Medical Physics Class Temperature and Kinetic Theory of Gases Part-2



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First year Pharmacy Students

Learning Goals

Looking forward at ...

- Kinetic Theory Model of an Ideal Gas
- Vapor Pressure and Humidity
- Dew, Fog, and Rain
- Boiling
- Thermal Expansion
- Thermal Expansion of water

Kinetic Theory; Model of an Ideal Gas

- Kinetic theory is an area of physics that was developed in the late nineteenth century
- By Rudolph Clausius, James Clerk Maxwell, Ludwig Boltzmann, and others.
- Kinetic theory provides an explanation for the behavior of a macroscopic system in terms of its microscopic components—atoms or molecules, which obey dynamical laws.
- In this section we shall use kinetic theory to provide an explanation for the pressure of an ideal gas in terms of a molecular model.



A container of gas consists of a large number of molecules moving randomly and colliding with the walls of the container.

- A gas contained in a volume of macroscopic dimensions consists of an enormously large number of molecules.
- These molecules move in a random, chaotic way throughout the volume of the container.
- When a molecule strikes a surface, it bounces off, exerting a small force on the surface.
- At any instant there will be many molecules colliding with the surface.
- The effect of these collisions is to produce a resultant force, which may be quite large.



A single molecule collides with a wall of the container; during the collision the molecule exerts a small force perpendicular to the surface.



At any instant a large number of molecules collide with the surface. The effect of all these collisions is a resultant force F and pressure P, which are effectively constant.

- The resultant force is not steady but fluctuates rapidly, depending on the number of molecules striking the surface at any instant.
- But, for a surface of macroscopic size, the number of molecules involved is so large that fluctuations in the net force are negligibly small.
- Thus the molecules exert a pressure on the container walls that is effectively constant.



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Kinetic Interpretation of Temperature

- In this section we shall derive the ideal gas law, using the more realistic model of molecules moving randomly in all directions.
- This derivation, first presented by James Clerk Maxwell in 1859, shows that the average kinetic energy of an ideal gas molecule equals $\frac{1}{2}kT$.
- A molecule of mass m traveling at speed v has kinetic energy

 $K = \frac{1}{2} mv^2$. Denoting the average values of K and v^2 by \overline{K} and $\overline{v^2}$, we may express Maxwell's result as:

$$\overline{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

Kinetic Interpretation of Temperature

- This equation shows that the temperature of an ideal gas is a measure of the average kinetic energy of its molecules.
- The phenomenon of thermal equilibrium is easy to understand. Two systems of gas that are initially at different temperatures have different values of average kinetic energy per molecule.
- When the systems are placed in thermal contact, the system with the higher temperature will lose energy as the system with the lower temperature gains energy.
- This process continues until the average molecular kinetic energies and hence also the temperatures of the two systems are the same.
- Thus thermal equilibrium is simply a consequence of the equal sharing of kinetic energy among the molecules of both systems.
- Although this equation is derived only for an ideal gas, it applies to any system, including liquids and solids.
- The average translational kinetic energy of the molecules in a body at absolute temperature T equals $\frac{3}{2}kT$.

$$\overline{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

Maxwell Distribution

- Maxwell carried his analysis a step farther and derived an expression for the distribution of molecular speeds.
- Maxwell's theoretical prediction is shown graphically in the Figure for oxygen at a temperature of 300 K.



Distribution of molecular speeds for oxygen at 300 K. The area under the curve between any two values of v gives the fraction of the molecules having speed somewhere in the interval between the two values of v. For example, the cross-hatched area is 0.053, meaning that 5.3% of the molecules have values of v between 375 m/s and 400 m/s.

Maxwell Distribution

- This figure indicates how the distribution changes with temperature.
- As *T* increases, the distribution becomes broader and shifts to the right, toward higher values of *v*. The
- Maxwell distribution has been sufficiently verified by experiments.



Distribution of molecular speeds for oxygen at 300 K and at 400 K.

