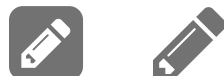




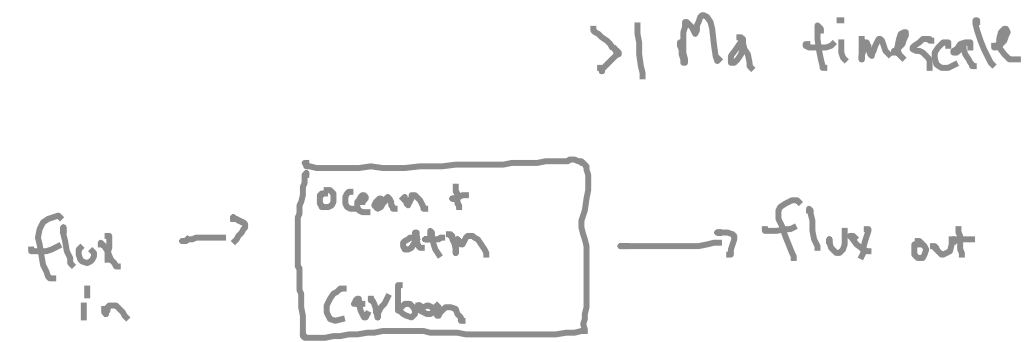
Lectures 18: CO₂ in seawater

1. The carbonate system
2. Examples

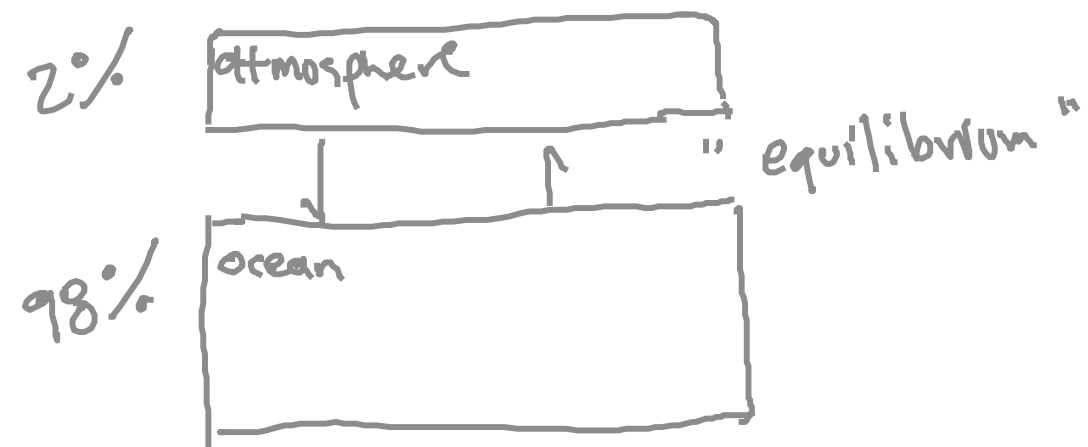
We acknowledge and respect the lək̓ʷəŋən peoples on whose traditional territory the university stands and the Songhees, Esquimalt and W̱SÁNEĆ peoples whose historical relationships with the land continue to this day.



Carbon on a new timescale..



