The Air We Breathe

Practice Problems:
All Ch. 1 problems with the blue codes or answers on Page 520

Consider this (1.1):

- What is the total volume of air that you exhale in a typical day?
- Discuss methods of estimation and calculation
  - Volume in 1 exhaled breath
  - Breathing rate (breaths per minute)
  - Number of exhaled breaths per day

Composition of Air

- Homogeneous mixture
- Type of matter composed of several substances in varying proportions
- Constituents of air are physically combined but not chemically combined

Major Components of Air

- Nitrogen, N₂ (78%)
- Oxygen, O₂ (21%)
- Argon, Ar (0.9)
- Carbon Dioxide, CO₂ (365 ppm)
- Water, H₂O (variable levels)
- Trace gases (CO, N₂O, CH₄, NH₃, SO₂, and VOCs) at less than 10 ppm
Concentration Units

- Relative concentration
  - 21% oxygen means 21 oxygen molecules out of 100 air molecules or 21 liters of oxygen in 100 liters of air.
  - Parts per million (ppm) and parts per billion (ppb) are used for trace levels of pollutants
    - 1% = 10,000 ppm; 1 ppm = 1000 ppb
- Absolute concentration
  - Microgram per cubic meter ($\mu g/m^3$)

Influence of T & P on V

- Volume (V) of a gas increases with increasing temperature (T) but decreases with increasing pressure (P)
- Hence, T and P values must be specified in the measurements of V or absolute concentrations of gases.
- The concentration of a chemical species in gaseous state stays constant in ppm units but is different in $\mu g/m^3$ units.

Units for Trace Quantities

- Concentrations
  - Parts per million, ppm ($10^{-6}$)
  - Parts per billion, ppb ($10^{-9}$)
  - Parts per trillion, ppt ($10^{-12}$)
- Amounts or mass
  - Microgram ($\mu g$ or $10^{-6}$ g)
  - nanogram (ng or $10^{-9}$ g)
  - picogram (pg or $10^{-12}$ g)
  - femtogram (fg or $10^{-15}$ g)
**Parts per million (PPM)**

- 1 second in 12 days
- 1 penny out of $10,000
- Pinch of salt on 20 pounds of chips
- 1 yard out of the length of $10^4$ football fields
- PPM is the unit of choice in air pollutions measurements

**Conversion of Concentration Units**

- Units of “ppm” useful for expressing low concentrations
- For example, can we have less than one particle of CO$_2$ as in 0.0365 CO$_2$ particles / 100 air particles? It is preferable to say 365 ppm of CO$_2$.
- Your Turn 1.4 on Page 7
- 9 ppm CO = ? % CO
- 75% N$_2$ = ? ppm N$_2$

**Nitrogen**

- Most abundant substance in air
- Relatively inert but form nitrogen oxides during combustion processes or lightning
- Industrially useful (e.g. ammonium or nitrate fertilizers, acrylonitrile

**Oxygen**

- Needed to sustain life via respiration and various physiological reactions
- Very reactive element capable of supporting combustion and oxidation
- Most abundant element in the Earth’s crust (as H$_2$O, rocks, and soil) and human body
- Isolated in 1770’s by Joseph Priestly
Argon (Ar)

- Non-reactive and exists as single atomic particles
- Also called inert, noble, or rare gas
- Belongs to Group 18 or VIII A that also include He, Ne, Kr, Xe, and Rn
- All Group VIII A elements except He have the stable configuration of 8 electrons in the outermost shell.
- Present in air at 0.9%

Composition of Inhaled and Exhaled Air

Exhaled air contains higher levels of carbon dioxide and water, which are the oxidation products of oxygen in the respiration process.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Inhaled Air (%)</th>
<th>Exhaled Air (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>78.0</td>
<td>75.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>21.0</td>
<td>16.0</td>
</tr>
<tr>
<td>Argon</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.04</td>
<td>4.0</td>
</tr>
<tr>
<td>Water</td>
<td>0.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Table 1.2

Consider this (1.3):

- How would life on earth be different if the oxygen content in the atmosphere were doubled to 40%?
- Burning, rusting, metabolic processes?

