Temperature

- We associate the concept of temperature with how hot or cold an object feels.
- Our senses provide us with a qualitative indication of temperature.
- However, our senses are unreliable for this purpose, e.g., taste the ice jelly with a plastic spoon or metal spoon will tell the “unreliable difference.”
- We need a technical definition of temperature.

Thermal Contact

- Two objects are in thermal contact with each other if energy can be exchanged between them.
  - The exchanges we will focus on will be in the form of heat or electromagnetic radiation.
  - The energy is exchanged due to a temperature difference.
Thermal Equilibrium

- **Thermal equilibrium** is a situation in which two objects would not exchange energy by heat or electromagnetic radiation if they were placed in thermal contact.
  - The thermal contact does not have to also be physical contact.

Zeroth Law of Thermodynamics

- If objects A and B are separately in thermal equilibrium with a third object C, then A and B are in thermal equilibrium with each other.
  - Let object C be the thermometer.
  - Since they are in thermal equilibrium with each other, there is no energy exchanged among them.

Zeroth Law of Thermodynamics, Example

- Object C (thermometer) is placed in contact with A until they achieve thermal equilibrium:
  - The reading on C is recorded.
- Object C is then placed in contact with object B until they achieve thermal equilibrium:
  - The reading on C is recorded again.
- If the two readings are the same, A and B are also in thermal equilibrium.

Temperature (Technical)

- **Temperature** can be thought of as the property that determines whether an object is in thermal equilibrium with other objects.
- Two objects in thermal equilibrium with each other are at the same temperature:
  - If two objects have different temperatures, they are not in thermal equilibrium with each other.
**Example.** A piece of copper is dropped into a beaker of water. If the water’s temperature rises, what happen to the temperature of copper? Under what conditions are the copper and water in thermal equilibrium?

**Answer:**

The copper’s temperature drops and the water temperature rises until both temperatures are the same. Then the metal and the water are in thermal equilibrium.

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**Thermometers**

- A **thermometer** is a device that is used to measure the temperature of a system.
- Thermometers are based on the principle that some physical property of a system changes as the system’s temperature changes.

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**Thermometers, cont**

- These properties include:
  - The volume of a liquid
  - The dimensions of a solid
  - The pressure of a gas at a constant volume
  - The volume of a gas at a constant pressure
  - The electric resistance of a conductor
  - The color of an object
- A temperature scale can be established on the basis of any of these physical properties.

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**Thermometer, Liquid in Glass**

- A common type of thermometer is a liquid-in-glass.
- The material in the capillary tube expands as it is heated.
- The liquid is usually mercury or alcohol.
Calibrating a Thermometer

- A thermometer can be calibrated by placing it in contact with some natural systems that remain at constant temperature.
- Common systems involve water:
  - A mixture of ice and water at atmospheric pressure: Called the \textbf{ice point} of water.
  - A mixture of water and steam in equilibrium: Called the \textbf{steam point} of water.

Problems with Liquid-in-Glass Thermometers

- An alcohol thermometer and a mercury thermometer may agree only at the calibration points. The discrepancies between thermometers are especially large when the temperatures being measured are far from the calibration points. This is because alcohol and mercury, in fact all substances, have different thermal expansion properties and the expansion may not be absolutely linear at all time.
- The thermometers also have a limited range of values that can be measured:
  - Mercury cannot be used under $-30^\circ$C because this is its freezing point.
  - Alcohol cannot be used above $85^\circ$C because this is its boiling point.

Celsius (Anders Celsius (1701 - 1744)) Scale

- The ice point of water is defined to be $0^\circ$C.
- The steam point of water is defined to be $100^\circ$C.
- The length of the column between these two points is divided into 100 increments, called degrees.

Example. A constant-volume gas thermometer is calibrated in dry ice (that is, carbon dioxide in the solid state, which has a temperature of $-80.0^\circ$C) and in boiling ethyl alcohol ($78.0^\circ$C). The two pressures are 0.900 atm and 1.635 atm respectively. (a) What Celsius value of absolute zero does the calibration yield? What is the pressure at (b) the freezing point of water and (c) the boiling point of water? (16)

Answer:

Since we have a linear graph, the pressure is related to the temperature as $P = A + B T$, where $A$ and $B$ are constants. To find $A$ and $B$, we use the data:

\[
0.900 \text{ atm} = A + (-80.0^\circ\text{C})B \\
1.635 \text{ atm} = A + (78^\circ\text{C})B
\]

Solving (1) and (2) simultaneously, we find:

\[
A = 1.272 \text{ atm} \\
B = 4.652 \times 10^{-3} \text{ atm/}^\circ\text{C}
\]

Therefore, $P = 1.272 \text{ atm} + (4.652 \times 10^{-3} \text{ atm/}^\circ\text{C}) T$.

