Practice problems:

Do these to learn the material. Check your answers against those in the back of the book or against your friends’ answers, or bring questions to office hours.


Discussion problems:

We will discuss these in class (3:30) on Wednesday the 11th. Be prepared to present answers to and to discuss any of these up at the blackboard.

1. The solubility of a gas in a liquid is given by Henry’s law, which says that the concentration of dissolved gas is proportional to the partial pressure of the gas. For the equilibrium

$$X(g) \rightleftharpoons X(aq)$$

the equilibrium constant is

$$K = \frac{[X]}{P_X}$$

For CO$_2$, the value of this constant is $3.4 \times 10^{-2}$ mol L$^{-1}$ atm$^{-1}$, and the partial pressure in the atmosphere is $3.94 \times 10^{-4}$ atm.

(a) What is the concentration of CO$_2$(aq) at equilibrium?

$$K = \frac{[X]}{P_X}$$

$$[X] = KP_X$$

$$= 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1} \cdot 3.94 \times 10^{-4} \text{ atm}$$

$$= 1.34 \times 10^{-5} \text{ mol L}^{-1}$$
(b) How many grams are dissolved in a liter of carbonated water at equilibrium CO$_2$ pressurized to 8 atm?

\[
\begin{align*}
[X] &= K P_x \\
&= 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1} \cdot 8 \text{ atm} \\
&= 2.72 \times 10^{-1} \text{ mol L}^{-1} \\
g \text{ CO}_2/\text{L} &= 2.72 \times 10^{-1} \text{ mol} \cdot \frac{44 \text{ g}}{1 \text{ mol}} \\
&= 15.2 \text{ g}
\end{align*}
\]

2. Dissolved CO$_2$ can react with water to form carbonic acid, H$_2$CO$_3$, according to the reaction

\[
\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) \quad K = 1.3 \times 10^{-3}
\]

The first acid dissociation constant of H$_2$CO$_3$ is

\[
K_{a1} = 2 \times 10^{-4} \text{ M}
\]

Simplify the problem by saying that further dissociation of HCO$_3^-$ does not occur, and calculate the pH of pure water in equilibrium with atmospheric CO$_2$. (Be careful with the H$_2$CO$_3$ concentration. Since you’re remaining in equilibrium with the atmosphere, it will not change during acid dissociation.)

The Big Idea here is that in order for the solution to stay in equilibrium with the air, the concentration of CO$_2$ in solution must stay at $1.34 \times 10^{-5}$ M (the answer from 1a). That is, $1.34 \times 10^{-5}$ M is not your initial concentration—it is your equilibrium concentration of CO$_2$(aq). Since

\[
\begin{align*}
K &= \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2(\text{aq})]} \\
1.3 \times 10^{-3} &= \frac{[\text{H}_2\text{CO}_3]}{[1.34 \times 10^{-5}]} \\
[\text{H}_2\text{CO}_3] &= 1.74 \times 10^{-8} \text{ M}
\end{align*}
\]

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The $K_a$ value given means that

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

and once again, the $H_2CO_3$ concentration is forced to be $1.74 \times 10^{-8}$ M at equilibrium. To the extent that some (most) of it dissociates in solution, additional $CO_2(aq)$ will react with $H_2O$ to make more, and additional $CO_2(g)$ will dissolve. So

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$[H^+][HCO_3^-] = K_a[H_2CO_3]$$

$$= 2 \times 10^{-4} \cdot 1.74 \times 10^{-8}$$

$$= 3.48 \times 10^{-12}$$

Since $x = [H^+] = [HCO_3^-]$, we have

$$x^2 = 3.48 \times 10^{-12}$$

$$x = 1.86 \times 10^{-6}$$

and a pH of 5.73.

3. The second acid dissociation constant of $H_2CO_3$ describes the reaction

$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq) \quad K_{a2} = 4.7 \times 10^{-11} \text{ M}$$

If you only consider the acid equilibria (ignore the effect of additional $H_2CO_3$ formation from $CO_2(aq)$ here), show that the fractional amount of each carbonate species is given by

$$\frac{[H_2CO_3]}{F} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

$$\frac{[HCO_3^-]}{F} = \frac{[H^+]K_{a1}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

$$\frac{[CO_3^{2-}]}{F} = \frac{K_{a1}K_{a2}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$
where

\[ F = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \]

(One way to do this is to solve for \( F \) in terms of one compound only by using the definitions of \( K_{a1} \) and \( K_{a2} \). Then repeat that for all three compounds.)

