PART I
INTRODUCTION TO THERMODYNAMICS

WHAT IS THERMODYNAMICS?

Thermodynamics is a study of gases, liquids and solids, their phase changes and interactions with the environment involving heat and work.

Since its inception in XVIII century it yielded many results of practical importance:
specific heats, theory of the steam engine operations

By the end of XIX century Thermodynamics was demonstrated to be a part of the more fundamental Statistical Mechanics, from which the it may be derived.

Thermodynamics is very well suited to serve as an illustration of a self-consistent empirical theory, a structure held together by logic and experimental evidence.
I will make my best effort to show students the beauty of this structure.

SOURCE: https://commons.wikimedia.org/wiki/File:Milan_Cathedral_from_Piazza_del_Duomo.jpg

MAIN DIRECTION OF OUR DISCOURSE

In our journey through this material, we will start by defining important state variables (P,T,V) used to describe fluids (gases and liquids). After a brief discussion of the State Equation (Ideal Gas Law) relating these state variables to each other, we will introduce concepts of Heat, Work and Internal Energy, and we will discuss their relations (First Law of Thermodynamics). We will proceed to discuss the standard gas processes at constant P, T or V and obtain valuable insights into the work, heat and internal energy changes in such processes. Our work up to that point will be summed up in the form of easy to use table. Next, we will look more carefully into the Ideal Gas Model and basic tenets of the Kinetic Theory of Gases, which will lead us to the first great insight: obtaining the Ideal Gas Law from the statistical treatment of the Newtonian Mechanics. The above discussion will bring forth the importance of the average speed and average kinetic energy of the single molecule, which in turn will introduce the question of the distribution of speeds and energies in the ideal gas. The answer will be provided without a proof (Maxwell-Boltzmann distribution of speeds, Boltzmann Energy Distribution). We will do our best to understand these functions and learn how to use them. We will then state (without proof) the Equipartition Theorem, that will allow us to generalize our ideal gas results (from the table) to the real gases. At this point, we will turn our attention to the Heat Engine, an important invention that revolutionized our world and started the Industrial Age. We will learn the general operating principles of the heat engines, (and their cousins: heat pumps) as well as about the laws limiting their efficiency. All of the above work will bring us to the doors of the Second Law of Thermodynamics. In the final chapter, we will discuss the concept of entropy as introduced by Clausius, and finally, we will consider the Boltzmann definition of entropy which together with the Second Law of Thermodynamics will give us another crucial insight into the link between the direction of irreversible processes and the Arrow of Time.

SOURCE:
https://commons.wikimedia.org/w/index.php?search=Boltzmann&title=Special:Search&profile=advanced&fulltext=1&advancedSearchcurrent=%7B%7D&ns0=1&ns6=1&ns12=1&ns14=1&ns100=1&ns106=1&searchToken=3at0ze21eohpkaw32dg7e6fft#/media/File:Zentralfriedhof_Vienna_-_Boltzmann.JPG

“THREE” LAWS OF THERMODYNAMICS

0th If A is in thermal equilibrium with B and B is in thermal equilibrium with C, then A is in thermal equilibrium with C.

1st The change of the internal energy of the isolated system is equal to the sum of the total work done on the system and the heat delivered to it.

2nd The total entropy change for any process is never negative.

3rd It is impossible for any procedure to lead to the isotherm T = 0 in a finite number of steps.

We will introduce and study them during our discussions.

State Variables: Macroscopic vs. Microscopic

A state variable is an element of the set of variables that describe the state of a dynamical system. Temperature, pressure, internal energy, enthalpy, entropy are examples of state variables in a thermodynamics system. These are macroscopic variables (attributable to the large ensembles of atoms/molecules)

In case of simple mechanical systems, position coordinates and their derivates are typical state variables. These are microscopic variables (attributable to single atoms/molecules)

ONE OF THE MAJOR ACCOMPLISHMENTS OF THE THEORY OF STATISTICAL MECHANICS WAS OBTAINING STATE VARIABLES FROM MICROSCOPIC VARIABLES DESCRIBING AVERAGE SINGLE MOLECULE!

