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Problems: See website,

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19.1 Temperature as a Measure of an average Kinetic Energy.

When objects at different temperatures are brought into contact heat is exchanged between them. They are said to be in **thermal contact**. Once they are at the "same" temperature they are said to be in **thermal equilibrium**.

We can only talk about **temperature T** in a situation with extremely large numbers of molecules involved. Every mole of a substance, i.e. the molecular or atomic mass in grams, contains Avogadro's number of molecules or atoms:

(19.1)
$$N_A = 6.022 \cdot 10^{23} \frac{molecules}{mole}$$

Caution:

n = number of moles,
N = number of molecules, N_A = Avogadro's number = number of molecules in 1 mole=$6.02 \cdot 10^{23}$,
$N = nN_A$

These individual molecules have a kinetic energy of translation

(19.2)
$$KE = \frac{1}{2}mv^2$$

The molecules have an **average** translational kinetic energy:

(19.3)
$$\overline{KE} = \frac{1}{2}m\overline{v^2} = \frac{\frac{1}{2}\sum_{i=1}^{N} m_i v_i^2}{N} = \frac{1}{2}\frac{\sum_{i=1}^{N} m_i \left(v_{ix}^2 + v_{iy}^2 + v_{iz}^2\right)}{N}$$

This average kinetic energy is a direct measure of the temperature T. Usually we write this relationship as:

(19.4)

$$\frac{3}{2}k_B T = \frac{1}{2}m\overline{v^2};\ k_B = 1.38 \cdot 10^{-23}\ \text{Boltzmann constant}$$

$$[k_B] = \frac{J}{K°} = \frac{Joules}{Kelvin}$$

If we multiply (19.4) with Avogadro's number we get the relationship for moles rather than for individual molecules.

(19.5)

$$\frac{3}{2}k_B N_A T = \frac{1}{2}m \cdot N_A \overline{v^2} = \frac{3}{2}\underset{k_B N_A}{\underbrace{R}}\ T = \frac{1}{2}\underset{m \cdot N_A}{\underbrace{M}}\ \overline{v^2} =$$

$$k_B N_A = 1.38 \cdot 10^{-23} \cdot 6.02 \cdot 10^{23}\ = R\ \text{universal gas constant}$$

$$R = 8.314\ \text{J/mol} \cdot K° = 0.08206\ \text{atm} \cdot L/\text{mol} \cdot K°$$

If we take the squareroot of the mean squared velocity we get the so-called **rms (root-mean-squared) speed** of the molecule.

(19.6)
$$v_{rms} = \sqrt{\overline{v^2}} \equiv \sqrt{\frac{\sum_i v_i^2}{N}} \text{ for N molecules}$$

Problem: Calculate the rms speed of an oxygen molecule at 20° C.

From this definition it is also obvious that absolute 0.00000…temperature cannot be achieved, as that would require absolute 0 kinetic energy and speed. This is not possible as long as Heisenberg's uncertainty relations (quantum physics) are correct, and we believe they are correct under all circumstances in our physical universe.

(19.7)
$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$$

All substances maintain a fundamental vibration consistent with a zero point energy. The smallest possible energy of an oscillator is given by (this is a result from quantum-physics, which I mention here to give you a more complete picture of the fundamental laws of physics.)

(19.8)
$$E_0 = \frac{\hbar}{2}\omega \equiv \frac{hf}{2}$$

Quantum physics states that any energy is quantized, and consists of a finite number of multiple energy quanta, which, in the case of an oscillator, is equal to $\hbar\omega$.

Where (19.9)
$$\boxed{\hbar(hbar) = \frac{h}{2\pi} = 1.05 \cdot 10^{-34} Js = \text{Planck's constant}/2\pi}$$

(The horizontal bar symbol means division by 2π.)

Example: For a spring with spring constant 10.0N/m and an amplitude of oscillation of 10.0 cm, we get a total energy of $\frac{1}{2}kA^2 = 0.0500J$ With a mass of 0.200kg we get an angular frequency of

$\sqrt{\frac{k}{m}} = 7.07s^{-1}$ The fundamental oscillation has an energy of

$$0.5\hbar\omega = 7.46 \cdot 10^{-34} J = 4.66 \cdot 10^{-15} eV$$
$$1eV(electron\,Volt) = 1.6 \cdot 10^{-19} J$$

This is obviously a very small number, but it is not absolute 0.

19.2,3 Constant-Volume Gas Thermometer.

