

Chapter 18

Temperature & Kinetic Theory

Temperature & Kinetic Theory

- Thermal Equilibrium and Temperature
- Gas Thermometers
- Absolute Temperature Scale
- The Kinetic Theory of Gases

Temperature

Heat is the flow of energy due to a temperature difference. Heat always flows from objects at high temperature to objects at low temperature.

When two objects have the same **temperature**, they are in **thermal equilibrium**.

No Temperature Difference → No Heat flow

The Zeroth Law of Thermodynamics

If two objects are each in thermal equilibrium with a third object, then the two objects are in thermal equilibrium with each other.



Thermodynamics

“Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more.”

- Arnold Sommerfeld

Thermodynamics is the scientific study of work, heat, and the related properties of chemical and mechanical systems.

Temperature Measurement

Requirement:

A substance that exhibits a measurable change in one of its physical properties as the temperature changes.

Examples:

Volume change with temperature is a common physical property used for the measurement of temperature

The change of electrical resistance with temperature is also used to measure temperature.

Not a Good Temperature Measurement Instrument



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Mercury Thermometer

A mercury-in-glass thermometer, invented by German physicist Daniel Gabriel Fahrenheit.

Bulb – reservoir for the thermometric liquid

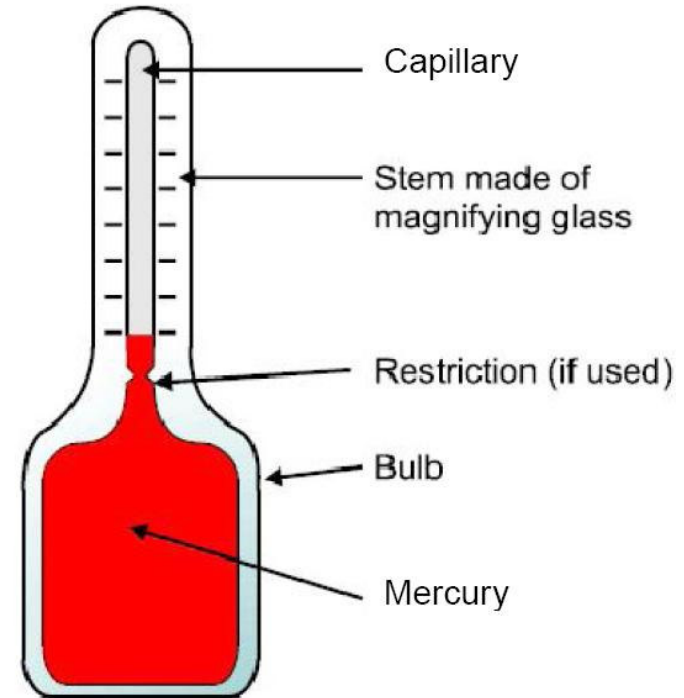
Stem – glass capillary tube through which the mercury or organic liquid fluctuates with changes in temperature

Scale – the scale is graduated in degrees, fractions or multiples of degrees

Contraction Chamber– an enlarged capillary bore which serves to reduce a long length of capillary, or prevent contraction of the entire liquid column into the bulb

Expansion Chamber– an enlargement of the capillary bore at the top of the thermometer to prevent build up of excessive pressures in gas-filled thermometers

http://www.omega.com/Temperature/pdf/INTRO_GLASS_THERM.pdf

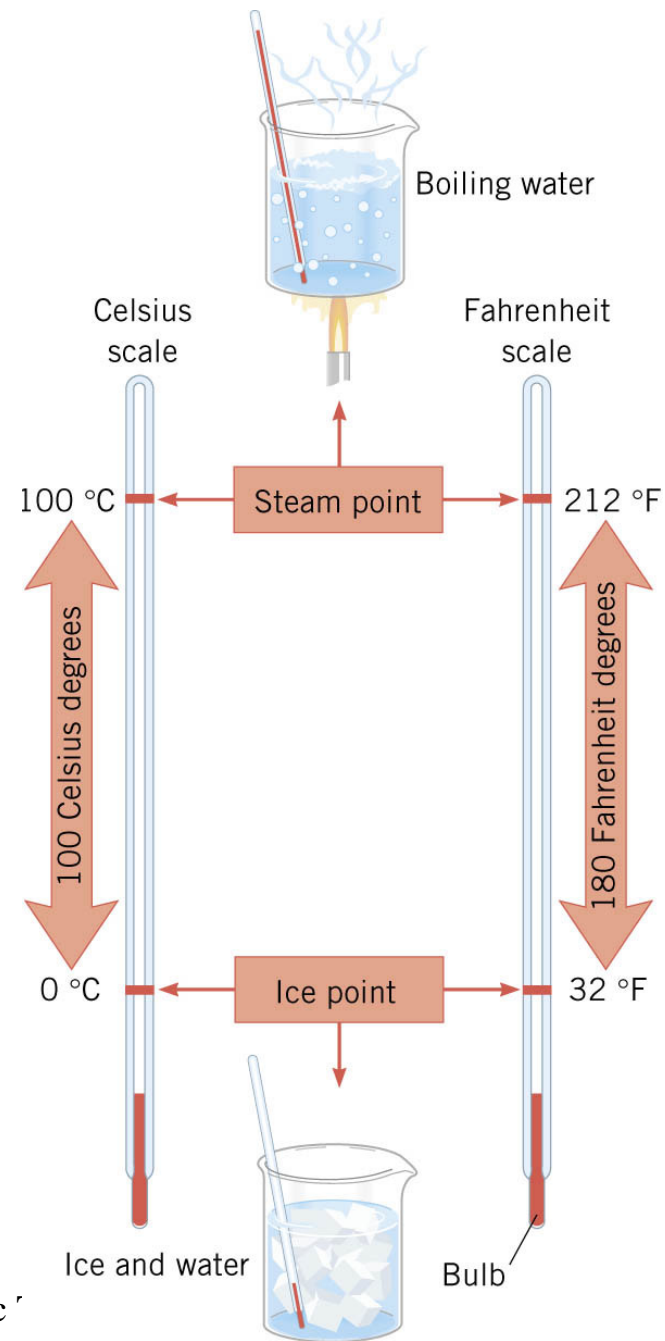


Temperature Calibration

Celsius and Fahrenheit are two different temperature scales but they are calibrated to the same reference points.

The two scales have different sized degree units and they label the steam point and the ice point with different temperature values.

The “Zero” values on both scales were picked for convenience and can cause problems.



Temperature Measurement

Calibration

This process ensures the accuracy of the measurement. It requires the availability of a repeatable set of states of matter. The boiling point of water and the freezing point of water are two examples.

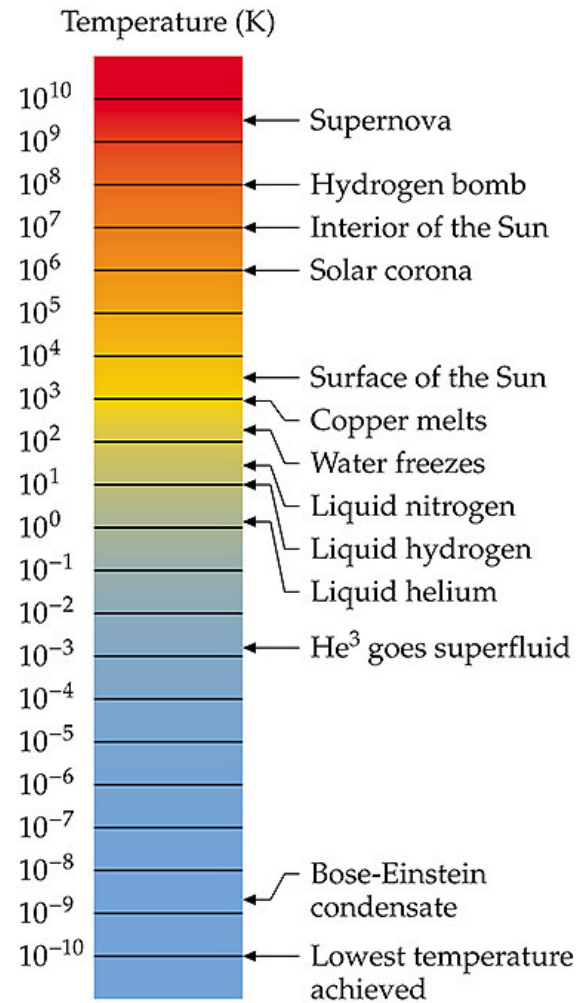
Transferability

The calibration needs to be transferable to other measuring instruments.

Standards

There needs to be agreed upon calibration procedures to allow transferability.

The Temperatures of Various Places & Phenomena



Temperature Scale

Anders Celsius devised the Celsius scale. This was published in *The Origin of the Celsius Temperature Scale* in 1742.

Celsius originally defined his scale "upside-down"

- boiling point of pure water at 0 °C and
- the freezing point at 100 °C.

One year later Frenchman Jean Pierre Cristin proposed to invert the scale. He named it Centigrade.

In later years, probably when the lower reference temperature was switch to the Triple Point, the name Celsius was restored.

Fahrenheit Temperature Scale

It was in 1724 that Gabriel Fahrenheit, an instrument maker of Däänzig and Amsterdam, used mercury as the thermometric liquid.

Fahrenheit described how he calibrated the scale of his mercury thermometer:

"placing the thermometer in a mixture of sal ammoniac or sea salt, ice, and water a point on the scale will be found which is denoted as zero. A second point is obtained if the same mixture is used without salt. Denote this position as 30. A third point, designated as 96, is obtained if the thermometer is placed in the mouth so as to acquire the heat of a healthy man." (D. G. Fahrenheit, Phil. Trans. (London) 33, 78, 1724)

On this scale, Fahrenheit measured the boiling point of water to be 212. Later he adjusted the freezing point of water to 32 so that the interval between the boiling and freezing points of water could be represented by the more rational number 180.

Temperatures measured on this scale are designated as degrees Fahrenheit ($^{\circ}$ F).

<http://www.cartage.org.lb/en/themes/sciences/Physics/Thermodynamics/AboutTemperature/Development/Development.htm>

Temperature Scales

	Absolute or Kelvin scale	Fahrenheit scale	Celsius scale
Water boils*	373.15 K	212 °F	100 °C
Water freezes*	273.15 K	32 °F	0 °C
Absolute zero	0 K	-459.67 °F	-273.15°C

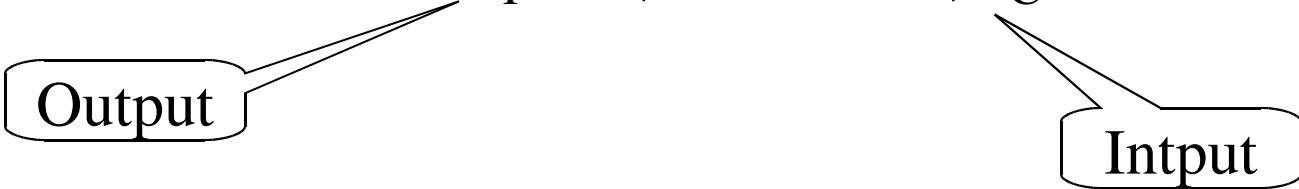
(*) Values given at 1 atmosphere of pressure.

- In general, as the temperature of a substance is lowered the atomic motion and vibrations slow down.
- Temperature can be related to molecular energy. Negative temperature values imply erroneous negative energy.
- The Kelvin temperature scale avoids this problem.

