# Thermodynamics

## Chapter 1

# Kinetic Molecular Theory of Gases

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# Introduction

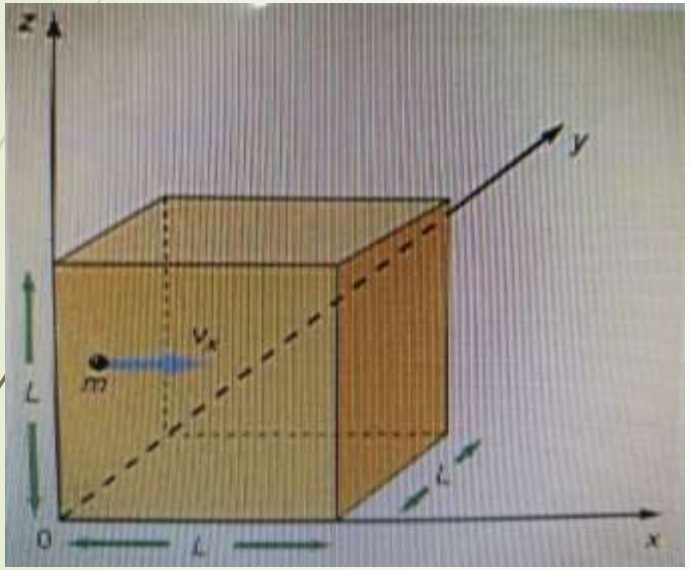
In 1859, after reading a paper on the diffusion of molecules by **Rudolf Clausius**, **Scottish physicist James Clerk Maxwell** formulated the Maxwell distribution of molecular velocities, which gave the proportion of molecules having a certain velocity Kinetic Molecular Theory states that gas particles are in constant motion and exhibit perfectly **elastic** collisions. they obey Newton's laws of motion. This means that the molecules move in **straight lines** until they collide with each other or with the walls of the container. Kinetic Molecular Theory can be used to explain both Charles' and Boyle's Laws. The average kinetic energy of a collection of gas particles is directly **proportional** to absolute temperature only.in a specific range.

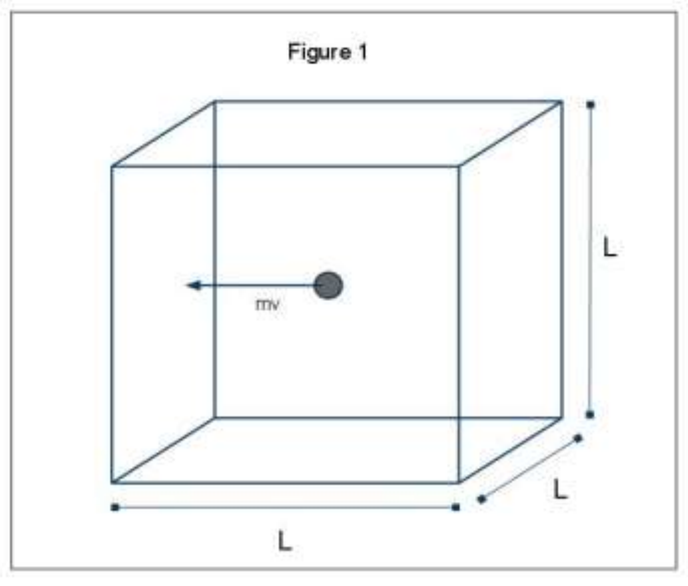
The basics of the **Kinetic Molecular Theory of Gases** (**KMT**) should be understood. A model is used to describe the behavior of gases. More specifically, it is used to explain macroscopic properties of a gas, such as pressure and temperature, in terms of its microscopic components, such as atoms. Like the ideal gas law, this theory was developed in reference to ideal gases, although it can be applied reasonably well to real gases. In order to apply the kinetic model of gases, The simplest kinetic **model** is based on four assumptions that :

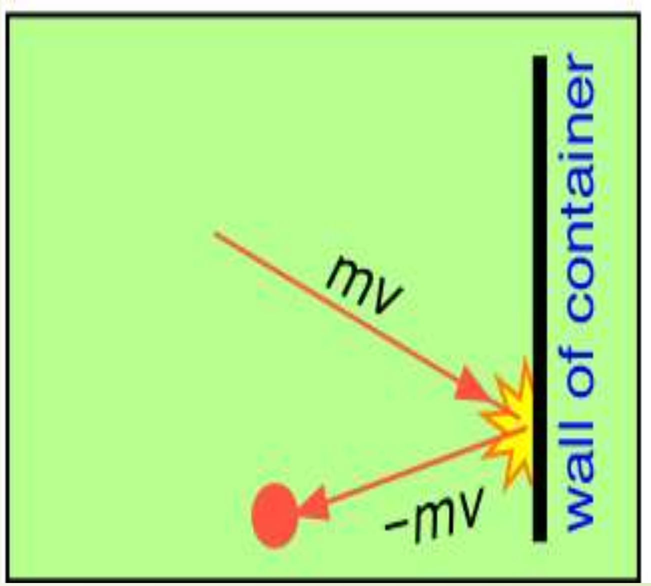
- Gases consist of large numbers of tiny particles that are far apart relative to their size.
- Collision between gas particles and between particles and container walls are elastic collisions (no energy loss) with each other and with the wall of container .
- Gas particles are in continuous, random, constant and linear motion.
- There are no forces of attraction between gas particles.

## Pressure :

The macroscopic phenomena of pressure can be explained in terms of the kinetic molecular theory of gases. Assume the case in which a gas molecule (represented by a sphere) is in a box, length *L* (Figure 1). Through using the assumptions laid out before, and considering the sphere is only moving in the x-direction, we can examine the instance of the sphere colliding elastically with one of the walls of the box.







The momentum of collision of one molecule is given by ;

$$\mathbf{M} = mu$$

since we are only considering the x dimension.

The total momentum change for this collision on the wall is then given by

$$\Delta M = mu - m(-u) = 2mu$$

Given that the amount of time it takes between collisions of the molecule with the wall is

$$t = \frac{L}{u}$$

we can give the frequency of collisions of the molecule against a given wall of the box per unit time as

$$t = \frac{2L}{u}$$

Solving for change of momentum per unit of time gives the force exerted by a molecule on the wall of container, according to the Newton's laws F = ma = mu / t = ΔM / t

$$F_x = \frac{\Delta M}{t} = 2mu \cdot \frac{u}{2L} = \frac{mu^2}{L}$$

With the expression that $F=mu^2/L$ one can now solve for the pressure exerted by the molecular collision, where area is given as the area of one wall of the box,

$$A = L^2$$

Any surface in contact with the gas is constantly bombarded by the molecules, it easy to see how a gas should exert a pressure on the walls of a container. *Pressure arises from the force due to the acceleration of molecules as they bound off a container's walls,* the pressure is ;

$$P_x = \frac{F_x}{A} = \frac{F_x}{L^2} = \frac{mu^2}{L} \cdot \frac{1}{L^2}$$

$$P_x = \frac{mu^2}{L^3} = \frac{mu^2}{V}$$

Where V is a volume

The expression can now be written in term of the pressure associated with collision of one molecule in x direction :

$$P_x = \frac{mu^2}{V}$$

The expression can now be written in terms of the total pressure associated with collisions from *N* number of molecules in x direction :

$$P_x = \frac{m\,(u^2{}_1 + u^2{}_2 + \ldots\ldots\ldots + u^2{}_n)}{V}$$

But the average square velocity of molecules

$$u^2{}_{ave} = \frac{(u^2{}_1 + u^2{}_2 + \ldots\ldots\ldots + u^2{}_n)}{N}$$

Then

$$u^2{}_{ave}\; N = (u^2{}_1 + u^2{}_2 + \ldots\ldots\ldots + u^2{}_n)$$

Then

$$P_x = \frac{m\,N\,u^2{}_{ave}}{V}$$

The expression can now be written in terms of the pressure associated with collisions in the y and z directions by

$$P_y = \frac{m\,N\,v^2{}_{ave}}{V}$$

$$P_z = \frac{m\,N\,w^2_{ave}}{V}$$

The average pressure in the container

$$P_{ave} = \frac{(Px + Py + Pz)}{3}$$

Then

$$P_{ave} = \frac{m\,N(u^2_{ave} + v^2_{ave} + w^2_{ave})}{3\,V}$$

But

$$C^2_{ave} = u^2_{ave} + v^2_{ave} + w^2_{ave}$$

Then

$$P_{ave} = \frac{m\,N\,C^2_{ave}}{3V}$$

Finally , the expression can now be written in terms of the pressure associated with collisions in all directions by

$$P = \frac{m\,N\,C^2}{3V}$$

**Above equation represent the Pressure of gases in a box by the kinetic Molecular Theory(KMT)**

# Relation between molecular kinetic energy of gas and temperature :

The **kinetic** energy of a **gas** is a measure of its temperature. The **kinetic** energy of a **gas** particle is directly proportional to the temperature. An increase in temperature increases the speed in which the **gas** molecules move. All **gases** at a given temperature have the same **kinetic** energy.