Historical Temperature Scales, Kelvin, Fahrenheit, Celsius. The 0 point of the Kelvin scale (or the absolute 0 point) can be obtained through extrapolation of the pressure-temperature relationship of an ideal gas, whose pressure is measured at the freezing point of water (triple point) at 0 degree Celsius and the steampoint of water at 100 degree Celsius. This is done with the *constant volume gas thermometer*.

(19.10)
$$\boxed{\begin{array}{l} PV = nRT \Rightarrow P = \frac{nR}{V}T \\ T \text{ in Kelvin degrees, } K° = K \end{array}}$$

According to this **Ideal Gas Law**, pressure in an ideal gas, maintained at *constant volume,* is directly proportional to temperature.

The slope of the P(T) graph depends on the number n of moles of the gas and its volume. The graph passes through P(0)=0 only if you use Kelvin degrees. Otherwise there will be an intercept depending on whether you Celsius or Fahrenheit degrees. If temperatures are measured with gas thermometers containing different gases at different initial pressures, the extrapolation of all straight lines intercepts the same 0 point of pressure at -273ºC. Obviously, the experiment can only be conducted with a very diluted regular gas, and as long as the gas does not turn liquid, or solid.

The graph shows several lines for different substances with different slopes, all converging to the absolute 0 K temperature point.
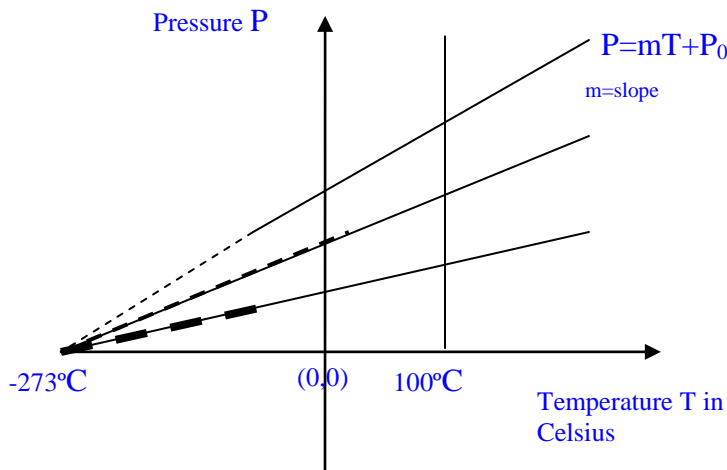
Problem: For dry ice (CO_2) solidification occurs at -80.00ºC and 0.9000 atm, for ethyl alcohol solidification occurs at 78.00ºC and 1.635 atm. These two exactly reproducible points are used as calibration points for the same amount of substance at the same volume, i.e. having the same slope m=nR/V. We get the slope of the straight line by

$$m = \frac{P_2 - P_1}{T_2 - T_1} = \frac{1.635 - 0.9}{78 - (-80)} \frac{atm}{C^\circ} = 4.652 \cdot 10^{-3} \frac{atm}{C^\circ}$$ Having the slope we can easily find the intercept value

$$1.635 = m(78C^\circ) + P_0 \Rightarrow P_0 = 1.272 atm \Rightarrow$$

(19.11) $$P(T) = 4.625 \cdot 10^{-3} \frac{atm}{C^\circ} \cdot T + 1.272 atm$$

This allows us to find the pressure of these gases at any temperature, and vice versa. Specifically, we find that 0 atm pressure is obtained at -273ºC.
At a 100ºC the gases have a pressure of 7.737atm.

The most common temperature measurements use Cº which are related to the scientific units of Kelvin through:

(19.12)

$$\boxed{\begin{array}{l} \text{0 point Kelvin} = -273.16 \text{ Celsius.} \\[2mm] T_F = \frac{9}{5}T_C + 32^\circ F; \\[2mm] \Delta T_F = \Delta \frac{9}{5}T_C; T_C = \frac{5}{9}T_F - \frac{5}{9} \cdot 32 C^\circ = \frac{5}{9}T_F - \frac{160}{9}C^\circ \end{array}}$$

