

Temperature: Average KE of the particles. Depends on average speed only of particles (atoms or molecules)
 A bucket of water at 50° has the same temperature as a cup of water at 50°

Thermal Energy: Average KE and the mass of the particles Depends on speed and the mass of the particles.
 A bucket at 50° has more thermal energy than a cup at 100°. Bucket of \$50 bills has more money than a cup of \$100's. While the particles are going faster in the cup, there are so many more in the bucket.

Heat: Transfer of energy between objects that have different temperatures. The direction of heat flow depends on temperature. From hot objects (more energy) to cold objects (less energy).

Thermal Expansion: As objects are heated the molecules move faster and they expand. This is why the liquid in a thermometer rises when heated. It is how a thermostat works. It is why there are gaps in sidewalks, bridges, & railroad tracks. It is why they don't fill bottles to the top, they might explode if the liquid expands to much.

$\Delta l = \ell_o \alpha \Delta T$ Gives the change in length. The original length ℓ_o is multiplied by α , the coefficient of linear expansion, and the change in temperature.

How long will a 5 m section of steel railroad track expand ($\alpha = 12 \times 10^{-6}$, from table 13-1, p 343) to if it is heated from 15° to 25°C?

$$\Delta l = \ell_o \alpha \Delta T = (5)(12 \times 10^{-6})(25 - 15) = 0.0006m \text{ so it will be } 5m + 0.0006m = 5.0006m$$

Kinetic Molecular Theory: Gas molecules collide with each other and their surroundings.

1. Large number of gas molecules (N) moving in random directions and a variety of speeds.
 2. They are far apart, with the separation distances being vast compared to the diameter of each particle.
 3. Molecules obey laws of mechanics. They attract each other, but we ignore this since the speeds and KE are huge.
 4. Collisions with each other and container walls are assumed to be perfectly elastic. Conservation of p and KE.
- * The higher the temperature the faster the molecules move. The particles vary in speed, so we can only measure an average. Half will be going faster and half slower than the average. Average KE is a reflects this speed.

$$\overline{KE} = \frac{3}{2} k_B T$$

Average KE = 3/2 (Boltzman's Constant, 1.38×10^{-23}) (Temperature in degrees Kelvin)

We can calculate the speed of the molecules on average

$$v_{rms} = \sqrt{\frac{3k_B T}{\mu}} = \sqrt{\frac{3RT}{M}}$$

The **Root Mean Square Velocity** = Square root of $[(3)(1.38 \times 10^{-23})(\text{Temp in Kelvin})/(\text{mass})]$

Gas Laws

Pressure: $P = F/Area$ Measured in N/m^2 called a **Pascal**. Collisions against an object are felt as pressure.

Universal Gas Law: $PV = nRT$ (Static cases) or $\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$ (Changing cases)

Pressure is measured in Pascals

$$1 \text{ atm} = 101300 \text{ Pa} = 1 \times 10^5 \text{ Pa}$$

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

Volume is measured in meters cubed

$$1000 \text{ L} = 1 \text{ m}^3$$

Gas constant

$$8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

Static cases: One container under a specific set of conditions.

What is the temperature of 30 mol of gas at 4 atm of pressure occupying 200 L?

$$PV = nRT \quad (4 \times 10^5 \text{ Pa})(0.200 \text{ m}^3) = (30 \text{ mol})(8.315 \text{ J/mol} \cdot \text{K})T$$

Changing cases: One container under changing conditions, or gas moved from one container to another.

Boyle's Law: Pressure and Volume are inversely proportional. As one goes up the other goes down.

200 L of gas at 4 atm of pressure is moved to a 400 L container, what is its new pressure?
(n and T aren't mentioned, so they must stay the same, and must cancel)

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} \quad PV = P_2V \quad (4 \times 10^5 \text{ Pa})(0.200\text{m}^3) = P_2(0.400\text{m}^3)$$

Charles' Law: Temperature and Volume are directly proportional. As one goes up the other goes up.

