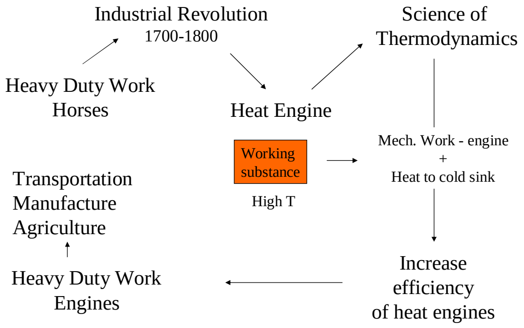
Concepts of Thermodynamics

Chapter 1

Relationship of Heat and Temperature to Energy and Work

Thermodynamics



Industrial Revolution
1700-1800

Heavy Duty Work
Horses

Heat Engine

Working substance

High T

Science of Thermodynamics

Mech. Work - engine
+
Heat to cold sink

Increase efficiency of heat engines

Heavy Duty Work
Engines

Transportation
Manufacture
Agriculture

Science of Thermodynamics

⇩

Four Fundamental Laws
interrelationships and inter-conversion
heat and mechanical energy

⇩

Concepts -
- Temperature, T
- Internal energy, U
- Enthalpy, H
- Entropy, S
- Gibbs free energy, G

Thermodynamics describes matter, their transformations and energy exchanges on a macroscopic scale using macroscopic (bulk) properties such as pressure, density, volume, and temperature.

Thermodynamics is useful in predicting the equilibrium position of chemical reactions at different temperatures and pressures, hence useful in selecting optimizing reaction conditions and yields. It also predicts the feasibility of chemical processes.

Further thermodynamics enables the calculation of the usable energy production from a reaction.

Energy technologies, design, etc..

In the microscopic view, descriptions of matter entails parameters such as the molecular dimensions which are of the order of the size of molecules, molecular electron distributions, bond angles, bond lengths, molecular geometry etc.

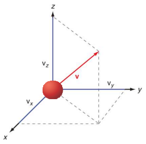
A thermodynamic description of matter does not make reference to the details of the molecular structure and associated parameters, e.g. *n* moles of a *gaseous substance* can be *completely described* by 2 of the 3 *macroscopic variables* pressure, volume, and temperature.

Only a few macroscopic variables are needed to describe a thermodynamic system.

Macroscopic variables; P, V and T

An (ideal) gas at a macroscopic level with a *known chemical composition* (*n* moles) is completely described by the measurable quantities volume, V, pressure, P, and temperature, T. How is P related to T and V, ..?

To understand such relationships a gaseous systems can be looked from the molecular point of view. Pressure in a gas arises from the molecular collisions on the container walls.



$$\mathrm{v}^2 = \mathbf{v}\cdot\mathbf{v} = \mathrm{v}_x^2 + \mathrm{v}_y^2 + \mathrm{v}_z^2$$

$$P = \frac{F}{A} = \frac{ma_i}{A} = \frac{m}{A}\left(\frac{d\mathrm{v}_i}{dt}\right) = \frac{1}{A}\left(\frac{d\boxed{m\mathrm{v}_i}}{dt}\right) = \frac{1}{A}\left(\frac{dp_i}{dt}\right)$$

An Ideal Gas

An ideal gas can be modeled as consisting *of point masses* (i.e. occupational volume is zero) with *no interaction with one another*; an ideal gas.

Gaseous samples that are dilute (i.e. at relatively low pressure and at relatively high temperature) can be considered as ideal gases.

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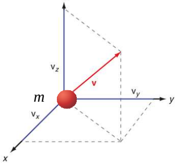
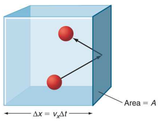
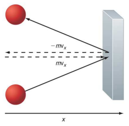
n moles of a gas in a cube (for simplicity) of volume V.