Air Quality Improvement

Improvement in the design of combustion engines lead to the reduction of CO and Nox levels. Phasing out the use of tetraethyl lead in leaded gasoline is responsible for the sharp decrease in lead.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Percent Decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>57</td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>25</td>
</tr>
<tr>
<td>Ozone</td>
<td>20</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>50</td>
</tr>
<tr>
<td>PM</td>
<td>**</td>
</tr>
<tr>
<td>Lead</td>
<td>94</td>
</tr>
</tbody>
</table>

Table 1.1

*These are overall percent changes. Changes for a particular urban area may differ.


1999-1999 PM10 standards were first set in 1999.
Criteria Air Pollutants

- Carbon monoxide, CO
- Sulfur dioxide, SO₂
- Ozone, O₃
- Nitrogen oxides, NOₓ
- Particulate matter, PM₁₀ & PM₂.₅
- Lead, Pb

All 6 pollutants are regulated by National Ambient Air Quality Standard

Sources of Environmental Data

- Environmental Protection Agency
  
  www.epa.gov

- Also check out www.scorecard.org

Find current pollutant levels for Murfreesboro (Nashville)

CO, NOₓ, SO₂, and O₃

Are we above or below or at accepted levels?

Effects of Criteria Pollutants

- CO binds hemoglobin in blood and prevents the transport of O₂ to tissues in body for metabolism.
- O₃ leads to respiratory problems
- NOₓ and O₂ leads to respiratory problems and acid rain
- Particulate matter has been linked to increased mortality and morbidity.
- Lead is associated with neurological disorder.

Table 1.3

Major Gaseous Air Pollutants for Selected Cities in the United States, 1996 and 2000

<table>
<thead>
<tr>
<th>City</th>
<th>Carbon Monoxide</th>
<th>Ozone**</th>
<th>Sulfur Oxides***</th>
<th>Nitrogen Oxides****</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1996 ppm</td>
<td>0.12 ppm</td>
<td>0.08 ppm</td>
<td>0.01 ppm</td>
</tr>
<tr>
<td></td>
<td>2000 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atlanta</td>
<td>4.28</td>
<td>0.14</td>
<td>0.032</td>
<td>0.027</td>
</tr>
<tr>
<td>Boston</td>
<td>2.37</td>
<td>0.18</td>
<td>0.036</td>
<td>0.031</td>
</tr>
<tr>
<td>Chicago</td>
<td>2.13</td>
<td>0.09</td>
<td>0.032</td>
<td>0.032</td>
</tr>
<tr>
<td>Detroit</td>
<td>4.55</td>
<td>0.12</td>
<td>0.059</td>
<td>0.021</td>
</tr>
<tr>
<td>Houston</td>
<td>3.89</td>
<td>0.20</td>
<td>0.011</td>
<td>0.045</td>
</tr>
<tr>
<td>Indianapolis</td>
<td>3.40</td>
<td>0.12</td>
<td>0.041</td>
<td>0.018</td>
</tr>
<tr>
<td>Los Angeles</td>
<td>7.50</td>
<td>0.18</td>
<td>0.046</td>
<td>0.023</td>
</tr>
<tr>
<td>New Orleans</td>
<td>4.00</td>
<td>0.11</td>
<td>0.035</td>
<td>0.018</td>
</tr>
<tr>
<td>New York City</td>
<td>4.66</td>
<td>0.12</td>
<td>0.055</td>
<td>0.042</td>
</tr>
<tr>
<td>Pittsburgh</td>
<td>4.24</td>
<td>0.11</td>
<td>0.070</td>
<td>0.020</td>
</tr>
<tr>
<td>San Francisco</td>
<td>2.28</td>
<td>0.10</td>
<td>0.007</td>
<td>0.022</td>
</tr>
<tr>
<td>Saint Louis</td>
<td>6.22</td>
<td>0.13</td>
<td>0.102</td>
<td>0.025</td>
</tr>
</tbody>
</table>

