Vapor Pressure
(Nazaroff & Alvarez-Cohen, Section 3.B.1)

When a liquid comes in contact with the air, a fraction of it will go into vapor phase and mix with the air. An equilibrium is reached in the absence of perturbing processes.

If the liquid is a pure substance $A$, the partial pressure $P_A$ at equilibrium, called vapor pressure, can be obtained directly from a table. See next slide.

In the presence of perturbing processes, the situation may be kept away from equilibrium.
- When the partial pressure of the substance is less than the vapor pressure, a condition called subsaturation, there is net evaporation.
- Conversely, when the partial pressure exceeds the vapor pressure, a condition called supersaturation, there is net condensation.

Vapor pressures of some organic substances (at 25°C)

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>Molecular Weight (g/mole)</th>
<th>Vapor pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>C$_3$H$_6$O</td>
<td>58</td>
<td>28600</td>
</tr>
<tr>
<td>Benzene</td>
<td>C$_6$H$_6$</td>
<td>78</td>
<td>12800</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>C$<em>{20}$H$</em>{12}$</td>
<td>252</td>
<td>$7 \times 10^{-7}$</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl$_3$</td>
<td>119.4</td>
<td>26000</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>C$_{10}$H$_8$Cl$_2$O</td>
<td>380</td>
<td>$7 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C$_2$H$_5$OH</td>
<td>46</td>
<td>0.082</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>C$<em>{10}$H$</em>{10}$</td>
<td>106</td>
<td>1280</td>
</tr>
<tr>
<td>Ethylene dibromide</td>
<td>CH$_2$Br$_2$</td>
<td>176</td>
<td>270</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH$_3$OH</td>
<td>32</td>
<td>0.18</td>
</tr>
<tr>
<td>n-octane</td>
<td>C$<em>8$H$</em>{18}$</td>
<td>114</td>
<td>1890</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C$_{10}$H$_8$</td>
<td>128</td>
<td>10.6</td>
</tr>
<tr>
<td>Phenol</td>
<td>C$_7$H$_8$O</td>
<td>94</td>
<td>26</td>
</tr>
<tr>
<td>2,3,7,8-TCDD</td>
<td>C$_2$H$_8$O$_2$Cl$_4$</td>
<td>322</td>
<td>$2 \times 10^{-7}$</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>C$_2$Cl$_4$</td>
<td>166</td>
<td>2550</td>
</tr>
<tr>
<td>Toluene</td>
<td>C$_8$H$_8$</td>
<td>92</td>
<td>3850</td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>C$_3$H$_7$Cl$_3$</td>
<td>133.4</td>
<td>16800</td>
</tr>
<tr>
<td>Trichloroethylene (TCE)</td>
<td>C$_2$HCl$_3$</td>
<td>131.4</td>
<td>9900</td>
</tr>
</tbody>
</table>

(Nazaroff & Alvarez-Cohen, Table 3.B.1 on page 94)
**Air-water equilibrium**  
(Nazaroff & Alvarez-Cohen, Section 3.B.2)

In the environment, water is often in contact with air, and chemicals are exchanged between the water and air.

An equilibrium is reached in the absence of perturbing processes.

At equilibrium, a fixed ratio is established between the concentration \([A]\) of substance A in the water and its partial pressure \(P_A\) in the air:

\[
[A] = K_H P_A
\]

or, in reverse,

\[
P_A = H[A]
\]

This is known as **Henry's Law**, and \(H = 1/K_H\) is called Henry's Law "constant".

It varies from species to species and is also a function of temperature.

---

### Table: Henry's Law Constants

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>(K_H) (M/atm)</th>
<th>(H) (atm/M)</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>62</td>
<td>0.0181</td>
<td>25°C</td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>0.18</td>
<td>5.6</td>
<td>20°C</td>
</tr>
<tr>
<td>Benzopyrene</td>
<td>C₁₆H₁₂</td>
<td>2040</td>
<td>4.9 x 10⁻⁴</td>
<td>20°C</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>0.034</td>
<td>29</td>
<td>25°C</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>0.0010</td>
<td>1000</td>
<td>20°C</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl₃</td>
<td>0.31</td>
<td>3.2</td>
<td>20°C</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>C₈H₁₀</td>
<td>0.11</td>
<td>9.1</td>
<td>20°C</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>HCHO</td>
<td>6300</td>
<td>1.6 x 10⁻⁴</td>
<td>25°C</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H₂S</td>
<td>0.115</td>
<td>8.7</td>
<td>20°C</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>0.0015</td>
<td>670</td>
<td>20°C</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C₁₀H₈</td>
<td>2.2</td>
<td>0.45</td>
<td>20°C</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>2.1 x 10⁵</td>
<td>4.8 x 10⁻⁴</td>
<td>25°C</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>0.00087</td>
<td>1500</td>
<td>20°C</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td>0.001384</td>
<td>720</td>
<td>20°C</td>
</tr>
<tr>
<td>Phenol</td>
<td>C₆H₅O</td>
<td>2200</td>
<td>4.5 x 10⁻⁴</td>
<td>20°C</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>SO₂</td>
<td>1.24</td>
<td>0.81</td>
<td>25°C</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>C₂Cl₄</td>
<td>0.083</td>
<td>12</td>
<td>20°C</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₇H₈</td>
<td>0.15</td>
<td>6.7</td>
<td>20°C</td>
</tr>
<tr>
<td>Trichloroethane</td>
<td>C₆H₅Cl₂</td>
<td>0.055</td>
<td>18</td>
<td>20°C</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>C₃H₅Cl₂</td>
<td>0.11</td>
<td>9.1</td>
<td>20°C</td>
</tr>
</tbody>
</table>