$$K.E. = \frac{1}{2} m_g C^2$$

Where $m_g$ is the mass of gas **= m N,** Then we can write

$$P = \frac{2}{2} \cdot \frac{1}{3} \frac{m N C^2}{V} = \frac{2}{3V} \cdot \frac{1}{2} m N C^2$$

$$P = \frac{2}{3V} \cdot \frac{1}{2} m_g C^2$$

$$PV = \frac{2}{3} K.E.$$

$$K.E. = \frac{3}{2} PV$$

From the ideal gas law, and for one mole of gas ( n = 1 )

$$P V_{mol} = n R_o T = R_o T$$

Where $R_o$ is universal gas constant = 8.3145 J/mol K, then

$$K.E. = \frac{3}{2} R_o T$$

## Relation between Speed of gas molecules and pressure :

From

$$P = \frac{1}{3} \frac{m N C^2}{V}$$

Then

$$P = \frac{1}{3} \frac{m_g C^2}{V}$$

$$C^2 = 3 P \frac{V}{m_g} = \frac{3 P}{\rho}$$

Then

$$C = \sqrt{\frac{3 P}{\rho}}$$

$\rho$ is the density of gas ( $\frac{kg}{m^3}$ )

## Relation between Speed of gas molecules and tempeature :

For one mole of gas we can write

$$P = \frac{1}{3} \frac{m \, NAvo \, C^2}{V_{mol}}$$

Where $N_{avo}$ is Avogadro's number = 6.0221 x $10^{23}$ /mol

From the ideal gas law, and for one mole of gas ( n = 1 )

$$P\ V_{mol} = n\ R_o\ T = R_o\ T$$

Where $\mathbf{R_o}$ is universal gas constant = 8.3145 J/mol K

$$P\ V_{mol} = \frac{1}{3}\ m\ N_{avo} C^2$$

$$R_o\ T = \frac{1}{3}\ m\ N_{avo}\ C^2$$

$$C^2 = \frac{3T}{m}\ \frac{R_o}{N_{avo}}$$

$$C = \sqrt{\frac{3kT}{m}}$$

Where **k** is Boltzmann constant = $\frac{R_o}{N_{avo}}$ = 1.38066 x $10^{-23}$ J/K

If divided **k** by **m** ( mass of one molecule )

$$\frac{k}{m} = \frac{R_o}{m\ N_{Avo}}$$

And Molecular weight of gas $\mathbf{M = m\ N_{avo}}$

$$C^2 = 3T\,\frac{R_o}{M}$$

Gas constant **R** is

$$R = \frac{R_o}{M}$$

Obtained

$$C^2 = 3T\,R$$

$$C = \sqrt{3T\,R}$$

**The kinetic molecular theory can be used to explain each of the experimentally determined gas laws.**

### The Link Between *P* and *n*

The pressure of a gas results from collisions between the gas particles and the walls of the container. Each time a gas particle hits the wall, it exerts a force on the wall. An increase in the number of gas particles in the container increases the frequency of collisions with the walls and therefore the pressure of the gas.

### Avogadro's Hypothesis ($V \alpha N$)

As the number of gas particles increases, the frequency of collisions with the walls of the container must increase. This, in turn, leads to an increase in the pressure of the gas. Flexible containers, such as a balloon, will expand until the pressure of the gas inside the balloon once again balances the pressure of the gas outside. Thus, the volume of the gas is proportional to the number of gas particles.

At constant temperature

$$PV = Constant$$

## Dalton's Law of Partial Pressures

$$(P_t = P_1 + P_2 + P_3 + \dots)$$

Imagine what would happen if six ball bearings of a different size were added to the molecular dynamics simulator. The total pressure would increase because there would be more collisions with the walls of the container. But the pressure due to the collisions between the original ball bearings and the walls of the container would remain the same. There is so much empty space in the container that each type of ball bearing hits the walls of the container as often in the mixture as it did when there was only one kind of ball bearing on the glass plate. The total number of collisions with the wall in this mixture is therefore equal to the sum of the collisions that would occur when each size of ball bearing is present by itself. In other words, the total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual gases.

## Gauge Pressure

A gauge is often used to measure the pressure difference between a system and the surrounding atmosphere. Gauge pressure is the pressure relative to atmospheric pressure. Therefore, it is positive for pressures above atmospheric pressure, and negative for pressures below it. This pressure is the gauge pressure and can be expressed as:

$$p_g = p_s - p_{atm}$$

Where:

$p_g$ = gauge pressure
$p_s$ = system pressure (absolute pressure )
$p_{atm}$ = atmospheric pressure

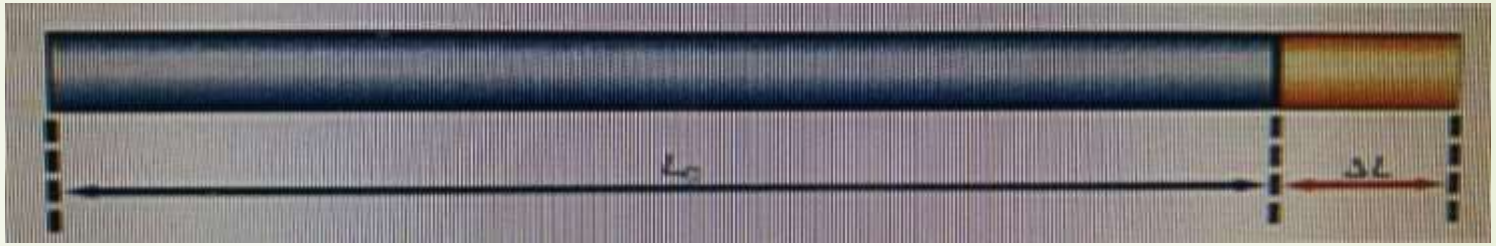
## Atmospheric Pressure

Standard sea-level pressure, by definition, equals 760 mm (29.92 inches) of mercury, 14.70 pounds per square inch, $1,013.25 \times 10^3$ dynes per square centimetre, $1.01325 \times 10^5$ Newtons per square metre, 1,013.25 millibars, one standard atmosphere, or 101.325 kilopascals.

# Expansion of Material

## Linear Expansion of Solids

It is a well-known fact that most materials expand when heated. This expansion is called thermal expansion. If a long thin rod of length $L_0$, at an initial temperature $T_i$, is heated to a final temperature $T_f$, then the rod expands by a small length $\Delta L$, as shown in figure 1

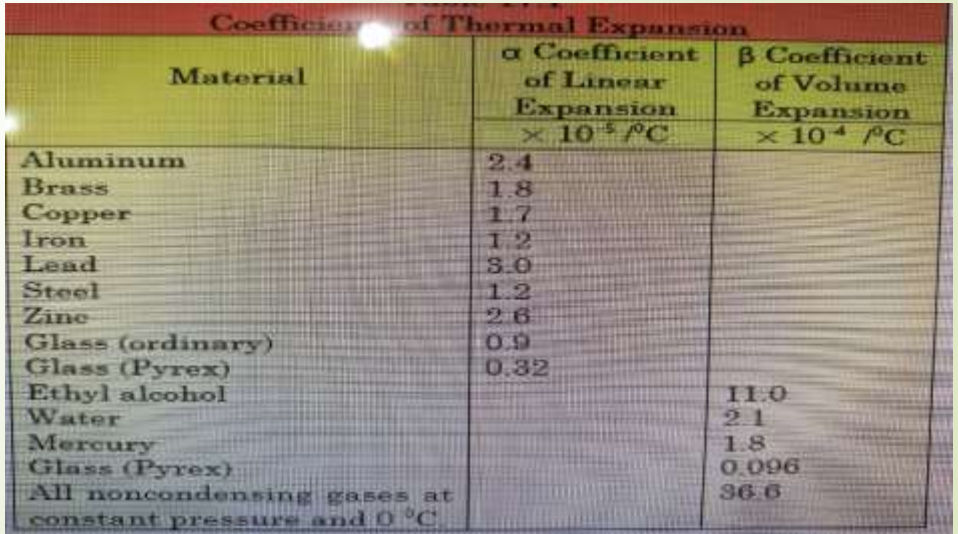


**( Fig. 1 ) Linear Expansion**

It is found by experiment that the change in length $\Delta L$ depends on the temperature change, $\Delta T = T_f - T_i$; the initial length of the rod $L_0$, and a constant that is characteristic of the material being heated. The experimentally observed linearity between $\Delta L$ and $L_0\Delta t$ can be represented by the equation

$$\Delta L = aL_0\Delta T \qquad (1)$$

We call the constant **a** the coefficient of linear expansion. The change in length is rather small, but it is, nonetheless, very significant.



Coeffici[illegible] of Thermal Expansion

| Material | α Coefficient of Linear Expansion × 10⁻⁵ /°C | β Coefficient of Volume Expansion × 10⁻⁴ /°C |
|---|---|---|
| Aluminum | 2.4 | |
| Brass | 1.8 | |
| Copper | 1.7 | |
| Iron | 1.2 | |
| Lead | 3.0 | |
| Steel | 1.2 | |
| Zinc | 2.6 | |
| Glass (ordinary) | 0.9 | |
| Glass (Pyrex) | 0.32 | |
| Ethyl alcohol | | 11.0 |
| Water | | 2.1 |
| Mercury | | 1.8 |
| Glass (Pyrex) | | 0.096 |
| All noncondensing gases at constant pressure and 0 °C | | 36.6 |

## Example 1

Expansion of a railroad track. A steel railroad track was 30.0 m long when it was initially laid at a temperature of −6.70 $^0$C. What is the change in length of the track when the temperature rises to 35.0 $^0$C? If the coefficient of linear expansion for steel $a_{steel} = 1.20 \times 10^{-5}/^0C$.