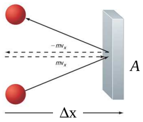
Collisions are elastic

$$\mathrm{v}^2 = \mathbf{v}\cdot\mathbf{v} = \mathrm{v}_x^2 + \mathrm{v}_y^2 + \mathrm{v}_z^2$$

Pressure due to the collision of one molecule;

$$P = \frac{F}{A} = \frac{ma_i}{A} = \frac{m}{A}\left(\frac{d\mathrm{v}_i}{dt}\right) = \frac{1}{A}\left(\frac{dm\mathrm{v}_i}{dt}\right) = \frac{1}{A}\left(\frac{dp_i}{dt}\right)$$

Acceleration of particle i; a_i *Momentum of particle i;* p_i



Δt $\Delta x = v_x \Delta t$

Change in momentum per molecule per collision *Δp* = mv$_x$-(-mv$_x$)=2mv$_x$

Change in momentum from N_{coll} collisions, Δp_{Total};

where N_{coll} = # collisions per unit time on area A

$$\Delta p_{Total} = (2m\mathrm{v}_x)(N_{coll})$$
$$= (2m\mathrm{v}_x)\left(\frac{nN_A}{V}\frac{A\mathrm{v}_x\Delta t}{2}\right)$$
$$= \frac{nN_A}{V} A\Delta t\, m\langle \mathrm{v}_x^2\rangle$$

$$F = \frac{\Delta p_{Total}}{\Delta t} = \frac{nN_A}{V} Am\langle \mathrm{v}_x^2\rangle$$
$$P = \frac{F}{A} = \frac{nN_A}{V} m\langle \mathrm{v}_x^2\rangle$$

It can be shown that; $\boxed{\frac{m\langle \mathrm{v}_x^2\rangle}{2}} = \frac{k_B \boxed{T}}{2}$ Thermodynamic temperature T (Kelvin scale)

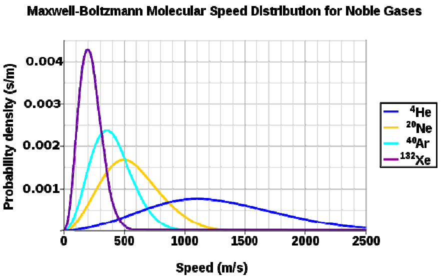
Gives; $P = \frac{nN_A}{V} m\langle \mathrm{v}_x^2\rangle = \frac{nN_A}{V} kT = \frac{nRT}{V}$

Ideal gas Law

Molecular collisions with the wall are elastic, meaning that translational energy of the particle is conserved. Collision imparts a linear momentum to the wall, which results in pressure. Force is the rate of change of momentum and pressure is force per unit area.

KE of a molecule is directly related to the temperature at the molecular level.

$$f(v) = \sqrt{\left(\frac{m}{2\pi kT}\right)^3} 4\pi v^2 e^{-\frac{mv^2}{2kT}},$$ (assume for now)



http://en.wikipedia.org/wiki/Maxwell%E2%80%93Boltzmann_distribution

Maxwell's Velocity Distribution Law $f(v) = \underline{\sqrt{\left(\frac{m}{2\pi kT}\right)^3} 4\pi v^2 e^{-\frac{mv^2}{2kT}},}$

Average energy E of a molecule $E = \int_0^\infty \frac{1}{2}m\mathrm{v}^2 f(\mathrm{v})d\mathrm{v}$

$$E = \int_0^\infty \frac{1}{2}\cdot \mathrm{m}\cdot \mathrm{v}^2 \cdot \left[\underline{\sqrt{\left(\frac{\mathrm{m}}{2\cdot\pi\cdot \mathrm{k}\cdot \mathrm{T}}\right)^3}\cdot 4\cdot\pi\cdot \mathrm{v}^2\cdot \mathrm{e}^{-\left(\frac{\mathrm{m}\cdot \mathrm{v}^2}{2\cdot \mathrm{k}\cdot \mathrm{T}}\right)}}\right] d\mathrm{v}$$

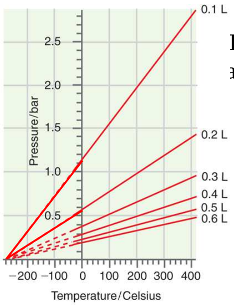
Using the standard integral;

$$\int_0^\infty e^{-ax^2} x^4 dx = \frac{3\pi^{1/2}}{8a^{5/2}}$$

$$\mathrm{E} = \frac{3}{2}\cdot \mathrm{k}\cdot \mathrm{T}$$

E: only a function of temperature T!