Comparison of Temperature Scales

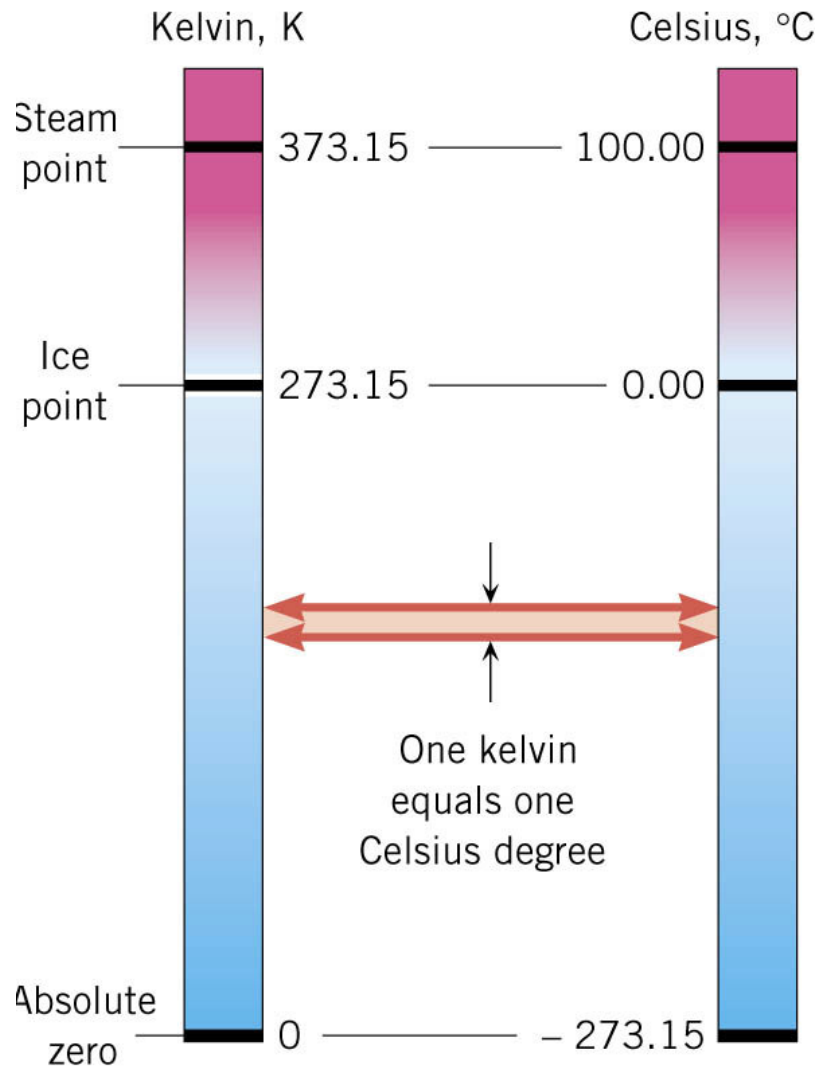
The temperature scales are related by:

Fahrenheit/Celsius $T_F = (1.8 \text{ }^\circ\text{F}/^\circ\text{C})T_C + 32^\circ\text{F}$

Output 

Absolute/Celsius $T = T_C + 273.15$

Comparison of Temperature Scales



Absolute Temperature and the Ideal Gas Law

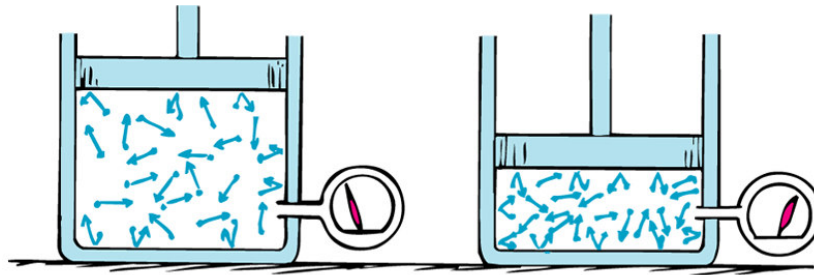
Experiments done on dilute gases (a gas where interactions between molecules can be ignored) show that:

For constant pressure $V \propto T$ Charles' Law

For constant volume $P \propto T$ Gay-Lussac's Law

For constant temperature

$$P \propto \frac{1}{V} \quad \text{Boyle's Law}$$

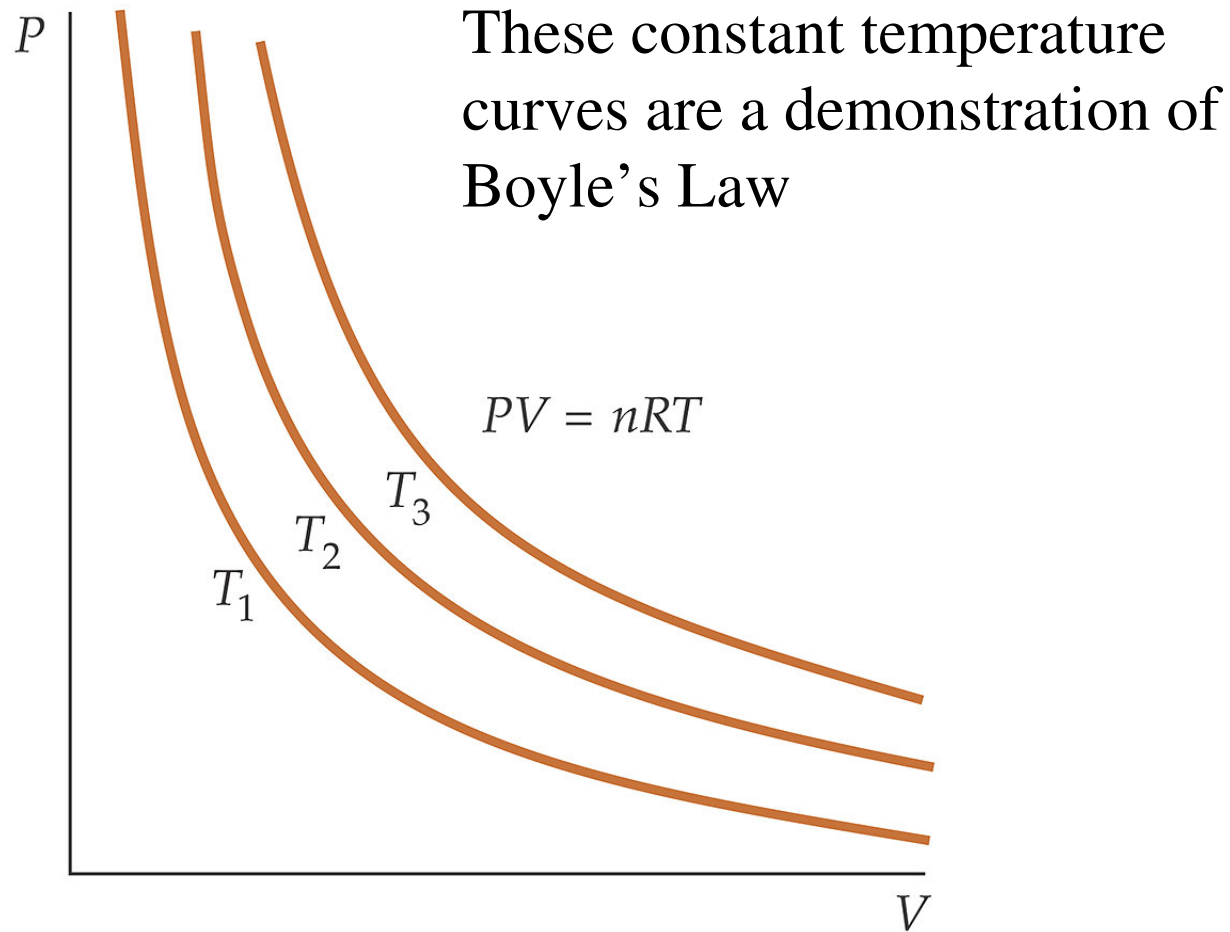


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For constant pressure and temperature

$$V \propto N \quad \text{Avogadro's Law}$$

The P-V Diagram for the Ideal Gas Law



The Ideal Gas Equation of State

Putting all of these statements together gives the **ideal gas law** (microscopic form):

$$PV = NkT$$

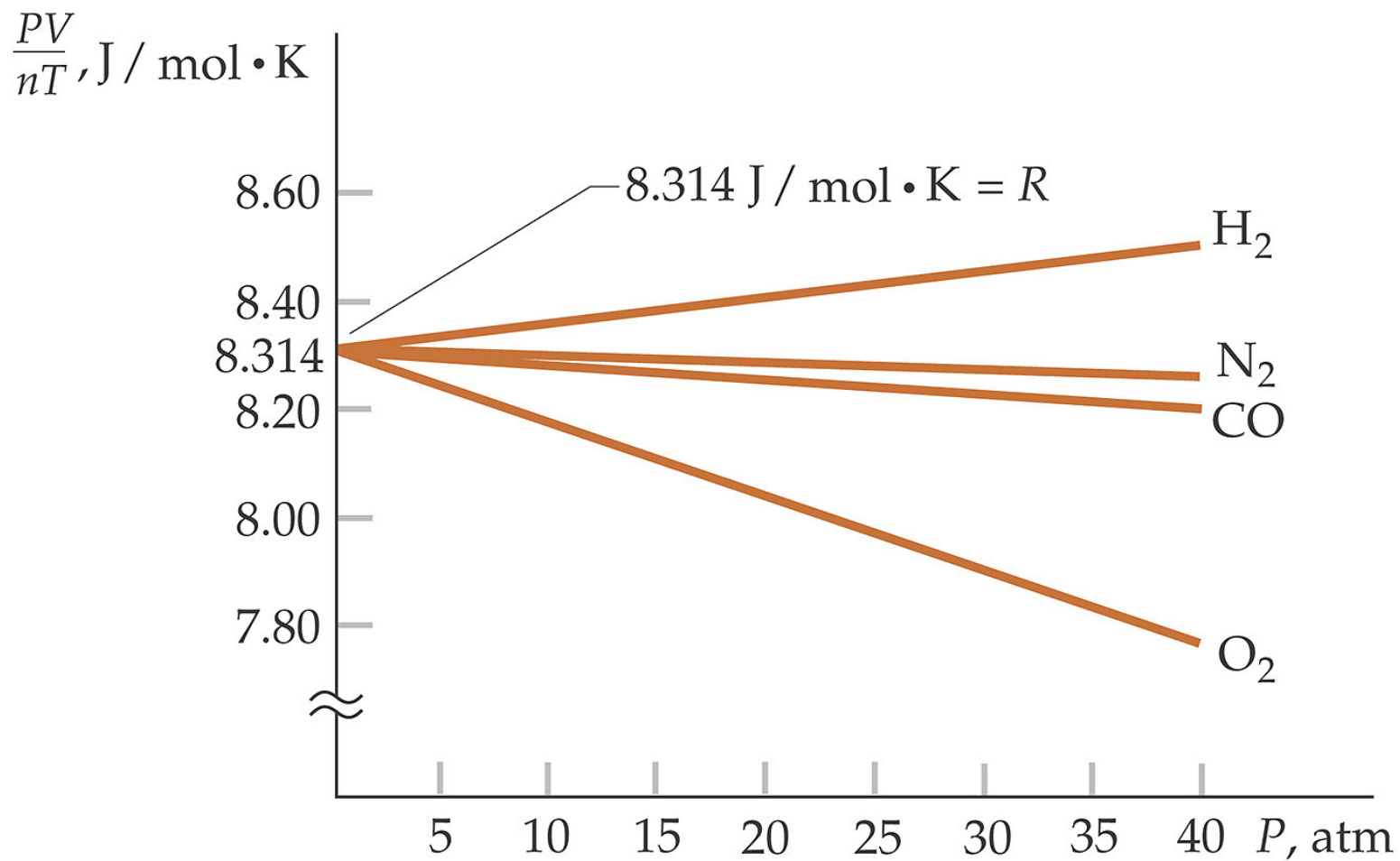
$k = 1.38 \times 10^{-23}$ J/K is
Boltzmann's constant

The ideal gas law can also be written as (macroscopic form):

$$PV = nRT$$

$R = N_A k = 8.31$ J/K/mole is
the universal gas constant and
 n is the number of moles.

