Temperature

Thermodynamics quantifies the transfer of thermal energy ("Heat") between objects at differing temperature.

Higher temperature corresponds to an increased **kinetic activity** at the molecular level.

Entropy is greater for a high temperature state versus the same state at lower temperature

Thermal equilibration for two systems at different temperatures subsequently placed in **thermal contact** leads to a maximization of the combined system entropy and a minimization of the combined system **free energy**:

1) Systems with higher temperature transfer heat energy during collisions between molecules from this system and molecules within the lower temperature system.

2) The higher temperature system cools, losing entropy and becoming more ordered. The lower temperature system heats up, gains entropy and becomes less ordered.

   Entropy increases or minimally remains unchanged during the interaction

3) The system reaches equilibrium if **thermal isolation** is maintained.

4) **Zeroth Law of Thermodynamics**: if system **A** and system **C** are in thermal equilibrium with system **B**, then systems **A** & **C** are also in thermal equilibrium.

Thermometry

Most **thermometers** indicate temperature change through a changing physical state of matter from which the thermometer is constructed.

Mercury thermometers rely on thermal expansion or contraction of the mercury liquid contained within a glass capillary tube.

Resistivity temperature dependence can indicate temperature via a **thermocouple**

Temperature Scale

Fahrenheit or Celsius temperature scales have calibrations based on the boiling and freezing points of water at one atmosphere of pressure.

Kelvin temperature scale has an **absolute zero point** corresponding to zero molecular activity. There are no negative temperature values below zero Kelvin.

Temperature Scales and Conversion Factors

The three primary scales we consider are Centigrade, Fahrenheit and Kelvin.

Celsius or Centigrade [At 1 ATM of pressure]

Freezing H_2O $= 0^0 C$ **Boiling H_2O** $= 100^0 C$

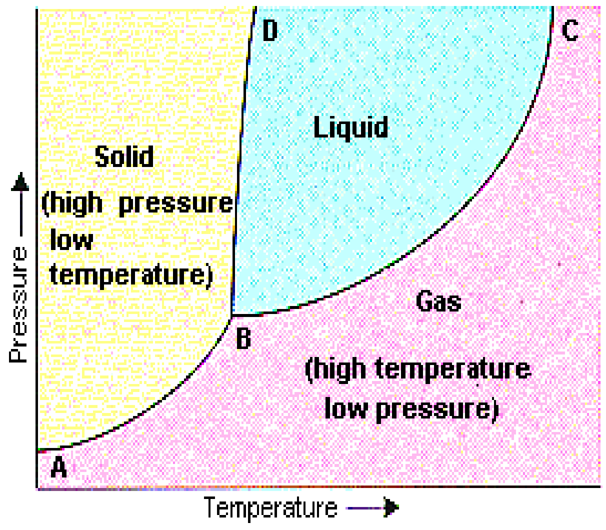
Fahrenheit [At 1 ATM of pressure]

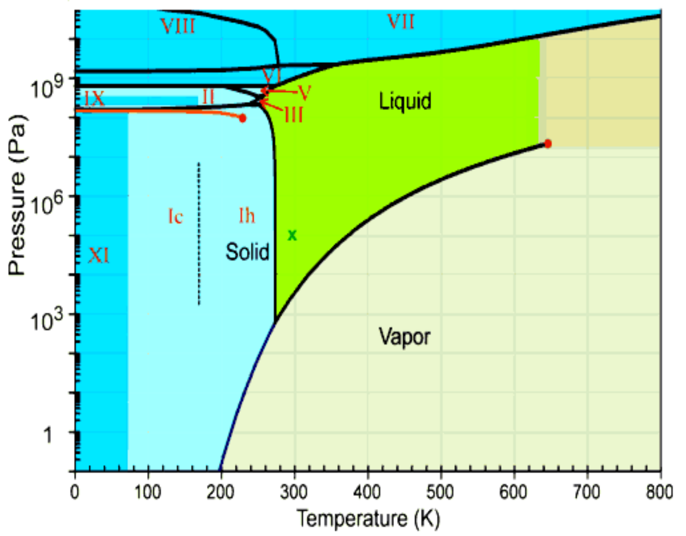
Freezing H_2O $= 32^0 F$ **Boiling H_2O** $= 212^0 F$