**Solution**

The change in length becomes

$$\Delta L = aL_0\Delta T$$

$$\Delta L = (1.20 \times 10^{-5}/^0C)(30.0\ m)(35.0\ ^0C - (-6.70\ ^0C)$$

$$\Delta L = 0.0150\ m = 1.50\ cm$$

Even though the change in length is relatively small, 1.50 cm in a distance of 30.0 m, it is easily measurable. The new length of the track becomes

$$L = L_0 + \Delta L$$

$$L = 30.0\ m + 0.0150\ m = 30.0150\ m$$

As you can see the new length is essentially the same as the old length. Why then is this thermal expansion so significant? Associated with this small change in length is a very large force. We can determine the force associated with this expansion by computing the force that is necessary to compress the rail back to its former length. The amount that a body is stretched or compressed is given by Hooke’s law as

$$\frac{F}{A} = Y\ \frac{\Delta L}{L_0}$$

We can solve this equation for the force that is associated with a compression. Taking the compression of the rail as 0.0150 m, Young’s modulus Y for steel as $2.10 \times 10^{11}$ N/m$^2$, and assuming that the cross-sectional area of the rail is 130 cm$^2$, the force necessary to compress the rail is

$$F = AY\,\frac{\Delta L}{L_0}$$

$$\mathbf{F} = (0.013\ \mathrm{m}^2)\ 2.10 \times 10^{11}\ \mathrm{N/m}^2\ (\ 0.0150\ \mathrm{m}\ /\ 30.0\ \mathrm{m}\ )$$

$$\mathbf{F} = 1.37 \times 10^6\ \mathrm{N}$$

This force of $1.37 \times 10^6$ N that is necessary to compress the rail by 1.50 cm, is also the force that is necessary to prevent the rail from expanding. It is obviously an extremely large force. It is this large force associated with the thermal expansion that makes thermal expansion so important. It is no wonder that we see and hear of cases where rails and roads have buckled during periods of very high temperatures.

The expansion of the solid can be explained by looking at the molecular structure of the solid. The molecules of the substance are in a lattice structure. Any one molecule is in equilibrium with its neighbors, but vibrates about that equilibrium position. As the temperature of the solid is increased, the vibration of the molecule increases. However, the vibration is not symmetrical about the original equilibrium position. As the temperature increases the equilibrium position is displaced from the original equilibrium position. Hence, the mean displacement of the molecule from the original equilibrium position also increases, thereby spacing all the molecules farther apart than they were at the lower temperature. The fact that all the molecules are farther apart manifests itself as an increase in length of the material. Hence, linear expansion can be explained as a molecular phenomenon. The large force associated with the expansion comes from the large molecular forces between the molecules. A more sophisticated approach to linear expansion can be found by writing equation 12.1 in the calculus form

$$dL = a L dT$$

which can be written as

$$\frac{dL}{L} = a\,dT \qquad (2)$$

and then integrated as

$$\int \frac{dL}{L} = \int a\, DT$$

The rod has the length $L_0$ when it is at the temperature $t_0$, and these values become the lower limits of integration, while the rod has the length L when it is at the temperature t, and these values become the upper limits of the integration. Assuming that the coefficient of thermal expansion a is a constant it can be taken outside of the integral to yield

$$\int \frac{dL}{L} = a \int dT$$

Upon integrating we obtain

$$\ln L \,|^{L}_{Lo} = a \;\; t \,|^{T}_{To}$$

$$\ln L - \ln L_0 = a \;( T - T_0 )$$

$$\ln \left(\frac{L}{L_0}\right) = a\, ( T - T_0 )$$

$$\frac{L}{L_0} = e^{\,a\,(T - T_0)}$$

and the final length of the rod after the expansion becomes

$$L = L_0\, e^{\,a\,(T - T_0)} \qquad (3)$$

## Example 2

The new length of the railroad track. Find the new length of the steel railroad track of $t_1$ when it expands from the initial temperature of − 6.70 $^0$C to the final temperature of 35.0 $^0$C? The original length of the track was 30.0 m long. If the coefficient of linear expansion for steel is $\alpha_{steel} = 1.20 \times 10^{-5}/^0C$.

## Solution

The new length of the track, found from equation 3, is

$$\mathbf{L = L_0\, e^{\alpha (T - T_0)}}$$

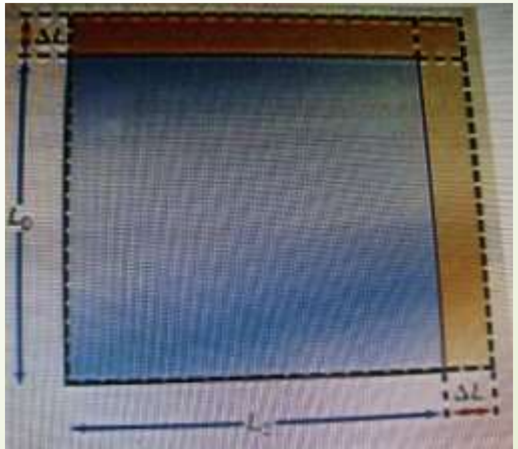
$$\mathbf{L = (30.0\ m)exp[(1.20*10^{-5}/\ ^0C)(35.0\ ^0C - (-\ 6.70\ ^0C))]}$$

$$\mathbf{L = 30.0150\ m}$$

which is the same length we obtained in the simpler version in example 1.

## Area Expansion of Solids

For the long thin rod, only the length change was significant and that was all that we considered. But solids expand in all directions. If a rectangle of thin material of length $L_1$ and width $L_2$, at an initial temperature of $t_i$, is heated to a new temperature $t_f$, the rectangle of material expands, as shown in figure 2



**( Fig. 2 ) Area Expansion**

original area of the rectangle is given by

$$A = L_1L_2 \qquad (4)$$

The change in area of the rectangle caused by a change in temperature of the material is found by differentiating equation 4 with respect to the temperature T. That is

$$\frac{dA}{dT} = L_1\frac{dL_2}{dT} + L_2\frac{dL_1}{dT}$$

Let us now divide both sides of this equation by equation 4 to get

$$\frac{1}{A}\frac{dA}{dT} = \frac{L_1}{L_1L_2}\frac{dL_2}{dT} + \frac{L_2}{L_1L_2}\frac{dL_1}{dT}$$

which yields

$$\frac{1}{A}\frac{dA}{dT} = \frac{1}{L_2}\frac{dL_2}{dT} + \frac{1}{L_1}\frac{dL_1}{dT}$$

But found before

$$a = \frac{1}{L}\frac{dL}{dT}$$

Thus

$$\frac{1}{L_1}\frac{dL_1}{dT} = a\,, \qquad \text{and } \frac{1}{L_2}\frac{dL_2}{dT} = a$$

Hence

$$\frac{1}{A}\frac{dA}{dT} = a + a = 2\,a$$

The change in area dA of a material, caused by a change in temperature dt, is

$$dA = 2aAdT \qquad (5)$$

Equation 5 gives us the area expansion dA of a material of original area A when subjected to a temperature change dT. Note that the coefficient of area expansion is twice the coefficient of linear expansion. Although we have derived this result for a rectangle it is perfectly general and applies to any area. For example, if the material was circular in shape, the original area $A_0$ would be computed from the area of a circle of radius $r_0$ as

$$A_0 = \pi r_0^2$$

We would then find the change in area from equation 5.

$$\Delta A = 2\alpha A_0 \Delta T$$

The new area can be found by adding the change in area $\Delta A$ to the original area $A_0$ as

$$A = A_0 + \Delta A \qquad (6)$$

or using the same calculus approach we used with equation 2 that culminated with equation 3 we would obtain for the final area of the material.

$$A = A_0\, e^{2\alpha (T - T_0)} \qquad (7)$$

**Example 3**

The change in area. An aluminum sheet 2.50 m long and 3.24 m wide is connected to some posts when it was at a temperature of −10.5 $^0$C. What is the change in area of the aluminum sheet when the temperature rises to 65.0 $^0$C? If the coefficient of linear expansion for aluminum, is $\alpha_{Al} = 2.4 \times 10^{-5}/^0C$.

**Solution**

The original area of the sheet, found from equation 4, is

$$A_0 = L_1 L_2$$

$$A_0 = (2.50\ \text{m})(3.24\ \text{m}) = 8.10\ \text{m}^2$$

The change in area, found from equation 5, is

$$\Delta \mathbf{A} = \mathbf{2a A_0 \Delta T}$$

$$\Delta \mathbf{A} = 2(2.4 \times 10^{-5}/{}^0\mathrm{C})(8.10\ \mathrm{m}^2)(65.0\ {}^0\mathrm{C} - (-10.5\ {}^0\mathrm{C})$$

$$\Delta \mathbf{A} = 0.0294\ \mathrm{m}^2 = 294\ \mathrm{cm}^2$$

The new area of the sheet becomes

$$\mathbf{A = A_0 + \Delta A}$$

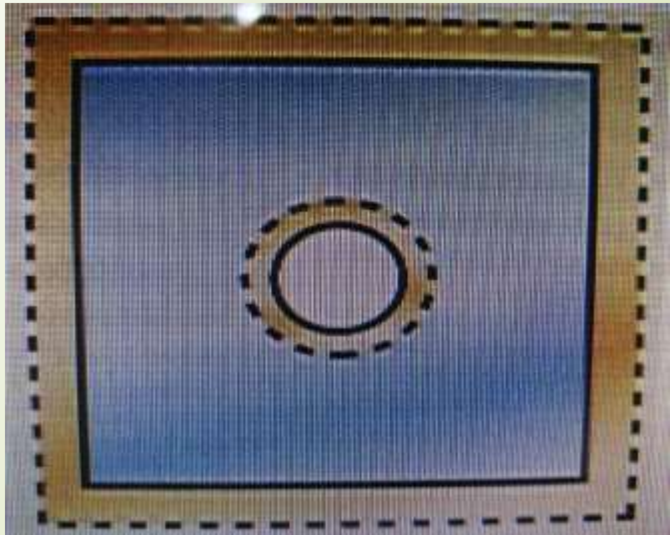
$$\Delta \mathbf{A} = 8.10\ \mathrm{m}^2 + 0.0294\ \mathrm{m}^2$$

$$\Delta \mathbf{A} = 8.13\ \mathrm{m}^2$$

Again notice that the new area is essentially the same as the old area, and the significance of this small change in area is the very large force that is associated with this thermal expansion.