The Ideal Gas Constant - R



Gas Constants

$$k = 1.381 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K}$$

$$R = N_A k = 8.341 \text{ J/mol-K}$$

$$= 0.08206 \text{ L-Atm/mol-K}$$

Example:

A cylinder in a car engine takes $V_i = 4.50 \times 10^{-2} \text{ m}^3$ of air into the chamber at $30 \text{ }^\circ\text{C}$ and at atmospheric pressure. The piston then compresses the air to one-ninth of the original volume and to 20.0 times the original pressure.

What is the new temperature of the air?

Here, $V_f = V_i/9$, $P_f = 20.0P_i$, and $T_i = 30 \text{ }^\circ\text{C} = 303 \text{ K}$.

$$P_i V_i = NkT_i$$

$$P_f V_f = NkT_f$$

The ideal gas law holds for each set of parameters (before compression and after compression).

Example continued:

Take the ratio:
$$\frac{P_f V_f}{P_i V_i} = \frac{NkT_f}{NkT_i} = \frac{T_f}{T_i}$$

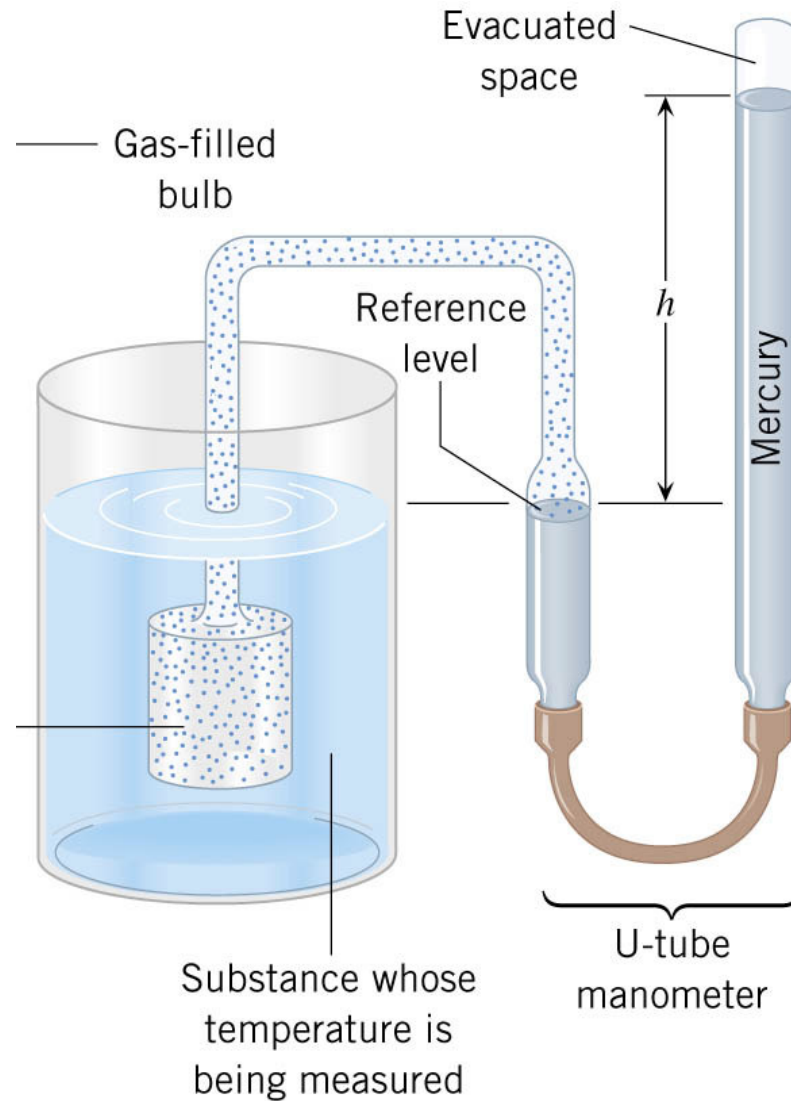
The final temperature is
$$T_f = \left(\frac{P_f}{P_i}\right)\left(\frac{V_f}{V_i}\right)T_i$$
$$= \left(\frac{20.0P_i}{P_i}\right)\left(\frac{V_i/9}{V_i}\right)(303 \text{ K}) = 673 \text{ K}$$

The final temperature is 673 K = 400 °C.

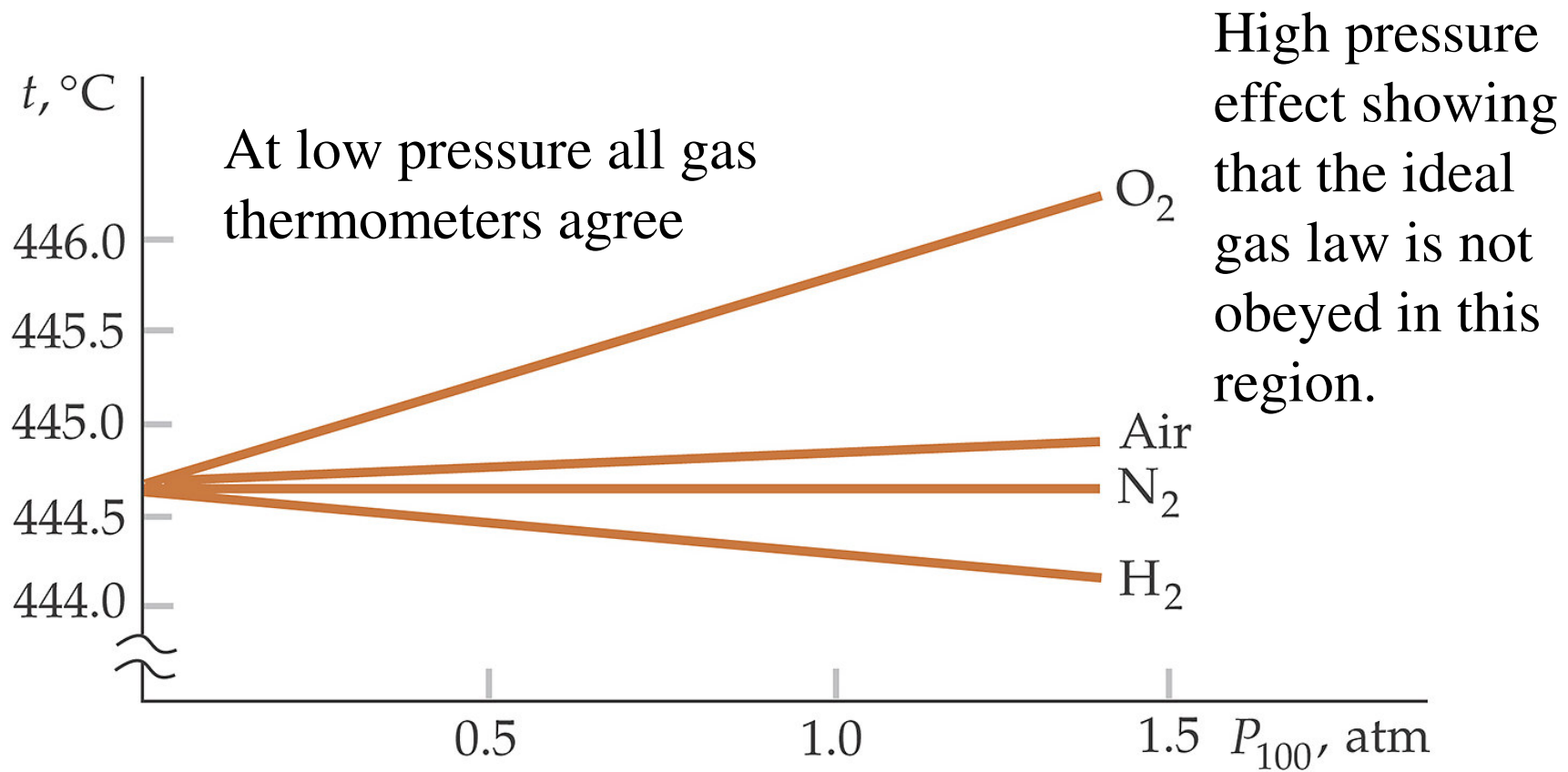
Constant Volume Gas Thermometer

- The agreement of thermometers at 0°C and 100°C doesn't guarantee close agreement at points in between or above 100°C .
- Among the various types of thermometers, gas thermometers agree closely with each other.
- The question becomes: how much agreement do you need and how much are you willing to pay for it in convenience, speed and cost.

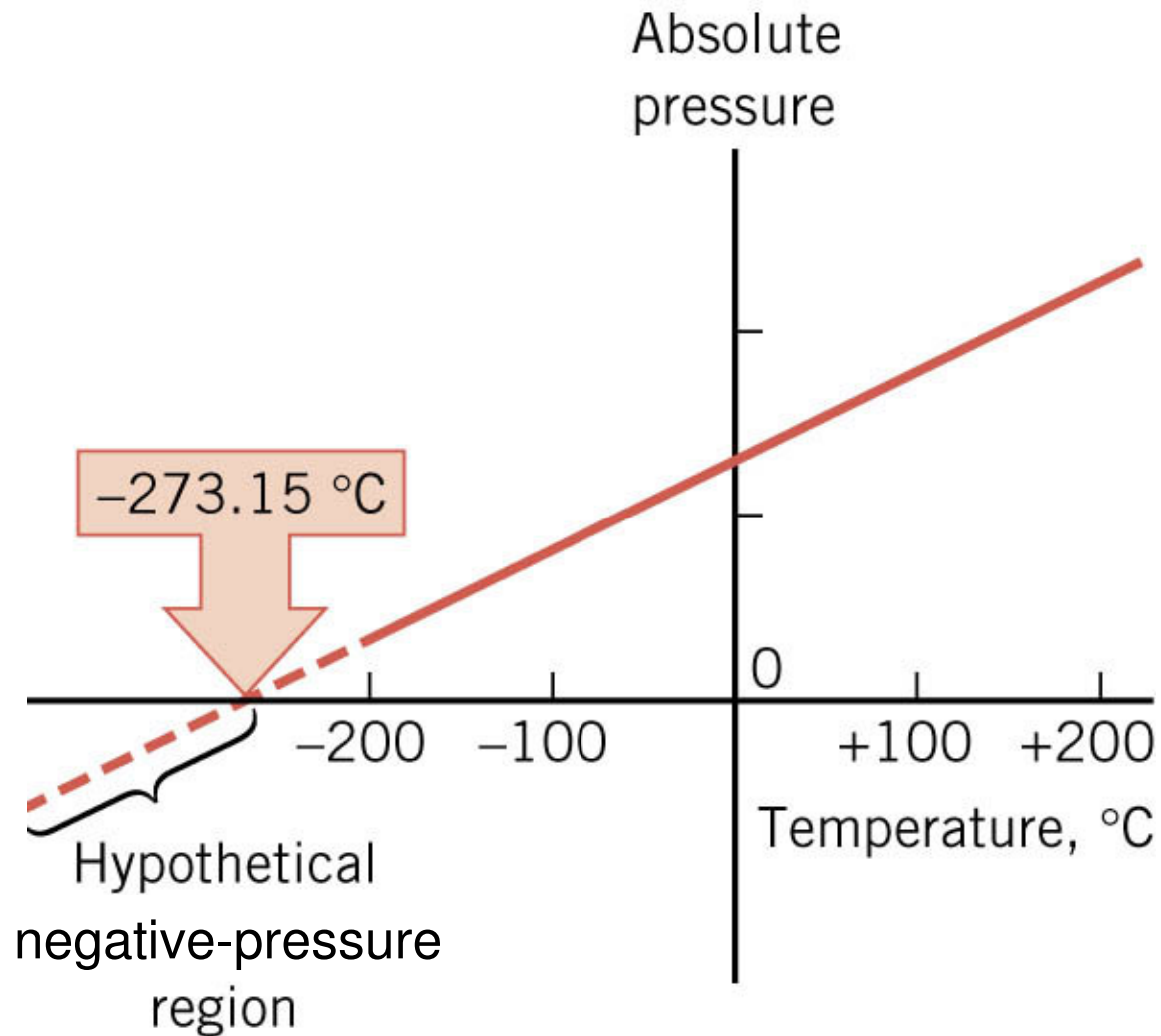
Constant Volume Gas Thermometer



Boiling Point of Sulphur



Constant Volume Gas Thermometer



The Triple Point of Water

At the triple point all three phases: ice, liquid and vapor, co-exist at the same time.