200 L of gas at 273 K are heated to 373 K, what is the new volume? (P and n aren't mentioned, so they must stay the same, and must cancel)

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \frac{0.200\text{m}^3}{273\text{K}} = \frac{V_2}{373\text{K}}$$

Combined Law: 200 L of gas at 3 atm and 273 K are moved to a 400 L container and heated to 373 K. What is the pressure? (n isn't mentioned, so they must stay the same, and must cancel)

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \frac{(3 \times 10^5 \text{ Pa})(0.200\text{m}^3)}{(273\text{K})} = \frac{P_2(0.400\text{m}^3)}{(373\text{K})} \quad \text{or} \quad \frac{(3\text{atm})(2\text{L})}{(273\text{K})} = \frac{P_2(4\text{L})}{(373\text{K})}$$

Heating and cooling curve

Heat: Q

Specific Heat Capacity: c , Ability to absorb or retain heat heat.

$$Q = mc\Delta T$$

Latent Heat: L , energy required to break intermolecular forces causing a phase / state change.

$$Q = mL$$

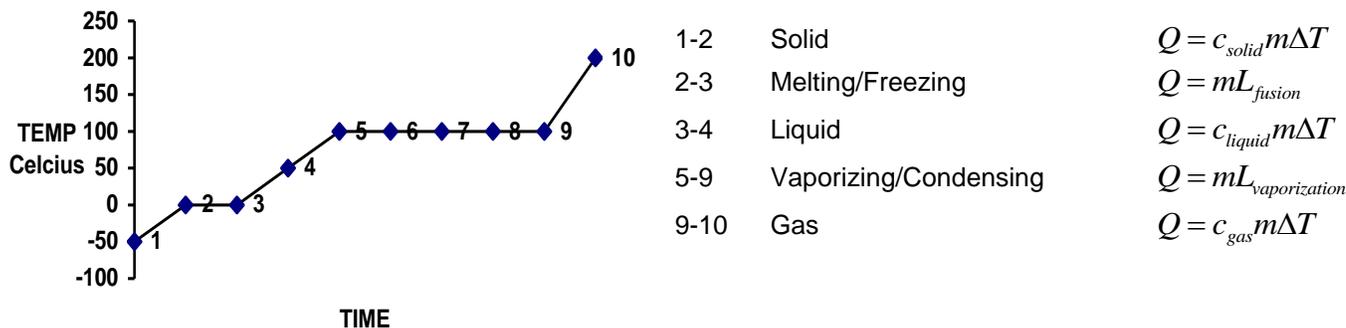
Latent Heat of Fusion:

L_F , energy required to melt a solid.

Latent Heat of Vaporization:

L_V , energy required to turn a liquid into a gas.

When phase / state is changing temperature cannot rise since the energy is required for the change.



How much energy does it take to melt 200 g of ice at 0°C and heat it to 60°C? It has to start as a solid, so it starts at point 2 on the graph. Melting is fusion so L is the Heat of Fusion for water from table 14-2, p. 377. Then it rises in temperature, so it must end around point 4. It is a liquid so you need the specific heat, c , of liquid water in table 14-1, p. 373. (Every substance has different melting plateau, different vaporizing plateau, and different specific heats. Also each substance has different specific heats for the three principle states of matter. This values must be given in chart form or be stated in the problem.)

Melting: $Q = mL_{\text{fusion}} \quad Q = (0.200\text{kg})(3.33 \times 10^5 \text{ J/kg}) = 66600\text{J}$

Heat: $Q = c_{\text{liquid}}m\Delta T \quad Q = (4180 \text{ J/kg} \cdot ^\circ\text{C})(0.200\text{kg})(60^\circ\text{C} - 0^\circ\text{C}) = 50160\text{J}$

Total is $66600 + 50160 = 116760\text{J}$

If you start with a solid below the freezing plateau (point 1) and go to a gas above the vaporization plateau (point 10) you must do all five equations using the correct specific heats for all three states and the correct latent heats for fusion and vaporization. The plateaus vary since all substances have different melting/freezing and vaporization/condensation points. The above graph is for water only. You have to use the tables.

