Thermodynamics

Unit: Heat & Thermodynamics

NGSS Standards: HS-PS2-6

MA Curriculum Frameworks (2006): N/A

AP Physics 2 Learning Objectives: 5.B.4.1, 5.B.5.4, 5.B.7.1, 7.B.2.1

Knowledge/Understanding:

- definition of thermodynamics
- conservation of energy & conversion of energy

Skills:

- calculate energy changes between internal energy and PV work

Language Objectives:

- Understand and correctly use the term "thermodynamics."
- Accurately describe and apply the concepts described in this section using appropriate academic language.
- Set up and solve word problems relating to conversion of heat energy into mechanical work.

Labs, Activities & Demonstrations:

- heat exchange dice game
- dice distribution game
- entropy (microstates) percentile dice game

Notes:

<u>thermodynamics</u>: the study of heat-related (thermal) energy changes (dynamics)

Thermodynamics is an application of the law of conservation of energy. In Physics 1, we studied changes between gravitational potential energy and kinetic energy. Thermodynamic changes involve the same principle; the details and the equations, however, are quite different.

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Thermodynamics

As was the case with gas laws, the topic of thermodynamics is studied by both chemists and physicists. Chemists tend to be more concerned with the heat produced and consumed by chemical changes and reactions. Physicists tend to be more concerned with the conversion between thermal energy (regardless of how it is produced) and other forms of energy, particularly mechanical.

thermal equilibrium: if we have two systems, "A," and "B," they are at thermal equilibrium if the heat transferred from A to B is the same as the heat transferred from B to A.

enthalpy: the "usable" heat content of an object or system; the heat that can be converted to other forms of energy.

entropy: the "unusable" thermal energy in a system. Energy in the form of entropy is unavailable because it has "escaped" or "spread out".

internal energy (U): the energy of a system due to the kinetic energy of its particles.

Particles have kinetic energy. If we add heat energy to a system, the energy causes the individual particles to move faster, *i.e.,* they gain kinetic energy. This energy is the internal energy of the system.

Because temperature is the average kinetic energy of the particles in a system, the internal energy of a system is related to temperature via the following equation:

$$U = \frac{3}{2} N k_B T = \frac{3}{2} nRT$$

where:

U = internal energy
N = number of particles
k_B = Boltzmann's constant $= 1.38 \times 10^{-23}\ \frac{\text{J}}{\text{K}}$
T = temperature
n = number of moles
R = gas constant $= k_B \cdot N_A = 8.31 \frac{\text{J}}{\text{mol}\cdot\text{K}}$

Similarly, the change in internal energy (ΔU) is related to the temperature change (ΔT) via the same equation:

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$$\Delta U = \frac{3}{2} N k_B \Delta T = \frac{3}{2} nR\Delta T$$

Laws of Thermodynamics

The laws of thermodynamics describe the behavior of systems with respect to changes in heat energy.

For historical reasons, the laws are numbered from 0−3 instead of 1−4.

0. If a system is at thermal equilibrium, every component of the system has the same temperature. (“You have to play the game.”)
1. Heat always flows from a region of higher enthalpy to a region of lower enthalpy. This means you can’t get more heat out of something than you put in. (“You can’t win.”)
2. In almost every change, some energy is irretrievably lost to the surroundings. Entropy is a measure of this “lost” energy. The entropy of the universe is always increasing, which means on any practical scale, you always get out less energy than you put in. (“You can’t break even.”)
3. In any closed system, the total energy (enthalpy + entropy + work) remains constant. If energy was “lost,” it turned into an increase in entropy. (“You can’t get out of the game.”)

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Zeroth Law

The zeroth law says that if you have multiple systems in thermal equilibrium (the heat transferred from "A" to "B" is equal to the heat transferred from "B" to "A"), then the systems must have the same temperature. The consequences of this are:

- If we have three (or more) systems "A," "B," and "C," and A is in thermal equilibrium with B, and B is in thermal equilibrium with C, this means that A, B, and C must all have the same temperature, and A is therefore in thermal equilibrium with C. (This is akin to the transitive property of equality in mathematics.)
- If an object with a higher temperature (a "hotter" object) is in contact with an object with a lower temperature (a "colder" object), heat will flow from the object with higher temperature to the object with lower temperature until the temperatures are the same (the objects are in thermal equilibrium).

First Law

Consider an isolated system—*i.e.,* a system where heat and other forms of energy cannot enter nor leave the system. This system is doing no work, but it has internal energy.