(a) At absolute zero, $P = 0 = 1.272 \text{ atm} + (4.652 \times 10^{-3} \text{ atm/}^\circ\text{C}) T$ which gives $T = -274^\circ\text{C}$.

(b) At the freezing point of water, $P = 1.272 \text{ atm} + 0 = 1.27 \text{ atm}$.

(c) At the boiling point, $P = 1.272 \text{ atm} + (4.652 \times 10^{-3} \text{ atm/}^\circ\text{C}) (100^\circ\text{C}) = 1.74 \text{ atm}$. 


Constant Volume Gas Thermometer

- The physical change exploited here is the variation of pressure of a fixed volume gas as its temperature changes.
- The volume of the gas is kept constant by raising or lowering the reservoir B to keep the mercury level at A constant. Consequently, the value of mercury height, \( h \), which represents the pressure, varies with the change in temperature.

Constant Volume Gas Thermometer, cont

- The thermometer is calibrated by using an ice water bath and a steam water bath.
- The pressures of the mercury under each situation are recorded.
  - The volume is kept constant by adjusting A.
  - The information is plotted.

Constant Volume Gas Thermometer, final

- To find the temperature of a substance, the gas flask is placed in thermal contact with the substance.
- The pressure is found on the graph.
- The temperature is read from the graph.

Absolute Zero Temperature with Different Gases

- The thermometer readings are virtually independent of the gas used.
- If the lines for various gases are extended, the pressure is always zero when the temperature is \(-273.15^\circ C\).
- This temperature is called absolute zero.
Absolute Temperature Scale, 1

- Absolute zero is used as the basis of the absolute temperature scale.
- The size of the degree on the absolute scale is the same as the size of the degree on the Celsius scale.
- To convert: 
  \[ T_C = T - 273.15 \]

Absolute Temperature Scale, 2

- The absolute temperature scale is now based on two new fixed points.
- Adopted by in 1954 by the International Committee on Weights and Measures.
- One point is absolute zero: 
  \[ T_C = T - 273.15 \]
  \[ = 0 - 273.15 = -273.15 \, ^\circ\text{C} \]
- The other point is the triple point of water:
  - This is the combination of temperature and pressure where ice, water, and steam can all coexist.

Absolute Temperature Scale, 3

- The triple point of water occurs at 0.01° C and a pressure with 4.58 mm of mercury: 
  \[ T_C = T - 273.15 \]
- This temperature was set to be 273.16 on the absolute temperature scale:
  - This made the old absolute scale agree closely with the new one.
  - The units of the absolute scale are kelvins.

Absolute Temperature Scale, 4

- The absolute scale is also called the kelvin scale:
  - Named for William Thomson, Lord Kelvin (1824 – 1907).
- The triple point temperature is 273.16 K.
- The kelvin is defined as 1/273.16 of the difference between (i) absolute zero and (ii) the temperature of the triple point of water.
Some Examples of Absolute Temperatures

- The figure at right gives some absolute temperatures at which various physical processes occur
- The figure is logarithmic
- The temperature of absolute zero cannot be achieved
  - Experiments have come close such as by using laser cooling method

Energy at Absolute Zero

- According to classical physics, the kinetic energy of the gas molecules would become zero at absolute zero temperature
- The molecular motion would cease
  - Therefore, the molecules would settle out on the bottom of the container
- Quantum theory modifies this and shows some residual energy would remain
  - This energy is called the **zero-point** energy

Fahrenheit Scale

- A common scale in everyday use in the US
- Named for Daniel Gabriel Fahrenheit (1686 - 1736)
- Temperature of the ice point is 32°F
- Temperature of the steam point is 212°F
- There are 180 divisions (degrees) between the two reference points

Comparison of Scales

- Celsius and Kelvin have the same size degrees, but different starting points
  \[ T_C = T - 273.15 \]
- Celsius and Fahrenheit have different sized degrees and different starting points
  \[
  \frac{T_F - 0}{212 - 32} = \frac{T_C - 0}{100 - 0}
  \]
  \[
  T_F = \frac{9}{5} T_C + 32 \]
Comparison of Scales, cont

- To compare changes in temperature
  \[ \Delta T_C = \Delta T = \frac{5}{9} \Delta T_F \]

- Ice point temperatures
  - \( 0^\circ C = 273.15 \text{ K} = 32^\circ F \)

- Steam point temperatures
  - \( 100^\circ C = 373.15 \text{ K} = 212^\circ F \)