HOMEWORK

1 Review important mechanical concepts of: Position, Velocity, Acceleration, Force, Kinetic Energy and Work, as they were introduced in your physics or Science classes.

2 Review Newton's Three Laws of Mechanics.

3 Review the Conservation of Energy Law.

	Definition	
Position		
Velocity		
Acceleration		
Linear Momentum		
Force		
Kinetic Energy		
Work		

III LAWS OD DYNAMICS

CONSERVATION OF ENERGY

LECTURE 1

O^{th} Law of Thermodynamics
Temperature and Pressure
Thermal Expansion of Solids and Fluids

Thermal Equilibrium

Two objects are in thermal equilibrium if and only if there is no net energy transfer between them. Once we define the temperature we will state that two objects in the thermal equilibrium have the same temperature.

Thermal Contact

Thermal Equilibrium
If two objects were placed in thermal contact and not exchange
exchange net energy then the objects are in thermal equlibrium.

0th Law of Thermodynamics

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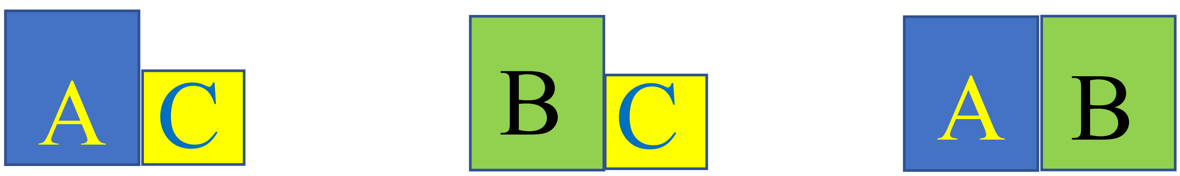


If objects A is in thermal equilibrium with an object C and object B is also in in thermal equilibrium with the object C, then A and B are in thermal equilibrium with each other.

Temperature

- We associate the concept of temperature with how “hot” or “cold” an objects feels.
- Our senses provide us with a qualitative indication of temperature, but our senses are unreliable for this purpose. For example; two objects at the same temperature will feel differently to a touch if one of them is a good thermal conductor while the other is not.
- We need a technical definition of temperature!

- **Temperature** can be thought of as the property that determines whether an object is in thermal equilibrium with other objects.
- Two objects in thermal equilibrium with each other are at the same temperature.
  - So, if two objects have different temperatures, they are not in thermal equilibrium with each other.

Thermometers

- Thermometer is a device used to measure the temperature of a system.
- In order to be effective thermometer needs to fulfill following general conditions

  Thermometer needs to have some linearly temperature-dependent physical parameter

  Thermometer needs to have a small "heat capacity."

  Since by introducing it into the system we will change the system temperature, we want that change to be negligible!

Thermometers are based on the principle that some easily observed physical property of a temperature-measuring device changes as the system's temperature changes.

- These properties may be: the liquid's volume, the length of the solid cylinder, the volume of a gas at constant pressure, the pressure of a gas at a constant volume, the electric resistance of a conductor, color of substance and the reflectivity
- A temperature scale can be established based on any of these physical properties.
- A thermometer can be calibrated by placing it in contact with some natural systems that remain at a constant temperature.

Using various phases of water is convenient.

One could use mixture of ice and water at atmospheric pressure. This is called the ice point of water. Triple point of water is the unique condition of pressure and temperature in which the water exists in three phases: ice, liquid and steam.

Liquid in glass Thermometers

- A common type of thermometer is a liquid-in-glass.
- The material in the capillary tube expands as it is heated.
- The liquid is usually mercury or alcohol.
- Inaccurate far from the calibration points.
- Useful only in the -30 to 80 C.