Constant Volume Gas Thermometers

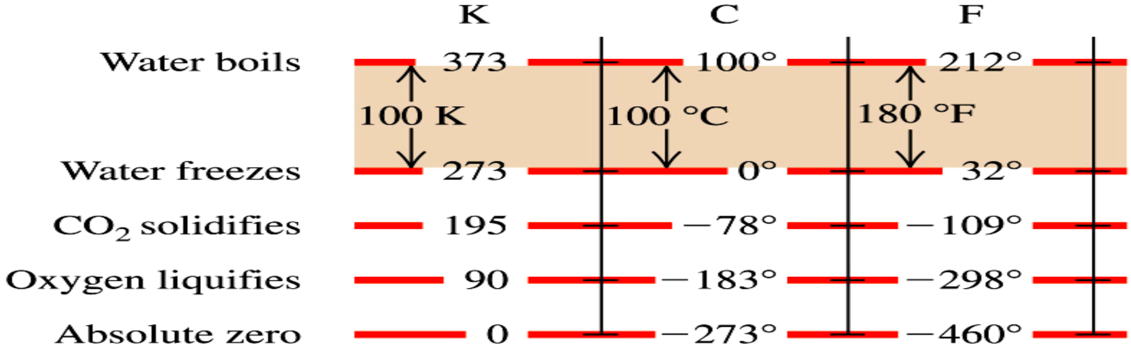
Using this type of thermometer plots of **P vs. T** for a variety of gases extrapolated to the **Pressure = Zero** point **[no pressure ➔ zero Kelvin]** intersects at a temperature $T = -273.15^0 C$ This is **absolute zero** on the Kelvin temperature scale.

The **triple point** of **H_2O** is the point where water, ice, and water vapor are coexistent in equilibrium. This equilibrium takes place at $0.01^0 C$ under $610.5 Pa$ of pressure. The Kelvin temperature scale unit is therefore $\frac{1}{273.16}$ the triple point of **H_2O**.





Covering a glass of ice water with plastic there is a coexistence of the three phases, but air is also present. Extract the air and the vapor pressure of water [pressure at which water vapor is in equilibrium with either the solid or the liquid] at the triple point is just under 610 Pa. At pressures lower than this, the liquid phase cannot exist as a stable phase.



Conversion from ^{o}C to Kelvin:

$$K={}^{0}C+273.15$$

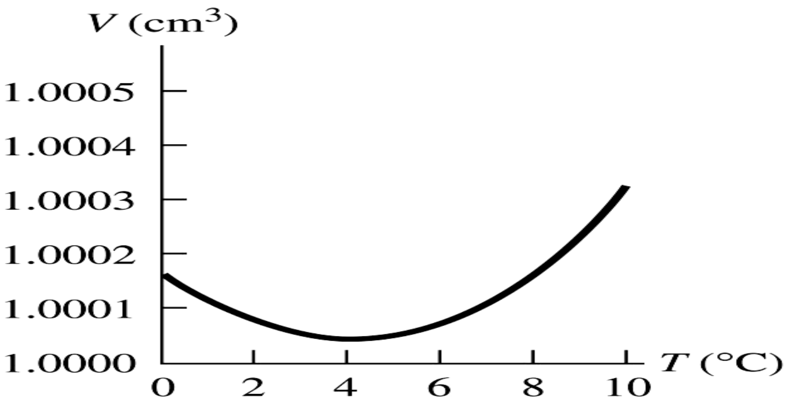
Between Celsius and Fahrenheit the conversions are:

$${}^{0}F=1.8\times{}^{0}C+32 \qquad {}^{0}C=({}^{0}F-32)\big/1.8$$

Thermal Expansion of Solids and Liquids

Most solids and liquids expand when heated and contract when cooled.

An exception to the rule is water around $4^{0}C$. Further cooling below $4^{0}C$ produces ice that is less dense than liquid water.



For a finite range of temperatures, thermal expansions / contractions are linear in **ΔT**. Constants of proportionality are **Coefficients of thermal expansion**.