Thermal Expansion

- Thermal expansion is the increase in the size of an object with an increase in its temperature
- Thermal expansion is a consequence of the change in the average separation between the atoms in an object
- If the expansion is small relative to the original dimensions of the object, the change in any dimension is, to a good approximation, proportional to the first power of the change in temperature, i.e., we can ignore \((\Delta t)^2\) and higher orders

Thermal Expansion, example

- As the washer shown at right is heated, all the dimensions will increase
- A cavity in a piece of material expands in the same way as if the cavity were filled with the material
- The expansion is exaggerated in this figure

Linear Expansion

- Assume an object has an initial length \( L_i \)
- That length increases by \( \Delta L \) as the temperature changes by \( \Delta T \)
- We define the coefficient of linear expansion as
  \[ \alpha = \frac{\Delta L}{L_i \Delta T} \]
- A convenient form is \( \Delta L = \alpha L_i \Delta T \)
Linear Expansion, cont

- This equation can also be written in terms of the initial and final conditions of the object:
  \[ L_f - L_i = \alpha L_i (T_f - T_i) \]

- The coefficient of linear expansion, \( \alpha \), has units of \((\text{oC})^{-1}\)

Linear Expansion, final

- Some materials such as calcite (CaCO₃) expand along one dimension, but contract along another as the temperature increases.

- Since the linear dimensions change, it follows that the surface area and volume also change with a change in temperature.

Table 19.1

<table>
<thead>
<tr>
<th>Material</th>
<th>Average Linear Expansion Coefficient ((\alpha))(°C)⁻¹</th>
<th>Material</th>
<th>Average Volume Expansion Coefficient ((\beta))(°C)⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>24 × 10⁻⁶</td>
<td>Alcohol, ethyl</td>
<td>1.12 × 10⁻⁴</td>
</tr>
<tr>
<td>Brass and bronze</td>
<td>19 × 10⁻⁶</td>
<td>Benzene</td>
<td>1.24 × 10⁻⁴</td>
</tr>
<tr>
<td>Copper</td>
<td>17 × 10⁻⁶</td>
<td>Acetone</td>
<td>1.5 × 10⁻⁴</td>
</tr>
<tr>
<td>Glass (ordinary)</td>
<td>9 × 10⁻⁶</td>
<td>Glycerin</td>
<td>4.85 × 10⁻⁴</td>
</tr>
<tr>
<td>Glass (Pyrex)</td>
<td>3.2 × 10⁻⁶</td>
<td>Mercury</td>
<td>1.82 × 10⁻⁴</td>
</tr>
<tr>
<td>Lead</td>
<td>29 × 10⁻⁶</td>
<td>Turpentine</td>
<td>9.0 × 10⁻⁴</td>
</tr>
<tr>
<td>Steel</td>
<td>11 × 10⁻⁶</td>
<td>Gasoline</td>
<td>9.6 × 10⁻⁴</td>
</tr>
<tr>
<td>Invar (Ni-Fe alloy)</td>
<td>0.9 × 10⁻⁶</td>
<td>Air at 0°C</td>
<td>3.67 × 10⁻⁵</td>
</tr>
<tr>
<td>Concrete</td>
<td>12 × 10⁻⁶</td>
<td>Helium²</td>
<td>3.665 × 10⁻⁵</td>
</tr>
</tbody>
</table>

Volume Expansion

- The change in volume is proportional to the original volume and to the change in temperature.
  \[ \Delta V = \beta V_i \Delta T \]

- \( \beta \) is the coefficient of volume expansion.

- For a solid, \( \beta = 3\alpha \)
  - This assumes the material is isotropic, i.e., the linear expansion is the same in all directions.
Area Expansion

The change in area is proportional to the original area and to the change in temperature:

\[ \Delta A = 2 \alpha A_i \Delta T \]

Example. The active element of a certain laser is made of a glass rod 30.0 cm long by 1.50 cm in diameter. If the temperature of the rod increases by 65.0°C, what is the increase in (a) its length, (b) its diameter, and (c) its volume? Assume that the average coefficient of linear expansion of the glass is \(9.00 \times 10^{-6}(°C)^{-1}\).