Thermocouple Thermometers

- Commonly used in variety of environments from low (-250C) to high (+1900C).
- Thermocouples utilize the thermoelectric effect: when conductor is subjected to temperature gradient ther will be a potential difference between the ends of the conductor.
- Using two different metals to complete the circuit in which the two arms of the thermocouple generate different voltages, produces a small difference in voltage easy to measure.
- That difference increases with temperature, and can typically be between 1 and 70 microvolts per degree Celsius (μV/°C) for the range of available metal combinations.
- Certain combinations have become popular as industry standards, driven by cost, availability, convenience, melting point, chemical properties, stability, and output. This coupling of two metals gives the thermocouple its name.

Temperature Scales

Celsius Scale

- The ice point of water is defined to be 0° C
- The steam point of water is defined to be 100° C
- The length of the column between these two points is divided into 100 increments, called degrees

Fahrenheit Scale

- A common scale in everyday use in the US
- Named for Daniel Fahrenheit
- Temperature of the ice point is 32 °F
- Temperature of the steam point is 212 °F
- There are 180 divisions (degrees) between the two reference points

Reamur Scale

- The ice point of water is defined to be 0° R
- The steam point of water is defined to be 80° R
- The length of the column between these two points is divided into 80 increments, called degrees

Kelvin (absolute) Scale

- Absolute zero is used as the basis of the absolute temperature scale.
- The size of the degree on the absolute scale is the same as the size of the degree on the Celsius scale
- The absolute scale is also called the Kelvin scale (for William Thomson, Lord Kelvin)
- The triple point temperature is 273.16 K
- No degree symbol is used with kelvins
- The kelvin is defined as 1/273.16 of the difference between absolute zero and the temperature of the triple point of water

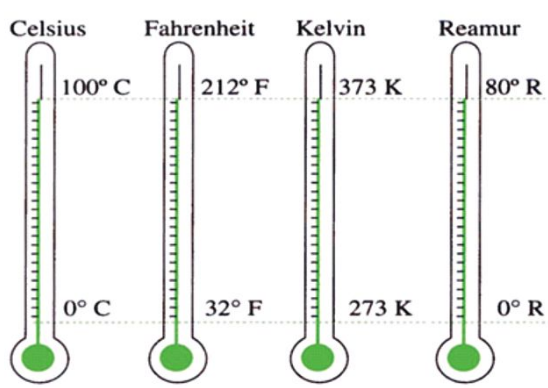


Figure 1 Different Scales of Temperature
SOURCE: https://commons.wikimedia.org/wiki/File:Skala_termometer.jpg

Example of Scale Conversions:

Celsius and Kelvin have the same size degrees, but different starting points

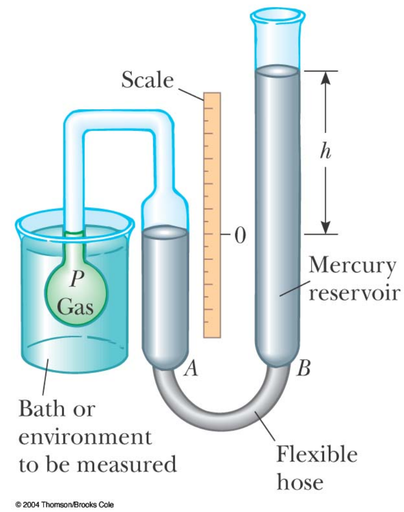
$$T_C = T - 273.15$$

Celsius and Fahrenheit have different sized degrees and different starting points

