Introduction to Mass and Energy Balances

• Mass and energy are conserved. They cannot be created or destroyed.
• This allows us to track materials and energy in the environment. Pollutants and energy must go somewhere.
• An individual chemical species may react and take a different form. For example, elemental mercury may react to form monomethylmercury (HgCH₃) but the amount of the element Hg does not change in that chemical process.
Units of Measurement

The large and the small – common prefixes

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Prefix</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-9}$</td>
<td>nano</td>
<td>n</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>micro</td>
<td>$\mu$</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>milli</td>
<td>m</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>centi</td>
<td>c</td>
</tr>
<tr>
<td>$10^{3}$</td>
<td>kilo</td>
<td>k</td>
</tr>
<tr>
<td>$10^{6}$</td>
<td>mega</td>
<td>M</td>
</tr>
<tr>
<td>$10^{9}$</td>
<td>giga</td>
<td>G</td>
</tr>
<tr>
<td>$10^{12}$</td>
<td>tera</td>
<td>T</td>
</tr>
</tbody>
</table>

Units - Concentrations in Liquids (Water)

Usually mass of substance per unit volume of mixture:
mg or $\mu$g per liter (L) of mixture or per cubic meter (m$^3$).
Alternatively, mass of substance per mass of mixture:
parts per million (ppm by weight) or parts per billion (ppb by wt.).

For dilute solutions in water,
1 mg/L = 1 g/m$^3$ = 1 ppm (by wt.)
1 $\mu$g/L = 1 mg/m$^3$ = 1 ppb (by wt.).

Examples: 1 ppm is about the same as one drop added to 15 gallons. 1 ppb is about the same as one drop in a large backyard swimming pool (70 m$^3$).
## Units - Concentrations in Solids (Coal)

Usually mass of substance per mass of mixture: $\mu g/g$ or $ng/g$ or parts per million (ppm by weight) or parts per billion (ppb by wt.).

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Elk/Norm/Hazard</th>
<th>Pittsburgh</th>
<th>Illinois 6</th>
<th>Wyodak</th>
<th>Wyodak</th>
<th>Ohio 5,6,7</th>
<th>ND Lignite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>low S bit</td>
<td>med S bit</td>
<td>high S bit</td>
<td>PRB</td>
<td>PRB</td>
<td>high S bit</td>
<td>lignite</td>
</tr>
<tr>
<td><strong>ANALYSIS (As Received):</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Carbon</td>
<td>74.87</td>
<td>76.62</td>
<td>67.70</td>
<td>53.20</td>
<td>51.19</td>
<td>71.07</td>
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<td>Hydrogen</td>
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<td>4.80</td>
<td>4.73</td>
<td>4.59</td>
<td>4.64</td>
<td>4.81</td>
<td>2.60</td>
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<tr>
<td>Oxygen</td>
<td>8.38</td>
<td>6.91</td>
<td>9.19</td>
<td>20.74</td>
<td>12.29</td>
<td>8.10</td>
<td>12.52</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.43</td>
<td>1.48</td>
<td>1.18</td>
<td>0.83</td>
<td>0.72</td>
<td>1.37</td>
<td>0.42</td>
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<tr>
<td>Sulfur</td>
<td>0.82</td>
<td>1.64</td>
<td>3.60</td>
<td>0.22</td>
<td>0.32</td>
<td>2.62</td>
<td>0.63</td>
</tr>
<tr>
<td>Ash</td>
<td>7.41</td>
<td>7.81</td>
<td>10.26</td>
<td>7.36</td>
<td>6.03</td>
<td>9.70</td>
<td>9.38</td>
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<td>Moisture</td>
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<td>1.44</td>
<td>3.31</td>
<td>13.06</td>
<td>25.81</td>
<td>2.33</td>
<td>35.88</td>
</tr>
<tr>
<td>Total</td>
<td>99.83</td>
<td>99.89</td>
<td>99.96</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Hg, ug/g</td>
<td>0.13</td>
<td>0.11</td>
<td>0.22</td>
<td>0.19</td>
<td>0.13</td>
<td>0.15</td>
<td>0.13</td>
</tr>
<tr>
<td>Cl, ug/g</td>
<td>1660</td>
<td>976</td>
<td>338 **</td>
<td>26</td>
<td>974</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Br, ug/g</td>
<td>25.0</td>
<td>17.0</td>
<td>3.7</td>
<td>2.4</td>
<td>1.2</td>
<td>23.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Cl/Br</td>
<td>66</td>
<td>57</td>
<td>91</td>
<td></td>
<td>22</td>
<td>42</td>
<td>19</td>
</tr>
</tbody>
</table>