Root Mean Square Speed

- It is convenient to be able to characterize the Maxwell distribution by a single number, typical of molecular speeds at a given temperature.
- For this purpose one may use either the average speed or the root mean square (rms) speed, defined as the square root of the average squared speed and denoted by v_{rms} .

$$v_{\rm rms} = \sqrt{v^2}$$

Root Mean Square Speed

- For the Maxwell distribution v_{rms} is approximately equal to the average speed.
- Since we have already derived an expression for the average molecular kinetic energy, it is easy to obtain an expression for v_{rms} .

 $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$

Thus

 $\overline{v^2} = \frac{3kT}{kT}$

and

$$v_{\rm rms} = \sqrt{\frac{3kT}{m}}$$

EXAMPLE 7 RMS Speed of Oxygen Molecules at Room Temperature

Calculate $v_{\rm rms}$ for oxygen molecules at a temperature of 300 K.

SOLUTION The molecular mass of oxygen is 32, which means that an oxygen molecule has a mass of 32 atomic mass units (32 u), where $u = 1.66 \times 10^{-27}$ kg. Applying Eq.

$$v_{\rm rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3kT}{32 \text{ u}}}$$
$$= \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{32(1.66 \times 10^{-27} \text{ kg})}}$$
$$= 484 \text{ m/s}$$

This speed, faster than a speeding bullet, is near the center of the molecular speed distribution shown in Fig. 12–8.



- If you fill a glass with water and leave it, within a day or two the water level in the glass will drop noticeably, unless the surrounding air is very damp.
- The water "evaporates." This means that water molecules leave the liquid and form a vapor or gas that mixes with the air.
- We can understand evaporation on a molecular level, using concepts of kinetic theory.



- The molecules in a liquid have a distribution of velocities, similar to the Maxwell-Boltzmann distribution of molecular velocities in a gas.
- Although intermolecular forces bind most of the molecules close together in the liquid, some of the molecules move fast enough to leave the surface of the liquid, like a rocket with a velocity greater than escape velocity leaving the earth.
- Since the molecules that evaporate are those with the greatest velocity and kinetic energy, the average kinetic energy of the molecules remaining in the liquid decreases, and so the temperature of the liquid decreases.



- You can feel the cooling effect of evaporation when you step out of a shower and water evaporates from your skin.
- The effect is more dramatic when the air is very dry. If you step out of a swimming pool in the desert, even though the air may be quite hot, you can be chilled by water evaporating from your skin.

- To better understand the process of evaporation, consider a liquid in a closed container with a piston (Fig. a).
- If the piston is raised, evaporation begins. Vapor fills the space above the liquid (Fig. b) and creates a pressure, called vapor pressure.
- As more and more molecules enter the vapor, some molecules begin to go from the vapor back into the liquid.
- Initially more molecules leave the liquid than enter it, and both the density and pressure of the vapor increases. There is soon reached an equilibrium state, in which as many molecules enter the liquid as leave it.



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- We say the vapor is then "saturated," since there can be no further increase in the number of molecules in the vapor (Fig. c).
- In this equilibrium state, vapor pressure reaches its maximum value, called saturated vapor pressure.
- If the piston is raised higher, more molecules enter the vapor phase until the vapor pressure again reaches the same saturated vapor pressure.



- As the temperature of a liquid increases, more of its molecules have sufficient kinetic energy to escape the liquid.
- Thus, as temperature increases, the rate at which molecules leave the surface of the liquid increases; that is, the rate of evaporation increases.
- An equilibrium state is not reached until the density of the vapor phase increases enough that the rate at which molecules reenter the liquid matches the new higher rate at which molecules leave the liquid (Fig. d).
- The higher-density equilibrium state is one of higher pressure. Thus, as temperature increases, saturated vapor pressure increases.



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Dew, Fog, and Rain

- When air containing water vapor is cooled sufficiently, some of the vapor condenses to the liquid state.
- This condensation begins when the air drops below the temperature at which the water vapor's partial pressure equals the saturated vapor pressure, in other words, when it drops below the temperature at which relative humidity is 100%.
- This temperature is called the dew point.
- Such condensation often occurs at night when dew forms on the ground, as the temperature of the ground falls and cools the surrounding air.