The zero point for the Fahrenheit scale is the freezing point for water (triple point, to be more exact), set by historical convention at **32 degree Fahrenheit, or 0 degree Celsius**. The boiling point for water is set at **212 F degree, and 100 Celsius** degree. From these definitions it is easy to construct the functional relationship between Fahrenheit and Celsius. (Two points define a straight line.) Let T_F be the y-axis, and T_C the x axis:
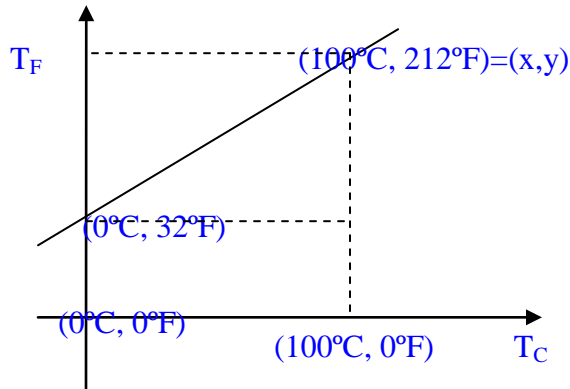
(19.13)
$$y = mx + b = \frac{212 - 100}{32 - 0} x + 32 = \frac{9}{5} x + 32$$

19.4 Thermal Expansion of Solids and Liquids.

Most solids and liquids expand slightly when the temperature is increased. The relative change in one dimension (linear expansion) is (for small temperature changes) directly proportional to the change in temperature. The **average coefficient of expansion** is denoted by α.

(19.14)
$$\frac{\Delta L}{L_i} = \alpha \Delta T \Rightarrow \Delta L = \alpha L_i \Delta T$$

$$[\alpha] = \frac{1}{C°}$$

If you write this as a differential relationship and integrate it you see that the above formula is an approximation:

$$\frac{dL}{L} = \alpha dT \underset{\text{integrate}}{\Rightarrow} \ln L = \alpha T + c; c \text{ is the constant of integration}$$

(19.15)
$$L = e^{\alpha T + c}; \text{ initial condition: } L(T=0) = L_0$$

$$L = L_0 e^{\alpha T}$$

If you expand the exponential formula using the McLaurin series:

(19.16)
$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + + +$$

we get:

(19.17)

$$L = L_0\left(1+\alpha T\right) = L_0 + L_0\alpha T \Rightarrow$$
$$\frac{\Delta L}{L_0} = \alpha T$$

Remember when we talked about stress and defined Young's modulus, or the elastic modulus through a similar relationship:

(19.18) $\text{stress} = \dfrac{F}{A} = Y\underbrace{\dfrac{\Delta L}{L_i}}_{\alpha \cdot \Delta T} = Y\alpha \cdot \Delta T$ ($Y_{Cu}=11\cdot E10$ N/m^2)

This means that thermal expansion increases the stress inside of materials.

Example:
Calculate the thermal stress in a copper bar of length 1.000m, if the temperature is increased from 0 to 100°C. (1.87E8 Pa) The copper bar expands by 1.7mm.

Note that if you have material with holes in it, the holes expand with the material, as if there were no holes in it.
For example, if you heat a copper ring with inner diameter 5.00 cm from 20 degree to 200 degree Celsius, the diameter will increase according to

$$\Delta L = \alpha L_i \Delta T = \underbrace{\frac{17\cdot 10^{-6}}{C°}}_{\alpha_{Cu}}\cdot 5.00cm \cdot 180C° = 0.015cm$$

(19.19)

$$\frac{\Delta L}{L} = 0.31\%$$

For a **volume expansion** of isotropic materials we want to find the relative expansion knowing the expansion in the linear directions. We use what we have learnt about calculating relative uncertainties, which is the same mathematics. Here is a little review: The relative change of any function is given by the total derivative of the natural log of that function. See the handout supplement on uncertainty calculations:
http://heisingart.com/230/230%20ch19%20supp1%20uncertainty%20calculations.pdf

(19.20)

$$\frac{df}{f} = d\ln f$$

(19.21)

$$f\left(x,y,z\right)$$
$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz \equiv \overrightarrow{grad}\,f \cdot d\vec{r} \equiv \left\langle \frac{\partial}{\partial x},\frac{\partial}{\partial y},\frac{\partial}{\partial z}\right\rangle\langle dx,dy,dz\rangle$$

In cases where the function is a simple polynomial the change of the function is particulary simple to calculate by using the logarithmic derivative process of (19.20)

$$f = \pi k x^2 y^{\frac{1}{2}} z$$

(19.22)
$$\ln f = \ln(\pi k) + 2\ln x + \frac{1}{2}\ln y + \ln z$$

$$d\ln f = 2\frac{dx}{x} + \frac{1}{2}\frac{dy}{y} + \frac{dz}{z}$$

Now, let us apply this to the volume expansion. Assume that we have homogeneous material which expands in all directions in the same way with α.