For **one-dimensional** thermal expansion / contraction of a solid with initial length **L_0**,

$$\Delta L = \alpha L_0 \Delta T$$

ΔT is the temperature change [T_f-T_0] and ΔL the deformation.

From this one-dimensional result, **area expansion / contraction** is found:

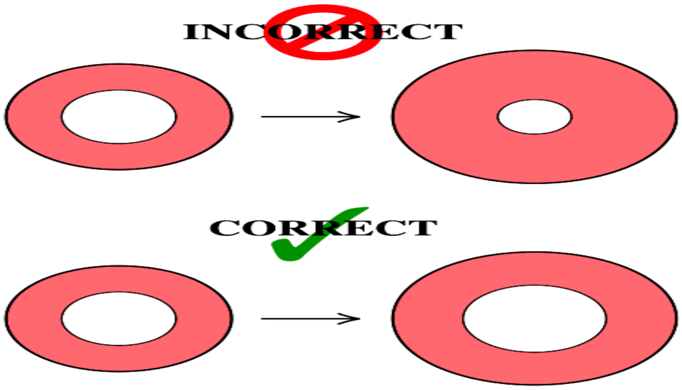
$$L^2 = [L_0 + \alpha L_0 \Delta T]^2 = L_0{}^2 + 2\alpha L_0{}^2 \Delta T + [\alpha L_0 \Delta T]^2$$

The last term is negligible since it is the product of two infinitesimal quantities, and

$$\Delta A = L^2 - L_0{}^2 = 2\alpha L_0{}^2 \Delta T$$

The **coefficient of area expansion is $\gamma = 2\alpha$**

$$\Delta A = \gamma L_0{}^2 \Delta T$$



More useful when dealing with liquids is a **three dimensional** result:

Volume changes have **coefficients of volume expansion for isotropic matter $\beta = 3\alpha$.**

$$\Delta V = \beta V_0 \Delta T$$

Liquid mercury constrained in a thermometer glass tube will volume expand / contract by an amount that may be calibrated with known temperature standards.

Ideal Gases

Temperature changes in gases depend also on other **macroscopic parameters** such as volume, pressure and particle number that additionally quantify the system.

The **equation of state** interrelates these macroscopic parameters in a single equation. An **ideal gas** is a low-density gas at high temperature where intermolecular interactions and the volume of the gas molecules are negligible.

The equation of state for an ideal gas is:

$$PV = NkT \qquad \textbf{Or} \qquad PV = nRT$$

$$P = pressure \qquad Pa$$

$$V = volume \qquad m^3$$

$$N = \#\, particles \qquad n = \#\, moles$$

$$T = temperature \qquad kelvin$$

$$k = Boltzmann\_Const. \quad 1.38x10^{-23}\, J/K$$

$$R = Universal\_Gas\_Const. \quad 8.31 J/mole \cdot K$$

One mole of a substance equals **$6.02\text{x}10^{23}$** units of the substance and is equal in weight to the substance gram molecular weight **[GMW]**.

Avogadro's number is $6.02\text{x}10^{23}$ molecules / mole.

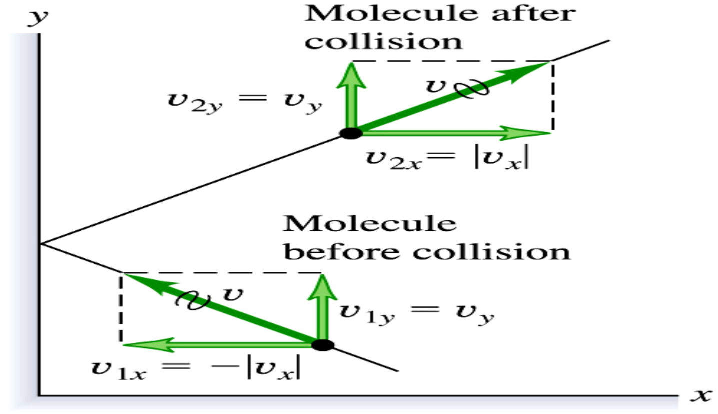
As an example, one mole of **H_2** gas is 2 grams and has **$6.02\text{x}10^{23}$ H_2** molecules.