*Second highest 8 hr avg
**Second highest 24 hr avg
***Second highest 24 hr avg
****Yearly avg
*Chaged to 80 ppb for 8 hr avg

Table 1.3 Page 8
Adverse Effects of Pollutants

- Dangerous element or factor with the possibility of causing loss or injury
- Toxicity
  - Intrinsic hazard of a substance
- Exposure
  - Amount of substance encountered that is related to its concentration or the duration of exposure

Risk Assessment of Pollutants

- Human population studies
  - Epidemiology of human exposure to contaminants in food or environment
- Animal studies
  - Establish lethal doses (LD$_{50}$) for small animals like mice and rabbits.
- Bacterial studies
  - Ames Test with Salmonella typhimurium

Atmosphere

- Troposphere: surface of Earth
- Stratosphere: includes ozone layer
- Mesosphere: highest layer

Composition, atmospheric pressure, and temperature in the three layers of atmosphere vary according to altitude.

Table 1.4 Page 11

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Limit, ppm</th>
<th>Limits, µg/m$^3$ (concentration approximately equivalent to ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>8-hr average 9</td>
<td>110.000</td>
</tr>
<tr>
<td></td>
<td>1-hr average 35</td>
<td>40,000.000</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>Annual arithmetic mean 0.053</td>
<td>180.000</td>
</tr>
<tr>
<td>Ozone</td>
<td>8-hr average 0.12</td>
<td>215.000</td>
</tr>
<tr>
<td></td>
<td>Annual arithmetic mean 0.08</td>
<td>157.000</td>
</tr>
<tr>
<td>Lead</td>
<td>Quarterly average 1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Particulates</td>
<td>≤ 10 µm (PM$_{10}$), 24-hr average* —</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>≤ 10 µm (PM$_{10}$), annual arithmetic mean* —</td>
<td>150.000</td>
</tr>
<tr>
<td></td>
<td>≤ 2.5 µm (PM$_{2.5}$), 24-hr average* —</td>
<td>30.000</td>
</tr>
<tr>
<td></td>
<td>≤ 2.5 µm (PM$_{2.5}$), annual arithmetic mean* —</td>
<td>85.000</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>Annual arithmetic mean 0.01</td>
<td>30.000</td>
</tr>
<tr>
<td></td>
<td>24-hr average 0.60</td>
<td>365.000</td>
</tr>
<tr>
<td></td>
<td>3-hr average 0.80</td>
<td>1200.000</td>
</tr>
</tbody>
</table>

*Refers to airborne particles that are present or equal to 10 µm or in diameter (PM$_{10}$) and equal to or smaller than 2.5 µm in diameter (PM$_{2.5}$).
*Excluded for information only. A 1999 Federal Court ruled the implementation of these standards, which EPA proposed in 1997. The EPA has asked the Supreme Court to reconsider that decision, which it has agreed to do.
Pressure defined as force exerted by “air” molecules per unit area.
- AP decreases with altitude; higher you go, fewer air molecules, less pressure.
- Outer space = vacuum

Mass and Weight
- Mass: Amount of matter in an object measured in kilogram or grams
- Weight: Measurement of mass due to gravitational constant (9.8 m/s²) and varies according to locations.
- Mass of an object is independent of locations whereas an object weighs less on the Moon or the outer space relative to its weight on the Earth.

Types of Matter
- Pure substances: Elements (atoms) and compounds (molecules or formula units)
- Mixtures: Physical combination of 2 or more substances in variable amounts
Elements and Compounds

- Elements are substances that cannot be broken down into simpler substances by chemical means.
- All known elements are listed on the Periodic Table.
- Compounds are pure substances made of 2 or more elements in a fixed, characteristic chemical composition and combination.
- Over 20 million and counting.