$$V = xyz; \frac{dV}{V} = \frac{dx}{x} + \frac{dy}{y} + \frac{dz}{z}$$

(19.23)
$$\frac{dx}{x} = \frac{dy}{y} = \frac{dz}{z} = \alpha\Delta T \text{ for isotropic material} \Rightarrow$$

$$\frac{dV}{V} = 3\alpha\Delta T$$

19.4a Anomaly of water with respect to expansion with temperature:
Water expands with temperature above 4° C, but it contracts below 4° Celsius. To put it differently, the density of water increases from 0 to 4.0°C, and it decreases above 4°C. It has a maximum for the density/temperature curve at 4°C

(19.24)
$$\rho(T = 4.0°C) = 1.000\frac{g}{cm^3}$$

$$\rho(T \neq 4.0°C) < 1.000\frac{g}{cm^3}$$

This means that water at 1° Celsius has a lesser density than water at 5° Celsius. It will therefore move to the top of a lake. (The buoyant force is larger than its weight.) With further cooling it will turn into ice which has an even smaller density. Therefore ice will form at the top of a lake and not at the bottom, which would be the case if water at 1°Celsius had a greater density than water at 4° C.

19.5 Macroscopic Description of an Ideal Gas.
The molar mass of each chemical element is the atomic mass, expressed in grams per mole. The same definition is applied to molecules. Thus, the atomic mass of water would be 18, and its molar mass would be 18 grams. **Every mole, or 18 grams, of water (vapor, ice, or liquid) contains Avogadro's number N_A of molecules**.
The density of water depends on its state (liquid, vapor, solid), its temperature, and the pressure it is under. The relationship expressing this is called **the equation of state**, which, for water is very complicated. The same relationship is relatively simple for an idealized gas, in which the gas particles have no chemical or other interactions with their neighbors. The ideal gases like Helium, Radon, Argon come close to this, so do Hydrogen and Oxygen molecules over some range of temperature and at low densities. We use the ideal gas law to illustrate and approximately calculate many of the thermodynamic quantities of gases.
The equation of state for an ideal gas is given by:

(19.25)

$$PV = nRT \text{ for n moles; R=universal gas constant}$$
$$[R] = \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}}; [E] = [P] \cdot [V] \Rightarrow 1J = 1Pa \cdot 1m^3 = \left(1.013 \cdot 10^5\right)^{-1} atm \cdot 10^3 L$$
$$R = 8.314 \text{ J} = 8.314 \cdot 9.8717 \cdot 10^{-3} L \cdot atm = 0.08207 L \cdot atm$$

P is pressure in Pascals, V is volume in m^3 or in atmospheres and liters.(1atm=1.013E5Pa) **Note that the product of volume and pressure has the dimension of energy, Joules.**

In order to obtain the gas law for **N particles**, rather than n moles, we have to make use of the fact, that the number of moles is equal to the number of particles N, divided by Avogadro's number N_A

(19.26) $N_A = 6.02 \cdot 10^{23} mol^{-1}$

Also, the universal gas constant for a single atom is given by Boltzmann's constant k_B.

(19.27) $n = \dfrac{N}{N_A}$ and $R = N_A \cdot k_B$

(19.28)

$$PV = nRT = \frac{N}{N_A} N_A \cdot k_B T = N k_B T$$

Note that in this equation, N stands for total number of individual particles, not moles.

(19.29)

$$k_B \equiv \frac{R}{N_A} = 1.38 \cdot 10^{-23} \frac{J}{K} \text{ Boltzmann's constant}$$

Pressure P, volume V, temperature T (and number of molecules) are the typical thermodynamic variables, very much like x, y, z in mechanics. The major thermodynamic **functions** like heat Q(P,V,T), internal energy U, entropy S can all be expressed in terms of such variables. These functions are all scalar functions. Pressure, volume, and temperature can be functions of space and time coordinates.

As we are always dealing with very large numbers of particles, we need to ultimately employ statistical models.

Problem:
Calculate the average pressure of outer space (universe) where we have typically about four protons per m^3 at a temperature of 1K.