All parts of a material expand at the same rate. For example, if there was a circular hole in the material, the empty hole would expand at the same rate as if material were actually present in the hole. We can see this in figure 3. The solid line represents the original material, whereas the dotted lines represent the expanded material.

Many students feel that the material should expand into the hole, thereby causing the hole to shrink. The best way to show that the hole does indeed expand is to fill the hole with a plug made of the same material. As the material expands, so does the plug. At the end of the expansion remove the plug, leaving the hole. Since the plug expanded, the hole must also have grown. Thus, the hole expands as though it contained material. This result has many practical applications.



**( Fig. 3 )**

**Example 4**

Fitting a small wheel on a large shaft. We want to place a steel wheel on a steel shaft with a good tight fit. The shaft has a diameter of 10.010 cm. The wheel has a hole in the middle, with a diameter of 10.000 cm, and is at a temperature of 20 $^0$C. If the wheel is heated to a temperature of 132 $^0$C, will the wheel fit over the shaft ? The coefficient of linear expansion for steel is found as a = $1.20 \times 10^{-5}/^0C$.

**Solution**

The present area of the hole in the wheel is not large enough to fit over the area of the shaft. We want to heat the wheel so that the new expanded area of the heated hole in the wheel will be large enough to fit over the area of the shaft. With the present dimensions the wheel can not fit over the shaft. If we place the wheel in an oven at 132 $^0$C, the wheel expands. We can solve this problem by looking at the area of the hole and the shaft, but it can also be analyzed by looking at the diameter of the hole and the diameter of the shaft. When the wheel is heated, the diameter of the hole increases by

$$\mathbf{\Delta L_H = a L_0 \Delta T}$$

$$\mathbf{\Delta L_H} = (1.20 \times 10^{-5}/^0C)(10.000\ cm)(132\ ^0C - 20\ ^0C) = 1.34 \times 10^{-2}\ cm$$

The new hole in the wheel has the diameter

$$\mathbf{L = L_0 + \Delta L}$$

$$\mathbf{L} = 10.000\ cm + 0.013\ cm = 10.013\ cm$$

Because the diameter of the hole in the wheel is now greater than the diameter of the shaft, the wheel now fits over the shaft. When the combined wheel and shaft is allowed to cool back to the original temperature of 20 $^0$C, the hole in the wheel tries to contract to its original size, but is not able to do so, because of the presence of the shaft. Therefore, the enormous forces associated with the thermal compression when the wheel is cooled, are exerted on the shaft by the wheel, holding the wheel permanently on the shaft.

# Volume Expansion of Solids and Liquids

All materials have three dimensions, length, width, and height. When a body is heated, all three dimensions should expand and hence its volume should increase. Let us consider a solid box of length $L_1$, width $L_2$, and height $L_3$, at an initial temperature $t_i$. If the material is heated to a new temperature $t_f$, then each side of the box undergoes an expansion dL. The volume of the solid box is given by

$$V = L_1L_2L_3 \qquad (8)$$

The change in volume of the box caused by a change in temperature of the material is found by differentiating equation 8 with respect to the temperature t. That is

$$\frac{dV}{dT} = L_2\,L_3\,\frac{dL_1}{dT} + L_1\,L_3\,\frac{dL_2}{dT} + L_1\,L_2\,\frac{dL_3}{dT}$$

Let us now divide both sides of this equation by equation 8 to get

$$\frac{1}{V}\,\frac{dV}{dT} = \frac{L_2\,L_3}{L_1L_2L_3}\,\frac{dL_1}{dT} + \frac{L_1\,L_3}{L_1L_2L_3}\,\frac{dL_2}{dT} + \frac{L_1\,L_2}{L_1L_2L_3}\,\frac{dL_3}{dT}$$

which yields

$$\frac{1}{V}\,\frac{dV}{dT} = \frac{1}{L_1}\,\frac{dL_1}{dT} + \frac{1}{L_2}\,\frac{dL_2}{dT} + \frac{1}{L_3}\,\frac{dL_3}{dT}$$

But found before

$$a = \frac{1}{L}\,\frac{dL}{dT}$$

Thus

$$\frac{1}{L_1}\,\frac{dL_1}{dT} = a\,, \qquad \frac{1}{L_2}\,\frac{dL_2}{dT} = a \qquad \text{and}\ \frac{1}{L_2}\,\frac{dL_2}{dT} = a$$

Hence

$$\frac{1}{V}\frac{dV}{dT} = a + a + a = 3\,a$$

The change in area dV of a material, caused by a change in temperature dt, is

$$dV = 3aVdT \qquad (9)$$

Equation 9 gives us the volume expansion dV of a material of original volume V when subjected to a temperature change dt. Note that the coefficient of volume expansion is three times the coefficient of linear expansion. Although we have derived this result for a solid box it is perfectly general and applies to any volume. We now define a new coefficient, called the coefficient of volume expansion β, for solids as

$$\beta = 3a \qquad (10)$$

Therefore, the change in volume of a substance when subjected to a change in temperature is

$$dV = \beta VdT \qquad (11)$$

Equation 11 gives the differential change in volume dV, caused by a differential change in temperature dt. When dealing with finite quantities, equation 11 is written in the finite form

$$\Delta V = \beta V\Delta T \qquad (12)$$

Although we derived equation 11 for a solid box, it is perfectly general and applies to any volume of a solid and even for any volume of a liquid. However, since a has no meaning for a liquid, we must determine β experimentally for the liquid. Just as a hole in a surface area expands with the surface area, a hole in a volume also expands with the volume of the solid. Hence, when a hollow glass tube expands, the empty volume inside the tube expands as though there were solid glass present. The new volume can be found by using the same calculus approach we used to obtain the final length of the material that culminated with equation 3. Using this same approach we obtain

$$V = V_0 e^{a(T-T0)} \qquad (13)$$

for the final volume of the material. The final volume can also be found by adding the change in volume $\Delta V$ to the original volume $V_0$ as

$$V = V_0 + \Delta V \qquad (14)$$

**Example 5**

An aluminum box 0.750 m long, 0.250 m wide, and 0.450 m high is at a temperature of −15.6 $^0$C. What is the change in volume of the aluminum box when the temperature rises to 120 $^0$C? If the coefficient of linear expansion for aluminum is $a_{Al} = 2.4 \times 10^{-5}/^0C$.

**Solution**

The original volume of the box, found from equation 8, is

$$V_0 = L_1L_2L_3$$

$$V_0 = (0.750\ m)(0.250\ m)(0.450\ m)$$

$$V_0 = 0.0844\ m^3$$

The change in volume, found from equation 12, is

$$\Delta V = 3aV_0\Delta T$$

$$\Delta V = 3(2.4 \times 10^{-5}/^0C)(0.0844\ m^3)(120\ ^0C - (-15.6\ ^0C)$$

$$\Delta V = 0.00082\ m^3 = 8.24\ cm^3$$

The new volume of the box becomes

$$V = V_0 + \Delta V$$

$$V = 0.0844\ m^3 + 0.00082\ m^3$$

$$V = 0.0852\ m^3$$

Again notice that the new volume is very close to the original volume.

## Example 6

An open glass tube is filled to the top with 25.0 $cm^3$ of mercury at an initial temperature of 20.0 $^0C$. If the mercury and the tube are heated to 100 $^0C$, how much mercury will overflow from the tube? If $\beta_{Hg} = 1.80 \times 10^{-4}\ /^0C$ and $\beta_{gl.} = 0.27 \times 10^{-4}\ /^0C$

## Solution

The change in volume of the mercury, found from equation 12 is

$$\boldsymbol{\Delta V_{Hg} = \beta_{Hg} V_0 \Delta T}$$

$$\Delta \mathbf{V}_{\mathbf{Hg}} = (1.80 \times 10^{-4}/^0C)(25.0\ cm^3)(100\ ^0C - 20\ ^0C)$$

$$\Delta \mathbf{V}_{\mathbf{Hg}} = 0.360\ cm^3$$

If the glass tube did not expand, this would be the amount of mercury that overflows. But the glass tube does expand and is therefore capable of holding a larger volume. The increased volume of the glass tube is found from equation 12 but this time with glass

$$\boldsymbol{\Delta V_{gl} = \beta_{gl} V_0 \Delta T}$$

$$\Delta \mathbf{V}_{\mathbf{gl}} = (0.27 \times 10^{-4}\ /^0C)(25.0\ cm^3)(100\ ^0C - 20.0\ ^0C)$$

$$\Delta \mathbf{V}_{\mathbf{gl}} = 0.054\ cm^3$$

That is, the tube is now capable of holding an additional 0.054 $cm^3$ of mercury. The amount of mercury that overflows is equal to the difference in the two volume expansions. That is,

$$\textbf{Overflow} = \boldsymbol{\Delta V_{Hg} - \Delta V_{gl}}$$

$$\textbf{Overflow} = 0.360\ cm^3 - 0.054\ cm^3$$

$$\textbf{Overflow} = 0.306\ cm^3$$

**Example 7**

The height of the mercury in a barometer is 76.0 cm at an initial temperature of 20.0 $^0$C. If the actual atmospheric pressure does not change, but the temperature of the air, and hence the temperature of the mercury and the tube, rises to 35.0 $^0$C, what will the barometer indicate erroneously for the atmospheric pressure? If $\beta_{Hg} = 1.80 \times 10^{-4}\ /^0C$ and $\beta_{gl} = 0.27 \times 10^{-4}\ /^0C$

