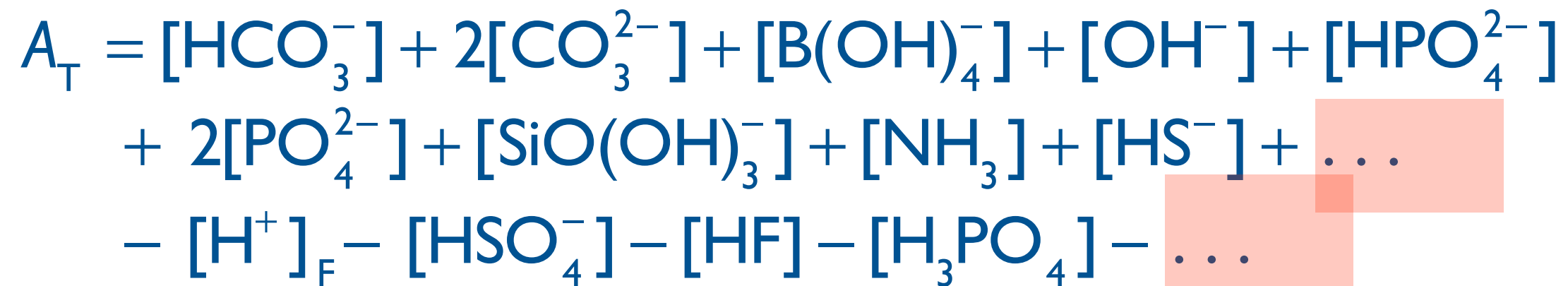
Strictly our definition of hydrogen ion concentration has been the “total” hydrogen ion concentration (*i.e.*, implicitly including the effect of the hydrogen sulfate species).

Implications

$$\begin{aligned} A_T = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] \\ & + 2[\text{PO}_4^{2-}] + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] + [\text{HS}^-] + \dots \\ & - [\text{H}^+]_F - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - \dots \end{aligned}$$

Although the titration approach will estimate total alkalinity well even if there are significant amounts of the various other species indicated here, if you wish to estimate other CO_2 parameters you need information (total concentrations, K_s) for all of these other acid/base systems!

Organic acids



It has been shown that organic acids in systems with significant biological activity can have a measurable contribution to the total alkalinity

LIMNOLOGY and OCEANOGRAPHY: METHODS

Limnol. Oceanogr.: Methods 5, 2007, 225–232
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Estimating the contribution of organic bases from microalgae to the titration alkalinity in coastal seawaters

J. Martín Hernández-Ayon^{1*}, *Alberto Zirino*^{2,3}, *A. G. Dickson*², *Tania Camiro-Vargas*¹, and *E. Valenzuela-Espinoza*¹

My advice

Don't use alkalinity measurements as one of your primary CO_2 parameters in systems with significant (potentially varying) amounts of nutrients, or in highly productive systems with significant alkalinity contribution from organic acids

How would you know?

Measure pH & C_T , predict A_T
compare result with measured A_T
worry about a significant discrepancy

History of concept

Marine Chemistry, 40 (1992) 49–63
Elsevier Science Publishers B.V., Amsterdam

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The development of the alkalinity concept in marine chemistry*

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(Accepted 27 March 1992)

How does alkalinity change with various processes?



Available online at www.sciencedirect.com



Marine Chemistry 106 (2007) 287–300

MARINE
CHEMISTRY

www.elsevier.com/locate/marchem

Total alkalinity: The explicit conservative expression and its application to biogeochemical processes

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Atmospheric CO₂ concentration at Mauna Loa Observatory, Hawaii