**Answer:**

(a) 
\[ \Delta L = \alpha L \Delta T = 9.00 \times 10^{-6}(°C)^{-1}(30.0 \text{ cm})(65°C) = 0.176 \text{ m m} \]

(b) 
\[ \Delta L = \alpha L \Delta T = 9.00 \times 10^{-6}(°C)^{-1}(1.50 \text{ cm})(65°C) = 8.78 \times 10^{-4} \text{ cm} \]

(c) 
\[ \Delta V = 3 \alpha V \Delta T = 3(9.00 \times 10^{-6}(°C)^{-1}) \left( \frac{30.0 \pi (1.50)^2}{4} \text{ cm}^3 \right)(65°C) = 0.0930 \text{ cm}^3 \]

Thermal Expansion, Example

- In many situations, joints are used to allow room for thermal expansion
- The long, vertical joint is filled with a soft material that allows the wall to expand and contract as the temperature of the bricks changes
- Thermal expansion has to be considered in many structure such as a bridge

Bimetallic Strip

- Each substance has its own characteristic average coefficient of expansion
- This can be made use of in the device shown, called a bimetallic strip
- It can be used in a thermostat
Water’s Unusual Behavior

- As the temperature increases from 0°C to 4°C, water contracts
  - Its density increases
- Above 4°C, water expands with increasing temperature
  - Its density decreases
- The maximum density of water (1.000 g/cm³) occurs at 4°C
- When temperature decreases from 4°C to 0°C, water expands

Thanks to this unusual behavior, marine life can survive when surface water freezes.

How can fish survive as water freezes in the pond? (d1s-15)

Answer:
The water in a pond begins freezing at the surface rather than the bottom. When the atmospheric temperature drops from, say 8°C to 4°C, the surface water also cools and consequently decreases in volume (as density goes up). This means that the surface water is denser than the water below it, which has not cooled and not as dense at the water on top. As a result, the surface water sinks, and the water from below is forced to the surface to be cooled.

But when the atmospheric temperature decreases further from 4°C to 0°C, the surface water expands as it cools, becoming less dense than the water below it – so the mixing process stops and eventually the surface water freezes.

As the water freezes (0°C), the ice remains on the surface because ice is less dense than water. The ice continues to build up at the surface, while water near the bottom remains at 4°C – so the fish can still survive.

An Ideal Gas

- For gases, the interatomic forces within the gas are very weak
  - We can imagine these forces to be nonexistent
- Note that there is no equilibrium separation for the atoms
  - Thus, no “standard” volume at a given temperature. The volume is entirely determined by the container holding the gas.

Gas: Equation of State

- **Equation of state** shows the volume, pressure and temperature of the gas of mass $m$ are related
  - These are generally quite complicated
  - If the gas is maintained at a low pressure, the equation of state becomes much easier to comprehend.
  - This type of a low density gas is commonly referred to as an **ideal gas**
### The Mole

- **Avogadro’s Hypothesis.** Equal volumes of gas at the same pressure and temperature contain equal numbers of molecules.
- The amount of gas in a given volume is conveniently expressed in terms of the number of moles.
- One **mole** of any substance is that amount of the substance that contains **Avogadro’s number** of constituent particles:
  - Avogadro’s number $N_A = 6.022 \times 10^{23}$ molecules/mole
  - The constituent particles can be atoms, or molecules (consists of atoms).

### Moles, cont

- The number of moles can be determined from the mass of the substance: $n = m / M$
  - $n$ is the number of moles
  - $m$ is the number of moles
  - $M$ is the molar mass of the substance

For example, 1 mole of Helium atom is $M = 4g$ (atomic mass of He is 4.00 u). For a molecular substance or a chemical compound, you can add up the molar mass from its molecular formula, eg, 1 mole of oxygen ($O_2$) is $M = 32 g$ (atomic mass of O is 16 u).

### Gas Laws

- When a gas is kept at a constant temperature, its pressure is inversely proportional to its volume (Boyle’s law), i.e., $PV$ is a constant.
- When a gas is kept at a constant pressure, its volume is directly proportional to its temperature (Charles and Gay-Lussac’s law), i.e., $V/T$ is a constant.

### Ideal Gas Law

- The equation of state for an ideal gas combines and summarizes the other two gas laws:
  $PV = nRT$
  - This is known as the **ideal gas law**
  - $n$ is the number of moles
  - $R$ is a constant of proportionality, called the Universal Gas Constant
    - $R = 8.314$ J/mol · K
  - Unit of PV is (Force/Area) x Volume = $F \times$ Distance $\rightarrow$ Joule (J)
**Ideal Gas Law**

From $PV = nRT$

to be specific, $R = 8.314 \text{ (N/m}^2\text{)} \times \text{m}^3 / \text{mol} \cdot \text{K}$

At sea level, the pressure of the atmosphere on the average is $1.013 \times 10^5 \text{ N/m}^2$. This is called 1 atmospheric pressure (atm).

So $1 \text{ N/m}^2 = \frac{1}{1.013 \times 10^5} \text{ atm}$

Given that $1 \text{ L} = (10 \text{ cm})^3 = (0.1 \text{ m})^3 = 10^{-3} \text{ m}^3$, so $1 \text{ m}^3 = 10^3 \text{ L}$.