**Not measured

*Coal analyses taken from DOE Toxics program*

Geoff Silcox, Chemical Engineering, U of Utah

## Units - Concentrations in Gases (Air)

Usually in volumetric terms:

\[
\text{volume of gaseous pollutant} \quad \frac{\text{volume of mixture}}{10^6} = \text{ppm (by volume)} = \text{ppmv}
\]

\[
\text{volume of gaseous pollutant} \quad \frac{\text{volume of mixture}}{10^9} = \text{ppb (by volume)} = \text{ppbv}
\]

\[
\text{volume of gaseous pollutant} \quad \frac{\text{volume of mixture}}{10^{12}} = \text{ppt (by volume)} = \text{pptv}
\]

Frequently in mass per unit volume: $\mu g/m^3$ or $mg/m^3$ or $ng/m^3$.

The relationship between volumetric and mass per volume depends on pressure, temperature, and the molecular weight of the pollutant. The ideal gas equation establishes that relationship.

Geoff Silcox, Chemical Engineering, U of Utah
Units - Concentrations in Gases (Air)

The Ideal Gas Equation

\[ PV = nRT \text{ or } PV = \frac{m}{M}RT \]

- \( n \) = number of moles of gas, kmol
- \( T \) = absolute temperature, K
- \( P \) = absolute pressure, kPa
- \( R \) = universal gas constant = 8.314 kJ/(kmol K)
  = 8.314 (kPa m³)/(kmol K)
- \( V \) = volume, m³
- \( M \) = molecular or atomic weight of gas, kg/kmol
- \( m \) = mass of gas, kg, where \( m = n \cdot M \)

Example. The ambient concentration of elemental mercury in the atmosphere of the Northern Hemisphere is about 0.4 pptv. Calculate the concentration as ng/m³ at temperature 300 K and pressure 1 atm.

\[
\frac{V_{\text{pol}}}{V_{\text{mix}}} = \frac{n_{\text{pol}}RT}{V_{\text{mix}}} \quad \text{ ppt } = \frac{V_{\text{pol}}}{V_{\text{mix}}} \times 10^{12} = \frac{m_{\text{pol}}}{M_{\text{pol}}} \frac{RT}{P} \times 10^{12} = \frac{m_{\text{pol}}}{V_{\text{mix}}} \frac{RT}{10^{12}}
\]

\[
m_{\text{pol}} = \left( \frac{\text{ppt}}{RT} \right) M_{\text{pol}} P \times 10^{-12} = \left( 0.4 \right) \frac{200.6 \text{ kg}}{\text{kmol}} \times 101 \text{kPa} \times 10^{-12} = \frac{8.314 \text{kPa m}^3}{\text{kmol K}} \times 300 \text{K} = 3.26 \times 10^{-12} \frac{\text{kg}}{\text{m}^3}
\]

1 kg = 10⁻¹² ng and our final concentration is 3 \( \frac{\text{ng}}{\text{m}^3} \)
Mercury in the Atmosphere

Observed atmospheric total gaseous mercury (TGM) concentrations over the Atlantic Ocean in 1994 [Slemr, 1996] (left panel) and 1996 [Temme et al., 2003] (right panel) are shown in black circles. The error bars represent the standard deviation of the observations within a grid box. Simulations are shown by solid lines.


Geoff Silcox, Chemical Engineering, U of Utah

Material Balances

Universal Balance Equation for Any Extensive Property

Integrated form:

\[
\text{accumulation} = \text{transport} + \text{generation}
\]

Rate form:

\[
\frac{\text{rate of change}}{\text{time}} = \frac{\text{rate of transport in}}{\text{time}} + \frac{\text{rate of generation}}{\text{time}} - \frac{\text{rate of transport out}}{\text{time}} - \frac{\text{rate of consumption}}{\text{time}}
\]

$\text{entering} \rightarrow \text{Checking account with some rate of interest} \rightarrow \text{leaving}$

Geoff Silcox, Chemical Engineering, U of Utah
Material Balances

At steady state,
\[
\text{rate of change of mass of water} = 0
\]

This is a poor assumption for the Great Salt Lake.