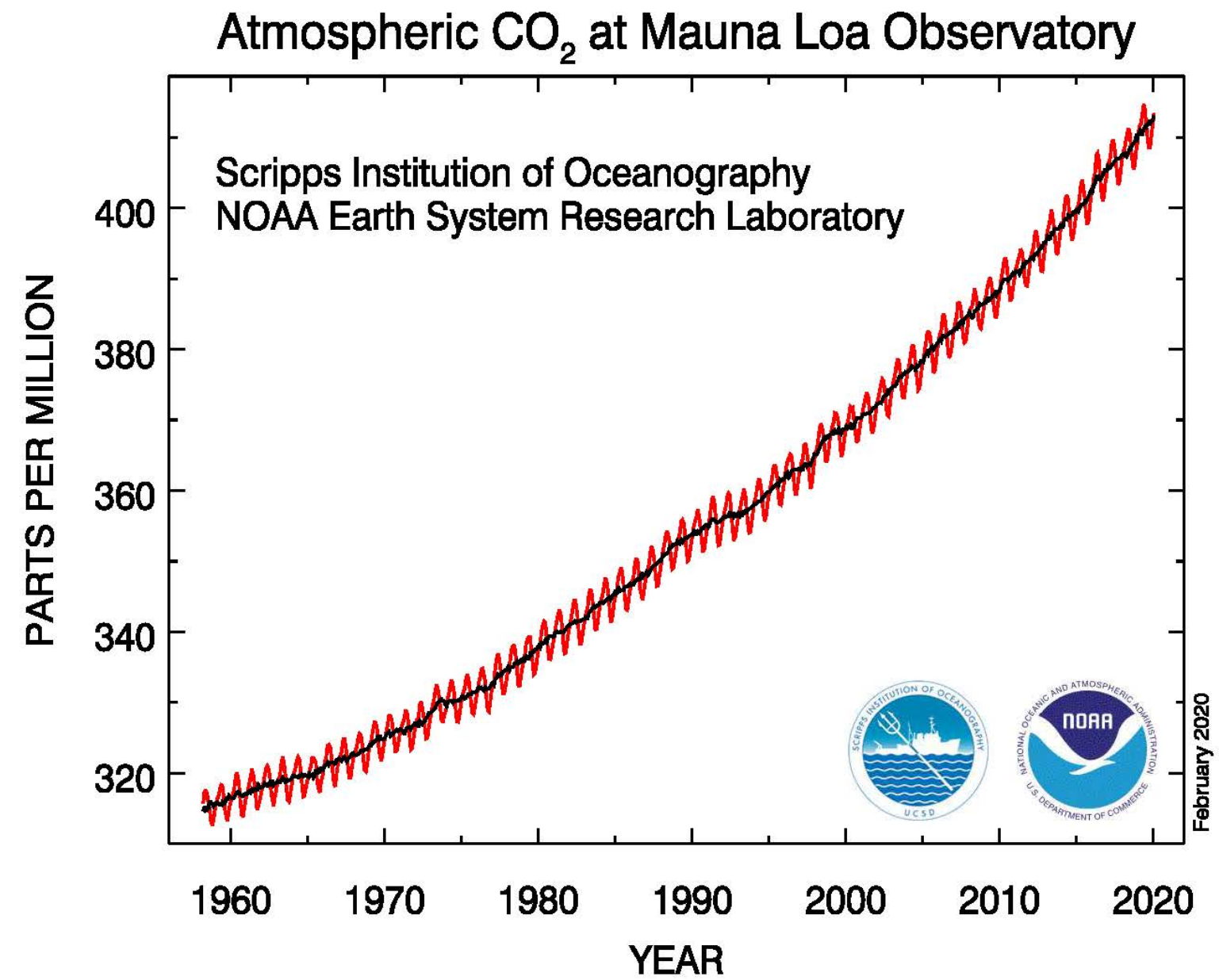
Now, we will consider:



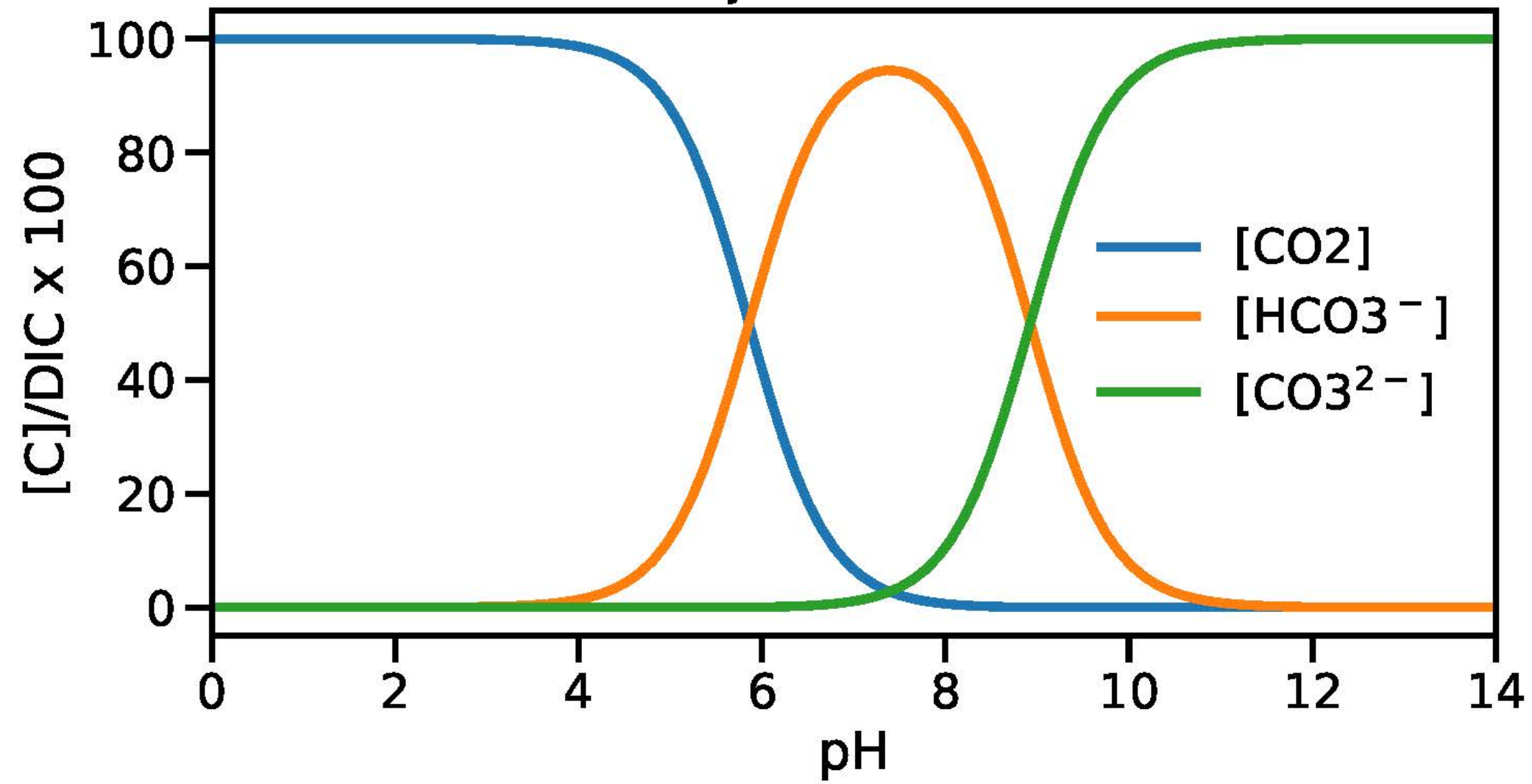
- C in atmosphere
- How much C has to be added to the ocean/atmosphere for a given rise in $p\text{CO}_2$?
 - Will that rate of change in the future? (Yes)



Motivation:

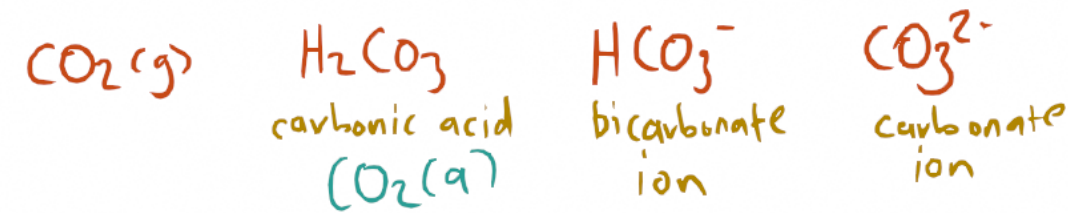


Carbon Speciation Bjerrum Plot

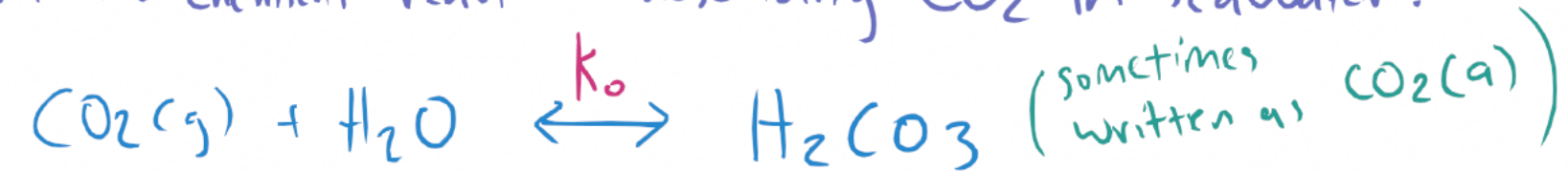


The Carbonate System (at equilibrium)

Where does CO_2 go? — reacts with seawater



Write the chemical reactions describing CO_2 in seawater.



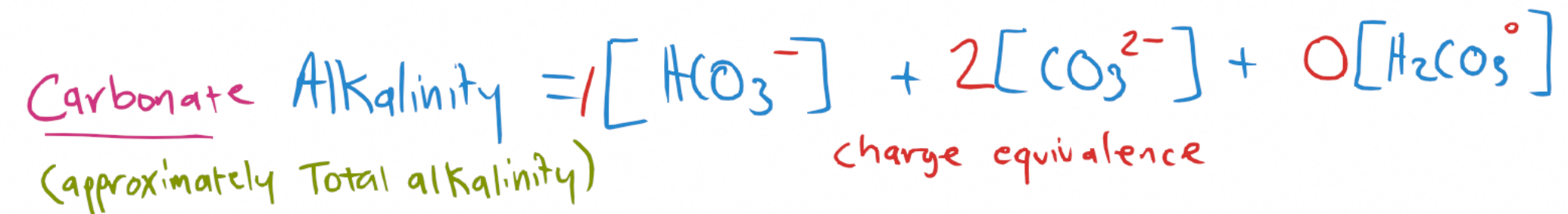
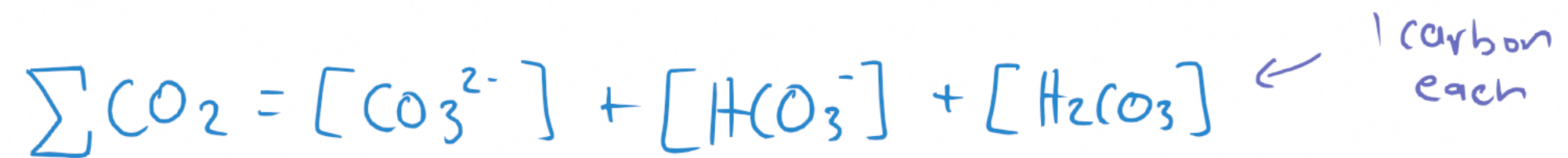
How could we determine where a CO_2 molecule goes?

- equilibrium constants K_0, K_1, K_2
- total carbon
- pH
- some property to describe how much the carbonic acid dissociates (alkalinity)



The Carbonate System (at equilibrium)

Dissolved inorganic Carbon: DIC



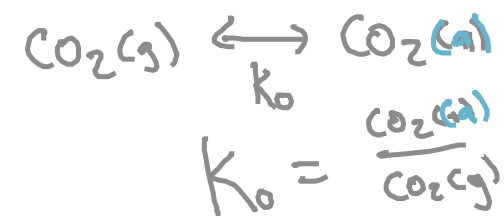
How many unknowns and how many equations?