$$P = \frac{nRT}{V} = \rho_m RT; \quad \rho_m = \frac{n}{V} = \text{molar density}$$



The pressure of a fixed amount of an i***deal gas*** is zero at T = -273.15^{o}C.

$$T/\mathrm{K} = T_C/^\circ\mathrm{C} + 273.15$$

↑

Thermodynamic temperature T (Kelvin scale)

Definitions in Thermodynamics

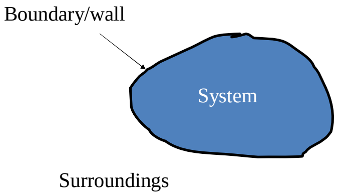
A thermodynamic system is defined as any part of the Universe under consideration. A thermodynamic *system* consists of *all the materials involved* in the process/part under study.

In thermodynamics, the *rest of the universe*, other than the system is referred to as the *surroundings*.

If a *system can exchange matter with the surroundings*, it is called an *open system*; if not, it is a *closed system*.

Both open and closed *systems can exchange energy with the surroundings.*

Systems that *does not exchange neither matter nor energy* with the surroundings are called *isolated systems*.



The Universe is the system *plus* it’s surroundings.

Surroundings are assumed infinite and remains at constant temperature and pressure. The immense size of the universe gives credence to this assumption.

The system and surrounding is separate by a boundary/wall; i.e. the wall contains the system.

A *diathermic system* allows heat flow into or out of the system.

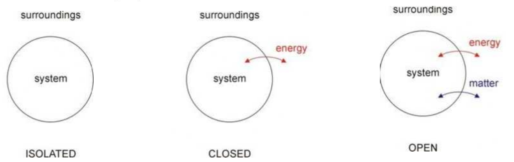
An *adiabatic system* prevents heat flow into or out of the system.

The boundary (wall) may be real or notional.

(a) **Isolated system:** A thermos bottle containing hot soup with the lid screwed on tightly

(b) **Closed system:** A cup of hot soup with a lid
Mass constant

(c) **Open system:** An open cup of hot soup



https://www.youtube.com/watch?v=7RawwstN-Pw cv

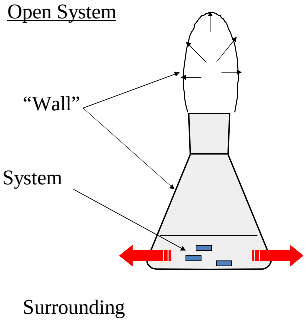
Properties of walls (boundary):

- rigid or moveable (allows changes in P and V during a process) (fixed volume container vs. a piston or balloon).
- adiabatic (insulating) or diathermal (conducts heat across the wall) e.g. Styrofoam vs. metallic containers.
- permeable (allowing material to pass through) or impermeable.

Thermodynamic Processes:

- *Isothermal process* implies constant temperature, *T*.
- *Isobaric process* implies constant pressure, *P*.
- *Isochoric process* implies constant volume, *V*.

Open System



Pushes (expansion) air outward
System works against
the atmosphere, expends
(loses) energy
$w < 0$

Loss of heat
System loses energy
in the form of heat
$q < 0$

System (open): The portion within the boundary (formed by the container and the edge of the gaseous cloud). Walls can be rigid or movable and permeable or non-permeable.

The exchange of energy and matter across the boundary (wall) between system and surroundings is central to the important concept of equilibrium.

The system and surroundings can be in equilibrium with respect to one or more of several different *system variables* such as pressure (P), temperature (T), and concentration.

Thermodynamic equilibrium refers to a condition in which equilibrium exists with respect to P, T and concentration.

A system comes to equilibrium with its surroundings when it establishes a constancy with respect to a given variable, only if that variable does not change with time, and if it has the same value in all parts of the system and surroundings.