Steady State Material Balances

Number of students at U: 29,012 (stock = M)
Rate of graduation: 6,997 per year (flow = F)

\[
\text{rate of change of enrollment} = \text{rate at which students enter} - \text{rate at which students leave} = 0
\]

\[
F = \text{students entering, yr}^{-1} \quad M = \text{number of students attending} \quad F = \text{students leaving, yr}^{-1}
\]

\[
\text{mean residence time of students} = \frac{\text{stock}}{\text{flow}} = \frac{M}{F} = \frac{29,000\ \text{students}}{7,000\ \text{students yr}^{-1}} = 4.1\ \text{yr}
\]

This equation holds only if the system is well mixed.
Steady Material Balances (Global Hg Cycle)

Flows in 10^3 kg/y
Stocks in 10^3 kg

Air (5000)
98% Hg^0, 2% Hg^+2

Estimated residence time in atmosphere
stocks = 5000x10^3 kg = 1 y
flows = 5000x10^3 kg/y

Estimated residence time in marine mixed layer
stocks = 10800x10^3 kg = 5 y
flows = 2200x10^3 kg/y

Land

Global Marine (mixed layer, 10,800)


Unsteady Material Balances

Entering flow
Flow rate \( Q = IV \)
Concentration \( C_a \)

Leaving flow
Flow rate \( Q = IV \)
Concentration \( C \)

\[
\frac{dC}{dt} = QC_a - QC + S - kVC
\]

at time \( < 0 \), \( C = C_0 \)

\( V \) = box volume, m³
\( C \) = concentration, mg/m³
\( S \) = rate at which pollutant is generated, mg/hr
\( Q = IV \) = total flow rate out of the box, m³/hr
\( k \) = reaction rate coefficient for consumption, hr⁻¹

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Energy Balances

The law of conservation of energy applied to a control volume

\[
\text{Time rate of change of energy within system} = \text{net rate of energy crossing boundary} + \text{rate of energy entering as work and heat} - \text{rate of energy exiting with mass}
\]

Mass and Energy Balances

Use mass and energy balances to estimate the mercury emissions from a 1000 MW<sub>e</sub> coal-fired power plant

Data:  Higher heating value of coal (HHV) = 29.3x10<sup>6</sup> J/kg (as received) = 12,600 Btu/lbm
Concentration of Hg in coal [Hg] = 0.1 μg/g (as received)
Overall efficiency of power plant = 0.3

\[
\eta = \frac{\text{desired result}}{\text{required input}} \\
\eta_{\text{overall}} = \frac{W_{\text{electrical}}}{HHV \cdot m_{\text{coal}}}
\]

\[
\eta_{\text{overall}} = \eta_{\text{boiler}} \cdot \eta_{\text{thermal}} \cdot \eta_{\text{generator}}
\]

The efficiencies are determined by experiment.
Mass and Energy Balances

Solve for mass flow rate of coal:

\[ \dot{m}_{\text{coal}} = \frac{W_{\text{electrical}}}{(HHV)\eta_{\text{overall}}} = \frac{1000 \times 10^6 \text{ J/s}}{(29.3 \times 10^6 \text{ J/kg}) 0.3} = 114 \text{ kg/s} \]

Solve for mass flow rate of Hg:

\[ \dot{m}_{\text{Hg}} = [\text{Hg}] \dot{m}_{\text{coal}} = 100 \frac{\mu g \text{ Hg}}{\text{kg coal}} \frac{114 \text{ kg coal}}{\text{s}} = 1.14 \times 10^4 \frac{\mu g}{\text{s}} \]

Change units to give mass flow rate of Hg per year:

\[ \dot{m}_{\text{Hg}} = 1.14 \times 10^4 \frac{\mu g}{\text{s}} \left( \frac{365 \times 24 \times 3600 \text{ s}}{\text{yr}} \right) \left( \frac{10^{-9} \text{ kg}}{1 \mu g} \right) = 359 \frac{\text{kg}}{\text{yr}} \]

Conclusions

(1) Our calculation to estimate the mercury flow rate may be off by a factor of two but it is more useful than no calculation at all.

(2) Simple calculations involving units and material and energy balances can help clarify discussions of policy, regulation, risk assessment, and law.

(3) Simple calculations can help detect errors and half truths.

(4) Simple models based on material and energy balances will allow you to explore the consequences of assumptions, policies, and regulations.

(5) Mathematics is a global language and can help avoid confusion.