Solution: $PV = nRT = Nk_B T \Rightarrow P = 4 \cdot 1.38 \cdot 10^{-23} \cdot 1 \approx 5 \cdot 10^{-23} Pa$

19.5a Van der Waals equation:

The behavior of real gases requires a modification of the ideal gas law. Experiment and theory confirm that we need to add an additional pressure term, and an additional volume term. This equation allows among other things to understand the liquification of gases when the pressure is increased and the temperature decreased. (See chapter 22.)

$$\left(P + \frac{a}{\left(V_{mol}^2\right)} \right)\left(V_{mol} - b\right) = RT$$

$\frac{a}{V_{mol}^2}$ is an internal pressure deriving from the attraction of the molecules to each-other

(19.30) b is the volume occupied by a single finite mole of particles

$$\left[\frac{a}{V_{mol}^2} \right] = pa = \frac{[a]}{m^6}mol^2 \Rightarrow [a] = \frac{pa \cdot m^6}{mol^2}$$

$$[b] = \frac{m^3}{mol}$$

For example: for carbondioxide we have a=.36 pa $\cdot m^6/mol^2$, and b=4.3$\cdot 10^{-5}m^3/mol$

We can use formula (19.25) to determine the density ρ of a gas at a particular pressure and temperature:

$$PV = Nk_BT \Rightarrow P = \frac{N}{V}k_BT = n_V k_BT$$

(19.31) $n_V = \frac{N}{V} = $ number density;

$$\rho = n_V \cdot m = \frac{N}{V}m = \frac{M}{V}; m = \text{mass of individual particle}; M = \text{total mass in the volume V.}$$

The number density n_V is related to the conventional mass density ρ by:

(19.32) $\rho = n_V \cdot m = \frac{\text{number of atoms}}{\text{volume}} \cdot \text{mass of one atom}$

By using the mass density we get in (19.31):

(19.33) $P = n_V k_BT = \frac{\rho}{m}k_BT = \frac{\rho}{M_{mol}}RT$

Solving for the density, we get:

(19.34) $$\boxed{\rho = \frac{M_{mol}}{RT}P = \frac{m}{k_BT}P}$$

Problem: Find the density of air at 0 degree Celsius and atmospheric pressure:
Air consists to 80% of nitrogen and 20% of oxygen. This gives us the molar mass of air at 0° C as:
(19.35) $M_{air} = 0.80 \cdot 28g + 0.20 \cdot 32g = 29g$

(19.36)
$$\rho_{air} = \frac{1atm \cdot 29g / mole}{273C° \cdot 0.082atm \cdot L / (K \cdot mole)} = 1.29\frac{g}{L} = 1.29\frac{kg}{m^3}$$

19.5b Barometric Formula.
Problem: How does the pressure in air vary with height? Assume that air behaves like an ideal gas.
We know that the pressure in any liquid changes according to:
(19.37)
$$P = P_0 - \rho gy \Rightarrow dP = -\rho gdy$$
In this formula we choose the 0 pressure point at the bottom of the liquid. Therefore the pressure decreases with increasing values for y.

From (19.34) we see that at constant temperature T, pressure P is proportional to the density ρ:
(19.38)
$$\rho = \frac{Pm_{molecule}}{k_B T}$$

With this substitution for ρ in (19.37) we get from $dP = -\rho gdy$
(19.39)

(19.40)
$$dP = -\frac{P \cdot m_{molecule}}{k_B T}gdy \Rightarrow \frac{dP}{P} = \frac{-mg}{k_B T}dy \Rightarrow \ln P\Big|_{P_0}^{P} = \frac{-mg}{k_B T}y + \text{constant}$$

(19.41)
$$P = P_0 e^{-\frac{m_{molecule}g}{k_B T}y} = P_0 e^{-\frac{M_{mol}g}{RT}y}$$

Both pressure and density decrease exponentially with the potential energy like
(19.42)
$$e^{-\frac{\text{potential energy of one molecule}}{k_B T}} = e^{-\frac{\text{potential energy}}{RT}}$$
The ratios $\frac{N_A m_{molecule}}{N_A k_B} = \frac{M_{mole}}{R}$ obviously being equal.
Therefore, we can also write:

(19.43)
$$\rho(y) = \rho_0 e^{-\frac{m_{molecule}g}{k_B T}y} = \rho_0 e^{-\frac{M_{mol}g}{RT}y}$$