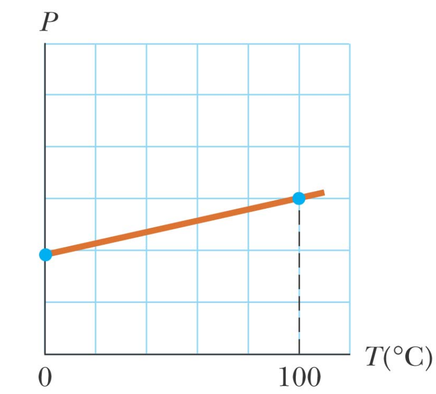
$$T_F = \frac{9}{5} T_C + 32$$

Ice point temperatures: $0^oC = 273.15\ K = 32^o\ F$ Steam point temperature: $100^oC = 373.15\ K = 212^o\ F$

Constant Volume Gas Thermometer

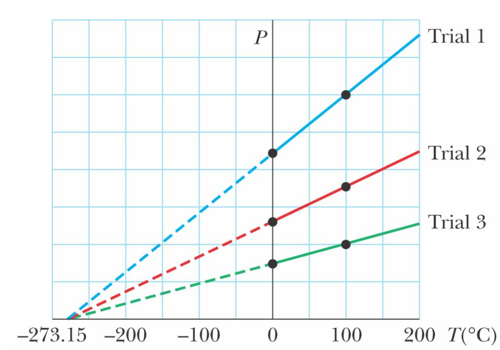


- The physical change exploited is the variation of pressure of a fixed volume gas as its temperature changes
- The volume of the gas is kept constant by raising or lowering the reservoir B to keep the mercury level at A constant.
- The thermometer is calibrated by using a ice water bath and a steam water bath.
- The pressures of the mercury under each situation are recorded
  - The volume is kept constant by adjusting A
- The information is plotted
- To find the temperature of a substance, the gas flask is placed in thermal contact with the substance
- The pressure is found on the graph
- The temperature is read from the graph



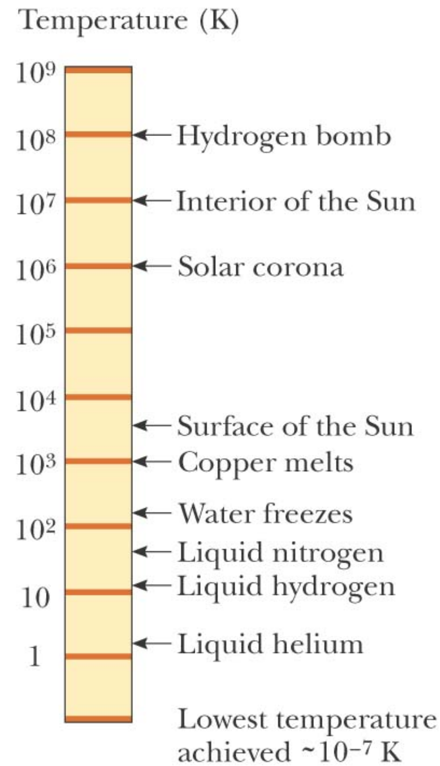
Absolute Zero

- The thermometer readings are virtually independent of the gas used
- If the lines for various gases are extended, the pressure is always zero when the temperature is
- –273.15o C
- This temperature is called **absolute zero**
- The absolute temperature scale is now based on two new fixed points (adopted by in 1954 by the International Committee on Weights and Measures)
  - One point is absolute zero
  - The other point is the triple point of water
- This is the combination of temperature and pressure where ice, water, and steam can all coexist
- The triple point of water occurs at 0.01^o C and 4.58 mm of mercury.
- This temperature was set to be 273.16 on the absolute temperature scale.
  - This made the old absolute scale agree closely with the new one



– The units of the absolute scale are **kelvins**

- The figure at right gives some absolute temperatures at which various physical processes occur
- The scale is logarithmic
- The temperature of absolute zero cannot be achieved
  – Experiments have come close



Energy at Absolute Zero

- According to classical physics, the kinetic energy of the gas molecules would become zero at absolute zero
- The molecular motion would cease
  – Therefore, the molecules would settle out on the bottom of the container
- Quantum theory modifies this and shows some residual energy would remain!
  – This energy is called the **zero-point** energy

BIG QUESTION :

How does one measure $T=10^6$ K or higher?