In addition, the **volume of 1mole of any gas at STP [1ATM and 273.15 K] is $22.4\text{x}10^{-3}$ m^3 = 22.4 L**.

Kinetic Theory of Gases

Taking gas molecules as randomly interacting identical molecules undergoing elastic collisions with each other and the container walls, derive the ideal gas equation of state:

In a cubical container, each wall imparts a momentum change in the colliding molecule:



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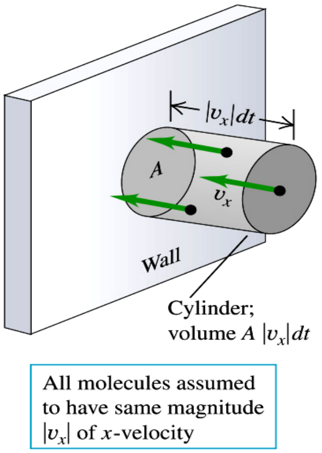
$$\Delta P_x = 2mv_x \qquad F = \frac{\Delta P}{\Delta t} = \frac{2mv_x}{\Delta t}$$

$\#of\_Collisions = \frac{1}{2}\frac{N}{V}Av_x dt$	 Copyright © 2004 Pearson Education, Inc., publishing as Addison Wesley.

$\Delta t = 2d / v_x$ **Gives the correct force on the wall in Newton's 2nd Law:**

$$F = \frac{2mv_x}{\Delta t} = \frac{mv_x^{\ 2}}{d}$$

Per Molecule.

For N molecules, $F = \frac{m}{d}\left[v_{x1}^{\;2} + v_{x2}^{\;2} + \ldots + v_{xN}^{\;2}\right]$

Taking the average $v_x^{\;2}$ **for the x-coordinate square velocities:**

$$\overline{v_x^{\;2}} = \frac{v_{x1}^{\;2} + v_{x2}^{\;2} + \ldots + v_{xN}^{\;2}}{N}$$

$v^2 = v_x^{\;2} + v_y^{\;2} + v_z^{\;2} = 3v_x^{\;2}$ **Motion in x, y, and z is identical.**

$$F = \frac{Nm\overline{v_x^{\;2}}}{d} = \frac{Nm}{d}\frac{\overline{v^2}}{3}$$

Pressure in the cube is: $P = \frac{F}{A} = \frac{Nm\overline{v^2}}{3dA} = \frac{1}{3}\frac{N}{V}m\overline{v^2}$

This relates the macroscopic pressure to microscopic molecular square velocity.

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

From **equipartition**, each molecular degree of freedom yields $\frac{1}{2}kT$ of energy.

Therefore, with 3 translation degrees of freedom $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$ and the gas temperature T is found to be directly related to kinetic activity as inferred earlier.

$$PV = NkT$$

RMS Velocity and Internal Energy

From $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$ The **RMS [root-mean-square] velocity** for a molecule is:

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

$v_{RMS} = \sqrt{\frac{3kT}{m}}$ **T is in Kelvin and m is the mass of the molecule in kilograms**.

The **RMS velocity** is the speed that molecules with average kinetic energy will posses.

The **internal energy** of the gas depends on the type of gas and its temperature:

For **monatomic gas** like **H_1** only molecular translation is possible and therefore by equipartition, $\frac{1}{2}kT$ for each translation degree of freedom ➔ $U = \frac{3}{2}kT$

For a **diatomic gas** like **H_2**, there exist the possibility that at high temperatures, rotational degrees of freedom in the gas molecules excite. Two rotation degrees of freedom plus the three degrees of translation freedom gives: $U = \frac{5}{2}kT$

At even higher temperatures, a diatomic molecule can also be exited into vibration modes with additional degrees of freedom that contribute to the internal energy: 7 total degrees of freedom gives: $U = \frac{7}{2}kT$.