**Solution**

The change in volume of the mercury, found from equation 12 is

$$\Delta V_{Hg} = \beta_{Hg} V_0 \Delta T$$

But the volume of the mercury in the tube is equal to the cross sectional area A of the tube times the height h of the mercury in the tube. Hence the volume of the mercury is given by V = Ah and the change in volume of the mercury can be written as $\Delta V = A\ \Delta h$. Hence the change in volume of the mercury, equation 12 can now be written as

$$\Delta(Ah)_{Hg} = \beta_{Hg} (Ah_o)(T_f - T_i)$$

Canceling the cross-sectional area A term from each side of the equation yields the equation for the change in height of the mercury in the tube caused by the thermal expansion of the mercury in the tube.

$$\Delta h_{Hg} = \beta_{Hg}\ h_o(T_f - T_i)$$

$$\Delta h_{Hg} = (1.80 \times 10^{-4}/^0C)(76.0\ cm)(35.0\ ^0C - 20\ ^0C)$$

$$\Delta h_{Hg} = 0.205\ cm$$

If the glass tube did not expand, this would be the change in height of the mercury in the tube and the new height of the mercury in the tube would be

$$h = h_0 + \Delta h_{Hg}$$

$$h = 76.0\ cm + 0.205\ cm = 76.205\ cm$$

But the glass tube does expand and is therefore capable of holding a larger volume of mercury. The increased volume of the glass tube will cause the mercury not to expand as high and the change in height is found from equation 12 but this time with glass as

$$\mathbf{\Delta h_{gl} = \beta_{gl}\, h_o(T_f - T_i)}$$
$$\mathbf{\Delta h_{gl}} = (0.27 \times 10^{-4}/{}^{0}\mathrm{C})(76.0\ \mathrm{cm})(35.0\ {}^{0}\mathrm{C} - 20\ {}^{0}\mathrm{C})$$
$$\mathbf{\Delta h_{gl}} = 0.0308\ \mathrm{cm}$$

That is, the tube is now capable of holding an additional height of 0.0308 cm of mercury. The actual height h of the mercury is equal to the original height $h_0$ of the mercury plus the increase in height $\Delta h_{Hg}$ caused by the expansion of the mercury minus the decrease in height $\Delta h_{gl}$ caused by the expansion of the glass. Hence, the reading of the barometer is

$$\mathbf{h = h_0 + \Delta h_{Hg} - \Delta h_g}$$
$$\mathbf{h} = (76.0\ \mathrm{cm}) + (0.2052\ \mathrm{cm}) - (0.0308\ \mathrm{cm})$$
$$\mathbf{h} = 76.174\ \mathrm{cm}$$

In a weather station the process is actually reversed. The barometer would be read directly as 76.174 cm of Hg. Then the correction for the thermal expansion of the mercury and the thermal expansion of the glass would then yield for the actual atmospheric pressure
p = 76.174 cm − (0.2052 cm) + (0.0308 cm) = 76.0 cm of Hg.

# Volume Expansion of Gases: Charles' Law

Consider a gas placed in a tank, as shown in figure 4 The weight of the piston exerts a constant pressure on the gas. When the tank is heated, the pressure of the gas first increases. But the increased pressure in the tank pushes against the freely moving piston, and the piston moves until the pressure inside the tank is the same as the pressure exerted by the weight of the piston. Therefore the pressure in the tank remains a constant throughout the entire heating process. The volume of the gas increases during the heating process, as we can see by the new volume occupied by the gas in the top cylinder. In fact, we find the increased volume by multiplying the area of the cylinder by the distance the piston moves in the cylinder.

If the volume of the gas is plotted against the temperature of the gas, in Celsius degrees, we obtain the straight line graph in figure 5.

If the equation for this straight line is written in the point-slope Form, we get

$$V - V_0 = m' (T - T_0)$$

where V is the volume of the gas at the temperature T, $V_0$ is the volume of the gas at $T_0 = 0\ {}^0C$, and m is the slope of the line. We can also write this equation in the form

$$\Delta V = m' \Delta T \qquad (15)$$

( Fig. 4 )

Note that equation 15, which shows the change in volume of a gas, looks like the volume expansion formula 12, for the change in volume of solids and liquids, that is,

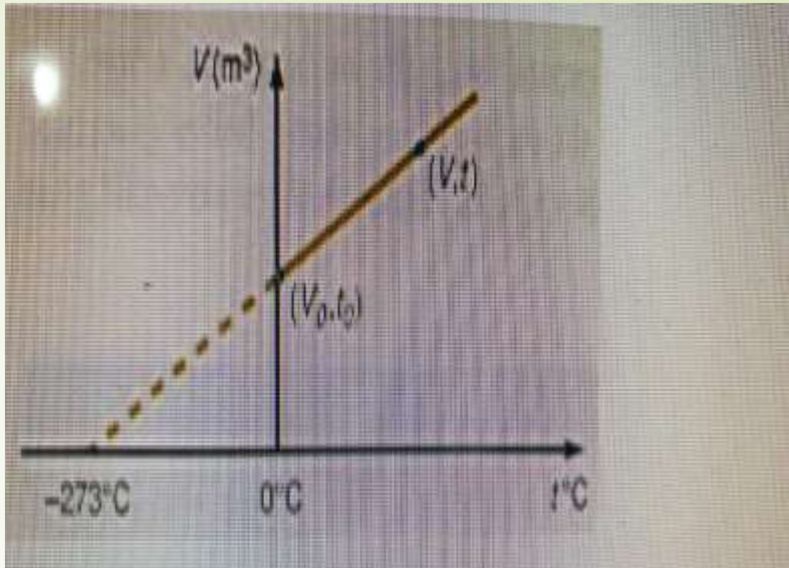
$$\Delta V = B v_0 \Delta T \qquad (12)$$

Let us assume, therefore, that the form of the equation for volume expansion is the same for gases as it is for solids and liquids. If we use this assumption, then

$$\beta V_0 = m'$$

Hence the coefficient of volume expansion for the gas is found experimentally as

$$\beta = \frac{m'}{V_0}$$



Plot of V versus t for a gas at constant pressure.

where m is the measured slope of the line. If we repeat this experiment many times for many different gases we find that

$$\beta = \frac{1}{273\ {}^0C} = \frac{3.66 \times 10^{-3}}{{}^0C}$$

For all noncondensing gases at constant pressure. This result was first found by the French physicist, J. Charles (1746-1823). This is a rather interesting result, since the value of β is different for different solids and liquids, and yet it is a constant for all gases. Equation 12 can now be rewritten as

$$V - V_0 = \beta V_0 (T - T_0)$$

For all noncondensing gases at constant pressure. This result was first found by the French physicist, J. Charles (1746-1823). This is a rather interesting result, since the value of β is different for different solids and liquids, and yet it is a constant for all gases. Equation 12 can now be rewritten as

$$\mathbf{V - V_0 = \beta V_0(T - T_0)}$$

Because $T_0 = 0\ {}^0C$, we can simplify this to

$$\mathbf{V - V_0 = \beta V_0\, T}$$

and

$$\mathbf{V = V_0 + \beta V_0\, T}$$

or

$$\mathbf{V = V_0\,(1 + \beta T)} \qquad \mathbf{(16)}$$

Note that if the temperature $T = -273\ {}^0C$, then

$$\mathbf{V = V_0\,[\,1 + (\tfrac{-273}{273})\,] = V_0\ \ (1 - 1) = 0}$$

That is, the plot of V versus t intersects the T-axis at $-273\ {}^0C$, as shown in figure 5. Also observe that there is a linear relation between the volume of a gas and its temperature in degrees Celsius. Since $\beta = 1/273\ {}^0C$, equation 16 can be simplified further into

$$\mathbf{V = V_0\,[\,1 + (\tfrac{T}{273})\,] = V_0 + [\,(\,\tfrac{273 + T}{273}\,)\,]}$$

It was the form of this equation that led to the definition of the Kelvin or absolute temperature scale in the form

$$T_K = T\,^0C + 273 \qquad (17)$$

With this definition of temperature, the volume of the gas is directly proportional to the absolute temperature of the gas, that is,

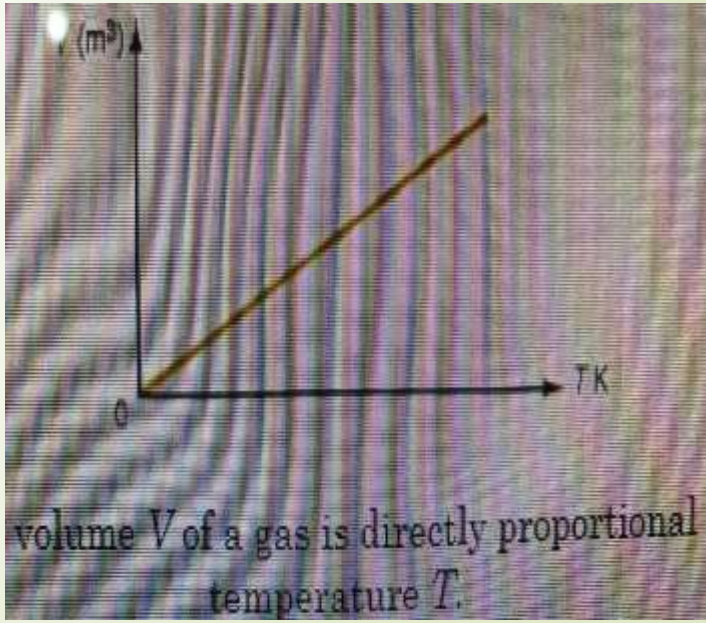
$$V = \frac{V_0}{273} T_K \qquad (18)$$

Changing the temperature scale is equivalent to moving the vertical coordinate of the graph, the volume, from the 0 0C mark in figure 5, to the −273 0C mark, and this is shown in figure 6. Thus, the volume of a gas at constant pressure is directly proportional to the absolute temperature of the gas. This result is known as Charles' law.