What does it mean that system is at this temperature?

PRESSURE

- The **pressure** *P* of the fluid at the level to which the device has been submerged is the ratio of the force to the area of the surface of the object

$$p = \frac{F}{A}$$

- Pressure is a scalar quantity
  If the pressure varies over an area, evaluate once needs to evaluate *dF* on a surface of area *dA* as *dF* = *P dA*
- Unit of pressure is **pascal** (Pa)

$$1\text{Pa} = \frac{1\text{N}}{1\text{m}^2}$$

Pressure in the uniform static fluid is constant at the same level

HYDROSTATIC PRESSURE EQUATION:

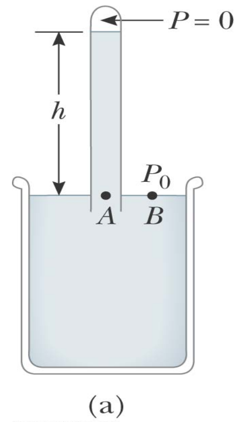
The pressure p at a depth *h* below a point in the liquid at which the pressure is p_0 is greater by an amount *ρgh.*

$$p = p_0 + \rho g h$$

- The liquid has a density of ρ./ We assume the density is the same throughout the fluid./

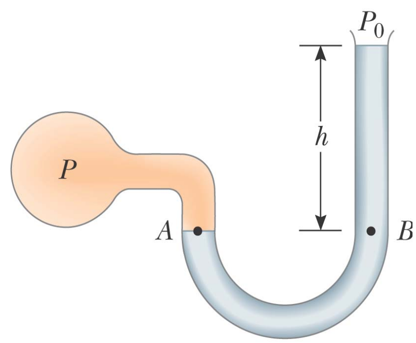
- If the liquid is open to the atmosphere, and *P*0 is the pressure at the surface of the liquid, then P_0 is *atmospheric pressure*
- *P*0 = 1.00 atm = 1.013×10^5 Pa

Torricelli's Barometer



- A long closed tube is filled with mercury and inverted in a dish of mercury.
  - The closed end is nearly a vacuum
- Measures atmospheric pressure as mm of mercury (Torrs)
  One 1 atm = 0.760 m (of Hg) =760 Torr

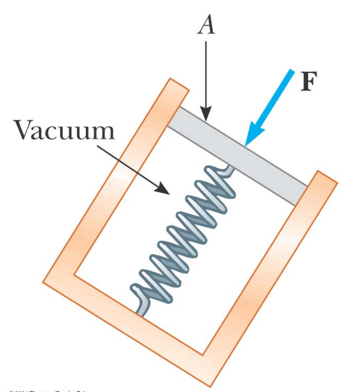
Manometer



- A device for measuring the pressure of a gas contained in a vessel
- One end of the U-shaped tube is open to the atmosphere
- The other end is connected to the pressure to be measured
- Pressure at *B* is $P_0+\rho gh$

- $P = P_0 + \rho gh$
- *P* is the **absolute pressure**
- The **gauge pressure** is $P - P_0$
  - This is also ρgh
  - This is what you measure in your tires

Measuring Pressure using calibrated spring



- To measure atmospheric pressure directly using mechanical device one could use a sealed container with calibrated spring attached to a piton. The external pressure acts on the piston compressed the spring.
  There are many other tools to measure very low pressures (high vacuum) such as capacitive baratrons, ionization gauges, and mass spectrometers.

IMPORTANT QUESTIONS:

1What is the total force acting on human body associated with the atmospheric pressure?
2What is the origin of atmospheric pressure?