Distribution of Molecular Speeds

From $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$ we can find the **RMS [root-mean-square] velocity** for a molecule within a monatomic gas at temperature T:

$$\overline{v^2} = 3kT * \frac{1}{m} \quad \rightarrow \quad v_{RMS} = \sqrt{\frac{3kT}{m}}$$

Where T is in Kelvin and m the mass of the molecule in kilograms.

The **RMS velocity** is the speed that molecules with average kinetic energy posses.

Velocities additionally of interest in this gas at temperature **T** include:

$$v_{Avg} = \sqrt{\frac{8kT}{\pi m}}$$

The average molecular speed.

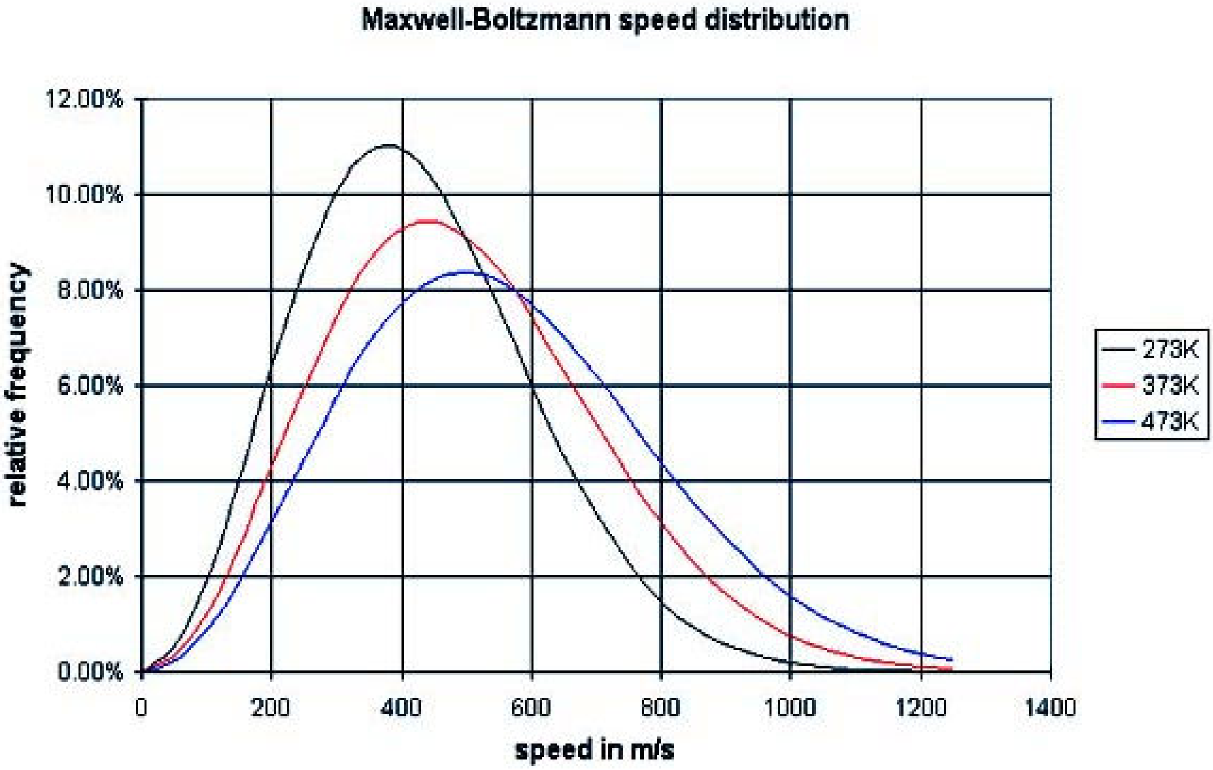
$$v_{Most\_Probable} = \sqrt{\frac{2kT}{m}}$$

The most probable velocity.

These may be derived from the **Maxwell Speed Distribution Law** which is a probability distribution function describing the relative probability of finding a molecule at a given velocity in a gas of given temperature.

$$P(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

Maxwell speed distributions for varying temperature look like:



The shape of the **Maxwell Speed Distribution Law** curves has implication for many physical processes where temperature is among the principle driving factors. As temperatures are increased, distributions are skewed further right to include molecules in the distribution tail with greater frequency and reaction rates increase.