

The Big Ideas – Thermodynamics

Objects in “thermal contact” exchange thermal energy via “heat.” They cease this process when they reach “thermal equilibrium.” We find experimentally—and give as the so-called “zeroth law of thermodynamics”—that two objects that are *separately* in thermal equilibrium with a third object, are also in thermal equilibrium with *each other*.

We can tell when thermal energy is being exchanged by monitoring a so-called “thermometric property” of the objects. A “thermometric property” is one that depends on the total internal energy of the objects, like density, length, resistivity, color, etc. It can be used to make a “thermometer.” For instance, mercury thermometers exploit thermal variations in the density of mercury.

The Celsius temperature scale is defined in terms of two so-called “fixed points”: One is a mixture of ice and water at atmospheric pressure (the “freezing point” of water) which is defined to have a temperature of 0°C. The other is a mixture of steam and water at atmospheric pressure (the “boiling point” of water) which is defined to have a temperature of 100°C. How one uses those fixed points to determine the size of 1 Celsius degree is not obvious.

At low enough pressures all gases approach the behavior of an “ideal gas.” Ideal gases in thermal equilibrium obey a simple law relating their pressure, volume, temperature, and number of molecules.

The ideal gas law is sometimes expressed in terms of the number of moles of gas particles (preferred by chemists) and sometimes in terms of the number of molecules (preferred by physicists.)

Relationships between pressure, density, and temperature are called “equations of state.”

Heat, like work, refers to a *transfer* of energy from one system to another. Objects do not “have” heat; they “have” internal energy. The internal energy of an object may be changed via mechanical processes (i.e., those that involve *work*) or via thermal processes (i.e., those that involve *heat*.)

Note that, although heat is the transfer of thermal energy *from* an object at a higher temperature *to* an object at a lower temperature that occurs *as a result* of the temperature difference, temperature itself is not a measure of *heat*. For instance, we can “warm” something (i.e., increase its temperature) by doing a suitable amount of *work* on it.

An archaic unit of heat—the calorie—created at a time when people thought heat itself *was* a sort of fluid that objects “contained”, is still used today even though we now know that it is simply an alternate unit of energy.

The “heat capacity” of an *object* is the change in internal energy (*not necessarily thermal energy!*) per unit change in temperature. By definition it is an *extensive* quantity—i.e., it depends on the *amount* of “stuff.” The “specific heat” of a *substance* is the change in internal energy per unit mass per change in temperature. By definition it is an *intensive* quantity—i.e., it depends only on the *identity* of the substance.

These two quantities have *very* unfortunate names!! For instance, the heat capacity of an object has nothing specifically to do with “heat” (it has to do with changes in *internal energy* which may be the result of heat or work) *nor* should it be taken to imply that objects have a finite capacity for “heat” (or *even* for changes in internal energy!) The “heat capacity” of an object is just the sum of the heat capacities of its constituent parts with heat capacity of each part depending on its own mass and the “specific heat” of the substance of which it is composed.

When different objects are in thermal contact with each other but do not exchange energy of any type with their surroundings, they will reach thermal equilibrium while conserving their initial energy. Devices in which such processes can be carried out are called *calorimeters* and the analysis of these processes is called *calorimetry*.

Calorimetry involves *nothing* more than the use of conservation of energy along with a knowledge of the connection between temperature and internal energy through quantities like *specific heats* and *latent heats* (see the next section.)

Melting and vaporizing are common examples of what are more generally called “changes of phase.” When a substance melts it changes from the solid “phase” to the liquid “phase.” When it vaporizes (by boiling) it changes from the liquid “phase” to the vapor or gas “phase.” During a phase change, the internal energy changes *without* a corresponding change in temperature. The “latent heat” of a *substance* is the change in internal energy (again, *not necessarily thermal energy!*) per unit mass that undergoes the phase change. By definition it is an *intensive* quantity—i.e., it depends only on the *identity* of the substance.

Calorimetry involving phase changes requires a knowledge of the corresponding latent heats.