THERMAL EXPANSION OF SOLIDES AND LIQUIDS (DIY)
(Annotate the following expressions for the thermal expansion of solids and liquids)

Length:

$$\Delta L = L_f - L_i = \alpha(T_f - T_i)L_i = \alpha L_i \Delta T$$

Volume:

$$\Delta V = V_f - V_i = \beta(T_f - T_i)V_i = \beta V_i \Delta T$$

Area:

$$\Delta A = A_f - A_i = \gamma(T_f - T_i)A_i = \gamma A_i \Delta T$$

Find out the meaning of all the equations and variables above

Answer the following questions:

1 How do α (linear expansion coefficient) and β (average coefficient of volume expansion) relate to each other?

ANSWER:

2 How do α (linear expansion coefficient) and **γ** (average coefficient of area expansion) relate to each other?

ANSWER:

Suggested Problems: Temperature and Pressure, Thermal Expansion

1 At what absolute temperature the temperatures measured using Celsius scale and Fahrenheit Scale are equal?

2. On a Weird temperature scale, the freezing point of water is –18.0°W and the boiling point is +62.0°W. Develop a *linear* conversion equation between this temperature scale and the Celsius scale.

3 As part of the science fair project student wants to use a mineral to duplicate Torricelli's barometer. How long will be the vertical glass tube in this barometer if the oil density is 1984 kg/m^3.

4 Mercury is poured into a U-tube with two cylindrical arms of different radii. The left arm of the tube has cross-sectional area A_1 of 10.0 cm^2, and the right arm has a cross-sectional area A^2 of 5.00 cm^2. Two hundred grams of water are then poured into the right arm.
(a) Determine the length of the water column in the right arm of the U-tube.
(b) Given that the density of mercury is 13.6 g/cm3, what distance *h* does the mercury rise in the left arm?

5 A telescope forms an image of part the sky with a uniform distribution of stellar sources, using the square silicon CCD detector originally at 20.0°C and 3.00 cm side. A star field is focused on the CCD. At this point the star field contains 6213 stars. To increase the Signal-To -Noise of the detector it is cooled to –90°C. How many star images then fit onto the chip? The average coefficient of linear expansion of silicon is 4.68×10^{-6} $(°C)^{-1}$.

6 A copper wire and a lead wire are joined together, end to end. The compound wire has an effective coefficient of linear expansion of 20.0×10^{-6} $(°C)^{-1}$. What fraction of the length of the compound wire is copper?

IDEAL GAS LAW

What is an ideal gas?
Ideal Gas Law
p-V Diagrams for Ideal Gas
p-V Diagrams for Various Gas Transformations

DEMO 1: Atmospheric Pressure: Can
DEMO 2: Liquid Nitrogen + Helium filled balloon.

4 Mid-lecture Quiz Questions

8 Suggested Problems

<u>READING ASSIGNMENT: 19</u>

What is an ideal gas?

An ideal gas is a theoretical gas composed of a set of randomly-moving point particles that interact only through elastic collisions. It is a gas in which the interatomic forces within the gas are very weak. Since the molecules of gas have large average inter-molecular separations, this is quite realistic condition. We shall treat these forces to be nonexistent, as result there is no equilibrium separation for the atoms, and thus there is no "standard" volume at a given temperature.

For a gas, the volume is entirely determined by the container holding the gas.

Equations involving gases will contain the volume, V, as a variable

Equation of State

- It is useful to know how the volume, pressure and temperature of the gas of mass m are related.
- The equation that interrelates these quantities is called the **equation of state.**
  - These are generally quite complicated.
  - If the gas is maintained at low pressure, the equation of state becomes much easier.
  - This type of a low-density gas is commonly referred to as **an ideal gas.**

Gas Laws

- They were discovered by XVIII/XIX century Scientists- founders of modern chemistry
- When a gas is kept at a constant temperature, its pressure is inversely proportional to its volume. **(Boyle's law)**
- When a gas is kept at a constant pressure, its volume is directly proportional to its temperature **(Charles and Gay-Lussac's law)**