Note that this result holds for all diprotic acids.

First express all concentrations in terms of \([\text{HCO}_3^-]\):

\[
K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}
\]

\[
[\text{H}_2\text{CO}_3] = \frac{[\text{H}^+][\text{HCO}_3^-]}{K_{a1}}
\]

\[
K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}
\]

\[
[\text{CO}_3^{2-}] = \frac{K_{a2}[\text{HCO}_3^-]}{[\text{H}^+]}
\]

Now substitute in:

\[
F = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]
\]

\[
= \frac{[\text{H}^+][\text{HCO}_3^-]}{K_{a1}} + [\text{HCO}_3^-] + \frac{K_{a2}[\text{HCO}_3^-]}{[\text{H}^+]}\]

\[
= \left( \frac{[\text{H}^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[\text{H}^+]} \right) [\text{HCO}_3^-]
\]

Common denominator:

\[
F = \left( \frac{[\text{H}^+]^2 + [\text{H}^+] K_{a1} + K_{a1} K_{a2}}{[\text{H}^+] K_{a1}} \right) [\text{HCO}_3^-]
\]

\[
\frac{[\text{HCO}_3^-]}{F} = \frac{[\text{H}^+] K_{a1}}{[\text{H}^+]^2 + [\text{H}^+] K_{a1} + K_{a1} K_{a2}}
\]

A clever way to get the other expressions came up in discussion section—use the expressions we got above:

\[
[\text{H}_2\text{CO}_3] = \frac{[\text{H}^+] [\text{HCO}_3^-]}{K_{a1}}
\]
\[
\frac{[\text{H}_2\text{CO}_3]}{F} = \frac{[\text{H}^+] \cdot [\text{HCO}_3^-]}{K_{a1}} \cdot \frac{[\text{H}^+]K_{a1}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}} \\
= \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}
\]

and the same approach works for \(\text{CO}_3^{2-}\).

4. Find the fractional amount of \(\text{H}_2\text{CO}_3\) and \(\text{CO}_3^{2-}\) at the pH where

\[
[\text{H}_2\text{CO}_3] = [\text{CO}_3^{2-}]
\]

Explain why this means that for most problems, both acid dissociation steps do not need to be considered at the same time. (Note that this result holds for all diprotic acids where \(K_{a1} \gg K_{a2}\).)

\[
\frac{[\text{H}_2\text{CO}_3]}{F} = \frac{[\text{CO}_3^{2-}]}{F} \\
\frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}} = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}} \\
[\text{H}^+]^2 = K_{a1}K_{a2} \\
[\text{H}^+] = \sqrt{K_{a1}K_{a2}}
\]

Rearrange the fractional concentration using \([\text{H}^+]^2 = K_{a1}K_{a2}\):

\[
\frac{[\text{H}_2\text{CO}_3]}{F} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}} \\
= \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + [\text{H}^+]^2} \\
= \frac{1}{2 + \frac{K_{a1}}{[\text{H}^+]}} \\
= \frac{1}{2 + \frac{K_{a1}}{\sqrt{K_{a1}K_{a2}}}}
\]
\[
\frac{1}{2 + \sqrt{K_{a1}/K_{a2}}}
\]

This means that as long as \( K_{a1} \) is much bigger than \( K_{a2} \) (it will never be smaller), this crossover point will always occur at very low values of \([H_2A]/F\) (or \([A^{2-}]/F\)). Also, if \( K_{a1} = K_{a2} \), then the fractional concentration of all species is 1/3. Here,

\[
\frac{K_{a1}}{K_{a2}} = \frac{2 \times 10^{-4}}{4.7 \times 10^{-11}} = 4.25 \times 10^6
\]

and so

\[
\frac{[H_2CO_3]}{F} = \frac{1}{2 + \sqrt{4.25 \times 10^6}} = 4.8 \times 10^{-4}
\]

So if your \( H_2CO_3 \) isn’t completely gone—that is, as long as more than 0.05% of your carbonate is in the form of \( H_2CO_3 \)—there will be negligible amounts (less than 0.05%) of \( CO_3^{2-} \). Once there’s any significant amount (more than 0.05%) \( CO_3^{2-} \), the dissociation of \( H_2CO_3 \) has essentially gone to completion (less than 0.05% remains).
Graded problem:

This should be written up and handed in before class begins on Wednesday the 11th. This problem may also be discussed in class.