$$P = 4.58 \text{ mmHg}$$

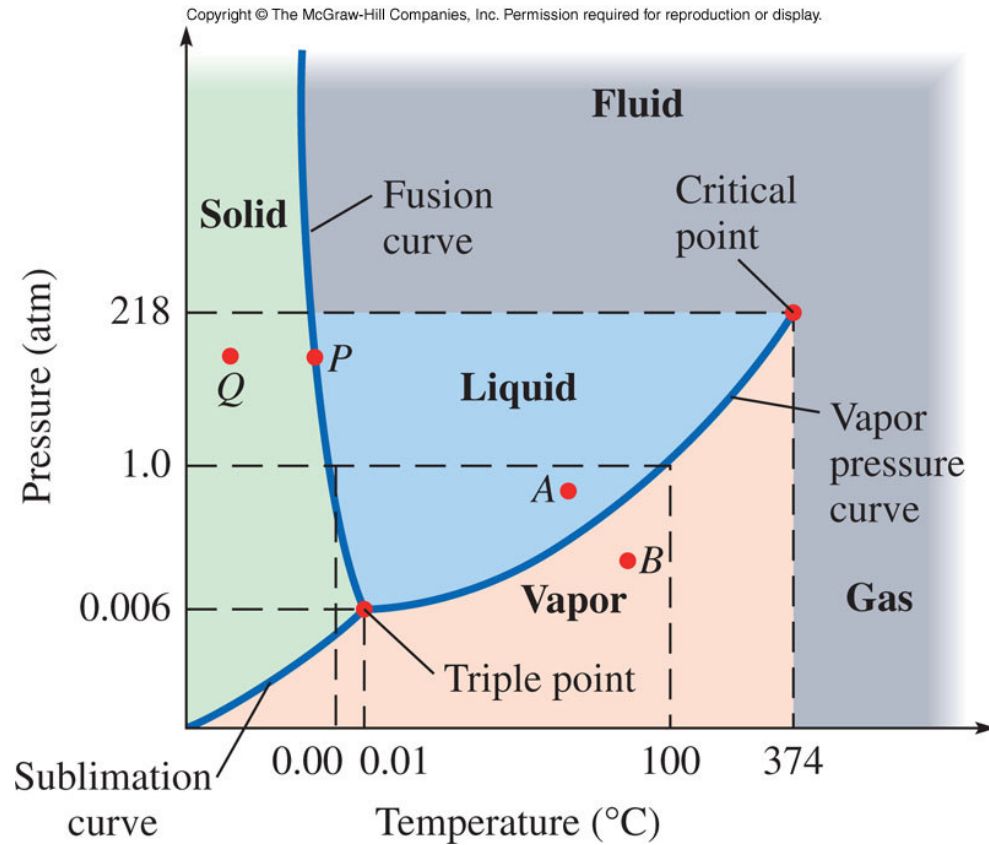
$$T = 0.01 \text{ }^{\circ}\text{C}$$

This doesn't occur at atmospheric pressure - it is only achieved under vacuum conditions.



The change to the triple point for calibration purposes was made in ~1947. The change was made due to the triple point's more precise reproducibility.

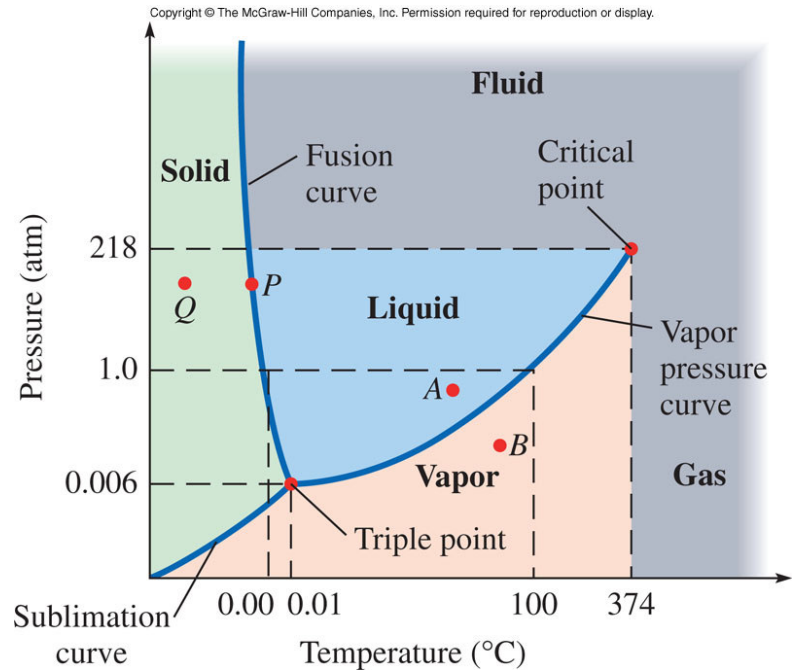
On a phase diagram, the **triple point** is the set of P and T where all three phases can coexist in equilibrium.



Sublimation is the process by which a solid transitions into a gas (and gas \rightarrow solid).

The **critical point** marks the end of the vapor pressure curve.

A path around this point (i.e. the path does not cross the curve) does not result in a phase transition.

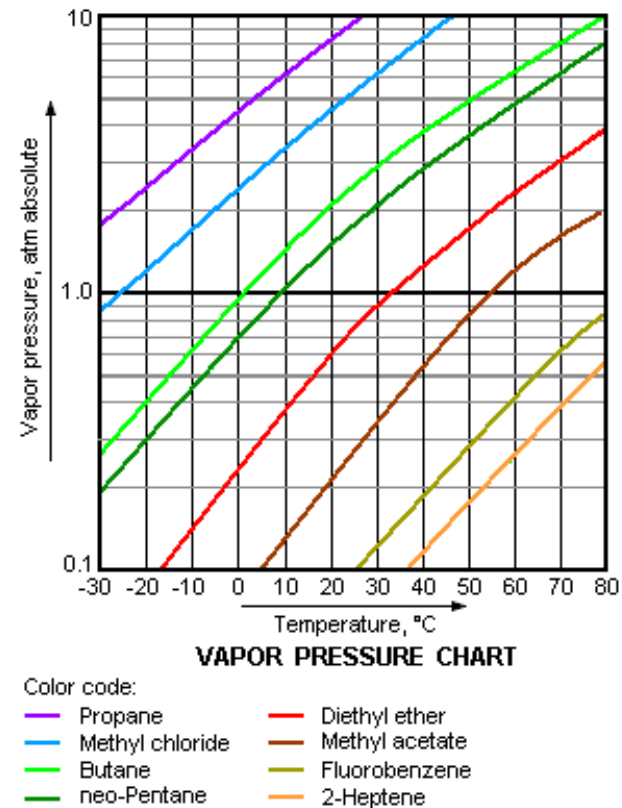


Past the critical point it is not possible to distinguish between the liquid and gas phases.

Vapor Pressure

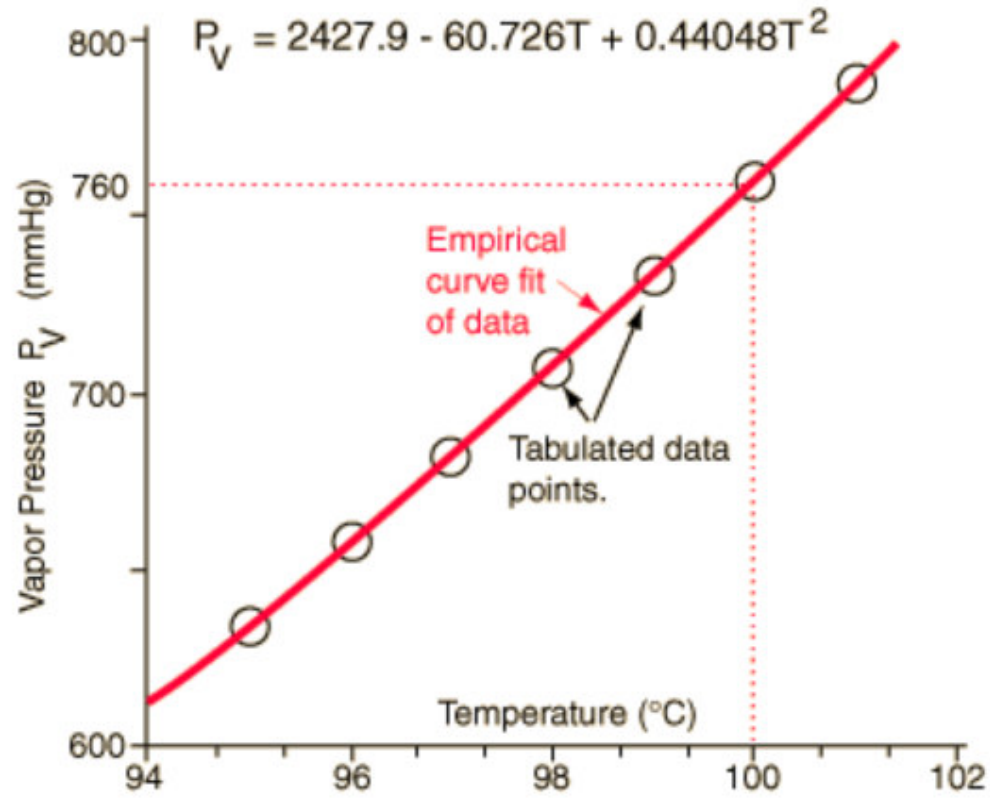
Vapor pressure is the pressure of a vapor in equilibrium with its non-vapor phases (i.e., liquid or solid). Most often the term is used to describe a liquid's tendency to evaporate. It is a measure of the tendency of molecules and atoms to escape from a liquid or a solid.

A liquid's atmospheric pressure boiling point corresponds to the temperature at which its vapor pressure is equal to the surrounding atmospheric pressure and it is often called the normal boiling point.



http://en.wikipedia.org/wiki/Partial_pressure

Vapor Pressure



Vapor pressure curve for water. Notice that at the boiling point the vapor pressure is atmospheric pressure (760 mmHg).