(Recall: The "molarity" unit \(M\) stands for mole per liter.)
The coefficient of proportionality in Henry's Law is a function of temperature. Hence, the amount of dissolved oxygen and carbon dioxide (among others) in water at equilibrium with the atmosphere will vary with temperature. This means that it varies with the season (summer ↔ winter) and latitude (tropics ↔ high latitudes).

As we see, the $K_H$ values drop with increasing temperature, which means that warmer water is less able to contain oxygen and carbon dioxide than colder water.

### Dissolution of oxygen in water

*(Nazaroff & Alvarez-Cohen, Example 3.B.1 on page 97)*

From the previous table, we note that $K_H$ for oxygen is 0.0015236 M/atm at 15°C. We also know that oxygen accounts for 20.9% of air in the atmosphere. Thus,

$$[O_2] = K_H P_o = (0.0015236 \text{ M/atm})(0.209 \times 1 \text{ atm}) = 3.184 \times 10^{-4} \text{ M} = 3.184 \times 10^{-4} \text{ mol/L}$$

Since the molecular weight of oxygen is 2 x 16 = 32 g/mol, we can convert the preceding number in mg/L:

$$\text{DO} = MW_{O_2} [O_2] = (32 \text{ g/mol})(3.184 \times 10^{-4} \text{ mol/L}) = 0.01019 \text{ g/L} = 10.19 \text{ mg/L}$$

DO stands for Dissolved Oxygen. It is always expressed in mg/L.
After repeating the procedure for various temperatures, we obtain the following table for the equilibrium level of dissolved oxygen in open water.

This quantity is called the *Saturated Value of Dissolved Oxygen* and is noted \( \text{DO}_s \).

<table>
<thead>
<tr>
<th>Temperature ((\degree C))</th>
<th>( \text{DO}_s ) (mg/L)</th>
<th>Temperature ((\degree C))</th>
<th>( \text{DO}_s ) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.6</td>
<td>13</td>
<td>10.6</td>
</tr>
<tr>
<td>1</td>
<td>14.2</td>
<td>14</td>
<td>10.4</td>
</tr>
<tr>
<td>2</td>
<td>13.8</td>
<td>15</td>
<td>10.2</td>
</tr>
<tr>
<td>3</td>
<td>13.5</td>
<td>16</td>
<td>10.0</td>
</tr>
<tr>
<td>4</td>
<td>13.1</td>
<td>17</td>
<td>9.7</td>
</tr>
<tr>
<td>5</td>
<td>12.8</td>
<td>18</td>
<td>9.5</td>
</tr>
<tr>
<td>6</td>
<td>12.5</td>
<td>19</td>
<td>9.4</td>
</tr>
<tr>
<td>7</td>
<td>12.2</td>
<td>20</td>
<td>9.2</td>
</tr>
<tr>
<td>8</td>
<td>11.9</td>
<td>21</td>
<td>9.0</td>
</tr>
<tr>
<td>9</td>
<td>11.6</td>
<td>22</td>
<td>8.8</td>
</tr>
<tr>
<td>10</td>
<td>11.3</td>
<td>23</td>
<td>8.7</td>
</tr>
<tr>
<td>11</td>
<td>11.1</td>
<td>24</td>
<td>8.5</td>
</tr>
<tr>
<td>12</td>
<td>10.8</td>
<td>25</td>
<td>8.4</td>
</tr>
</tbody>
</table>

EPA recommendation for a healthy fish population: \( \text{DO} \geq 5 \text{ mg/L} \)

For better fish, such as trout and salmon, water must have \( \text{DO} \geq 8 \text{ mg/L} \)

---

**In water**

One is often concerned not only by the presence of contaminants but also by the depletion of what should be there, especially

**DISSOLVED OXYGEN.**

Dissolved Oxygen (\( \text{DO} \), in short) is vital to aquatic life. As a rule, the more oxygen is dissolved in the water, the better for the fish and other desirable forms of life. Low \( \text{DO} \) levels do not make good habitats for fish and promote undesirable forms of life such as algae. Low oxygen levels are accompanied by murkiness, sliminess and, sometimes, odor.