Dew, Fog, and Rain

- For example, suppose air temperature during the day is 30°C with a relative humidity of 75%, meaning that the partial pressure of water vapor in the air is 75% of the saturated vapor pressure of 0.04 *atm* at 30°C, or 0.03 *atm*.
- Then, if the temperature of the air near the ground falls to 20°C at night, since the saturated vapor pressure of water at that temperature is only 0.02 *atm*, the partial pressure of water vapor in the air must drop by one third from 0.03 *atm* to 0.02 *atm*, meaning that one third of the water vapor must condense.

Dew, Fog, and Rain

- Fog results when a humid warm air mass mixes with cooler air and tiny droplets of water form as the temperature of the warm air drops below the dew point.
- Clouds form when air rises and is cooled below the dew point. When a cloud cools suddenly, condensation is more rapid, water droplets increase in size, and then come together to form larger drops, which fall as rain.

Boiling

- If the temperature of a liquid is raised enough so that the liquid's vapor pressure equals the pressure of the surrounding air, the liquid begins to boil.
- That is, bubbles of vapor form within the bulk liquid. These vapor bubbles push outward against the liquid, which is at approximately the same pressure as the air.
- Water boils at a temperature of 100°C when the surrounding air is at a pressure of 1.00 *atm* because the saturated vapor pressure of air at 100°C is 1.00 *atm*.
- If the surrounding air is at a lower pressure, water will boil at a lower temperature.
- For example, on a mountain at an elevation of 3000 *m*, where atmospheric pressure is only 0.7 *atm*, water boils at a temperature of 90°C, since its saturated vapor pressure at that temperature equals 0.7 *atm*.

Nearly all solids and liquids expand as they are heated.

The fractional increase in volume, $\Delta V/V$, is often found to be directly proportional to the increase in temperature, ΔT .

The constant of proportionality is called the "volume coefficient of expansion," denoted by β . Thus

$$\frac{\Delta V}{V} = \beta \ \Delta T$$

The change in volume ΔV is proportional to the original volume V, as well as to the temperature change ΔT .

 $\Delta V = \beta V \, \Delta T$

Thus, for example, if $1 \ liter (1000 \ cm^3)$ of water is heated from 20° C to 25° C, its volume increases by only about $1 \ cm^3$. But if the water in a swimming pool of volume $1000 \ m^3$ is heated over the same temperature interval, the water increases in volume by $1 \ m^3$, or $10^6 \ cm^3$. In both cases the ratio $\Delta V/V$ is 10^{-3} .

$$\frac{\Delta V}{V} = \beta \, \Delta T$$

 $\Delta V = \beta V \Delta T$

- In the case of solids, the volume expansion is accomplished by an increase in all linear dimensions.
- As a solid is heated, the distance between any two points in the solid increases.
- The fractional increase in length is normally the same in all directions.
- Thus, if a block of metal expands thermally by 0.1% in length, the block's height and width will each also increase by 0.1%.
- The increase in size is like a photographic enlargement the Figure.
- As a washer is heated from temperature T to temperature $T + \Delta T$, all its linear dimensions get bigger.
- The actual expansion, however, is much smaller than indicated here.
- The expansion shown here is 20%, which is approximately 100 times greater than the expansion of aluminum heated100°C.





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Thermal Expansion

- Instead of using a volume coefficient of expansion for solids, we normally use a linear expansion coefficient α , which is a measure of the fractional change in the linear dimensions of the solid.
- For a temperature change ΔT , a length l changes by Δl , where

$$\frac{\Delta l}{l} = \alpha \Delta T$$

 $\Delta l = \alpha l \Delta T$ show that the volume co

• It is possible to show that the volume coefficient of expansion for a solid equals 3 times its linear coefficient:

$$\beta = 3\alpha$$





- Coefficients of expansion for various materials are given in Table.
- For liquids there is no measure of linear expansion, since liquids must conform to the shapes of their containers.