6 unknowns and 4 equations

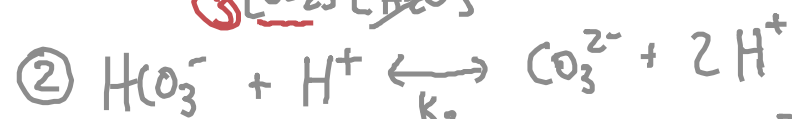
- 2 independent measurements to determine the system



The Carbonate System (at equilibrium)



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



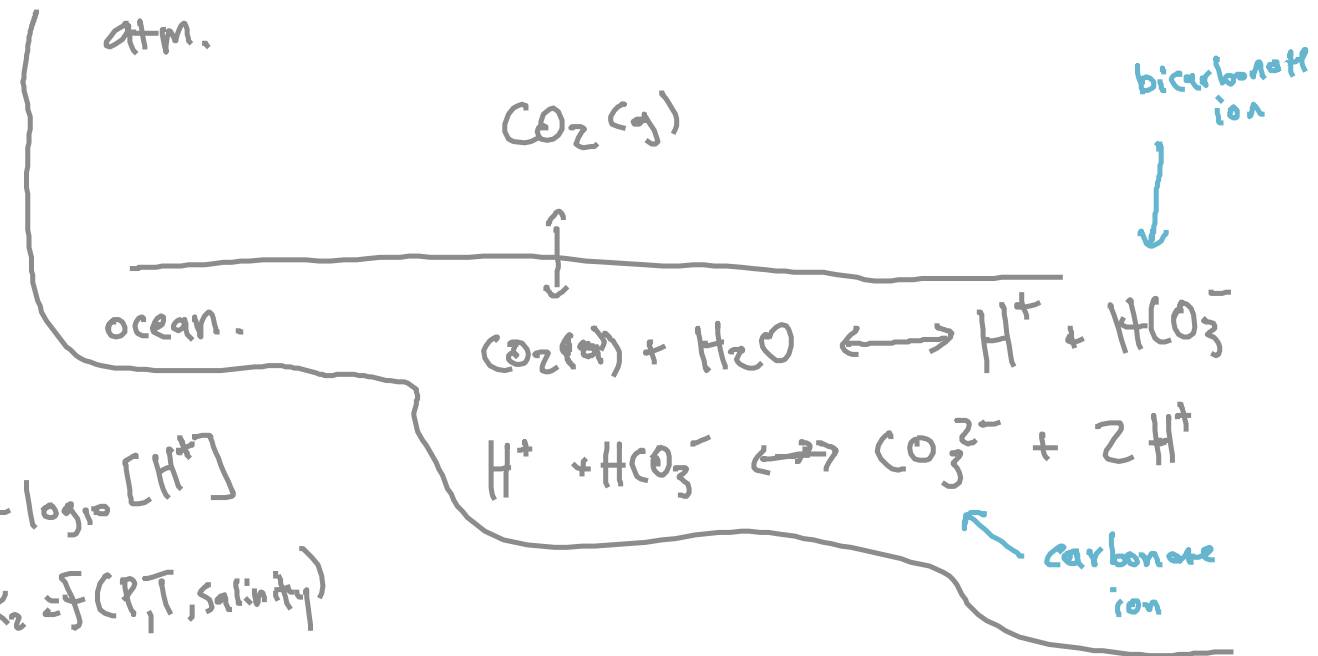
$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]^2}{[\text{HCO}_3^-][\text{H}^+]}$$



recall:
 $\text{pH} = -\log_{10} [\text{H}^+]$

$K_1, K_2 = f(P, T, \text{salinity})$

6 unknowns, 4 eqs.