$R = 8.314 \left( \frac{\text{N/m}^2}{\text{m}^3/\text{mol} \cdot \text{K}} \right) \times \frac{1}{1.013 \times 10^5} \text{ atm} \times \text{L/mol} \cdot \text{K}$

$= 0.08214 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$

■ From this, you can determine that 1 mole of any gas at atmospheric pressure and at $0^\circ \text{C}$ is 22.4 L.

($PV = nRT \rightarrow 1 \times V = 1 \times 0.08214 \times 273.15$, so $V = 22.4 \text{ L}$)

What is the height of water the atmospheric pressure can sustain at mean sea level?

**Answer:**

You school teachers previously had performed this demonstration and the glass was fully filled with water.

We first ask whether the pocket on top of the up-side-down glass needs to be a vacuum or not.

The answer is that the pocket needs not be fully vacummed, but it should not be fully expanded and filled with air.

If the pocket is fully expanded and filled with air, the weight of the paper cannot be ignored as there is no more water. There will be leakage and now the pressure inside the glass and the pressure outside will cancel each other.

The pressure asserted by water on the piece of paper is

$F/A = mg/A = \rho \times V \times g / A$

$= \rho \times h \times A \times g / A = h \rho g$

This downward pressure is sustained by the atmospheric pressure.

The weight of the pouch of air in the container is negligible as compare to the weight of water. Assume that the piece of small paper is of negligible weight as compared to the weight of water in the glass.

$h \rho g = 1.013 \times 10^5 \text{ N/m}^2$

$h \times 1 \times 10^3 \text{ kg/m}^3 \times 9.81 \text{ m/s}^2 = 1.013 \times 10^5 \text{ N/m}^2$

$h = 10.33 \text{ m} \quad \text{i.e., about 10 meter.}$

![Diagram](image-url)

**Ideal Gas Law, cont**

■ The ideal gas law is often expressed in terms of the total number of molecules, $N$, present in the sample

$PV = nRT = \left( \frac{N}{N_A} \right) RT = N k_B T$, where

$k_B$ is Boltzmann’s constant ($R/N_A$)

Given that Avogadro’s number $N_A = 6.022 \times 10^{23}$ molecules/mole, and $R = 8.314 \text{ J/mol} \cdot \text{K}$, we have Boltzmann’s constant $k_B = 1.38 \times 10^{-23} \text{ J/K}$

■ It is common to call $P$, $V$, and $T$ the thermodynamic variables of an ideal gas
Example. Natural gas is sold by volume. In the United States, the price charged is usually per cubic foot. Given the price per cubic foot, what other information would you need in order to calculate the price per mole?

Answer:

Conversion of the price per cubic foot of natural gas into the price per mole requires knowledge of the number of moles contained within the given volume. From the macroscopic ideal gas law, the number of moles in a sample is proportional to the volume, pressure, and temperature of the gas. Using the known volume and the additional quantities of pressure and temperature, the number of moles may be calculated and the price may be converted. The conversion could also be made if the density and the mass per molecule were known. The latter method works whether or not the gas is ideal.

\[
\frac{PV}{nRT} = \left( \frac{N}{N_A} \right) \frac{RT}{Nk_B T} = \frac{N}{N_A} \frac{RT}{Nk_B T} = \frac{PV}{nRT} = \frac{N}{N_A} \frac{RT}{Nk_B T} = 1 \text{ N/m}^2 = 1 \text{ Pascal (Pa)}
\]

Example. An automobile tire is inflated with air originally at 10.0°C and normal atmospheric pressure. During the process, the air is compressed to 28.0% of its original volume and the temperature is increased to 40.0°C. (a) What is the tire pressure? (b) After the car is driven at high speed, the tire air temperature rises to 85.0°C and the interior volume of the tire increases by 2.00%. What is the new tire pressure (absolute) in pascals?

Answer:

(a) Initially, \( P_1V_1 = nRT_1 \)

Finally, \( P_2V_2 = nRT_2 \)

\[
0.280P_f = \frac{1.00 \text{ atm}}{1.00 \text{ atm}} = \frac{313.15 \text{ K}}{283.15 \text{ K}} = 3.95 \text{ atm}
\]

Dividing these equations, giving

\[
P_f = \frac{0.280P_f}{3.95 atm} = 4.00 \times 10^5 \text{ Pa (abs)}
\]

(b) After being driven

\[
P_f (1.02)(0.280V_1) = nRT_f
\]

\[
P_f = 1.02P_f = 4.49 \times 10^5 \text{ Pa}
\]