In general, if the state of the gas is considered at two different temperatures, we have

$$V_1 = \frac{V_0}{273} T_{K\,1} \quad \text{, and} \quad V_2 = \frac{V_0}{273} T_{K\,2}$$

( Fig. 6 )



volume V of a gas is directly proportional temperature T.

Hence,

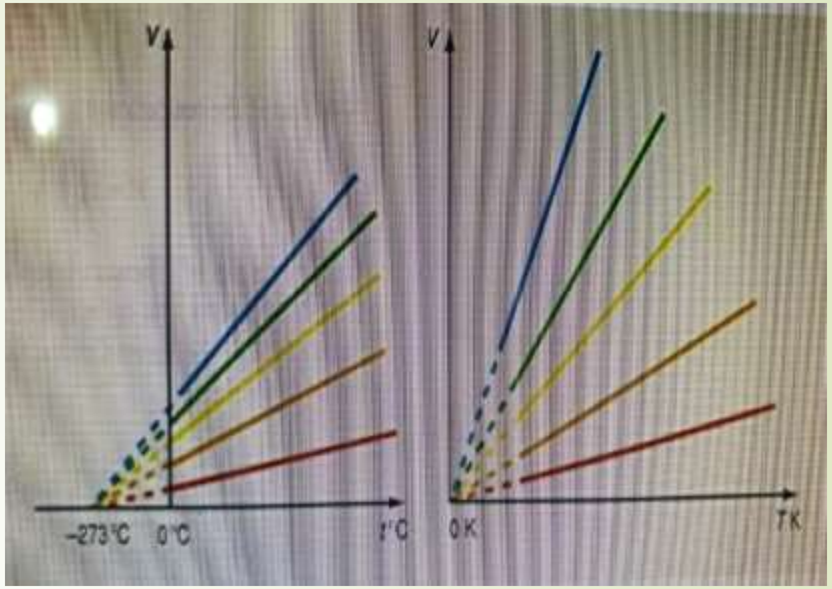
$$\frac{V_0}{273} = \frac{V_1}{T_{K\,1}} = \frac{V_2}{T_{K\,2}}$$

Therefore, at p = constant

$$\frac{V_1}{T_{K\,1}} = \frac{V_2}{T_{K2}} \qquad (19)$$

which is another form of **Charles' law**. Figures 6 and eq. 19 are slightly misleading in that they show the variation of the volume V with the temperature T of a gas down to −273 $^0C$ or 0 K.

However, the gas will have condensed to a liquid and eventually to a solid way before this point is reached. A plot of V versus T for all real gases is shown in figure 7. Note that when each line is extrapolated, they all intersect at −273 $^0$C or 0 K. Although they all have different slopes m, the coefficient of volume expansion ($\beta = m/V_0$) is the same for all the gases



**( Fig. 7 )**

## Charles' Law (V α T)

The average kinetic energy of the particles in a gas is proportional to the temperature of the gas. Because the mass of these particles is constant, the particles must move faster as the gas becomes warmer. If they move faster, the particles will exert a greater force on the container each time they hit the walls, which leads to an increase in the pressure of the gas. If the walls of the container are flexible, it will expand until the pressure of the gas once more balances the pressure of the atmosphere. The volume of the gas therefore becomes larger as the temperature of the gas increases.

For an ideal gas, the law,

$$PV = m\,R\,T \qquad \text{or} \qquad PV = n\,R_0\,T$$

At constant Pressure

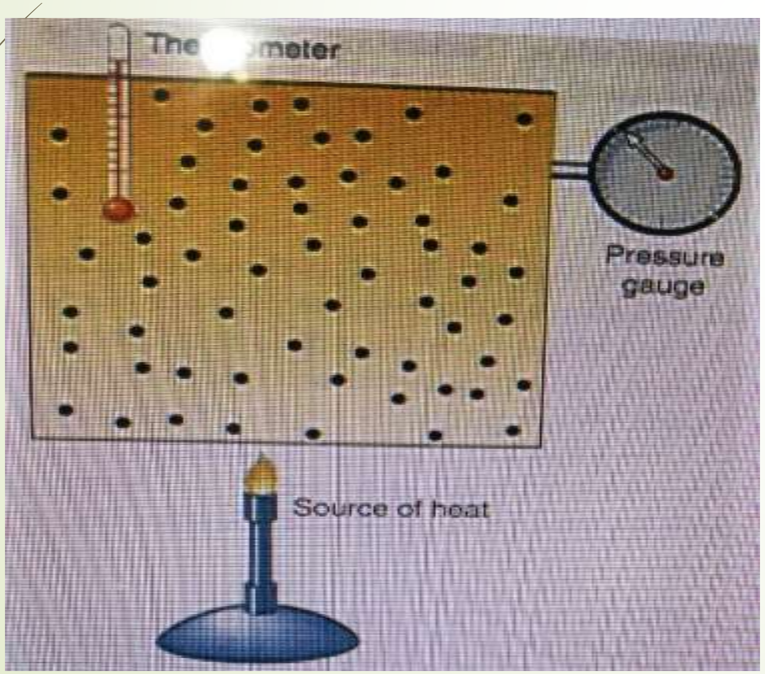
$$\frac{V}{T} = \frac{mR}{P} = \text{Constant} \qquad \text{or} \qquad \frac{V}{T} = \frac{n\,R_0}{P} = \text{Constant}$$

$$\frac{V}{T} = \text{Constant}$$

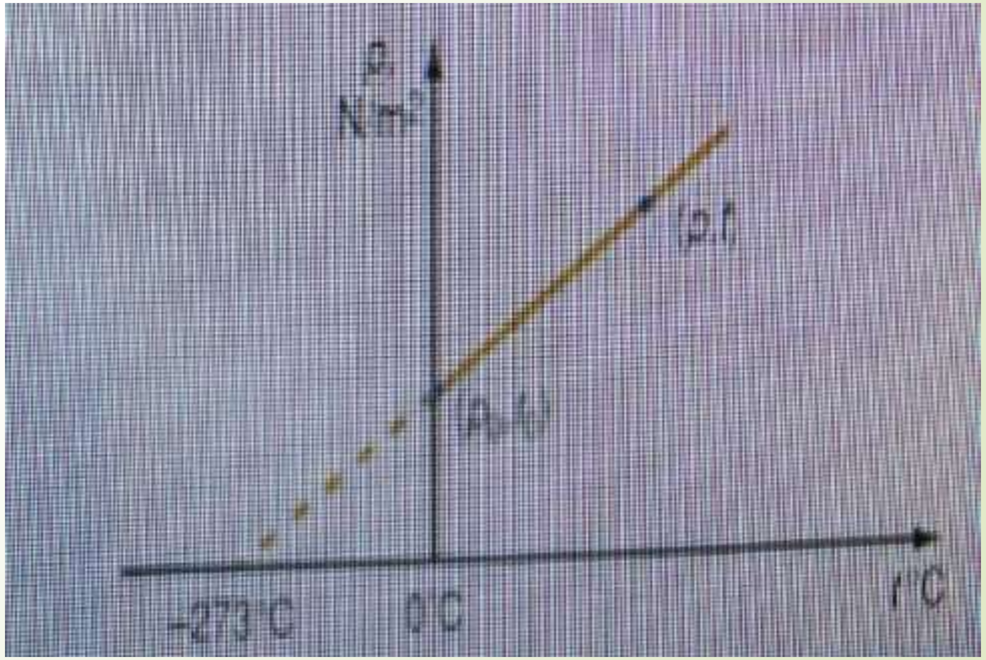
## Gay-Lussac's Law

Consider a gas contained in a tank, as shown in figure 8. The tank is made of steel and there is a negligible change in the volume of the tank, and hence the gas, as it is heated. A pressure gauge attached directly to the tank, is calibrated to read the absolute pressure of the gas in the tank. A thermometer reads the temperature of the gas in degrees Celsius. The tank is heated, thereby increasing the temperature and the pressure of the gas, which are then recorded. If we plot the pressure of the gas versus the temperature, we obtain the graph of figure 9. The equation of the resulting straight line is

$$p - p_0 = m'(t - t_0)$$



**( Fig. 8 )**



**( Fig. 9 )**

where p is the pressure of the gas at the temperature T, $\mathbf{P_0}$ is the pressure at the temperature $\mathbf{T_0}$, and m’ is the slope of the line. The prime is placed on the slope to distinguish it from the slope determined before.