Periodic Table

- At least 109 elements arranged in the order of increasing atomic number.
- Mendeleev and Meyer first proposed the Periodic Table based on 66 known elements at their time.
- Periodic trends of similar chemical & physical properties are observed in groups or vertical columns of elements in the Periodic Table.

Table 1.5: Classification of Matter

<table>
<thead>
<tr>
<th>Observable Properties</th>
<th>Atomic Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Cannot be broken down into</td>
</tr>
<tr>
<td></td>
<td>simpler substances</td>
</tr>
<tr>
<td>Compound</td>
<td>Fixed composition, but capable</td>
</tr>
<tr>
<td></td>
<td>of being broken down into</td>
</tr>
<tr>
<td></td>
<td>elements</td>
</tr>
<tr>
<td>Mixture</td>
<td>Variable composition of elements</td>
</tr>
<tr>
<td></td>
<td>and/or compounds</td>
</tr>
<tr>
<td></td>
<td>Only one kind of atom</td>
</tr>
<tr>
<td></td>
<td>Two or more atoms in fixed</td>
</tr>
<tr>
<td></td>
<td>combination</td>
</tr>
<tr>
<td></td>
<td>Variable assortment of atoms</td>
</tr>
<tr>
<td></td>
<td>and/or molecules</td>
</tr>
</tbody>
</table>
Classification of Elements

- “Staircase” in Periodic Table divides the metallic elements from the non-metallic elements.
- Metals are to the left of the “staircase”; groups 1-15.
- Non-metals are to the right of the “staircase”; groups 14 -18.

Metalloids

- Metalloids are elements with both metallic and non-metallic properties or characteristics intermediate between those of metals and non-metals.
- Metalloids include elements adjacent to the “staircase” such as Si, B, Ge, Sb, and Te.
- Metalloids in groups 13 to 17 are useful in making semiconductors.

Atom

- Smallest unit of an element that can exist as a stable, independent, and chemically indivisible entity.

H₂O As A Compound

- Formula shows 2 hydrogen atoms bonded to 1 oxygen atom, which is 16x the weight of a hydrogen atom.
- Therefore, the mass ratio of oxygen to hydrogen is about 8:1 or 11 g H to 89 g O in 100 g of H₂O (constant composition).
- H₂O has constant chemical and physical properties such as colorless, odorless with BP=100°C and FP=0 °C and serves as a universal solvent.
Molecules and Formulas

- Molecules are the combination of a fixed number of atoms bonded together in a certain geometric arrangement.
- Formulas are symbolic representation of elemental composition in molecules with numerical subscripts denoting the numbers of atoms bonded together.
- Compound: CO$_2$, H$_2$O, C$_6$H$_{12}$O$_6$
- Element: N$_2$, O$_2$, and O$_3$

Formulas and Names of Compounds

- Metals combined with non-metals to yield ionic compounds.
- Binary ionic compounds consisting of 2 elements are named with the metals first followed by non-metals that ends with “ide”.
- NaCl, sodium chloride
- MgBr$_2$, magnesium bromide

Naming Covalent Compounds

- 2 or more non-metals can combine with one another to yield covalent compounds.
- Subscripts in the formula indicate the ratio of atoms in the compounds and are denoted by prefixes in the compound names.
- CO$_2$ carbon dioxide, CO carbon monoxide, BF$_3$: boron trifluoride, CCl$_4$: carbon tetrachloride, PCl$_5$: phosphorous pentachloride, SF$_6$: sulfur hexachloride

Chemical Reactions

- Chemical reactions refer to the transformation of reactants into products via the re-arrangement of chemical bonds.
- Heat, light, sound, production of gas or precipitate, and changes in color or physical state may be observed.
- Chemical reactions are needed to obtain consumer items such as fuels, drugs, soaps, perfumes, and plastic products.
Combustion Reaction