Brief Total Alkalinity Intro

$$\text{Total Alkalinity, TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] + \text{minor components} - [\text{H}^+]$$

Conservative:
not a function of
T, pH, P

TA = charge from all dissolved
"conservative" anions

- charge from all
dissolved "conservative"
cations
[Na⁺]



Practice Problem: relative abundance of carbon species in seawater

Q1: Determine the relative abundances of carbon species in the ocean with the following measurements:

- pH: 8.1
- DIC: 2.1 mmol/kg
- $K_1 = e^{-13.4847}$
- $K_2 = e^{-20.5504}$



An exercise: relative abundance of carbon species in seawater

CA ≈ TA

Four eqs., six unknowns → measure two things to fully describe the system
unknowns: $[H^+][CO_3^{2-}][HCO_3^-][CO_2(aq)][DIC][TA]$

determine the relative abundances of carbon species in the ocean w/
the following measurements: pH = 8.1, DIC = 2.1 mol/kg

$$K_1 = e^{-13.4847}$$

$$K_2 = e^{-20.5504}$$

hint: start w/ DIC eq. and replace $[CO_2]$ and $[CO_3^{2-}]$

$$\text{ie: } [CO_2] = \frac{[HCO_3^-][H^+]}{K_1}$$

$$[CO_2(aq)] \approx$$

$$[HCO_3^-] \approx$$

$$[CO_3^{2-}] \approx$$



An exercise: relative abundance of carbon species in seawater

CA ≈ TA

Four eqs., six unknowns → measure two things to fully describe the system
unknowns: $[H^+][CO_3^{2-}][HCO_3^-][CO_2(aq)][DIC][TA]$

determine the relative abundances of carbon species in the ocean w/
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$$K_1 = e^{-13.4847}$$