Ideal Gas Law

- The equation of state for an ideal gas combines and summarizes the other gas laws

$$PV=nRT$$

This is known as the **Ideal Gas Law**

P is pressure; *V is volume* *n is number of moles of substance* $n=N/N_A$ *T is temperature*

R is a constant, called the Universal Gas Constant **R = 8.314 J/mol · K** = 0.08214 L · atm/mol · K

From this, you can determine that 1 mole of any gas at atmospheric pressure and at 0^o C is taking 22.4 liters of volume. (Avogadro's Law)

<u>The Mole</u>

- The amount of gas in a given volume is conveniently expressed in terms of the number of moles
- One **mole** of any substance is that amount of the substance that contains **Avogadro's number** of constituent particles
  - Avogadro's number $N_A = 6.022 \times 10^{23}$
  - The constituent particles can be atoms or molecules
- The number of moles can be determined from the mass of the substance: $n = m / M$
  - M is the molar mass of the substance
  - m is the mass of the sample
  - n is the number of moles

IDEAL GAS EQUATION IN ALTERNATIVE FORM

- The ideal gas law is often expressed in terms of the total number of molecules, N, present in the sample:

$$PV = nRT = (N/N_A)\, RT = Nk_B T$$

  - k_B is Boltzmann's constant
  - k_B = 1.38 x 10-23 J/K
- It is common to call P, V, and T the **thermodynamic variables** of an ideal gas

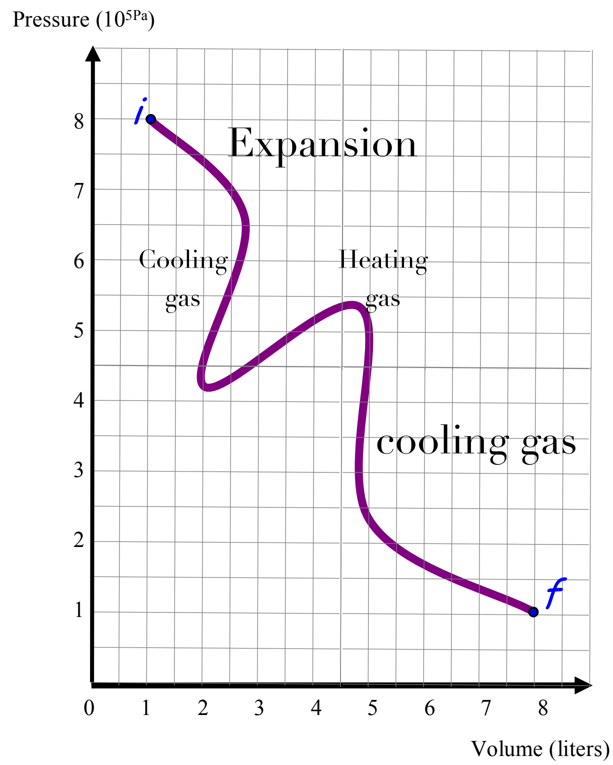
EXAMPLES OF OTHER STATE EQUATIONS (DIY):