- Combustion or burning is rapid combination of O₂ with another material to provide heat energy.
- Combustion of hydrocarbon fuels (e.g. methane, propane, gasoline, diesel) results in the production of CO₂ and H₂O as major products.
- CH₄ + O₂ → CO₂ + 2 H₂O

Physical State of Matter

- Physical states of reactants and products are usually denoted in chemical equations.
  - Solid (s)
  - Gas (g)
  - Liquid (l)
  - Aqueous solution (aq)

Conservation of Matter and Mass

- In a chemical reaction, matter and mass are conserved.
- Since matter is neither created nor destroyed in a chemical reaction, mass reactants = mass products.
- Composition of reactants are transformed and chemical equations have to be balanced for mass of elements in reactants and products.

Oxidation of Carbon

- C + O₂ → CO₂ Complete oxidation
- 2 C + O₂ → 2 CO Partial oxidation
Changes in Chemical Bonding via Reactions

\[ \text{N}_2 + \text{O}_2 \rightarrow 2 \text{NO} \]

\[ 2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} \]

Hydrocarbons

- Compounds composed of hydrogen and carbon only.
- Over 3 million compounds known and range from the smallest hydrocarbon of \( \text{CH}_4 \) (main constituent of natural gas) to hydrocarbon waxes with \( \text{C}_{40} \).
- Hydrocarbons have high energy content in fossil fuels like coal and petroleum.
- Gasoline (C5-C13) and diesel (C10-C30) are homogeneous hydrocarbon mixtures.

Combustion of Hydrocarbons

- Hydrocarbons are combustible in air.
- \( \text{CH}_4 + \text{O}_2 \) (in air) \( \rightarrow \) \( \text{CO}_2 + \text{H}_2\text{O} \)
- Equation balanced by filling in stoichiometric coefficients to give equal numbers of each type of atoms in reactants and products.
- \( \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \)
- Complete oxidation of hydrocarbons leads to the formation of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \).

Combustion of Gasoline

- Gasoline is a mixture of hydrocarbons that includes \( \text{C}_8\text{H}_{18} \).
- \( \text{C}_8\text{H}_{18} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \)
- Balance carbon first followed by hydrogen, and oxygen last.
- Coefficients must be whole numbers.
- \( 2 \text{C}_8\text{H}_{18} + 25 \text{O}_2 \rightarrow 16 \text{CO}_2 + 18 \text{H}_2\text{O} \) (100% combustion)
Incomplete Combustion

- Forms other products such as carbon monoxide, methanol, formaldehyde, benzene, and 1,3-butadiene.
- Catalytic converters help remove the emission of these volatile organic compounds that lead to ozone formation in the troposphere.
- Fuel quality and auto emission standards are necessary to protect air quality.

Urban Air Quality

**Table 1.9**

<table>
<thead>
<tr>
<th>City</th>
<th>Days with AQI &gt; 100</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1991</td>
</tr>
<tr>
<td>Atlanta</td>
<td>23</td>
</tr>
<tr>
<td>Boston</td>
<td>13</td>
</tr>
<tr>
<td>Chicago</td>
<td>22</td>
</tr>
<tr>
<td>Detroit</td>
<td>28</td>
</tr>
<tr>
<td>Houston</td>
<td>37</td>
</tr>
<tr>
<td>Indianapolis</td>
<td>12</td>
</tr>
<tr>
<td>Los Angeles</td>
<td>169</td>
</tr>
<tr>
<td>New Orleans</td>
<td>2</td>
</tr>
<tr>
<td>New York City</td>
<td>49</td>
</tr>
<tr>
<td>Pittsburgh</td>
<td>21</td>
</tr>
<tr>
<td>San Francisco</td>
<td>0</td>
</tr>
<tr>
<td>Saint Louis</td>
<td>32</td>
</tr>
</tbody>
</table>

Higher AQI (air quality index) means poorer air quality and greater risks to human health.
Green chemistry

- Designing of chemical products or processes that reduce or eliminate generation of hazardous substances.
- EPA promotes the synthesis of drugs, pesticides, and plastics using green chemistry.
- “preventive medicine” for improving the environment and avoidance of costly cleanup or remediation efforts.
- Examples include ibuprofen, disposable diapers, contact lens, and dry cleaning solvents.

