Chemical kinetics
(Nazaroff & Alvarez-Cohen, Section 3.A.2)

This is the answer to what happens when chemical equilibrium is not reached.

For example, take the two-way reaction

\[ A + B \rightleftharpoons C + D \]

As A and B come into contact with each other, they start to react one with the other, and the reaction rate can be expressed as

\[ R_{\text{forward}} = k_f [A][B] \]

This expression reflects the fact that the more of A and B there is, the more encounters occur, and the more reactions take place.

This rate depletes the amounts of both A and B, and generates amounts of C and D:

\[
\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -R_{\text{forward}} = -k_f [A][B] \\
\frac{d[C]}{dt} = +\frac{d[D]}{dt} = +R_{\text{forward}} = +k_f [A][B]
\]

But, at the same time, C and D come in contact, too, and carry their own (reverse) reaction, at a rate proportional to their amounts

\[ R_{\text{reverse}} = k_r [C][D] \]

This rate depletes the amounts of both C and D, and adds to the amounts of A and B:

\[
\frac{d[A]}{dt} = +\frac{d[B]}{dt} = +R_{\text{reverse}} = +k_r [C][D] \\
\frac{d[C]}{dt} = -\frac{d[D]}{dt} = -R_{\text{reverse}} = -k_r [C][D]
\]

Because the two reactions occur simultaneously, we subtract the rate of one from the other:

\[
\frac{d[A]}{dt} = +\frac{d[B]}{dt} = -R_{\text{forward}} + R_{\text{reverse}} = -k_f [A][B] + k_r [C][D] \\
\frac{d[C]}{dt} = +\frac{d[D]}{dt} = +R_{\text{forward}} - R_{\text{reverse}} = +k_f [A][B] - k_r [C][D]
\]
Finally, in a system with open boundaries, we can add the imports and exports:

\[ \nu \, \frac{d[A]}{dt} = + \sum_{\text{inlets}} Q_{\text{in}} [A]_{\text{in}} - \sum_{\text{outlets}} Q_{\text{out}} [A]_{\text{out}} + k_i V[C][D] - k_i V[A][B] \]

\[ \nu \, \frac{d[B]}{dt} = + \sum_{\text{inlets}} Q_{\text{in}} [B]_{\text{in}} - \sum_{\text{outlets}} Q_{\text{out}} [B]_{\text{out}} + k_i V[C][D] - k_i V[A][B] \]

\[ \nu \, \frac{d[C]}{dt} = + \sum_{\text{inlets}} Q_{\text{in}} [C]_{\text{in}} - \sum_{\text{outlets}} Q_{\text{out}} [C]_{\text{out}} + k_i V[A][B] - k_i V[C][D] \]

\[ \nu \, \frac{d[D]}{dt} = + \sum_{\text{inlets}} Q_{\text{in}} [D]_{\text{in}} - \sum_{\text{outlets}} Q_{\text{out}} [D]_{\text{out}} + k_i V[A][B] - k_i V[C][D] \]

where \( V \) is the volume of the system for which the budget is written.

Note: The variables here are concentrations ([…]’s), expressed in moles per liter (mol/L or M), not in mass per liter (such as mg/L). The latter would be obtained after invoking the molecular weights of the individual chemicals.

---

**Chemical Kinetics – Reaction order**
(Nazaroff & Alvarez-Cohen, Section 3.A.3)

The previous example assumed that it takes two chemicals for each reaction. This is not always the case. For example, when a substance dissolves in water

\[ \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \]

The forward reaction needs only one concentration

\[ R_{\text{forward}} = k_i [\text{H}_2\text{CO}_3] \]

**Nomenclature:**

- **Second-order reaction:** \[ \frac{d[A]}{dt} = - k [A][B] \]
- **First-order reaction:** \[ \frac{d[A]}{dt} = - k [A] \]
- **Zeroth-order reaction:** \[ \frac{d[A]}{dt} = - k \]

Note: The units of the \( k \) coefficients vary accordingly!
Chemical Equilibrium

(back to beginning of Nazaroff & Alvarez-Cohen, Section 3.A.2)

A system is in chemical equilibrium when
1. It does not vary in time (steady state);
2. It is well mixed;
3. There is no net flow of mass, heat or species with the surroundings;
4. The net rate of all chemical reactions is zero.

Such a state corresponds to a local minimum in “free energy”:

\[ \Delta G = \Delta G^\circ + RT \ln(Q) \]

where \( Q = \frac{[C][D]}{[A][B]} \) is called the reaction quotient.

For the reaction \( a \ A + b \ B \leftrightarrow c \ C + d \ D \)

\( \Delta G = 0 \) implies \( Q = \text{constant} \). There is a better to see this, though…

Many chemical reactions in the environment are two-way reactions.
Symbolically,

\[ A + B \leftrightarrow C + D \]

during which \( A \) and \( B \) react to produce \( C \) and \( D \), and at the same time \( C \) and \( D \) react to produce \( A \) and \( B \).