$$P - P_0 = m'(T - T_0)$$

Because $\mathbf{T_0}$ = 0 0C, this simplifies to

$$P - P_0 = m'T$$

or

$$p = m'T + P_0 \qquad (20)$$

It is found experimentally that the slope is

$$m' = P_0\,\beta$$

where $\mathbf{P_0}$ is the absolute pressure of the gas and β is the coefficient of volume expansion for a gas. Therefore equation 20 becomes

$$p = P_0\,\beta\,T + P_0$$

and

$$p = P_0(\beta T + 1) \qquad (21)$$

Thus, the pressure of the gas is a linear function of the temperature, as in the case of Charles’ law. Since β = 1/273 $^0$C this can be written as

$$p = P_0\left(\frac{T}{273} + 1\right)$$

$$p = P_0\left(\frac{T + 273}{273}\right)$$

But the absolute or Kelvin scale has already been defined as $T_K = T\,^0C + 273$ , therefore, equation becomes,

$$p = P_0\left(\frac{T_K}{273}\right)$$

Which shows that the absolute pressure of a gas at constant volume is directly proportional to the absolute temperature of the gas, a result known as Gay-Lussac's law, in honor of the French chemist Joseph Gay-Lussac (1778-1850). For a gas in different states at two different temperatures, we have

$$P_1 = P_0\left(\frac{T_{K1}}{273}\right) \quad , \quad \textbf{and} \qquad P_2 = P_0\left(\frac{T_{K2}}{273}\right)$$

Then

$$\left(\frac{P_0}{273}\right) = \left(\frac{P_1}{T_{K1}}\right) = \left(\frac{P_2}{T_{K2}}\right)$$

or , at V = constant

$$\frac{P_1}{T_{K1}} = \frac{P_2}{T_{K2}} \qquad (22)$$

Equation 22 is another form of Gay-Lussac's law. (Sometimes this law is also called Charles' law, since Charles and Gay-Lussac developed these laws independently of each other.)

**Gay-Lussac's Law** or called **Amonton's Law ($P \propto T$)**

The last postulate of the kinetic molecular theory states that the average kinetic energy of a gas particle depends only on the temperature of the gas. Thus, the average kinetic energy of the gas particles increases as the gas becomes warmer. Because the mass of these particles is constant, their kinetic energy can only increase if the average velocity of the particles increases. The faster these particles are moving when they hit the wall, the greater the force they exert on the wall. Since the force per collision becomes larger as the temperature increases, the pressure of the gas must increase as well.

For an ideal gas, the law,

$$\mathbf{PV = m\,R\,T} \quad \text{or} \quad \mathbf{PV = n\,R_0\,T}$$

At constant Volume

$$\frac{\mathbf{P}}{\mathbf{T}} = \frac{\mathbf{m\,R}}{\mathbf{V}} = \text{Constant} \quad \text{or} \quad \frac{\mathbf{P}}{\mathbf{T}} = \frac{\mathbf{n\,R_0}}{\mathbf{V}} = \text{Constant}$$

$$\frac{\mathbf{P}}{\mathbf{T}} = \text{Constant}$$

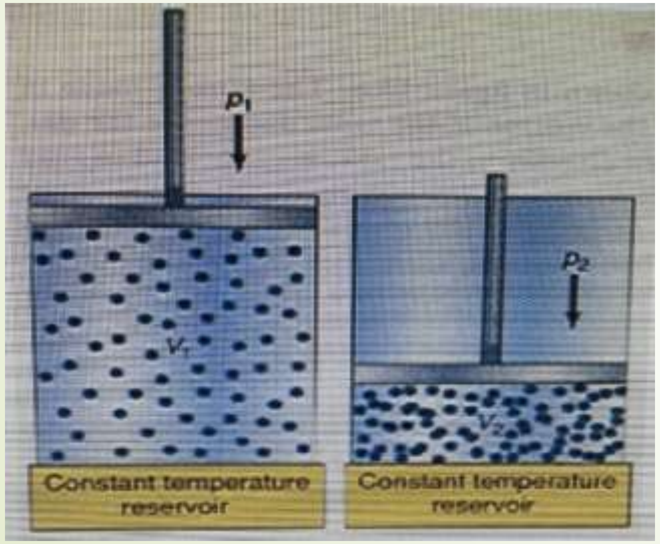
# Boyle's Law ($P \alpha 1/v$)

Consider a gas contained in a cylinder at a constant temperature, as shown in figure 10. By pushing the piston down into the cylinder, we increase the pressure of the gas and decrease the volume of the gas. If the pressure is increased in small increments, the gas remains in thermal equilibrium with the temperature reservoir, and the temperature of the gas remains a constant. We measure the volume of the gas for each increase in pressure and then plot the pressure of the gas as a function of the reciprocal of the volume of the gas. The result is shown in figure 11. Notice that the pressure is inversely proportional to the volume of the gas at constant temperature. We can write this as

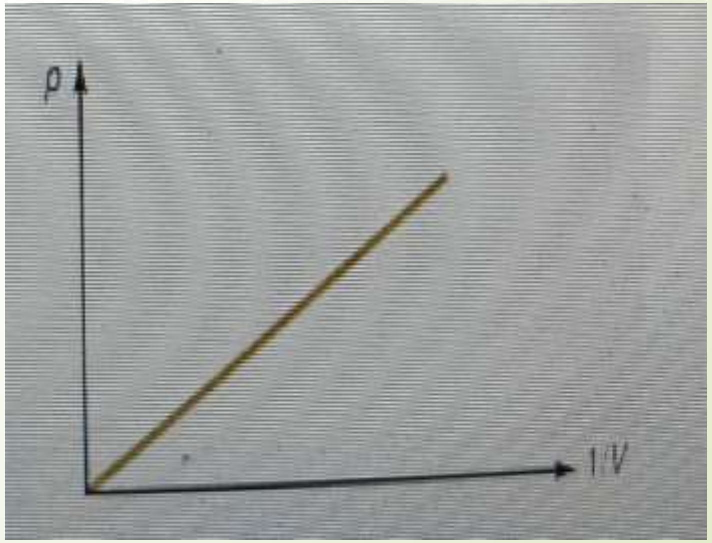
$$p \propto \frac{1}{V}$$

or

$$PV = \text{constant} \qquad (23)$$



( Fig. 10 )



( Fig. 11 )

That is, the product of the pressure and volume of a gas at constant temperature is equal to a constant, a result known as Boyle's law, in honor of the British physicist and chemist Robert Boyle (1627-1691). For a gas in two different equilibrium states at the same temperature, we write this as

$$\mathbf{P\,V = constant}$$

Then

$$\mathbf{P_1\,V_1 = constant \quad and \quad P_2\,V_2 = constant}$$

Therefore, at T = constant

$$\mathbf{P_1\,V_1 = P_2\,V_2} \qquad \mathbf{(\,24\,)}$$

Equation 24 is an another form of **Boyle's law**

Gases can be compressed because most of the volume of a gas is empty space. If we compress a gas without changing its temperature, the average kinetic energy of the gas particles stays the same. There is no change in the speed with which the particles move, but the container is smaller. Thus, the particles travel from one end of the container to the other in a shorter period of time. This means that they hit the walls more often. Any increase in the frequency of collisions with the walls must lead to an increase in the pressure of the gas. Thus, the pressure of a gas becomes larger as the volume of the gas becomes smaller.

For an ideal gas, the law, At constant Temperature

$$\mathbf{PV = m\,R\,T = \ Constant} \quad \text{or} \quad \mathbf{PV = n\,R_0\,T = \ Constant}$$

$$\mathbf{PV} = \text{Constant}$$

# Conclusion

## The Ideal Gas Law ( The three gas laws )

1. At P = constant

$$\frac{V_1}{T_{K1}} = \frac{V_2}{T_{K2}} \qquad (19)$$

2. At V = constant

$$\frac{P_1}{T_{K1}} = \frac{P_2}{T_{K2}} \qquad (22)$$

3. At T = constant

$$P_1 V_1 = P_2 V_2 \qquad (24)$$

can be combined into one equation, namely,

$$\frac{P_1 V_1}{T_{K1}} = \frac{P_2 V_2}{T_{K2}} \qquad (25)$$

Equation 25 is a special case of a relation known as the ideal gas law. Hence, we see that the three previous laws, which were developed experimentally, are special cases of this ideal gas law, when either the pressure, volume, or temperature is held constant. The ideal gas law is a more general equation in that none of the variables must be held constant. Equation 27 expresses the relation between the pressure, volume, and temperature of the gas at one time, with the pressure, volume, and temperature at any other time. For this equality to hold for any time, it is necessary that

$$\frac{PV}{T} = \text{constant} \qquad (26)$$

This constant must depend on the quantity or mass of the gas. A convenient unit to describe the amount of the gas is the mole. One mole of any gas is that amount of the gas that has a mass in grams equal to the atomic or molecular mass (M) of the gas. The terms atomic mass and molecular mass are often erroneously called atomic weight and molecular weight in chemistry. As an example of the use of the mole, consider the gas oxygen. One molecule of oxygen gas consists of two atoms of oxygen, and is denoted by O2. The atomic mass of oxygen is 16.00. The molecular mass of one mole of oxygen gas is therefore

$$M_{O2} = 2\,(16) = 32 \text{ g/mole}$$

Thus, one mole of oxygen has a mass of 32 g. The mole is a convenient quantity to express the mass of a gas because one mole of any gas at a temperature of 0 0C and a pressure of 1 atmosphere, has a volume of 22.4 liters. Also Avogadro's law states that every mole of a gas contains the same number of molecules. This number is called Avogadro's number NA and is equal to 6.022 × 1023 molecules/mole.