The minimum recommended amount of \( \text{DO} \) for a healthy fish population in a stream is 5 mg/L. The EPA recommends at least 8 mg/L for the more desirable cold-water species, such as trout and salmon, during their embryonic and larval stages and the first 30 days after hatching.

At the extreme, water may become *anoxic*, that is, completely lacking dissolved oxygen. Bacteria living in anoxic water produce methane (\( \text{CH}_4 \)), which is flammable, and hydrogen sulfide (\( \text{H}_2\text{S} \)), which has the smell of rotten egg.
Biochemical Oxygen Demand (BOD)
(Nazaroff & Alvarez-Cohen, pages 55-56 and 136-137)

Often, pollution in surface waters is not measured in terms of the concentrations of the individual contaminants but is measured in terms of their aggregate potential for oxygen depletion. This is called the \textit{Biochemical Oxygen Demand (BOD)}.

Substances contributing to BOD are food for bacteria, and the more the bacteria feed on these, the more they also take oxygen (like us humans, who both eat and breathe).

\[
\text{Few cells } + \text{ organic matter } + \text{ O}_2 \rightarrow \text{ more cells } + \text{ CO}_2 + \text{ H}_2\text{O} + \text{ etc.}
\]

The definition is:

1 mg/L of BOD will, after uptake by bacteria, decrease the DO level by 1 mg/L.

\textit{Note}: 1 mg/L of BOD may correspond to more or less than 1 mg/L of the offensive substance.

BOD is determined in the laboratory by measuring the depletion of dissolved oxygen in the contaminated water placed in a closed container, over the course of several days.

An interesting spill accident...

On 9 May 2000, an explosion occurred at the Wild Turkey Distillery in Lawrenceburg, Kentucky. Then, the rear wall of the 7-story bourbon Warehouse “K” collapsed. The estimate of bourbon in the warehouse at the time was between 15,000 to 20,000 casks of 53 gallons each (around a million gallons of whiskey), and this much alcohol cannot burn off all at once.

Torrents of burning alcohol poured from crushed barrels, flowing 300 feet downhill into the Kentucky River. This was the beginning of a local disaster. Firefighters arriving at the Wild Turkey Distillery were met by a stream of burning alcohol moving like lava flow downhill from flaming Warehouse K through a small patch of woods and then into the Kentucky River. It was immediately apparent that the burning warehouse was beyond saving, and firefighters began watering nearby Warehouse “I” some 260 feet upwind for exposure protection.

The air was filled with “the sweet smell of bourbon.”

Then came reports of a fish kill. On 15 May, an official of the Division of Water stated that the kill was “quite a decent size one.” Two days later other sources reported that the fish kill might possibly be the largest in state history.

In May 2000 a seven story warehouse containing 1 million gallons of whiskey burned in Lawrenceburg, KY. A similar fire in November 1699 in Bardstown, KY, destroyed seven such warehouses.

Alcohol is ethanol:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} - \text{C} - \text{O} & - \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

\[
\text{C}_2\text{H}_5\text{OH}
\]
By 19 May, the count of dead fish had reached tens of thousand. At that time, what officials described as “a slug of dead water” moving down the river had reached the confluence of the Kentucky River with the Ohio River. “The actual area of influence measures some 5 to 6 miles in length with a critical zone of 2 to 4 miles, moving at a rate of about 5 miles per day,” said Pete Pfeiffer of the state Department of Fish and Wildlife Resources. “They (the fish) were literally jumping over the dam. Someone said that there were so many dead fish across the mouth of Elkhorn Creek that you could literally walk across it.”

Officials had hoped that turbulence resulting from the plume of bourbon traveling over a series of locks and dams along the river would disperse the effect, but this was not the case. On 18 May, the EPA, assisted by contractors, began aeration of the affected area. Much like providing oxygen to a home aquarium, the EPA used 6 barges equipped with large oxygen compressors and trailing submerged perforated piping. The plan called for pumping oxygen back into the river where the DO level had dropped below 0.50 mg/L.

**FISH MAKE POOR PARTY ANIMALS**

According to a recent newspaper article, there was a liquor spill into the Kentucky River. Bourbon supposedly contaminated an eight mile stretch.