We will see later that, in general, the probability **to find a molecule in a particular energy E state is proportional to:**
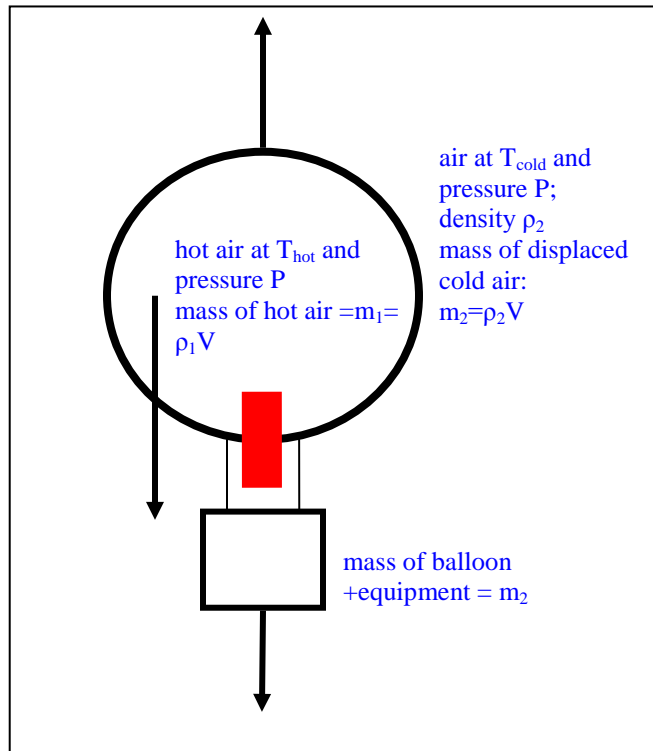
(19.44)
$$e^{-\frac{E}{k_B T}}$$

E is the total of all energies, potential and kinetic of the molecules.

Problem: At what height will the pressure of nitrogen gas drop to 80% of the original pressure, 0ºC.

(19.45)

$$0.8P_0 = P_0 e^{-\frac{m_{molecule} g}{k_B T} y} = P_0 e^{-\frac{M_{mol} g}{RT} y} = P_0 e^{-\frac{0.028 kg \cdot 9.8 \frac{m}{s^2}}{8.314 \cdot 273 J} y}$$

$$\ln 0.8 = -\frac{0.028 \cdot 9.8}{8.314 \cdot 273} y \Rightarrow y = \frac{0.223}{1.2E-4} = 1850m$$

Problem:
A hot air balloon consists of a balloon with volume of 5000 m^3. The ballast, i.e. everything of the system with the exception of the air inside the balloon, has a mass of 2500kg. The surrounding air is at a temperature of 0ºC. To which temperature does the air inside of the balloon have to be raised for the balloon to take off?
This is a buoyancy problem and an ideal gas problem.

Let us call the mass of air in the balloon m_1 and the remaining mass of the baloon and the equipment m_2.

The weight of the displaced cold air with density ρ2 must be equal to the weight of the hot air plus the additional weight m2g.When the air inside of the balloon is heated, its density and weight decrease.

(19.46) $m_1 g = \rho_1 V g$

The buoyancy of the hot air, which is equal to the weight of the displaced cold air will lift the balloon:

(19.47) $\underbrace{\rho_2 V g}_{\substack{\text{buoyancy=} \\ \text{weight of displaced} \\ \text{cold air}}} = \underbrace{\rho_1 V g}_{\substack{\text{weight of the hot} \\ \text{air in the balloon}}} + \underbrace{m_2 g}_{\text{remaining weight}}$

We need to figure out how the density varies with temperature and assume that air behaves like an ideal gas.

Formula (19.34) $\rho = \frac{P m_{molecule}}{k_B T} = \frac{P M_{mol}}{RT}$ is applicable.

In our problem pressure is constant (the balloon is open to the outside air), so, the density varies inversely with the temperature. The ratio between the densities at hot and cold temperatures is therefore: (the constants cancel)

(19.48)
$$\frac{\rho_{1hot}}{\rho_{2cold}} = \frac{T_{cold}}{T_{hot}} \Rightarrow \rho_{1hot} = \rho_{2cold}\frac{T_{cold}}{T_{hot}}$$

Inserting the density of hot air ρ_{1hot} in equation (19.47) we get:

$$\rho_2 Vg = \rho_1 Vg + m_2 g = \rho_2 \frac{T_{cold}}{T_{hot}}Vg + m_2 g; \rho_{2cold} = 1.29 kg / m^3$$

(19.49)
$$\rho_2 V = \rho_2 \frac{T_{cold}}{T_{hot}}V + m_2 \Rightarrow \rho_2 VT_{hot} = \rho_2 T_{cold}V + m_2 T_{hot}$$

$$T_{hot}\left(\rho_2 V - m_2\right) = \rho_2 T_{cold}V \Rightarrow T_{hot} = \frac{\rho_2 T_{cold}V}{\rho_2 V - m_2} = 446°K = 173°C$$