Kinetic Theory of the Ideal Gas

Kinetic Theory of the Ideal Gas

An **ideal gas** is a dilute gas where the particles act as point particles with no interactions except for elastic collisions with the walls of the container.

Molecular Picture of a Gas

The **number density** (n_v) of particles is N/V where N is the total number of particles contained in a volume V .

If a sample contains a single element, the number of particles in the sample is $N = M/m$. M is the total mass of the sample divided by the mass per particle (m).

Avogadro's Number - N_A

One **mole** of a substance contains the same number of particles as there are atoms in 12 grams of ^{12}C . The number of atoms in 12 grams of ^{12}C is Avogadro's number.

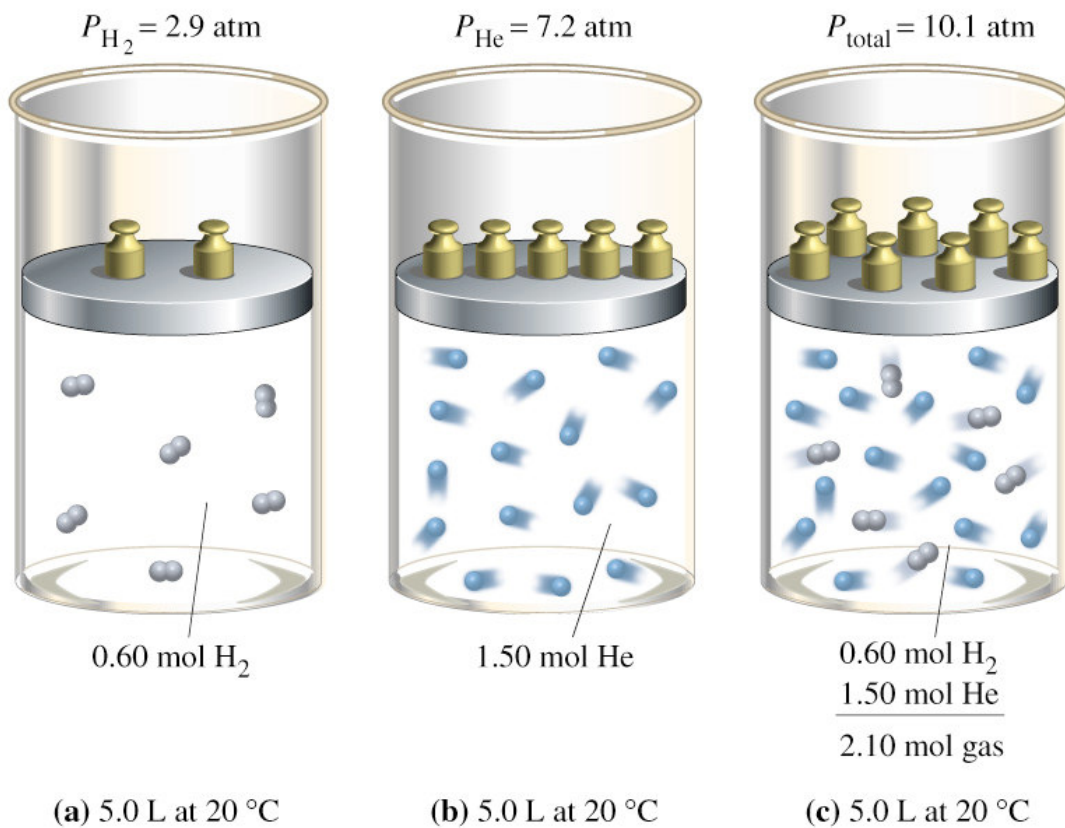
$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

The Law of Partial Pressures

In a mixture of ideal gases, each gas has a partial pressure which is the pressure which the gas would have if it alone occupied the volume.

The total pressure of a gas mixture is the sum of the partial pressures of each individual gas in the mixture.

http://en.wikipedia.org/wiki/Partial_pressure



Gas particles have random motions. Each time a particle collides with the walls of its container there is a force exerted on the wall. The force per unit area on the wall is equal to the pressure in the gas.

The pressure will depend on:

- The number of gas particles
- Frequency of collisions with the walls
- Amount of momentum transferred during each collision

The Equipartition Theorem

“When a substance is in equilibrium, there is an average energy of $\frac{1}{2}kT$ per molecule or $\frac{1}{2}RT$ per mole associated with each degree of freedom.” Tipler & Mosca

The pressure in the gas is

$$P = \frac{2}{3} \frac{N}{V} \langle K_{\text{tr}} \rangle$$

Where $\langle K_{\text{tr}} \rangle$ is the root mean square (RMS) average of the translational kinetic energy of the gas particles; it depends on the temperature of the gas.

$$\langle K_{\text{tr}} \rangle = \frac{3}{2} kT$$

The average kinetic energy also depends on the rms speed of the gas

$$\langle K_{\text{tr}} \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m v_{\text{rms}}^2$$

where the rms speed is

$$\langle K_{\text{tr}} \rangle = \frac{3}{2} kT = \frac{1}{2} m v_{\text{rms}}^2$$

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

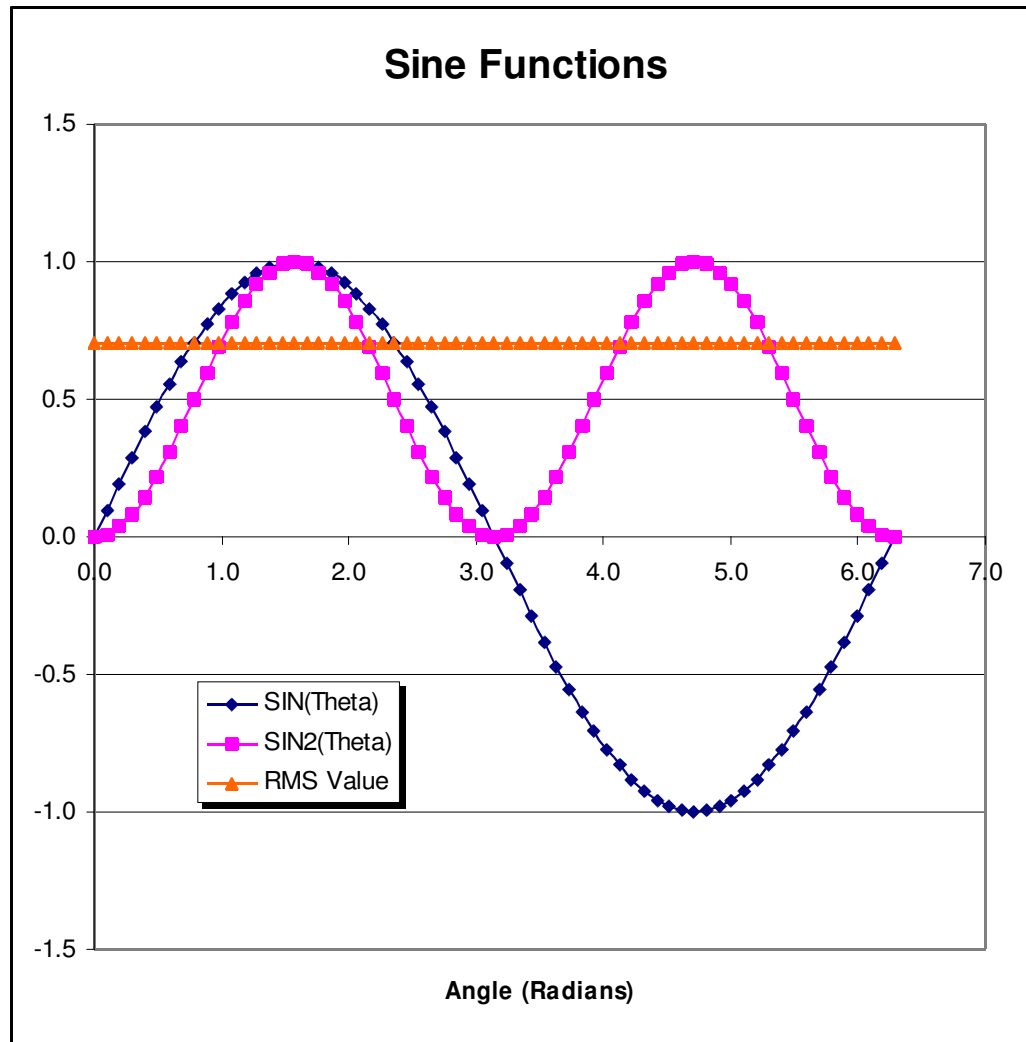
Root Mean Squared

The root mean squared (rms) method of averaging is used when a variable will average to zero but its effect will not average to zero.

Procedure

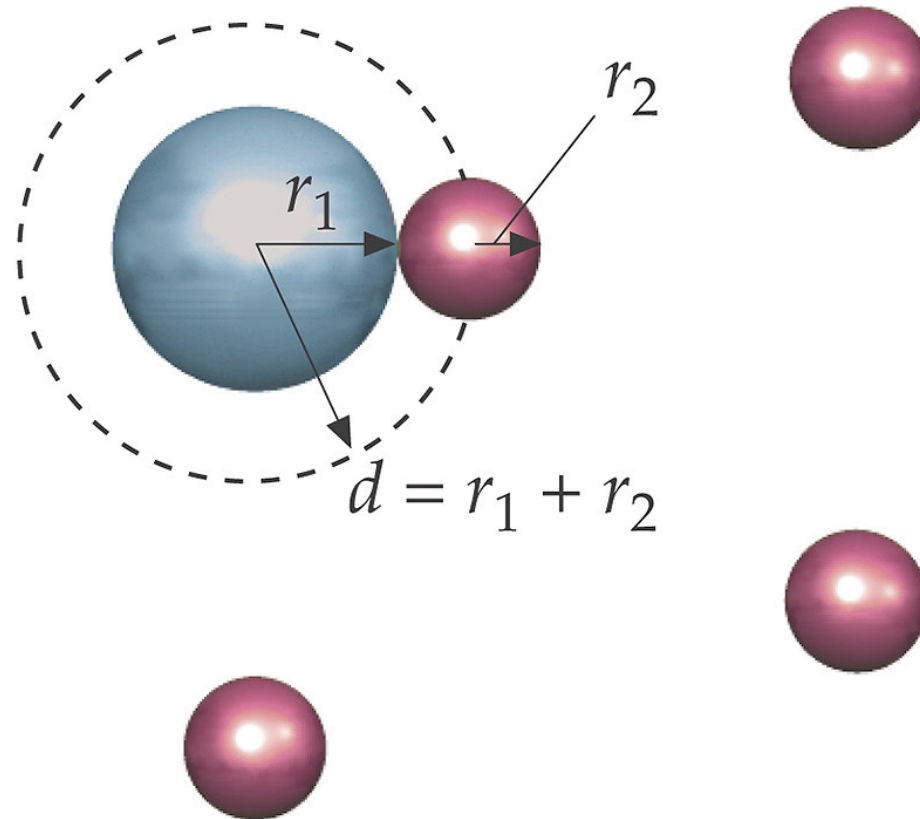
- Square it (make the negative values positive)
- Take the average (mean)
- Take the square root (undo the squaring operation)