Solids	α, (C°) ⁻	Liquids and gases	β, (C°) ⁻¹
Aluminum	2.4×10^{-5}	Ethyl alcohol	1.1 × 10 ⁻³
Brass	1.9×10^{-5}	Mercury	1.8×10^{-4}
Brick	1×10^{-5}	Olive oil	7.2×10^{-4}
Concrete	1.2×10^{-5}	Water	2.1×10^{-4}
Copper	1.7×10^{-5}	Air	3.67×10^{-3}
Diamond	1.2×10^{-6}	Hydrogen	3.66×10^{-3}
Glass	4 $\times 10^{-6}$ to 1 $\times 10^{-5}$	Nitrogen	3.67×10^{-3}
Gold	1.4×10^{-5}	C	
Graphite	2×10^{-6}		
Ice	5.1×10^{-5}		
Paraffin	1×10^{-4}		
Steel	1.2×10^{-5}		
Wood, parallel to fiber	5 $\times 10^{-6}$ to 1×10^{-5}		
Wood, across fiber	3×10^{-5} to 6×10^{-5}		

 Table 12-2
 Coefficients of thermal expansion

EXAMPLE : Overflow of an Expanding Liquid

A glass container that has a volume of 1.0 liter and is filled with alcohol is initially refrigerated at a temperature of 7° C. How much of the alcohol will overflow if the container is placed in a warm room where the temperature is 27° C? The linear coefficient of expansion for the glass is 1.0×10^{-5} (C°)⁻¹.

SOLUTION The volume coefficient of expansion for the glass is 3 times its linear coefficient, or $3.0 \times 10^{-5} (C^{\circ})^{-1}$. Thus

 $\Delta V_{\text{glass}} = \beta_{\text{glass}} V \Delta T$

 $= [3.0 \times 10^{-5} (\text{C}^{\circ})^{-1}](1.0 \times 10^{3} \text{ cm}^{3})(20 \text{ C}^{\circ})$

 $= 0.60 \text{ cm}^3$

From Table 12–1 we find that the volume coefficient of expansion for alcohol is 1.1×10^{-3} —much larger than the coefficient for glass. Therefore the alcohol will expand more than the glass.

$$\Delta V_{alc} = \beta_{alc} V \Delta T$$

= [1.1 × 10⁻³ (C°)⁻¹](1.0 × 10³ cm³)(20 C°)
= 22 cm³

Since the volume of the glass container increases by only about 1 cm³, about 21 cm³ of the alcohol will overflow.

Thermal Expansion of Water

In many cases the simple linear dependence of ΔV on ΔT expressed by Eq. 12–20 is valid over all temperature ranges commonly encountered, with a constant value for β . However, for some substances the variation of volume with temperature is more complicated. Water is such a substance. Figure below shows the density of water as a function of temperature. Notice that at most temperatures the density of water decreases as its temperature increases; that is, water expands as it is heated. But in the temperature range from 0°C to 4°C water contracts as it is heated.



Thermal Expansion of Water

But in the temperature range from 0°C to 4°C water contracts as it is heated. Water is one of the few materials that have this property. This has an important effect on the rate at which lakes freeze. As air temperatures drop, the temperature of the water in a lake drops also, with the cooling occurring first at the surface of the lake. For temperatures above 4°C this cooling proceeds very efficiently. As water cools, it becomes more dense and sinks to a lower level in the lake, as warmer, less dense water rises to take its place.



Thermal Expansion of Water

Thus there is a natural mixing of warmer and colder water, causing rapid cooling of water beneath the surface. However, when the water reaches a uniform temperature of 4° C, the process changes. Cooling of the surface water below 4° C decreases its density. Thus it stays at the surface, and further cooling of the water beneath proceeds more slowly. The surface of the lake may freeze. But in even the coldest weather, large lakes do not freeze solid. The water at the bottom of the lake remains at 4° C, enabling the marine life there to survive.



The End Part-2

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