Internal energy is similar to potential energy—it is a property of a system that is not doing work currently, but has the potential to do work in the future.

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According to the First Law, the internal energy of a system increases $(\Delta U > 0)$ if heat is added to the system $(\Delta Q > 0)$ or if work is done on the system $(W > 0)$. The internal energy decreases if the system gives off heat or the system does work on its surroundings. In equation form, the First law looks like this:

$$\Delta U = \Delta Q + \Delta W^{*}$$

The First Law is simply the law of conservation of energy—the change in internal energy comes from the heat added to or removed from the system combined with the work done on or by the system.

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[*] Some texts, including the AP formula sheet, use Q and W instead of ΔQ and ΔW. These notes use Δ in front of energy terms as a reminder that nonzero values of these quantities reflect changes of energy to the system and the surroundings.

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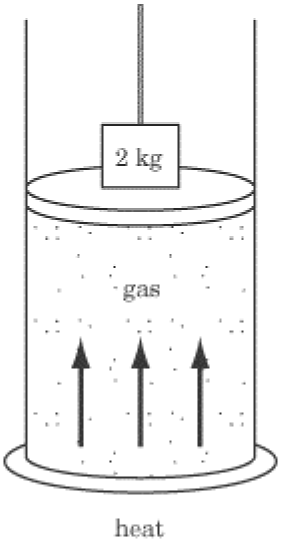
Sample Problem



Q: A cylinder containing a gas has a piston with a weight on top. The combined mass of the piston plus the weight is 2 kg. Heat is added, and the piston rises a distance of 0.2 m with a constant velocity. If this process occurred while keeping the temperature of the gas in the container constant, how much heat was added to the gas?

A: No gas was added to the system, and the temperature does not change. Therefore, the internal energy of the system (the combined kinetic energy of the molecules) remains constant $(\Delta U = 0)$.

Work was done by the system to raise the piston:

$$W = Fd = -(mg)d = -(2)(10)(0.2) = -4\text{ N}\cdot\text{m}$$

(Note that the work is negative because it is done by the system on its surroundings.)

Applying the First law:

$$\Delta U = \Delta Q + \Delta W$$
$$0 = \Delta Q + (-4)$$
$$\Delta Q = +4\text{ J}$$

(Recall that the work-energy theorem tells us that one newton-meter of work is equivalent to one joule of energy.)

Second Law

The Second law tells us that heat energy cannot flow from a colder system to a hotter one unless work is done on the system. This is why your coffee gets cold and your ice cream melts.

One consequence of this law is that no machine can work at 100% efficiency; all machines generate some heat, and some of that heat is always lost to the surroundings.

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Entropy

The Second Law is most famous for its formulation in terms of entropy. Recall that entropy is the thermal energy in a system that is unavailable (or "unusable") because it has "escaped" or "spread out".

For example, when an egg falls to the floor and breaks, gravitational potential energy is converted to a combination of enthalpy (the measurable increase in temperature of the egg), and entropy (heat energy that is radiated to the environment and "lost"). Over time, the heat in the egg is also radiated to the environment and "lost" as the egg cools off. Ultimately, all of the gravitational potential energy is converted to entropy, which is the heat energy that is dissipated and cannot be recovered.

Entropy is sometimes called "disorder" or "randomness", but in the thermodynamic sense this is not correct. The entropy of your room is a *thermodynamic* property of the heat energy in your room, not a commentary on the amount of dirty laundry on the floor! A quantitative study of entropy requires advanced calculus and probability, both of which are beyond the scope of this course.

A consequence of the Second law is that over time, systems (and the universe) tend toward greater entropy. The only way to reduce the entropy of a system is to do work on it.

A quantitative definition of the second law is:

$$dS = \frac{\delta Q_{rev}}{T}$$

In an algebra-based physics class, we simplify this to:

$$\Delta S = \frac{Q_{rev}}{T} \geq \frac{Q}{T}$$

In other words, a change in entropy is given by the amount of heat that is added or removed *by a reversible process* at a given temperature. Because actual heat transfer in a finite amount of time cannot be completely reversible, some heat is lost to the surroundings and the actual entropy change is always greater than the actual heat change at a given temperature. The concept of a reversible process is an idealization that represents the maximum amount of work that could theoretically be extracted from the process.