Root Mean Squared Average

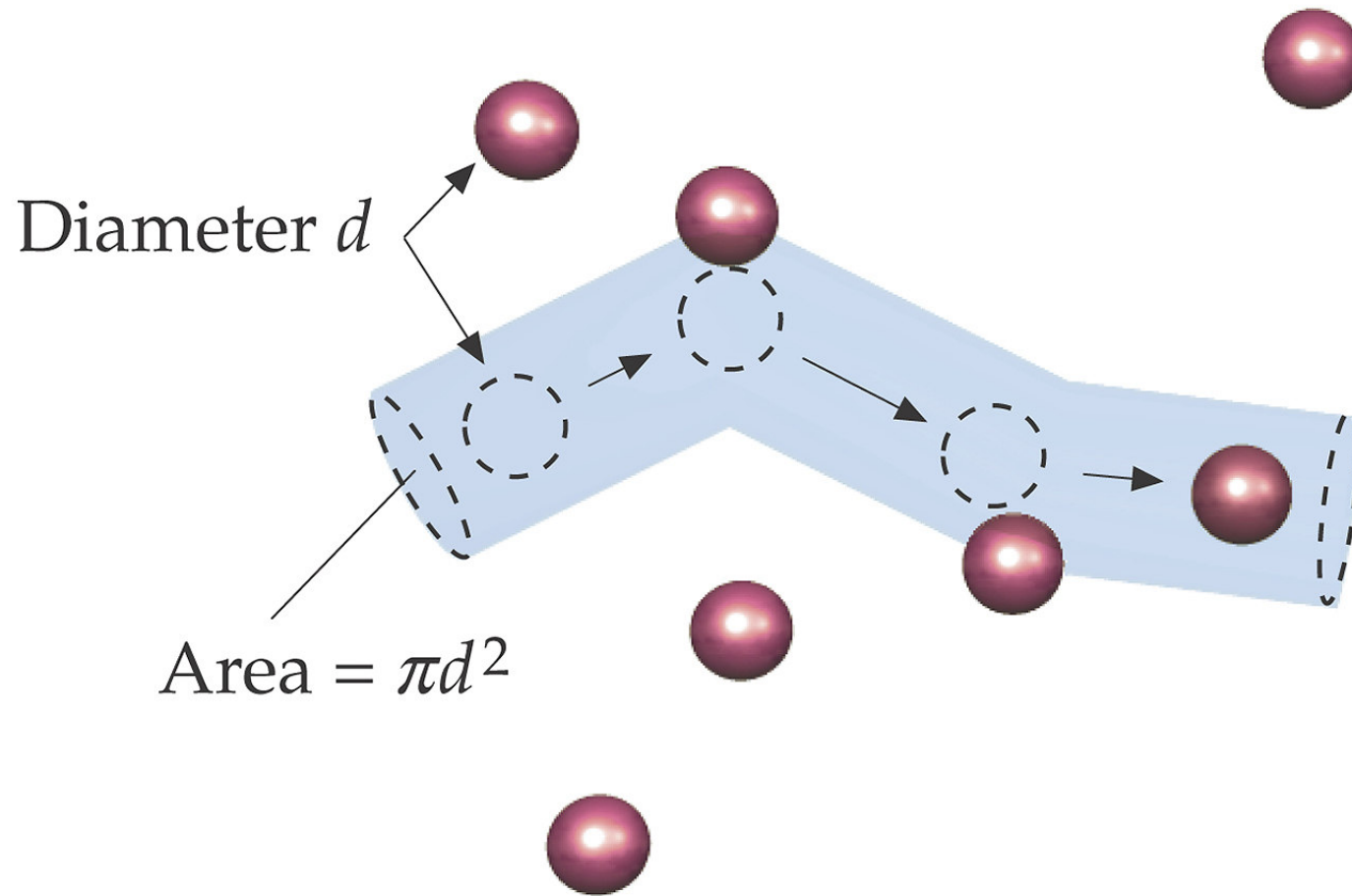


Mean Free Path

The molecule collides with any gas atom that approaches within a distance of $d = r_1 + r_2$ of the molecule.



Mean Free Path



Mean Free Path

Assumptions:

- Gas of similar molecules
- Molecular diameter is d
- Collisions occur with any molecule in a cylinder $\pi d^2 vt$
- All collisions are elastic.
- All but one of the molecules are at rest

Mean Free Path

Number density $n_v = \frac{N}{V}$

Number of in the cylinder $n_v \pi d^2 v t$

Mean Free Path $\frac{\text{Total Path}}{\# \text{ Collisions}} = \lambda = \frac{vt}{n_v \pi d^2 vt} = \frac{1}{n_v \pi d^2}$

For a more realistic situation when all atoms are in motion.

$$\lambda = \frac{1}{\sqrt{2} n_v \pi d^2}$$

τ Collision rate

$$\lambda = v_{avg} \tau$$

$\frac{1}{\tau}$ Collision frequency

Mean Free Path

How far does a molecule travel before it collides with another molecule ?

For air at room temperature, the mean free path can be expressed as:

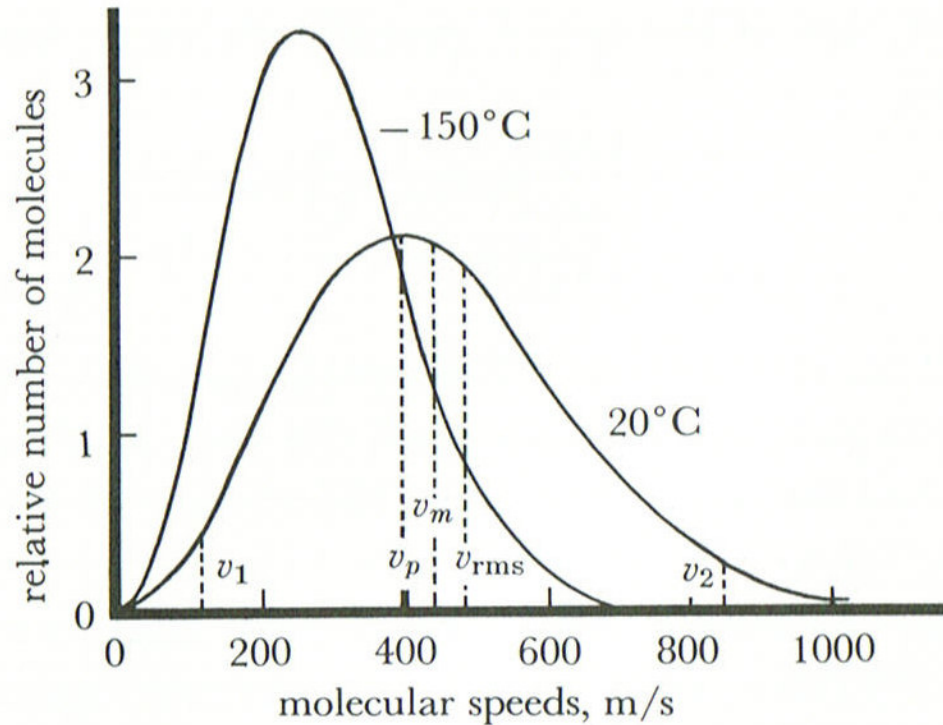
$$\lambda = \frac{5 \times 10^{-3}}{P}$$

P = pressure in torr

Distance will be in cm.

Pressure	Mean Free Path
1 atm	6.7×10^{-6} cm
1 torr	5×10^{-3} cm
1 millitorr	5 cm
10^{-6} torr	50 m
10^{-9} torr	50 km

The Maxwell-Boltzmann Distribution



The distribution of speeds in a gas is given by the Maxwell-Boltzmann Distribution.

Figure 16-7 Maxwell's distribution curve for molecular speeds at two temperatures. The ordinate is in per cent, for a 10 m/s range of speeds. Example: At 20°C, about 2% of the molecules have speeds between 395 and 405 m/s.

Example:

What is the temperature of an ideal gas whose molecules have an average translational kinetic energy of 3.20×10^{-20} J?

$$\langle K_{\text{tr}} \rangle = \frac{3}{2} kT$$

$$T = \frac{2\langle K_{\text{tr}} \rangle}{3k} = 1550 \text{ K}$$

Example:

What are the rms speeds of helium atoms, and nitrogen, hydrogen, and oxygen molecules at 25 °C?

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

On the Kelvin scale $T = 25 \text{ °C} = 298 \text{ K}$.

Element	Mass (kg)	rms speed (m/s)
He	6.64×10^{-27}	1360
H ₂	3.32×10^{-27}	1930
N ₂	4.64×10^{-26}	515
O ₂	5.32×10^{-26}	482

Molecular Velocity

How fast are the molecules moving ?
equation for rms velocity

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

k = Boltzmann's constant

T = temperature of the gas (K)

m = mass of the molecule

Not surprising:

The hotter it is, the faster they move.

The lighter they are, the faster they move.

At room temperature:

Molecule	v_{rms} (m/sec)	v_{rms} (miles/hour)
H ₂	1700	3790
N ₂	450	1000
Ar	380	850

<http://www.uccs.edu/~tchriste/courses/PHYS549/549lectures/gasses.html>

Most Probable Speed - Previous Slide Had V_{rms}

TABLE I. Most Probable Speed v_0 for Various Species (in 10^4 cm sec^{-1}).

Species	100 K	200 K	300 K
H ₂	9.08	12.84	15.72
He	6.42	9.08	11.12
H ₂ O	3.03	4.29	5.25
N ₂	2.43	3.44	4.21
CO	2.43	3.44	4.21
O ₂	2.27	3.21	3.93
A	2.03	2.87	3.52
Electron	551	779	954
Average kinetic energy (eV)	0.0129	0.0258	0.0388

The speed of sound is about 340 m/s.