Air Pollutant Sources

- Transportation (auto emissions)
- Burning of fossil fuels in power plants
- Petrochemical refineries
- Industries (e.g. smelting, paper, and semiconductor production).
- Municipal and medical waste incinerators.
- Natural processes (wildfires and volcanic eruptions)

Coal and Acid Rain

- Major US source of electric power
- Coal + O₂ → H₂O + CO₂ + other products
- Coal contains 1-3 % S that forms SO₂.
- Ash particulates speed up or catalyze the conversion of SO₂ into SO₃.
- Aerosol containing SO₂ is formed that this leads to acid rain!

Formation of Acid Rain

- Sulfur → Sulfur Dioxide → Sulfur Trioxide → Sulfuric Acid (a component of acid rain)
Automobile emissions

- Source of CO, Pb, NO\textsubscript{x}, O\textsubscript{3}, SO\textsubscript{2}, and other pollutants
- Only small amounts emitted from the tailpipe of each vehicle
- Mobile source emission is significant with over 220 million vehicles!
- Auto inspection is usually required in cities due to the large numbers of cars.

Problems of Hydrocarbon Fuels

- Incomplete combustion leads partially oxidized pollutants.
  - Not enough O\textsubscript{2}
  - Insufficient time in engine
  - Needs better engine design
- Evaporative emissions of smaller hydrocarbons from gasoline.

Ways to Reduce CO

- Better engine design
- Use of oxygenated fuels containing ethanol or MTBE
- Sensors that adjust O\textsubscript{2}/fuel to achieve more complete combustion.
- Catalytic converters assist in the conversion of CO to CO\textsubscript{2}

Lead in Transportation Fuels

- Tetraethyl lead (TEL) is added to boost octane or reduce engine knock.
- Leaded gasoline has been phased out in the U. S. but TEL is still used in aviation gasoline.
- Lead (Pb) released into the environment poses health risk as a developmental toxin.
- Lead can harm catalytic converters
Nitrogen Oxides

- N$_2$ and O$_2$ in air forms NO$_x$ at high temperatures (combustion and lightning)
- NO$_x$ = NO + NO$_2$
- NO$_x$ emissions in cars can be reduced by catalytic converters
- NO$_x$ can lead to acid rain

Chemical Releases in the U.S.

![Figure 1.15 Page 34](https://example.com/figure1.15.png)

Table 1.11

<table>
<thead>
<tr>
<th>Phases of Matter</th>
<th>Source</th>
<th>Pollutant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid/particulate</td>
<td>Floor tile</td>
<td>Asbestos</td>
</tr>
<tr>
<td></td>
<td>Pets</td>
<td>Pet dander, dust</td>
</tr>
<tr>
<td></td>
<td>Plants</td>
<td>Mold, mildew, bacteria, viruses</td>
</tr>
<tr>
<td>Liquid/gas</td>
<td>Carpet</td>
<td>Styrene</td>
</tr>
<tr>
<td></td>
<td>Cigarette smoke</td>
<td>Formaldehyde, carbon monoxide</td>
</tr>
<tr>
<td></td>
<td>Clothes</td>
<td>Dry-cleaning fluid, moth balls</td>
</tr>
<tr>
<td></td>
<td>Electric arcing</td>
<td>Glucose</td>
</tr>
<tr>
<td></td>
<td>Faulty furnace or space heater</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td></td>
<td>Furniture</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td></td>
<td>Glues and solvents</td>
<td>Acetone, toluene</td>
</tr>
<tr>
<td></td>
<td>Paint and paint thinners</td>
<td>Methanol, methylene chloride</td>
</tr>
<tr>
<td></td>
<td>Soil and rocks under house</td>
<td>Radon</td>
</tr>
</tbody>
</table>