The mass of any gas will now be represented in terms of the number of moles, n. We can write the constant in equation 28 as n times a new constant, which shall be called R, that is,

$$PV = n R_0 T \qquad (27)$$

To determine this constant $\mathbf{R_0}$ let us evaluate it for 1 mole of gas at a pressure of 1 atm and a temperature of 0 $^0$C, or 273 K, and a volume of 22.4 L. That is,

$$PV = n\,T\,R_0$$

$$(1\ \text{atm})(22.4\ \text{L}) = (1\ \text{mole})(273\ \text{K})\,R_0$$

$$R_0 = 0.08205\ \text{atm L / mole K}$$

Converted to SI units, this constant is

$$R_0 = 0.08205 \times (\,1.013{\times}10^5\ \text{N/m2}\,)\,(\,10^{-3}\ \text{m}^3\,)\ \ /\ \text{mole K}$$

$$R_0 = 8.314\quad \text{J / mole K}$$

We call the constant $\mathbf{R_0}$ **the universal gas constant**, and it is the **same for all gases**. We can now write equation 27 as

$$PV = n\,R_0\,T \qquad (\,27\,)$$

Equation 27 is called **the ideal gas equation**. An ideal gas is one that is described by the ideal gas equation. Real gases can be described by the ideal gas equation as long as their density is low and the temperature is well above the condensation point (boiling point) of the gas. Remember that the temperature T must always be expressed in Kelvin units, and

$$R_0 = R_g\,M_g\ , \qquad R_g = \frac{R_0}{M_g} \qquad \text{and} \qquad n = \frac{m}{M_g}$$

Then

$$PV = n\,R_0\,T = \frac{m}{M_g}\,(R_g\,M_g\,)\,T$$

Equation 27 can now be rewritten as

$$PV = m\,R_g\,T \qquad (\,28\,)$$

Let us now look at some examples of the use of the ideal gas equation.

## Example 8

Find the temperature of the gas. The pressure of an ideal gas is kept constant while 3.00 $m^3$ of the gas, at an initial temperature of 50.0 $^0C$, is expanded to 6.00 $m^3$. What is the final temperature of the gas?

**Solution**

The temperature must be expressed in Kelvin units. Hence the initial temperature becomes

$$\mathbf{T_K = T\ {}^0C + 273 = 50.0 + 273 = 323\ K}$$

We find the final temperature of the gas by using the ideal gas equation in the form of equation 25, namely,

$$\frac{P_1V_1}{T_{K1}} = \frac{P_2V_2}{T_{K2}} \qquad (25)$$

However, since the pressure is kept constant, $\mathbf{P_1 = P_2}$, and cancels out of the equation. Therefore, obtained equation ( 19 )

$$\frac{V_1}{T_{K1}} = \frac{V_2}{T_{K2}} \qquad (19)$$

and the final temperature of the gas becomes

$$T_{K2} = \frac{V_1}{V_2} T_{K1}$$

$$T_{K2} = \frac{6.00\ m^3}{3.00\ m^3}\ (323\ K)$$

$$T_{K2} = 646\ K$$

$$T_2 = 646\ K - 273 = 373\ {}^0C$$

## Example 9

Find the volume of the gas. A balloon is filled with helium at a pressure of $2.03 \times 10^5$ N/m$^2$, a temperature of 35.0 $^0$C, and occupies a volume of 3.00 m$^3$. The balloon rises in the atmosphere. When it reaches a height where the pressure is $5.07 \times 10^4$ N/m$^2$, and the temperature is −20.0 $^0$C, what is its volume?

## Solution

First we convert the two temperatures to absolute temperature units as

$$T_{K1} = 35.0\ ^0C + 273 = 308\ K$$

and

$$T_{K2} = -20.0\ ^0C + 273 = 253\ K$$

We use the ideal gas law in the form ( equation 25 )

$$\frac{P_1V_1}{T_{K1}} = \frac{P_2V_2}{T_{K2}} \qquad (25)$$

Solving for $V_2$ gives, for the final volume,

$$V_2 = \left(\frac{P_1}{P_2}\right)\left(\frac{T_{K2}}{T_{K1}}\right)V_1$$

$$V_2 = \left(\frac{2.03\times105\ N/m^2}{5.07\ \times104\ N/m^2}\right)\left(\frac{253\ K}{308\ K}\right)(3.00\ m^3)$$

$$V_2 = 9.87\ m^3$$

# Example 10

What is the pressure produced by 2.00 moles of a gas at 35.0 $^0$C contained in a volume of 5.00 × $10^{-3}$ $m^3$ ?

## Solution

We convert the temperature of 35.0 $^0$C to Kelvin by

$$\mathbf{T = 35.0\ ^0C + 273 = 308\ K}$$

We use the ideal gas law in the form

$$\mathbf{PV = n\,R_0\,T} \qquad (27)$$

Solving for P,

$$\mathbf{P = \frac{n\,R_0\,T}{V}}$$

$$\mathbf{P} = \frac{(2.00\text{ moles})(8.314\text{ J /mole K})(308\text{ K})}{5.00 \times 10^{-3}\text{ m}^3}$$

$$\mathbf{P} = 1.02 \times 10^6\ \text{N/ m}^2$$

**Example 11**

Compute the number of molecules in a gas contained in a volume of 10.0 $cm^3$ at a pressure of $1.013 \times 10^5$ $N/m^2$, and a temperature of 300 K.

**Solution**

The number of molecules in a mole of a gas is given by Avogadro's number $N_A$ ($6.022 \times 10^{23}$ ) and hence the total number of molecules N in the gas is given by

$$\mathbf{N = nN_A}$$

Therefore we first need to determine the number of moles of gas that are present. From the ideal gas law,

$$\mathbf{PV = n\, R_0\, T} \qquad (27)$$

$$\mathbf{n = \frac{PV}{R_0\, T}}$$

$$\mathbf{n =} \frac{[\,(1.013\times105\ N/m^2)(10.0\ cm^3 \times 10^{-6})\,]}{[\,(8.314\ J/mole\ K)(300\ K)\,]}$$

$$\mathbf{n =} 4.06 \times 10^{-4} \text{ moles}$$

The number of molecules is now found as

$$\mathbf{N = nN_A =} (4.06 \times 10^{-4} \text{ mole})\ 6.022\times10^{23}$$

$$\mathbf{N =} 2.45 \times 10^{20} \text{ molecules}$$

## Example 12

An automobile tire has a volume of 81,900 $cm^3$ and contains air at a gauge pressure of $2.07 \times 10^5$ $N/m^2$ when the temperature is $0.00\ ^0C$. What is the gauge pressure when the temperature rises to $30.0\ ^0C$?

## Solution

When a gauge is used to measure pressure, it reads zero when it is under normal atmospheric pressure of $1.013 \times 10^5$ $N/m^2$. The pressure used in the ideal gas equation must be the absolute pressure ( system pressure ), that is, the total pressure, which is the pressure read by the gauge plus atmospheric pressure. Therefore,

$$\mathbf{P_{absolute} = P_{gauge} + P_{atm}}$$

Thus, the initial pressure of the gas is

$$\mathbf{P_1 = P_{gauge} + P_{atm}}$$

$$\mathbf{P_1} = 2.07 \times 10^5\ N/m^2 + 1.01 \times 10^5\ N/m^2$$

$$\mathbf{P_1} = 3.08 \times 10^5\ N/m^2$$

The initial volume of the tire is $V_1$ = 81,900 $cm^3$ and the change in that volume is small enough to be neglected, so $V_2$ = 81,900 $cm^3$. The initial temperature and the final temperature are

$$\mathbf{T_1 = 0.00\ ^0C + 273 = 273\ K \quad and \quad T_2 = 30.0\ ^0C + 273 = 303\ K}$$

We use the ideal gas law in the form ( equation 25 )

$$\frac{P_1 V_1}{T_{K1}} = \frac{P_2 V_2}{T_{K2}} \qquad (25)$$

Solving the ideal gas equation for the final pressure,,  we get

$$P_2 = \left(\frac{V_1}{V_2}\right)\left(\frac{T_{K2}}{T_{K1}}\right) P_1$$

$$P_2 = \left(\frac{81{,}900\ \mathrm{cm}^3}{81{,}900\ \mathrm{cm}^3}\right)\left(\frac{303\ \mathrm{K}}{273\ \mathrm{K}}\right)\left(3.08\times10^5\ \mathrm{N/m}^2\right) = 3.42 \times 105\ \mathrm{N/m}^2$$

Or , we can write at constant volume

$$P_2 = \left(\frac{T_{K2}}{T_{K1}}\right) P_1$$

$$P_2 = \left(\frac{303\ \mathrm{K}}{273\ \mathrm{K}}\right)\left(3.08\times10^5\ \mathrm{N/m}^2\right) = 3.42 \times 105\ \mathrm{N/m}^2$$

$$P_2 = 3.42 \times 105\ \mathrm{N/m}^2$$

Where **$P_2$** is absolute pressure, expressing this pressure in terms of gauge pressure we get

$$P_{2gauge} = P_{2absolute} - P_{atm}$$

$$P_{2gauge} = 3.42 \times 10^5\ \mathrm{N/m}^2 - 1.01 \times 10^5\ \mathrm{N/m}^2$$

$$P_{2gauge} = 2.41 \times 10^5\ \mathrm{N/m}^2$$