$$10^4 \text{ cm/s} = 100 \text{ m/s} = 223.7 \text{ mi/hr}$$

Extra Slides

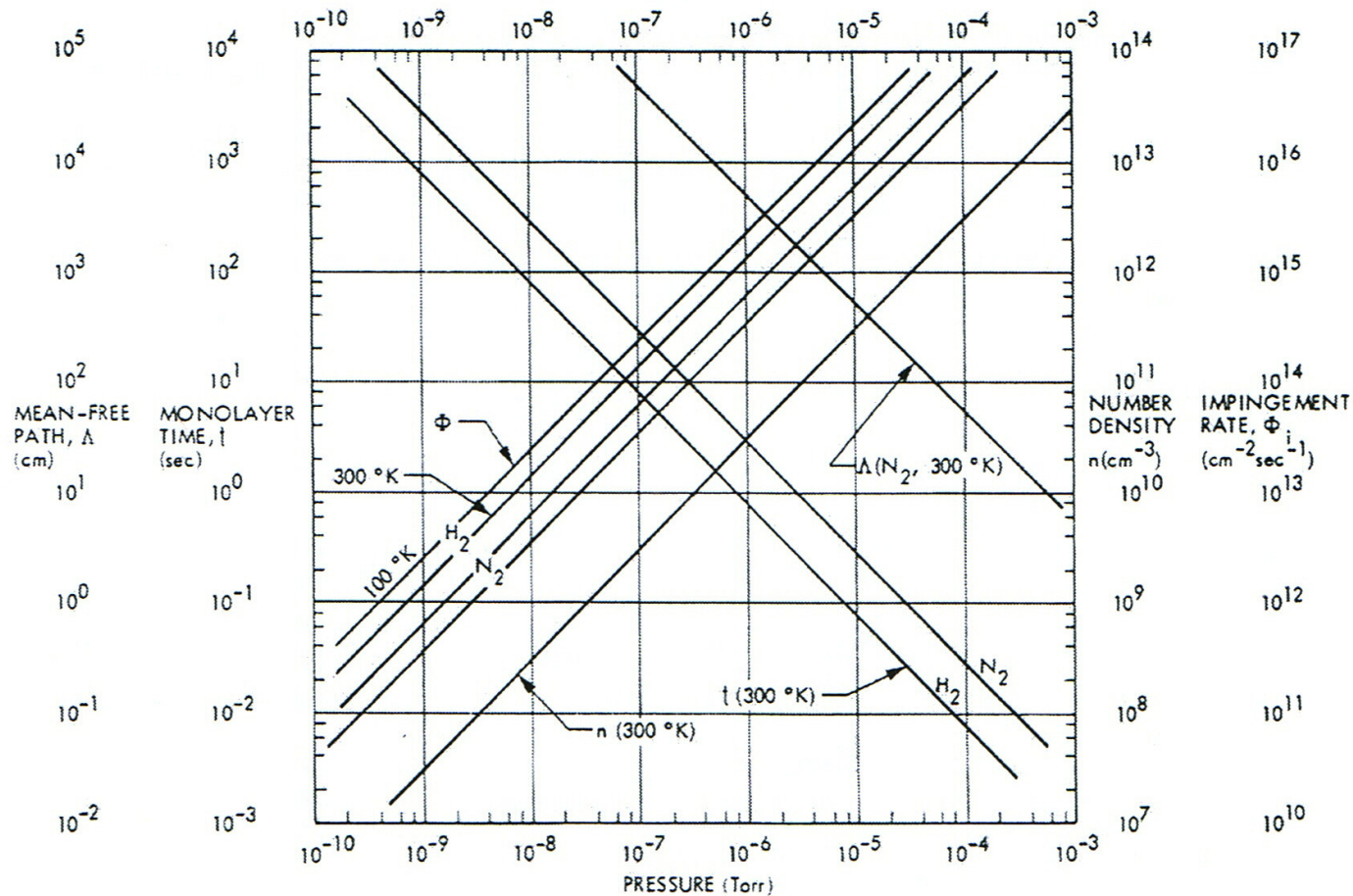
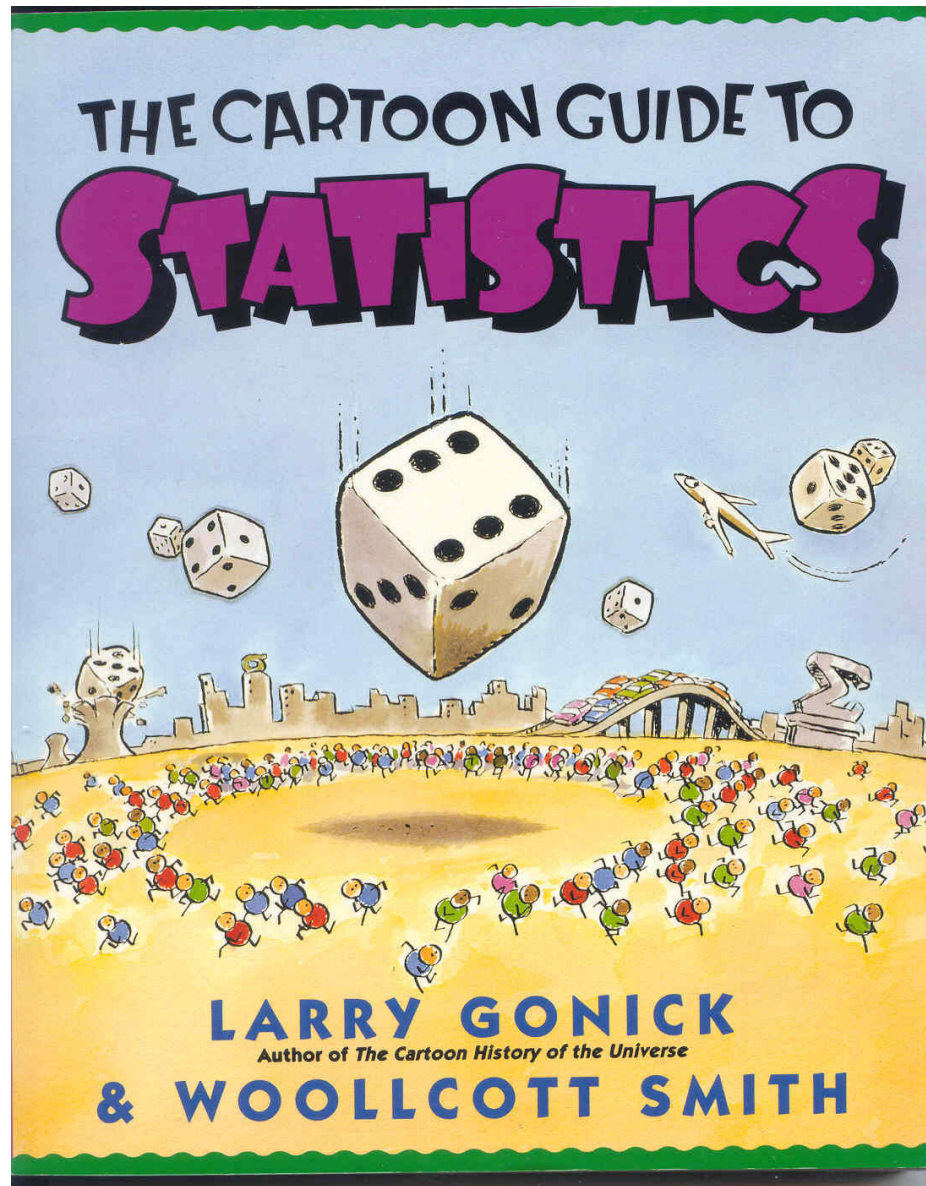


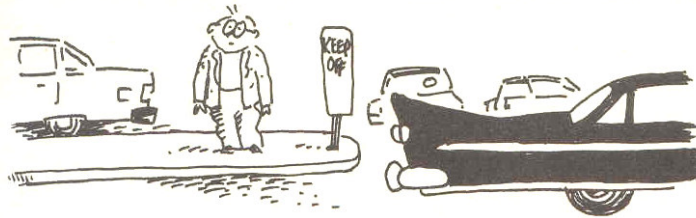
FIG. 1. Dependence of mean free path, monolayer time, number density, and molecular impingement rate as a function of pressure (in Torr). The mean free path Δ is shown for N_2 molecules in a background 300 K N_2 gas while the monolayer time t is shown for H_2 and N_2 at 300 K. The number density n is shown for a 300 K gas and is independent of the molecular species. The impingement rate Φ depends upon both the temperature and species and is given for H_2 and N_2 at 100 and 300 K.

Statistics



THE MEDIAN

IS ANOTHER KIND OF CENTER: THE "MIDPOINT" OF THE DATA, LIKE THE "MEDIAN STRIP" IN A ROAD.



TO FIND THE MEDIAN VALUE OF A DATA SET, WE ARRANGE THE DATA IN ORDER FROM SMALLEST TO LARGEST. THE MEDIAN IS THE VALUE IN THE MIDDLE.

3 5 7 7 38
 ↑
 THE MEDIAN

IF THE NUMBER OF POINTS IS *EVEN*—IN WHICH CASE THERE IS NO MIDDLE, WE AVERAGE THE TWO VALUES AROUND THE MIDDLE... SO IF THE DATA ARE

3 5 7 7 WE AVERAGE 5 AND 7 TO GET $\frac{5 + 7}{2} = 6$
 ↑
 MIDDLE SPACE

THIS GIVES US A GENERAL RULE: ORDER THE DATA FROM SMALLEST TO LARGEST.

IF THE NUMBER OF DATA POINTS IS *ODD*, THE MEDIAN IS THE MIDDLE DATA POINT.

IF THE NUMBER OF POINTS IS *EVEN*, THE MEDIAN IS THE AVERAGE OF THE TWO DATA POINTS NEAREST THE MIDDLE.



Statistics Basics

Statistics is based on probability. The typical question asked is:

What is the probability that a particular event will occur?

Averages are the result of a statistical calculation.

$$x_{avg} = \frac{x_1 + x_2 + x_3 + x_4 + x_5}{5}$$

$$x_{avg} = \frac{x_1}{5} + \frac{x_2}{5} + \frac{x_3}{5} + \frac{x_4}{5} + \frac{x_5}{5} = \frac{1}{5} \sum_{i=1}^5 x_i$$

$$x_{avg} = \frac{1}{5} \sum_{i=1}^5 x_i = \sum_{i=1}^5 \left(x_i \frac{1}{5} \right) = \sum_{i=1}^5 x_i p(x_i)$$

$p(x)$ is the probability distribution

The probability distribution function is subject to the following condition

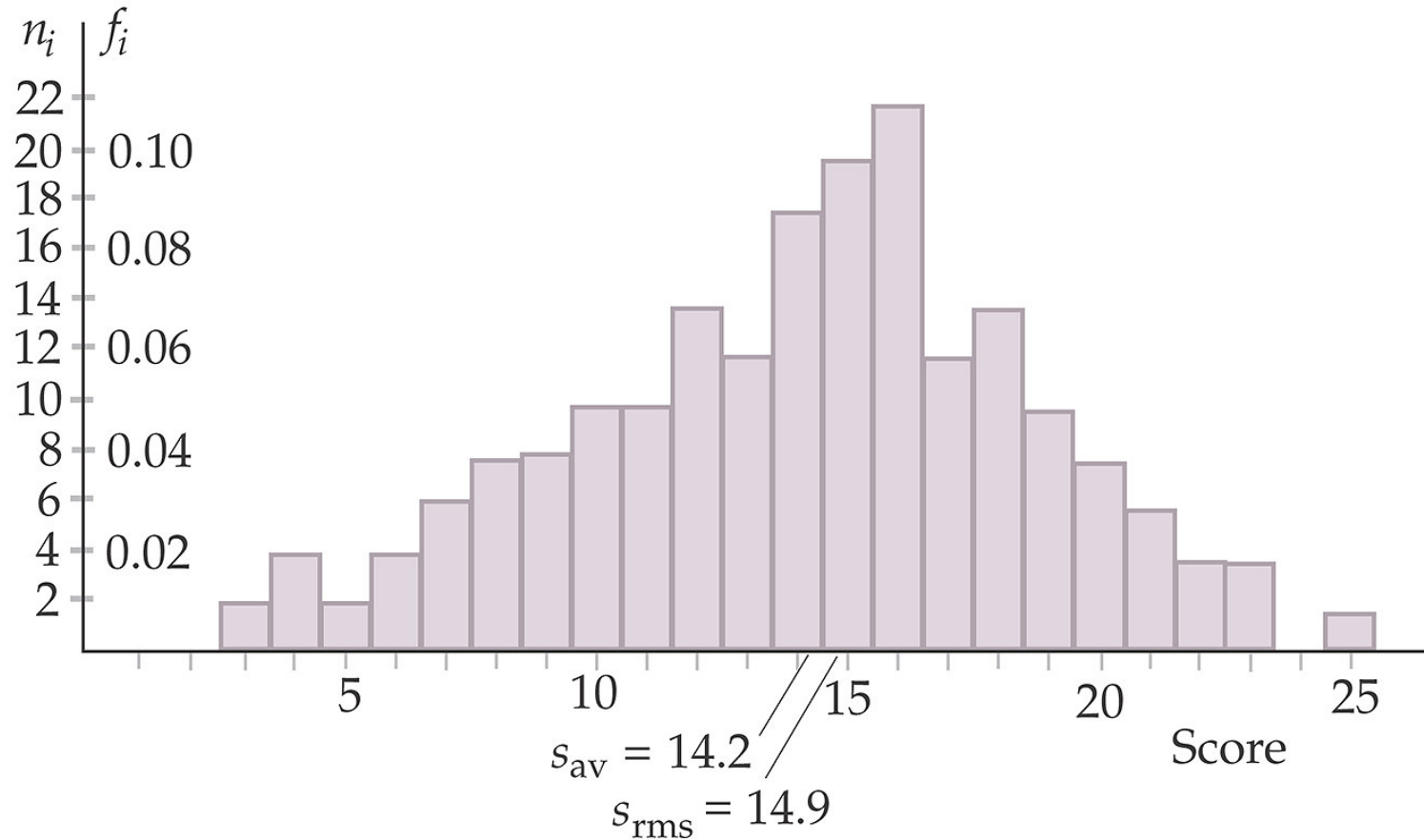
$$\sum_{i=1}^5 p(x_i) = 1$$

This means that the probability of all events must sum to 1

For our example $p(x_i) = 1/5$ independent of x .