1) Vanderval's Eqn

2) Crystal's

Phase Space and P-V Diagrams

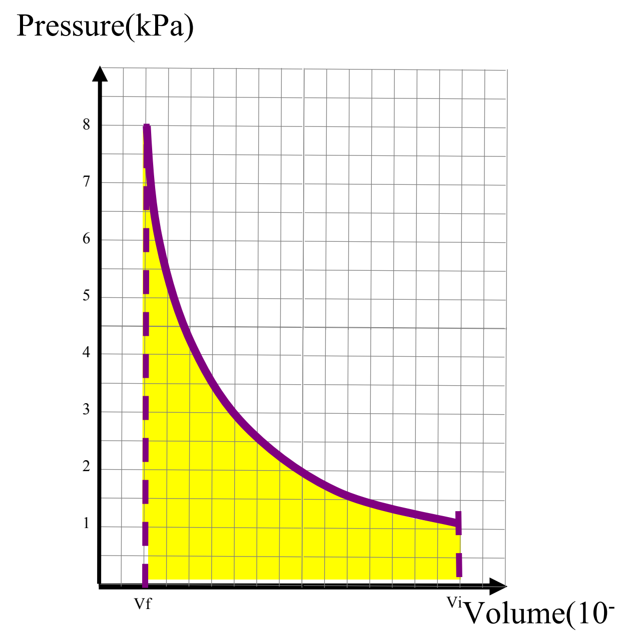
- *If the system has well-defined Pressure, Volume and Temperature, we are able to represent its state at every moment in time as a point on a P-V , P-T or V-T diagram.*
- *The change of these parameteres corresponds to the change of the coordinates on such* ***"phase space diagram."***
- P-V diagram is used when the pressure and volume are known at each step of the process.
- The state of the gas at each step can be plotted on a graph called a ***P-V*** **diagram.**
  This allows us to visualize the process through which the gas is progressing by drawing the curve on a P-V diagram from intial state i to final state *f.*
  This curve is called the *path.*



Pressure-volume diagram is used to describe a thermal cycle involving the following two variables: Volume (on the X axis) Pressure (on the Y axis)
This is in fact enough information to fully describe a simple system from a thermodynamic standpoint. Each point on the diagram has coordinates (V,p) which fully describe the ideal gas system at any point of time!

Also, the p-V diagrams are very useful when one wants to calculate the work done by the system, the integral of the pressure with respect to volume. One can often quickly calculate this using the PV diagram as it is simply the area enclosed by the cycle.

area under graph is work



Suggested Problems: Ideal Gas Equation

1. Show that 1 mole of any gas at atmospheric pressure and at 0o C is taking 22.4 liters of volume.

2. 100 grams of oxygen and 100 grams of hydrogen gas occupy separate, equal sections of 200-liter tank. The divide is removed and the gases are allowed to mix and react with each other. The temperature is kept constant at 110 °C, throughout the process
   a) find the pressure of each gas in the separate containers
   b) find the pressure after the reaction ends.

3. A 2.0-L bottle of generic soft-drink contains 12.50 g of carbon dioxide dissolved in its volume. After opening of the bottle, the evaporating carbon dioxide is trapped in a cylinder at 1.00atm and 17.0°C, what volume does the gas occupy?

4. A 6.0 g of water is placed in a 1.50-L pressure cooker and heated to 400°C. What is the pressure inside the container?

5. A hot-air balloon and its cargo (not including the air inside) have mass of 180 kg. The temperature of the air outside is at 11.0°C and 101.4 kPa. The volume of the balloon is 420 m^3. what must be the temperature of the hot air inside the balloon for it to lift off? (Air density at 11.0°C is 1.25 kg/m^3.)

6. A tank having a volume of 0.200 m3 contains helium gas at 150 atm. How many balloons can the tank blow up if each filled balloon is a sphere 0.300 m in diameter at an absolute pressure of 1.20 atm?

7. At 30.0m below the surface of the sea (density=1 025 kg/m3), where the temperature is 4.00°C, a diver exhales an air bubble having a volume of 1.2 cm^3. If the surface temperature of the sea is 23.0°C, what is the volume of the bubble just before it breaks the surface?

8. Long-term space missions require reclamation of the oxygen in the carbon dioxide exhaled by the crew. In one method of reclamation, 1.00 mol of carbon dioxide produces 1.00 mol of oxygen and 1.00 mol of methane as a byproduct. The methane is stored in a tank under pressure and is available to control the attitude of the spacecraft by controlled venting. A single astronaut exhales 1.09 kg of carbon dioxide each day. If the methane generated in the respiration recycling of three astronauts during one week of flight is stored in an originally empty 150-L tank at –45.0°C, what is the final pressure in the tank? [Source: Serway and Jewet 2003]