Equations of State of Gases and the Ideal Gas Law

An equation of state relates the state variables (P, V, T, n) that characterizes a gaseous sample.

An ideal (dilute) gas can be modeled as consisting *of point masses* (occupational volume is zero) with *no interaction with one another*; an ideal gas.

$$PV = nN_Ak_BT = nRT \quad \textit{Ideal Gas Law}$$

P, T are intensive variables, V and n are extensive variables.

For an ideal gas mixture; $PV = nRT = \left(\sum_i n_i\right)RT = \sum_i n_iRT$

$$P = \sum_i \boxed{\frac{n_i\,RT}{V}} = \sum_i \boxed{P_i} = P_1 + P_2 + P_3 + \ldots$$

P_i = partial presssure of gas i

$$\frac{P_i}{P} = \frac{\dfrac{n_iRT}{V}}{\sum_i \dfrac{n_iRT}{V}} = \frac{\dfrac{n_iRT}{V}}{\dfrac{nRT}{V}} = \frac{n_i}{n} = x_i$$

x_i = mole fraction of gas i

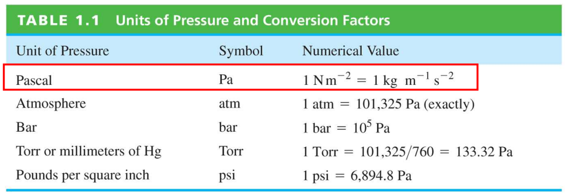


TABLE 1.1 Units of Pressure and Conversion Factors

Unit of Pressure	Symbol	Numerical Value
Pascal	Pa	$1\ \mathrm{N\,m^{-2}} = 1\ \mathrm{kg\ m^{-1}\ s^{-2}}$
Atmosphere	atm	1 atm = 101,325 Pa (exactly)
Bar	bar	1 bar = 10^5 Pa
Torr or millimeters of Hg	Torr	1 Torr = 101,325/760 = 133.32 Pa
Pounds per square inch	psi	1 psi = 6,894.8 Pa

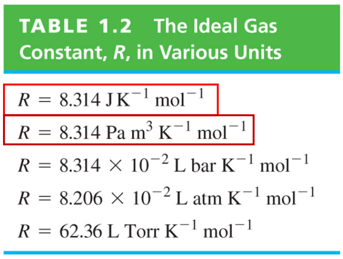


TABLE 1.2 The Ideal Gas Constant, *R*, in Various Units

$R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$

$R = 8.314\ \mathrm{Pa\,m^3\,K^{-1}\,mol^{-1}}$

$R = 8.314 \times 10^{-2}\ \mathrm{L\,bar\,K^{-1}\,mol^{-1}}$

$R = 8.206 \times 10^{-2}\ \mathrm{L\,atm\,K^{-1}\,mol^{-1}}$

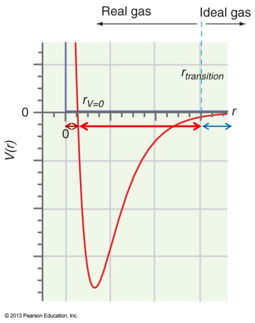
$R = 62.36\ \mathrm{L\,Torr\,K^{-1}\,mol^{-1}}$

Real Gases

The ideal gas law only holds for gases at low densities. Deviations from the ideal gas show up for real gases at low temperatures and high pressures.

The ideal gas assumes that the atoms or molecules of a gas do not interact with one another and can be treated as point masses have a limited range of validity.

The potential energy of interaction of two gas molecules as a function of the distance between them is not zero as the ideal gas concept assumes.



The intermolecular potential can be divided into regions;

PE ~ 0; $r > r_{transition}$

PE < 0 (attractive interaction)
$r_{transition} > r > r_{v=0}$

PE > 0 positive (repulsive interaction); $r < r_{v=0}$

$r_{transition}$ not uniquely defined and depends on the energy of the molecule. It is on the order of the molecular size.

Ideal gas pressure

Container ‘free’ space

$$PV = nRT$$

No interactions between gas molecules.

The pressure from the collisions impinging on the wall, where each colliding molecule is neither attracted or repelled by other molecules.