1. A paper appeared in the Journal of Chemical Education (J. Chem. Educ., 1983, 60 (3), p. 198) with the abstract “Hot chickens have economic implications that can be better understood through chemistry.” The full text of the paper is:

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Le Chatelier’s Principle, Coupled Equilibrium, and Egg Shells

Chickens can not perspire, so when they get hot they pant. This seemingly trivial fact leads to a serious economic loss for egg producers. In hot weather, chickens lay eggs with thin shells which are easily (and frequently) broken. A little reflection shows that this is an inevitable consequence of Le Chatelier’s Principle and the well-known carbonate equilibrium system,

\[ \text{CO}_2(g) = \text{H}_2\text{CO}_3(aq) = \text{H}^+ + \text{HCO}_3^-(aq) \]

(chicken breath)

When the chicken pants, the equilibrium is perturbed by the rapid loss of carbon dioxide. Because this affect cascades through all of these equilibria, the effect is a loss of solid calcium carbonate which ultimately produces weaker egg shells.

Ted Odom, while a graduate student at the University of Illinois, found the deceptively simple “solution” to this problem—give the chickens carbonated water. Now the equilibrium has been perturbed in the opposite direction. The addition of aqueous carbon dioxide shifts all of the equilibria to the right and results in stronger egg shells. Moreover, the chickens seem to like the carbonated water, and there are rumors that they spend their spare time singing familiar jingles about “spirit” and “the real thing.”

Philosophical questions about which came first are left to the reader, but in this case, at least, Le Chatelier’s Principle comes before the egg (shell).

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You have seen most of the relevant reactions and equilibrium constants, except:

\[ \text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \quad K_{sp} = 6 \times 10^{-9} \text{ M}^2 \]

Assume that blood pH stays regulated at 7.4 (not entirely true; pH will go up with panting). Calculate the solubility of CaCO$_3$(s) in grams per liter given equilibrium between CO$_2$(aq) and CO$_2$(g) for both

(a) CO$_2$ partial pressure of 0.04 atm (typical of exhaled air), and

(b) atmospheric composition (3.94 $\times$ 10$^{-4}$ atm) CO$_2$.

(Hyperventilation, in humans or chickens, cycles air through the lungs much more quickly, resulting in far less build-up of respiratory CO$_2$.)

Food for thought: how much harder is this problem to solve if [H$^+$] depends only on the carbonate equilibria?
The key idea here is that both the pressure of CO\(_2\) (g) and the concentration of H\(^+\) (aq) are set—that is, we know their concentrations at equilibrium. This is enough to pin down all other concentrations:

\[
[\text{CO}_2(aq)] = 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1} \cdot P_{\text{CO}_2} = 1.36 \times 10^{-4} \text{ M}
\]

\[
1.3 \times 10^{-3} = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2(aq)]} \\
[\text{H}_2\text{CO}_3] = 1.76 \times 10^{-7} \text{ M}
\]

This gets us to the CO\(_3^{2-}\) concentration:

\[
K_{a1}K_{a2} = \frac{[\text{H}^+][\text{HCO}_3^-][\text{H}^+][\text{CO}_3^{2-}]}{[\text{H}_2\text{CO}_3][\text{HCO}_3^-]} = \frac{[\text{H}^+]^2[\text{CO}_3^{2-}]}{[\text{H}_2\text{CO}_3]} = 1.6 \times 10^{-21} \\
[\text{CO}_3^{2-}] = \frac{1.6 \times 10^{-21}}{[\text{H}^+]^2}
\]

and with pH = 7.4,

\[
[\text{H}^+] = 10^{-7.4} = 4.0 \times 10^{-8}
\]

so

\[
[\text{CO}_3^{2-}] = 1.0 \times 10^{-6} \text{ M}
\]

The solubility equilibrium:

\[
[\text{Ca}^{2+}][\text{CO}_3^{2-}] = 6 \times 10^{-9} \\
[\text{Ca}^{2+}] = 6 \times 10^{-3}
\]

Because the CO\(_3^{2-}\) concentration is directly proportional to P\(_{\text{CO}_2}\), part b (~100 times less CO\(_2\)) gives 100 times smaller [CO\(_3^{2-}\)] and thus 100 times larger [Ca\(^{2+}\)].