Thermodynamics

System and environment: Think of the amount of energy in universe as constant. But, energy can be added to or subtracted from a system (engine, etc.). Energy comes from or goes to the greater universe (environment). Energy can transfer between systems. A ball colliding with another can transfer energy to that ball. Energy can change forms. If you calculate potential energy that energy can change into kinetic energy, electrical energy, thermal energy, etc.

Internal Energy All matter has some amount of energy. Objects feel warm to the touch (internal energy: due to heat content or thermal energy of the object) caused by vibration of atoms that make up the object. If energy is added to an object it can start moving or become hotter. If energy is subtracted it can slow down or become colder. Or it can be a combination of motion and heat. Most of the beginning problems we do are done pretending that no energy is lost to the environment in the form of friction and air resistance. We often assume the energy stays in one form or that 100% is transferred when energy changes form. In real life energy is lost to the environment. Also objects become a little hotter in collisions increasing internal energy. 100% of the energy put into problems will not be available to cause motion, electricity, or power a heat engine. So many of the problems are not realistic. They ask for a theoretical unattainable maximum assuming no energy loss or perfect energy transfer.

Heat Transfer

Conduction: Objects touch transferring energy

Convection: Fluids (gases & liquids) carry heat as they flow. Hot air or water rise, carrying heat. Convection currents.

Radiation: Electromagnetic radiation, as in infrared frequencies of light. Why does a thermos have an inner container separated from the outer by a vacuum? Why is the inside reflective?

Zeroth Law of Thermodynamics: Two objects, each in thermal equilibrium with a third object, are in thermal equilibrium with each other.

Internal Energy: It is the sum total of all the energies of the individual molecules that make up a system.

U Internal energy is the potential thermal energy that all objects contain.

First Law of Thermodynamics: Statement of conservation of energy.

$\Delta U = Q + W$ ΔU : the change in the system's internal energy. Q : heat added. W : the work done on system.

+ Q means heat is added to the system, while - Q means heat is given out by the system.

+ W means work is done on the system, while - W means work is performed by the system.

Adiabatic: If no heat enters or leaves system, then system is said to be perfectly isolated from its environment. Process that happens so rapidly so that heat does not have time to flow in or out of the system. If a gas filled cylinder is compressed very rapidly, heat won't have time to escape.

$$Q = 0$$

$$\Delta U = W$$

Change in internal energy is the work done

Isothermal: If temp of the system does not change during process

A good approximation is one that proceeds so slowly that temperature rise is negligible. Compress a gas filled cylinder very slowly so that molecules don't speed up and temperature does not rise.

$$\Delta U = 0$$

$$Q = -W$$

Heat added equals the negative of the work done.

Isobaric: If pressure is kept constant during the process.

$$W = -P\Delta V$$

Work to raise a piston in a gas cylinder.

$$W = Fd$$

$$W = P \text{ Area } \text{distance} = P\Delta V$$

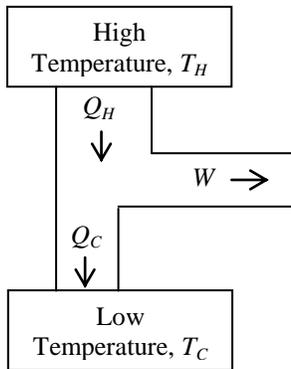
Second Law of Thermodynamics:

First Law is a statement of conservation of energy. A ball with PE falls so energy becomes KE. Then it hits the ground causing the molecules to vibrate. The KE is transferred to internal energy and the ball comes to a stop. Have you ever seen the reverse? If internal energy caused the ball to rise energy would still be conserved, so why isn't it reversible.

"Heat flows naturally from a hot object to a cold object; heat will not flow spontaneously from a cold to a hot object."

Heat Engines

Mechanical energy can be obtained from thermal energy, only when heat is allowed to flow from a high temperature to a low temperature. Example: steam engines, internal combustion engines, and human respiration. Remember thermal energy is not heat (heat is the transfer of energy because of a temperature difference). A piece of cold wood has high thermal energy (fuel) that can be burned. This is true for gasoline and the food you eat. If this energy can be tapped it can do work. But there is always a by-product: heat rising above a fire, the hot exhaust of a car, and human body heat are the by-products.