The rate of reaction between \( A \) and \( B \) is \( R_{\text{forward}} = k_f [A][B] \)
The rate of reaction in the reverse direction is \( R_{\text{reverse}} = k_r [C][D] \)

Chemical equilibrium occurs when the two rates equal each other so that the rate of depletion of \( A \) and \( B \) equals the rate of their replenishment:

\[ k_f [A][B] = k_r [C][D] \]

That is, when:

\[ \frac{[C][D]}{[A][B]} = \frac{k_f}{k_r} = \text{const.} \]
**Equilibrium constant**

from equilibrium the equilibrium equation \( k_f [A] [B] = k_r [C] [D] \)
we can write

\[
\frac{[C][D]}{[A][B]} = \frac{k_r}{k_f} = K
\]

The “constant” \( K \) is determined in the laboratory. Like most chemical “constants,” it varies with temperature.

Generalization to reaction with arbitrary numbers in the stoichiometry:

\[
aA + bB \leftrightarrow cC + dD
\]

\[
R_{\text{forward}} = k_f [A]^a [B]^b \quad R_{\text{reverse}} = k_r [C]^c [D]^d
\]

Equilibrium exists when \( k_f [A]^a [B]^b = k_r [C]^c [D]^d \)

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

**Important particular case: Water dissociation**
(Nazaroff & Alvarez-Cohen, Section 3.C.2)

Water always tends to dissociate a little, via the reaction

\[
H_2O \leftrightarrow H^+ + OH^-
\]

There is an equilibrium constant for this, and it is:

\[
\frac{[H^+][OH^-]}{[H_2O]} = 1.83 \times 10^{-16} \text{ moles/L}
\]

Since \([H_2O]\) is always the same and equal to 55.4 moles/L (see Lecture 2), we can write:

\[
[H^+][OH^-] = (1.83 \times 10^{-16} \text{ mol/L})[H_2O] = (1.83 \times 10^{-16} \text{ mol/L})(55.4 \text{ mol/L}) = 1.01 \times 10^{-19} \text{ (mol/L)^2}
\]
**pH of Pure Water**

In the absence of any other ion (pure water!), to any $[H^+]$ ion there is a companion $[OH^-]$ ion. Thus,

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

It follows

$$[H^+] = \sqrt{1.01 \times 10^{-14} \text{ (mol/L)}}^2 = 1.0 \times 10^{-7} \text{ mol/L}$$

$$pH = -\log_{10}[H^+] = 7.0$$

---

**Inorganic impurities in water and air**

First, a distinction needs to be made between organic and inorganic compounds:

"organic" compounds = those with carbon, except for these basic elements: C, CO, CO$_2$, HCO$_3^-$ and CO$_3^{2-}$

Acids & Bases:
- acids make $H^+$
  - common acids are HCl, HOCI, H$_2$S, H$_2$SO$_4$, H$_2$SO$_3$, HNO$_3$
- bases make $OH^-$
  - common bases are NH$_3$, NaOH, CaCO$_3$, Ca(OH)$_2$

$OH^-$ takes away $H^+$ via $OH^- + H^+ \rightarrow H_2O$

Dissolution in water $\rightarrow$ ions
- cations are positive, anions are negative
- most common ions are NH$_4^+$, Na$^+$, Ca$^{2+}$, Cl$^-$, SO$_4^{2-}$, HCO$_3^-$, CO$_3^{2-}$
Electroneutrality Principle
(Nazaroff & Alvarez-Cohen, page 45)

It can almost always be assumed that the initial water solution is electrically neutral, that is, it has no net electric charge. Then, conservation of electrons demands that this state of neutrality persist over time. Therefore, for every extra electron on an anion in the solution, there must be a missing electron from a cation in the same solution, and

\[ \sum z_i [A_i] = 0 \]

where \( z_i \) = charge of ion \( A_i \) (+ for cation, – for anion), most often +1, +2, – 1 or – 2

\([A_i]\) = molar concentration of ion \( A_i \).

Example: The Carbonate System
(Nazaroff & Alvarez-Cohen, section 3.C.4)

Carbon dioxide \( \text{CO}_2 \) from the atmosphere partially dissolves in water. In water, it then forms carbonic acid \( \text{H}_2\text{CO}_3 \). In turn, \( \text{H}_2\text{CO}_3 \) dissolves into \( \text{H}^+ \) and bicarbonate ion \( \text{HCO}_3^- \), and \( \text{HCO}_3^- \) into another \( \text{H}^+ \) and carbonate ion \( \text{CO}_3^{2-} \).