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An interesting way to look at entropy is the idea that the Second Law defines the positive direction for time. If all we had were Newton's Laws, then there would be no difference between time going forward and time going backward. For example, imagine a ball that goes up and then falls down. If we reversed time, the ball falling down would become the ball going up, and the ball going up would become the ball falling down. However, because entropy can only increase over time, the Second law states that time moves in the direction of entropy increase.

This is an example of the hierarchy of thinking among physicists. A very few laws, such as the conservation of momentum and the conservation of energy, are believed to form the basis of how all objects behave and all events occur in the universe. Defining time based on the conservation of energy means that time itself follows naturally from the conservation of energy.

Third Law

The Third law tells us that in an isolated system, the total energy of the system must be constant. (An isolated system is a system for which it is not possible to exchange energy with the surroundings.) This makes intuitive sense; because energy must be conserved, if no energy can be added or taken away, then the total energy cannot change.

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Thermodynamic Quantities and Equations

Because energy is complex and exists in so many forms, there are many thermodynamic quantities that can be calculated in order to better understand the energy of different portions of a system. The following is a list of some of the more familiar ones:

Selected Thermodynamic Quantities

Variable	**Name**	**Description**
Q	heat	Thermal energy (heat) transferred into or out of a system.
W	work	Mechanical energy transferred into or out of a system.
H	enthalpy	Energy contained in the chemical potential of the particles.
S	entropy	Energy that is inaccessible because it has spread to the surroundings or has spread to separate microstates and cannot be utilized by the particles of the system.
U	internal energy	Total non-chemical energy contained within the particles of a system. $\Delta U = \Delta Q + \Delta W$
G	Gibbs' free energy	Total non-work energy (chemical energy plus heat) of a system. $\Delta G = \Delta H - T\Delta S$
A	Helmholtz free energy	Useful work that can be obtained from a system. $\Delta A = \Delta U - T\Delta S$

In AP Physics 2, we will leave chemistry to the chemists and concern ourselves with internal energy:

$$\Delta U = \Delta Q + \Delta W$$

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Conjugate Variables

Because thermodynamic equations relate energy in different forms, each term in any thermodynamic equation must have units of energy. For example, in the equation:

$$\Delta U = \Delta Q + \Delta W$$

The terms ΔU, ΔQ and ΔV each represent types of energy.

However, energy cannot be measured directly; it can only be calculated from other quantities. (Recall that in mechanics, we measured mass, velocity and height in order to calculate kinetic and gravitational potential energy.) It is therefore useful to express thermodynamic quantities in terms of pairs of conjugate variables that we can measure directly:

<u>conjugate variables</u>: pairs of variables X and y for which:

- X is an intensive variable (a variable that represents a property of the individual particles of a gas, *e.g.,* pressure)
- y is an extensive variable (a property that represents a property of a specific quantity of a gas, *e.g.,* volume)
- The quantity $X\Delta y$ has units of energy.

The ideal gas law (see page 163) is an example of a thermodynamic relationship that uses pairs of conjugate variables:

$$PV = nRT = Nk_BT$$

$$P\Delta V = nR\Delta T = Nk_B\Delta T$$

In the above equations, the pairs of conjugate variables are pressure and volume, and number of particles (or moles of particles) and temperature.

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The left side of this equation, $P\Delta V$ is the work done by a gas when it expands (because the gas pushes on the surroundings), or the work that is done by the surroundings when compressing the gas:

$$\Delta W = -P\Delta V$$

This allows us to calculate work from quantities we can measure—pressure and volume. We have defined the system to be the gas, which means positive work is work that enters the system, *i.e.,* work done *on* the gas. Because positive work (work done on the gas) causes a decrease in volume and negative work (work done by the gas) results in an increase in volume, we need a negative sign.

Summary of Thermodynamics Equations Used in AP Physics 2

Most of the thermodynamics problems encountered in AP Physics 2 are applications of the equations in this section:

Equation	**Variables that are Changing**
$\Delta U = \frac{3}{2} nR\Delta T = \frac{3}{2} Nk_B\Delta T$	internal energy *vs.* temperature
$P\Delta V = nR\Delta T = Nk_B\Delta T$	volume *vs.* temperature
$\Delta U = \Delta Q + \Delta W$	internal energy *vs.* heat & work

Problems will involve a change in a state variable (pressure, volume and/or temperature). You will need to:

1. Determine whether the change involves heat transfer, work, and/or a change in internal energy.
2. Apply algebraic combinations of one or more of these equations to answer the question.

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