Efficiency: ratio of useful work done to the heat input.

$$e = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

Carnot Efficiency: an unattainable maximum theoretical efficiency.

Carnot imagined a gas cylinder moved from hot to cold and expanding and contracting. He also imagined that all the processes could be done **reversibly**. He imagined this because it happened so slowly that equilibrium was maintained throughout. Real processes happen fast and involve turbulence thus making reversal along the same path impossible. He showed that even under these ideal circumstances 100% efficiency is impossible.

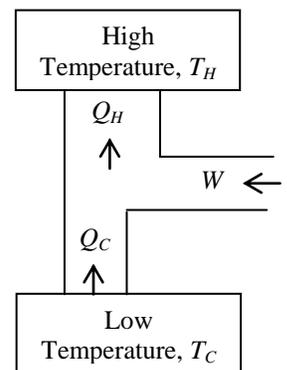
$$e_c = \frac{T_H - T_C}{T_H} = 1 - \frac{T_C}{T_H}$$

Second Law Revisited

No device is possible whose sole effect is to transform an amount of heat completely into work.

Refrigerator

(Heat Pump diagrammed to the right) Pumps heat away from one area to another. You do work to make this happen. The work comes from electrical energy. But, what's happening to Q_H ? It's getting bigger. So overall a refrigerators actually produce heat. As an example, in the process of lowering the inside air volume 40 degrees they may raise an equal volume of outside air by 100 degrees. If you fan yourself to keep cool, you do work and generate even more heat.



Entropy

A measure of how much energy or heat is unavailable for conversion to work. This is why heat is sometimes called the graveyard of energy. As Carnot showed not all the heat energy in even a perfect engine can be used to do work. Entropy is thought of as disorganization. As we use more energy we get more heat as a by-product. Look at oil. It is composed of large well organized molecules. When we burn it to produce work, we get smaller less organized molecules and heat. The small gas by-products of combustion, CO_2 and H_2O , are more difficult to burn and extract further work from. Gases are less organized than liquids, which are less organized than solids. Perhaps all highly organized molecules will turn into small atoms of gas evenly distributed throughout the universe and they may eventually reach an even average temperature. If there is no heat difference there can be no work. So life and machines can't exist. This is called the heat death of the universe.

Second Law Re-Revisited

Natural processes tend to move toward a state of greater disorder (entropy).

The entropy of an isolated system never decreases. It can only stay the same or increase. And entropy can only really stay the same for idealized (reversible) processes. So it always increases.

The total entropy of any system and the environment increases as a result of any natural process.

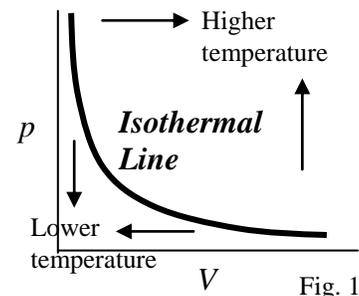
pV Diagrams

Boyles Law: Pressure and volume are inversely proportional.

This is a part of the ideal gas law and was derived when the number of moles and the temperature remained constant.

$$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2} \quad \boxed{p_1 V_1 = p_2 V_2}$$

Isothermal: If temperature is constant the process is termed isothermal. (iso: same, isothermal: same temperature). So a hyperbolic curve is generated under conditions of constant temperature. Pressure and volume are indirectly proportional. Moving up or to the right from the isotherm increases temperature. Moving left or down decreases temperature.



Isobaric

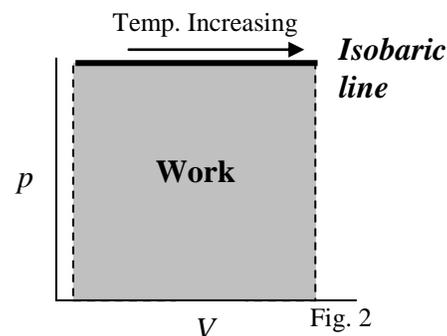
Same Pressure: generated under conditions of constant pressure.

$$\boxed{p = \frac{F}{A}} \quad \text{If we multiply pressure by a change in volume } \frac{F}{A} \times \Delta V \text{ then}$$

$$\frac{F}{A(m^2)} \times \Delta V(m^3) = F \cdot d \quad \text{and since } W = F \cdot d, \text{ then } W = -P\Delta V.$$

Work is $W = -P(V_2 - V_1)$, the area under the **pV** curve (shaded area Fig.2).