I immediately called one of my trusted sources who lives in the area. He confirmed it. "It wuz sumtin to behold. Them fish went totally crazy. They wuz jumpin an stannin on der tails. Carryin on like a bunch o’ wild turkeys, they wuz, yessir. Never seen nuttin like it, nope, never. Bit of a problem though. Seems none of dem fish could hole his likker. Guess maybe they drank too much. They all started turnin wheels up. We gathered up a parcel. They wuz still mighty tasty. Even o' Aunt Myrtle musta et a bunch. Never saw her go after fish like that before."
Acid-base chemistry – The example of ammonia in water
(Nazaroff & Alvarez-Cohen, Section 3.C.1)

Ammonia (NH₃) is often generated on farms as a by-product of animal manure. Because of its nitrogen content, it is a good soil nutrient, but in water, it affects the pH.

In water, ammonia forms the ammonium ion (NH₄⁺) via

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad \text{with} \quad \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.70 \times 10^{-5} \text{ M}
\]

Between air and water, Henry's Law constant of NH₃ is 62 M/atm.

If the concentration of ammonia in the air is 50 ppm, what is the pH of the water?
(Assume no CO₂ is present.)

Answer:
First determine [NH₃] in water:

\[
[\text{NH}_3] = 62P_{\text{NH}_3} = (62 \text{ M/atm})(50 \times 10^{-6} \text{ atm}) = 3.10 \times 10^{-3} \text{ M}
\]

Use this in the equilibrium relation:

\[
[\text{NH}_4^+][\text{OH}^-] = (1.70 \times 10^{-5})[\text{NH}_3] = 5.27 \times 10^{-4} \text{ M}^2
\]

Finally, apply the constant of dissociation of water and electroneutrality:

\[
[\text{H}^+][\text{OH}^-] = 10^{-14} \Rightarrow [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} \Rightarrow [\text{NH}_4^+] = 5.27 \times 10^{-4}[\text{H}^+]
\]

\[
[\text{H}^+] + [\text{NH}_4^+] = [\text{OH}^-] \Rightarrow [\text{H}^+] + 5.27 \times 10^{-4}[\text{H}^+] = \frac{10^{-14}}{[\text{H}^+]} \Rightarrow [\text{H}^+] = 4.36 \times 10^{-11} \Rightarrow pH = -\log_{10}(4.36 \times 10^{-11}) = 10.4
\]

Ammonia can act as a strong base!

Does that mean that we could dump ammonia in lakes that have become acidified by acid rain???
Consider:

1. Equilibrium between water and atmosphere would mean that much of the ammonium in the water would leak as ammonia in the air and be swept away with the wind. The system has a big leak!

2. Ammonia in the air has a pungent odor. So, these lakes would smell bad.

3. Ammonia even at dilute concentrations is highly toxic to aquatic animals, and for this reason it is classified as dangerous for the environment.

Answer: Very bad idea!

So, what would be a better idea to remedy acid lakes?

Examples of harmful organic chemicals

**Formaldehyde:** HCHO
- component in resins for bonding & laminating
- also found in wood combustion & tobacco smoke
- creates odor and irritates mucous membranes
- may cause cancer
- New building smell !!!

**Chlorofluorocarbons:** ex. CClF₂ and CHClF₂ (known as R-22)
- unknown to nature
- used as refrigerants, propellants, foaming agents
- causes depletion of stratospheric ozone
- → skin cancer at ground level

**Benzene:** C₆H₆
- basic block of aromatic compounds
- used as solvent, gasoline additive
- produced by incomplete petroleum combustion
- found in tobacco smoke
- known human carcinogen
Vinyl Chloride: $\text{C}_2\text{H}_3\text{Cl}$

Trichloroethylene (TCE): $\text{C}_2\text{H}_3\text{Cl}_2$

Perchloroethylene (PCE, “perc”): $\text{C}_2\text{Cl}_4$

solvents, cleaners
feedstocks for other chemicals
contaminate soil & groundwater

Dichloromethane: $\text{CH}_2\text{Cl}_2$

Trichloroethane (TCA): $\text{C}_2\text{H}_3\text{Cl}_3$

same as above

Dioxin:
- compounds with two benzene rings bridged by two oxygen atoms and some chlorine replacing hydrogen
- not produced intentionally rather a by-product after release of chlorinated compounds also produced during incineration of plastics (PVC)
- one of the most toxic organic substances caused by humans persistent in the environment hurts wildlife and damages ecosystems.

Herbicides and insecticides
- used in agriculture to control monocultures toxic to humans inside the factory where they are manufactured residuals find their way on our food and in our groundwater.