$$K_2 = e^{-20.5504}$$

hint: start w/ DIC eq. and replace $[CO_2]$ and $[CO_3^{2-}]$

$$\text{ie: } [CO_2] = \frac{[HCO_3^-][H^+]}{K_1}$$

$$DIC = \frac{[HCO_3^-][H^+]}{K_1} + [HCO_3^-] + \frac{K_2[HCO_3^-]}{[H^+]}$$

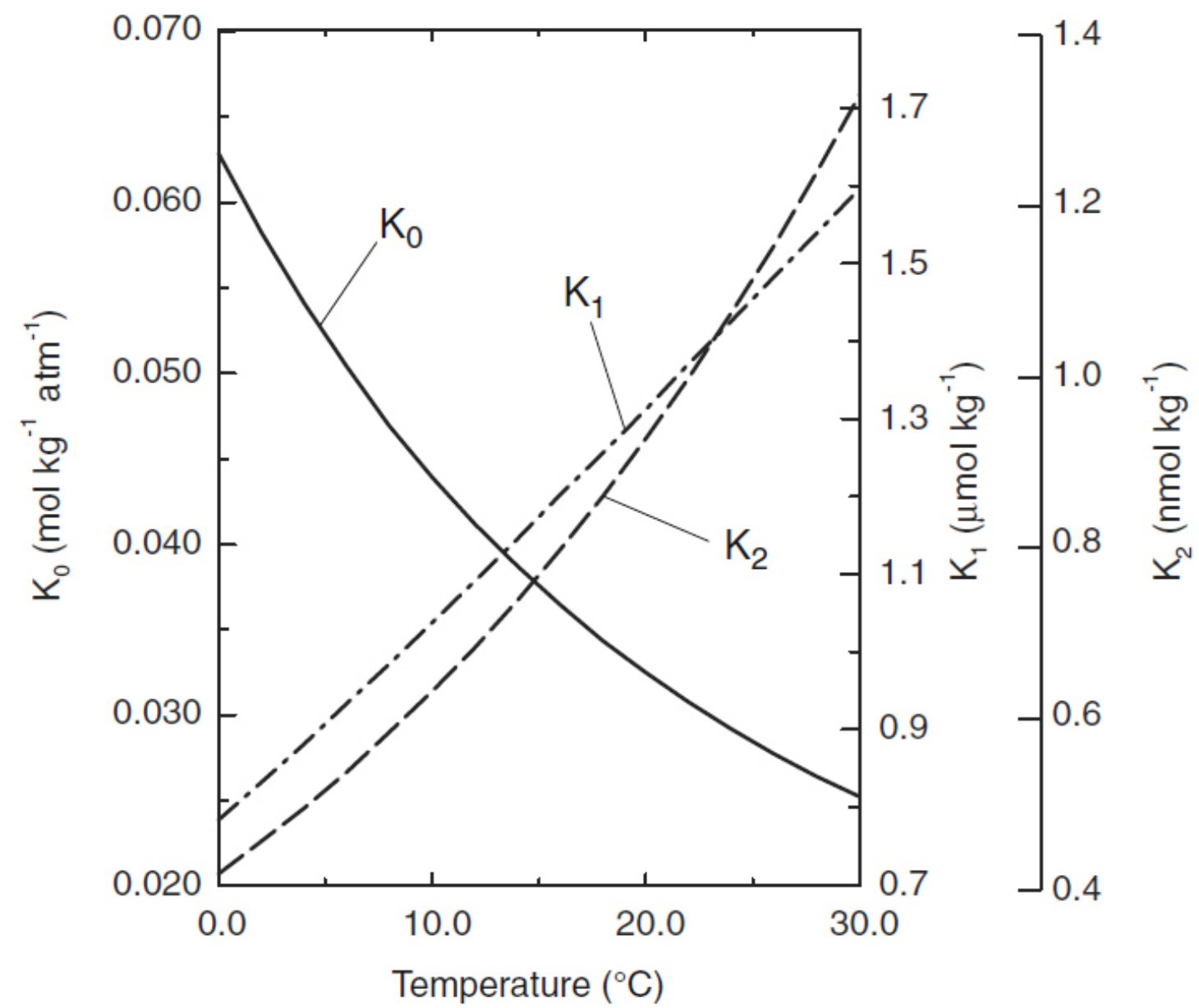
$$[CO_2(aq)] \approx 0.5\%$$

$$[HCO_3^{2-}] \approx 86.5\%$$

$$[CO_3^{2-}] \approx 13\%$$

$$DIC = a \left(1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} \right) = 1.82 \text{ mol/kg}$$





What does warming do to equilibrium $p\text{CO}_2$?

$$\frac{K_2}{K_0 K_1} \alpha p\text{CO}_2 \approx \frac{1}{K_0}$$

• Assume fixed ALK
and DIC. How does
 $p\text{CO}_2$ change when
T increases?

$p\text{CO}_2 \uparrow$ as $T \uparrow$



An exercise: relative abundance of carbon species in seawater

recall:

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

$$p\text{CO}_2 = \frac{[\text{CO}_2(\text{aq})]}{K_0} \quad \leftarrow \text{replace w/ eq 1}$$

$$p\text{CO}_2 = \frac{1}{K_0} \cdot \frac{[\text{HCO}_3^-][\text{H}^+]}{K_1} \quad \leftarrow \text{replace w/ eq 2}$$

$$p\text{CO}_2 = \frac{1}{K_0} \cdot \frac{[\text{HCO}_3^-]}{K_1} \cdot \frac{K_2[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]}$$

$$p\text{CO}_2 = \frac{K_2}{K_0 K_1} \cdot \frac{2[\text{HCO}_3^-]^2}{[\text{CO}_3^{2-}]}$$

$$p\text{CO}_2 = \frac{K_2}{K_0 K_1} \cdot \frac{2(\text{DIC} - \text{CA})^2}{\text{CA} - \text{DIC}}$$

↑ only constant at fixed T, P, salinity

$$\text{DIC} = \cancel{[\text{CO}_2(\text{aq})]} + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad \text{CA} \approx \text{TA}$$

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

$$\text{DIC} = a + b$$

$$\text{CA} = a + 2b$$

$$\text{DIC} - b = a$$

$$\text{CA} = \text{DIC} - b + 2b$$

$$\text{CA} = \text{DIC} + b$$

$$b = \text{CA} - \text{DIC}$$

$$[\text{CO}_3^{2-}] = \text{CA} - \text{DIC}$$

$$2\text{DIC} - \text{CA} = [\text{HCO}_3^-]$$

↑ calculation from previous slide

In []: 1