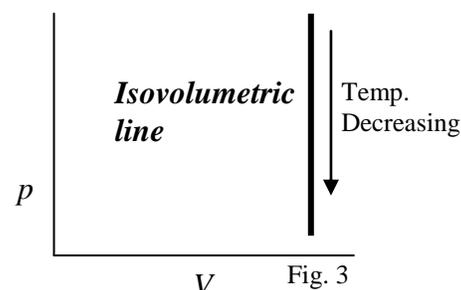
Work is the area under any pV curve. But it would require calculus to accurately solve for the area under the isothermal line in Fig 1. So many of the processes in this class will be represented by straight lines to facilitate the computation of work, heat added, and change in internal energy.



Isovolumetric (Isochoric)

Same Volume. An isovolumetric line is generated under conditions of constant volume (Fig. 3).

There is **no work done**, since there is no area under the curve.



The Full Cycle ABCA

A to B: p is constant, so this is an isobaric process. The temperature increases by going to the right, so ΔT is positive. Plug $+\Delta T$ into the $\boxed{Q = nc\Delta T}$ where c_p is used, $Q = nc_p\Delta T$. Then Q must also be positive (heat is added) to make this step take place. The temperature increase also causes an increase in ΔU . The volume is increasing while the gas expands, so W is negative. $W = -P\Delta V, W = -P(V_2 - V_1)$. **Work is the area under the AB curve.** (Shaded area, Fig. 2)

B to C: Isovolumetric, V is constant. The equation $Q = nc_v\Delta T$ applies.

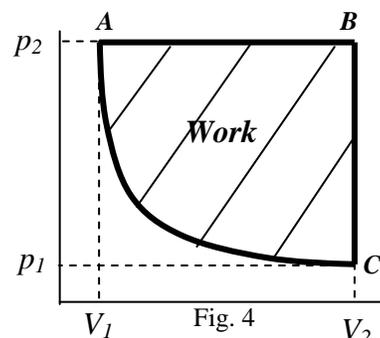
Temperature is decreasing, so ΔT is negative. Q must also be negative to make this step take place. If temperature decreases, then ΔU decreases (negative). $\boxed{\Delta U = nc_v\Delta T}$ also applies. The pressure drops even though volume stays the same. The drop in internal energy means the molecules of gas slow down. And slower molecules exert less pressure. $W = 0$. **The area under the curve is zero.**

The drop in internal energy means the molecules of gas slow down. And slower molecules exert less pressure. $W = 0$. **The area under the curve is zero.**

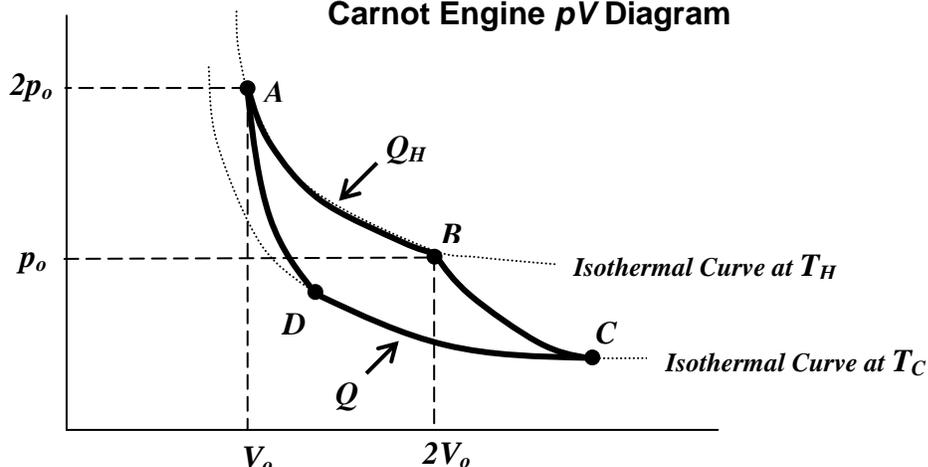
C to A: Isothermal, $\Delta U = Q + W$ so $\Delta T = 0$. As a result $Q = nc\Delta T$ and $\Delta U = nc_v\Delta T$ both become irrelevant.