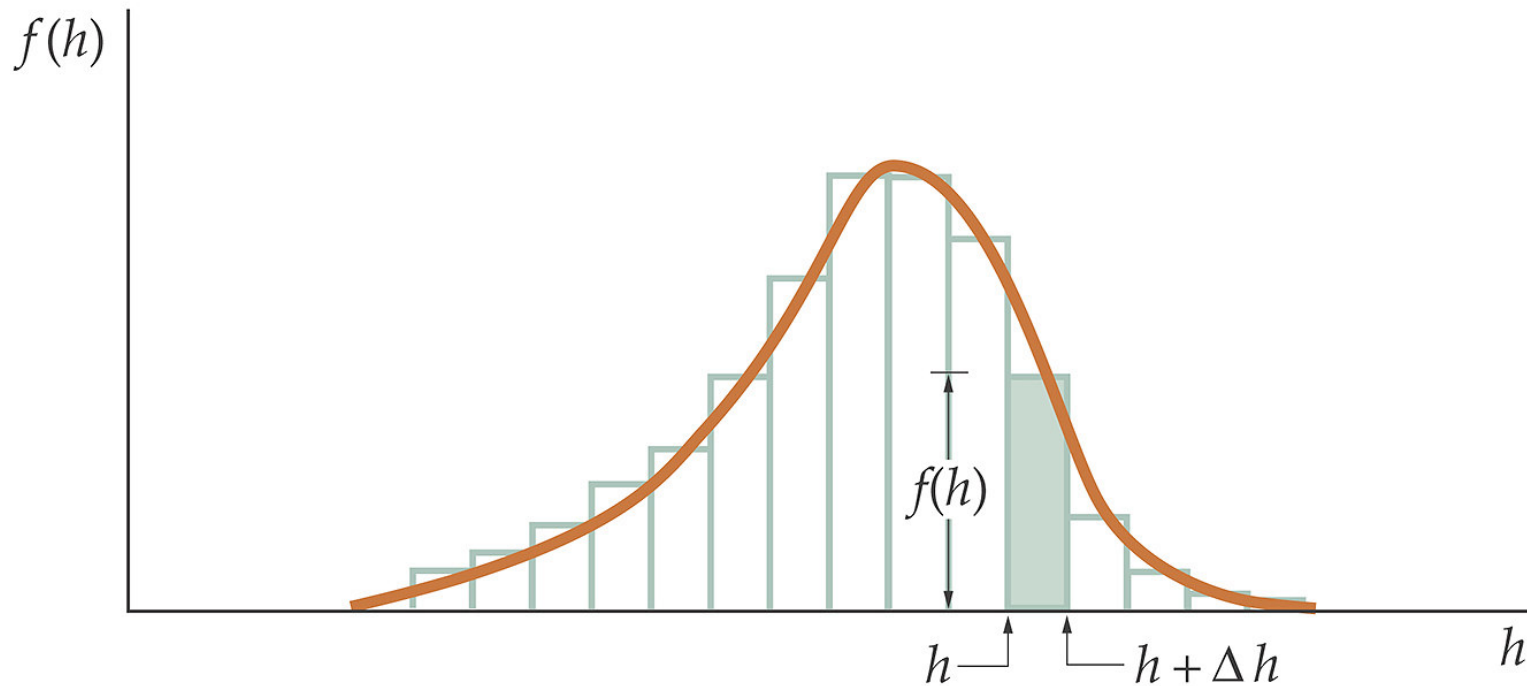
Discrete Distribution Function

Quiz Grades



Continuous Distribution Function

The finite distribution of heights can be approximated by a continuous function (solid line).



Maxwell-Boltzmann Distribution

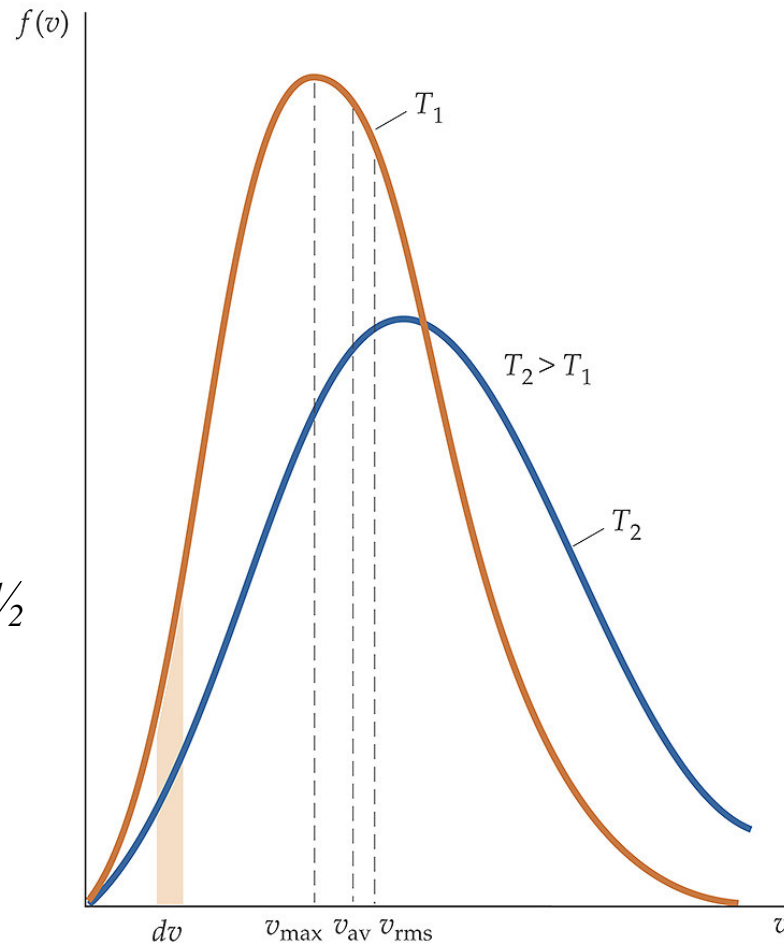
$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} v^2 \exp \left[\frac{-mv^2}{kT} \right]$$

$$f(E) = \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT} \right)^{3/2} E^{1/2} \exp \left[\frac{-E}{kT} \right]$$

$$f(E) = n(E)P(E)$$

Density of states $n(E) = \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT} \right)^{3/2} E^{1/2}$

Boltzman probability factor $P(E) = \exp \left[\frac{-E}{kT} \right]$



Redundant Slides

A carbon-12 atom by definition has a mass of exactly **12 atomic mass units (12 u)**.

$$12 \text{ u} = \left(\frac{12 \text{ g}}{\text{mole}} \right) \left(\frac{1 \text{ mole}}{6.022 \times 10^{23}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 1.66 \times 10^{-27} \text{ kg} \times 12$$

This is the conversion factor between the atomic mass unit and kg ($1 \text{ u} = 1.66 \times 10^{-27} \text{ kg}$). N_A and the mole are defined so that a 1 gram sample of a substance with an atomic mass of 1 u contains exactly N_A particles.

The atomic mass M_A (from the periodic table) is the gram weight of a mole of that substance. “u” is the average nucleon mass.

Example:

Air at room temperature and atmospheric pressure has a mass density of 1.2 kg/m^3 . The average molecular mass of air is 29.0 u .

How many air molecules are there in 1.0 cm^3 of air?

$$\text{number of particles} = \frac{\text{total mass of air in } 1.0 \text{ cm}^3}{\text{average mass per air molecule}}$$

The total mass of air in the given volume is:

$$m = \rho V = \left(\frac{1.2 \text{ kg}}{\text{m}^3} \right) \left(\frac{1.0 \text{ cm}^3}{1} \right) \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 = 1.2 \times 10^{-6} \text{ kg}$$

Example continued:

$$\begin{aligned}\text{number of particles} &= \frac{\text{total mass of air in } 1.0 \text{ cm}^3}{\text{average mass per air molecule}} \\ &= \frac{1.2 \times 10^{-6} \text{ kg}}{(29.0 \text{ u/particle})(1.66 \times 10^{-27} \text{ kg/u})} \\ &= 2.5 \times 10^{19} \text{ particles}\end{aligned}$$

Atomic Mass Unit & Nucleon Binding Energy

Mass of proton :	$1.6726 \times 10^{-27} \text{ kg}$	1.6726E-27
Mass of neutron:	$1.6749 \times 10^{-27} \text{ kg}$	1.6749E-27
Mass of electron:	$0.00091 \times 10^{-27} \text{ kg}$	9.1000E-31
Avg of proton & neutron mass:	$1.6738 \times 10^{-27} \text{ kg}$	1.6738E-27
1 u =	$1.66 \times 10^{-27} \text{ kg}$	1.6600E-27

Carbon Mass (= 6p + 6n)		2.0085E-26
12u		1.9920E-26
Missing Mass		1.6500E-28
Missing Energy (Joules) ($E = mc^2$)		1.485E-11
Missing Energy (eV) ($E = E(\text{J})/1.602\text{E-}19$)		92696629.21
		9.27E+07
Missing Energy (Mev) per nucleon		7.72E+06

Missing Mass/u 9.94%

Pressure Conversion Table

	mbar	Pascals (N/m ²)	atmospheres	Torr (mm Hg)	microns (μm Hg)	psi (lb/in ²)	dyne/cm ²	molecules / m ³
1 mbar =	1	100	9.87x10 ⁻⁴	0.75	750	0.0145	1000	2.65x10 ²²
1 Pa =	0.01	1	9.87x10 ⁻⁶	7.5x10 ⁻³	7.5	1.45x10 ⁻⁴	10	2.65x10 ²⁰
1 atm =	1010	10,100	1	760	7.6x10 ⁵	14.69	1.01x10 ⁶	2.69x10 ²⁵
1 Torr =	1.333	133.3	1.31x10 ⁻³	1	1000	0.0193	1333	3.53x10 ²²
1 μm =	1.33x10 ⁻³	0.133	1.31x10 ⁻⁶	0.001	1	1.93x10 ⁻⁵	1.333	3.53x10 ¹⁹
1 psi =	68.94	6.89x10 ³	0.068	51.71	5.17x10 ⁴	1	6.89x10 ⁴	1.83x10 ²⁴
1 dyne/cm ² =	0.001	0.10	9.87x10 ⁻⁷	7.50x10 ⁻⁴	0.75	1.45x10 ⁻⁵	1	2.65x10 ¹⁹
1 molecule/m ³ =	3.77x10 ⁻²³	3.77x10 ⁻²¹	3.72x10 ⁻²⁶	2.83x10 ⁻²³	2.83x10 ⁻²⁰	5.47x10 ⁻²⁵	3.77x10 ⁻²⁰	1