Point masses - occupation volume of all molecules = 0.

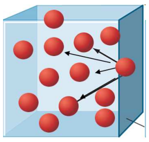
V = empty/free space of the container

Real P ≠ Ideal P
Actual ‘free space’ ≠ V

As the gas density is increased molecules approach one another to within a few molecular diameters and experiences a long-range attractive Van der Waals forces.

The strength of the attractive interaction is proportional to the polarizability of the electron charge in a molecule and is, therefore, substance dependent.

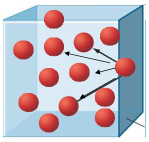
In the attractive region, P is lower because the *attractive interaction* brings the atoms or molecules closer. So the pressure measured P, is lower than the P of the ideal gas equation (IGE), PV = nRT.



A correction has to be made to account for two body attractive forces. P (ideal) in the IGE must be replaced by (*P (measured/real)* + ‘correction accounting the attractive forces’).

$$\text{IDE P} \Rightarrow P + \frac{na^2}{V}$$

The volumes excluded for molecules is no more negligible and the V in the IGE must be replaced by (*V* – ‘correction accounting the excluded volumes)



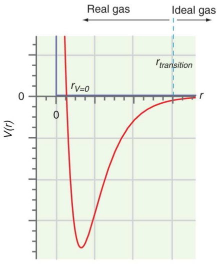
$$\text{IDE V} \Rightarrow V - nb$$

$$\left(P + \frac{na^2}{V}\right)\left(V - nb\right) = RT$$

Van der Waals equation of state

P, T , V and n relationship in a real gas, in general.

$$\left(P+\frac{n^2a}{V^2}\right)\left(V-nb\right)=nRT \quad PV=nRT$$



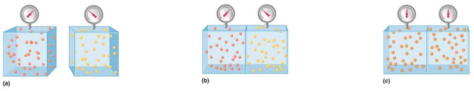
a, b; experimentally determined and positive quantities.

Zeroth Law of Thermodynamics

Temperature equilibrium between multiple systems or system(s) and surroundings is referred to as *thermal equilibrium*.

Two systems that have the same temperature are in thermal equilibrium. Temperature and thermal equilibrium *characterizes the walls* between a system(s) and its surroundings.

$$P = \rho_m RT$$



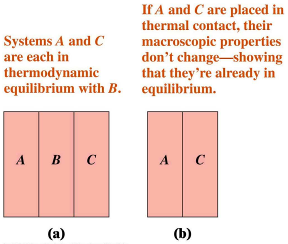
Same *molar density* in both systems

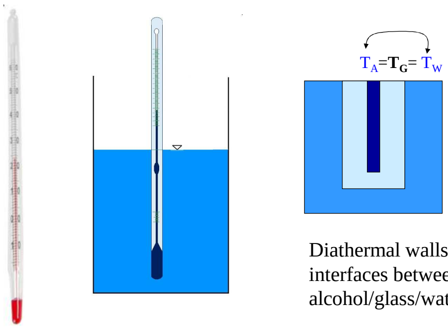
Adiabatic wall – systems not in thermal equilibrium. No heat exchange.

Diathermal wall – systems in thermal equilibrium.

Zeroth Law of Thermodynamics

Two systems that are separately in thermal equilibrium with a third system are also in thermal equilibrium with one another.





Diathermal walls; interfaces between alcohol/glass/water.

The thermometer measures the temperature of mercury/dyed alcohol, which can be equated to the temperature of the water.

Equipartition Theorem

The law of equipartition of energy states *that each quadratic term in the classical expression for the energy contributes* ½$k_B T$ *to the average energy*.

For instance, the translational motion of *an atom or molecule* has three degrees of freedom (number of ways of absorbing energy), corresponding to the x, y and z components of its momentum.

Since these components of momenta appear quadratically in the kinetic energy, every atom has an average kinetic energy of (3/2) $k_B T$ in thermal equilibrium.

http://chemwiki.ucdavis.edu/Physical_Chemistry/Statistical_Mechanics/Equipartition_Theorem