The **First Law of Thermodynamics** simplifies to $W = Q$. **Work is the area under the CA curve** and it is positive, since the gas is compressed.

ABCA: The Net Work done is the stripped area bounded by ABCA (Fig. 4). Upon returning to **A** the temperature is the same as it was at the start, so $\Delta U = 0$ for the cycle. So $W = Q$ for the whole cycle.



Carnot Engine pV Diagram



A to B: Isothermal (Done slowly: Heat added has time to convert into work without raising internal energy of the gas)

Lies along the T_A isotherm. Temperature is constant. $\Delta U = 0$ $\Delta U = Q - W$ so $W_{AB} = Q$

Work is positive since the gas is expanding. The gas pressure starts out high and this pressure causes the volume to expand. If this process is done slowly the temperature of the gas does not change.

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \quad \frac{(2p_o)(V_o)}{T} = \frac{(p_o)(2V_o)}{T} \quad \text{This process is } Q_H, \text{ so } W_{AB} = Q_H.$$

B to C: Adiabatic (Done rapidly: Short time period prevents heat from being added, so Internal energy turns to work)

Drops from the T_A isotherm line to the T_B . So temperature and internal energy are both decreasing. But no heat is added. $Q = 0$ $\Delta U = Q - W$ so $W_{BC} = -\Delta U$. Work is *negative* since the gas is expanding. All the

work comes from internal energy. If work is increasing, then internal energy must be decreasing. The gas pressure starts out high and this pressure causes the volume to expand. But while the gas pressure appears to be cut in half to $p_o/2$ the volume moves from $2V_o$ to about $3V_o$. Plugging in to the ideal gas law shows that

temperature cannot be the same.

$$\frac{(p_o)(2V_o)}{T_{A \text{ isothermal}}} = \frac{(p_o/2)(3V_o)}{T_{????}}$$

C to D: Isothermal (Logic is similar to **AB** above, but work will calculate negative, gas is being compressed.)

Lies along the T_B isotherm. Temperature is constant. $\Delta U = 0$ and $W_{CD} = Q$. The gas pressure starts out low and this pressure causes the volume to compress. **This process is Q_C , so $W_{CD} = Q_C$.**

D to A: Adiabatic. (Logic is similar to **BC** above, but work will calculate negative, gas is being compressed.)

Rises from T_B isotherm line to the T_A . So temperature and internal energy are both increasing. But no heat is added. $Q = 0$ so $W_{DA} = -\Delta U$. All the work goes into increasing the internal energy of the gas.

The Cycle ABCDA: This is a heat engine. The **Net Work** done in the entire cycle is the sum of the areas under the **AB**, **BC**, **CD**, and **DA** curves. **AB** and **BC** are positive work since the gas expands doing work by the system. **CD** and **DA** are negative work since work is done on the engine and the gas is compressed. In other words, the **Net Work** is the area enclosed by **ABCDA**. If it returns to the same temperature at **A**, then during the entire process $\Delta U = 0$ and $W = Q$, the net work must have come from the net heat added $W = Q_H - Q_C$. This would be for a reversible ideal engine (Carnot) which does not exist. The ideal efficiency for this reversible, Carnot, engine is

$$e_c = \frac{T_H - T_C}{T_H} \quad \text{The real efficiency is } e = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \quad \text{with } Q_H \text{ being generated during the } \mathbf{AB} \text{ process on the}$$

T_H isotherm and Q_C being generated during the **CD** process on the T_C .

Refrigerators: Run in reverse. Counterclockwise. **ADCBA**. Follow the steps above backwards and change the signs.