Thus, the following reactions take place in water exposed to the atmosphere:

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \leftrightarrow \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}
\end{align*}
\]

In addition, water \( \text{H}_2\text{O} \) always decomposes slightly into \( \text{H}^+ \) and \( \text{OH}^- \):

\[
\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-
\]

Electroneutrality requires:

\[ [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \]
The equilibrium relations are:

\[
\begin{align*}
\text{CO}_2 \text{ in the water} & \leftrightarrow \text{CO}_2 \text{ in the air} & [\text{CO}_2] = K_p, P_{\text{CO}_2}, K_p = 0.034 \text{ M/atm} \\
\text{CO}_2 \text{ in the water} + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{CO}_3 & [\text{H}_2\text{CO}_3] = [\text{CO}_2] = 1.58 \times 10^{-3} \\
\text{H}_2\text{CO}_3 & \leftrightarrow \text{H}^+ + \text{HCO}_3^- & [\text{H}^+] [\text{HCO}_3^-] = 2.834 \times 10^{-2} \text{ M} \\
\text{HCO}_3^- & \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} & [\text{H}^+] [\text{CO}_3^{2-}] = 4.68 \times 10^{-11} \text{ M} \\
\text{H}_2\text{O} & \leftrightarrow \text{H}^+ + \text{OH}^- & [\text{H}^+] [\text{OH}^-] = 10^{-14} \text{ M}^2
\end{align*}
\]

Do we have enough equations?

Number of unknowns = 6 for [CO\textsubscript{2}], [H\textsubscript{2}CO\textsubscript{3}], [HCO\textsubscript{3}\textsuperscript{-}], [CO\textsubscript{3}\textsuperscript{2-}], [H\textsuperscript{+}] and [OH\textsuperscript{-}]

Number of equations = 6 = 5 (above) + 1 (electroneutrality at bottom of previous slide).

So, yes, we have enough equations to solve the problem.

For a partial pressure of CO\textsubscript{2} in the atmosphere equal to 350 ppm, we have

\[
[\text{CO}_2] = (0.034 \text{ M/atm}) (350 \times 10^{-6} \text{ atm}) = 1.24 \times 10^{-5} \text{ M}
\]

From the first chemical equilibrium, we deduce:

\[
[H_2CO_3] = (1.58 \times 10^{-3}) [CO_2] = (1.58 \times 10^{-3})(1.24 \times 10^{-5} \text{ M}) = 1.88 \times 10^{-8} \text{ M}
\]

We solve the remaining simultaneous equations and obtain:

\[
\begin{align*}
[\text{HCO}_3^{-}] &= 2.31 \times 10^{-6} \text{ M} \\
[\text{CO}_3^{2-}] &= 4.67 \times 10^{-11} \text{ M} \\
[\text{OH}^-] &= 4.33 \times 10^{-9} \text{ M} \\
[\text{H}^+] &= 2.31 \times 10^{-6} \text{ M}
\end{align*}
\]

Thus, the pH of natural (clean) water is

\[
pH = -\log_{10}[\text{H}^+] = 5.64
\]

Clean, natural water is slightly acidic.

And, it is getting increasingly acidic. There is fear that coral in the sea will not survive.
**Question:** What can be done about coral erosion short of curbing CO₂ in the atmosphere?

**Answer:** Use calcium, or simply rely on the calcium that is naturally there.

\[
\begin{align*}
\text{CaCO}_3 & \leftrightarrow \text{Ca}^{++} + \text{CO}_3^- \\
\text{CO}_3^- + \text{H}^+ & \leftrightarrow \text{HCO}_3^- \\
\text{HCO}_3^- + \text{H}^+ & \leftrightarrow \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \leftrightarrow \text{H}_2\text{O} + \text{CO}_2 \\
\text{CO}_2 \text{ in water} & \leftrightarrow \text{CO}_2 \text{ in air}
\end{align*}
\]

The net effect of limestone is to deliver calcium ions (Ca⁺⁺) that displace protons (H⁺), and thus reduce acidity. There is efficiency in this because one Ca⁺⁺ eliminates two H⁺'s.
But think:

- If a body of water has become too acidic because of some acid input, it is better to eliminate that acid source than to remediate the water body.

- Often, acidity comes from acid precipitation (rain / snow) over the lake.

- This atmospheric acidity is primarily in the form of sulfuric acid (H$_2$SO$_4$) and nitric acid (HNO$_3$).

- Sulfuric acid is the consequence of burning coal with sulfur content, creating SO$_2$ in the combustion fumes that later turn into H$_2$SO$_4$.

- Nitric acid originates from NO$_2$ out of tailpipes of gas and diesel engines.

- Solutions therefore consist in
  - Scrubbing the SO$_2$ from fumes before release through the smokestack.
  - Burning low-sulfur coal.
  - Burning some fuel other than coal for electricity.
  - Getting electricity from windmills or other non-fuel alternatives.
  - Regulate tailpipe emissions.
  - Have people drive better cars.
  - Have people drive less.
  - Reduce food shipment by consuming local foods.