In thermodynamics we are concerned with the so-called thermodynamic “state” of the system which is specifically characterized by “state variables”—things like pressure, volume, internal energy, and temperature. The “state” of a system and, therefore, the values of its “state variables” can be altered either mechanically or thermally—that is, by processes that involve either work or heat.

Note that many of the quantities used to specify the thermodynamic state of a system can only be sensibly defined for a system that is in “thermal equilibrium.”

A “quasistatic process” is one in which the system is always approximately in thermal equilibrium. The state of a given amount of gas can be fully specified by its pressure and volume. Furthermore, the work it does on its surroundings can be determined in terms of how its pressure changes as its volume changes.

On a PV diagram, the work done by the gas in any quasistatic process is simply the area of the curve representing the process. Since the internal energy of a gas is a “state variable” the change in the internal energy of a gas depends only on its initial and final “states.” The work done by the gas, however, depends on the details of the *process* by which the gas changes its state.

The “first law of thermodynamics” (FLT) says that, in *any* process, the change in the internal energy of a system is equal to the thermal energy transfer *to* (positive Q) or *from* (negative Q) the system minus the work done *by* (positive W_{sys}) or *on* (negative W_{sys}) the system.

The FLT is *nothing* more than an energy bookkeeping equation in a form that recognizes both mechanical and thermal means of transferring energy from one system to another. Please note that *many* books use different conventions for the signs for Q and W . It is especially common for texts to define *positive* work as work done *on* the system (rather than work done *by* the system, as is the case in this class.) In that case the FLT is written purely with “+” signs. A “cyclic process” is one in which the initial and final states are the same. For a cyclic process, $\Delta E^{\text{int}} = 0$ so $Q = W$.

Several important thermodynamic processes involve holding some specific state variable constant or disallowing work or heat.

In an “**isobaric**” process, the pressure is held (approximately) constant. Since pressure is a state variable such a process is necessarily performed quasistatically. The work is easily calculated as $W = P\Delta V$.

In an “**isovolumetric**” (or “**isochoric**”) process, the volume is held (approximately) constant. Note that no work is done in an isovolumetric process, so the FLT gives $Q = \Delta E^{\text{int}}$.

In an “**isothermal**” process, the temperature is held (approximately) constant. Since temperature is a state variable, such a process is necessarily performed quasistatically. Note that, for an ideal gas, the pressure is inversely proportional to volume in an isothermal process and the work is easily calculated.

In an “**adiabatic**” process, $Q = 0$. Because Q is *not* a state variable, such a process may be performed quasistatically or *nonquasistatically* as, for instance, in a “free expansion.” The FLT gives the work.

The ideal gas law is the natural result of a very simple model of a gas (in which molecules behave like particles that undergo elastic contact collisions with walls and other molecules) and an interpretation of temperature as a measure of the average energy per molecule.

In this model the pressure arises from the average force of the collisions between the molecules and the walls and is directly associated with the density and the average translational kinetic energy of the molecules. The ideal gas law then reveals temperature as a pure function of the average translational kinetic energy.

In a quasistatic adiabatic expansion, an ideal gas loses energy by doing work. Thus its pressure drops more rapidly than it does for an isothermal process in which the energy is kept constant by simultaneously adding thermal energy by heat.

A cyclic process may be exploited to construct a “heat engine”—a device that trades thermal energy from a hot reservoir for work at the cost of some exhaust or waste thermal energy

In all cases we distinguish between the thermal energy *to* the system *from* the “hot” reservoir— Q_{hot} —and the thermal energy *from* the system *to* the “cold” reservoir— Q_{cold} . The first law of thermodynamics connects these thermal energies with the net work done per cycle. A “perfect heat engine” is one for which there is no waste thermal energy, that is, it uses all thermal energy *from* the hot reservoir to do *work*.

Although perfect heat engines are *completely* compatible with the first law of thermodynamics, they are not allowed by nature. These observations form the basis for the Kelvin-Planck and Clausius statements of the “Second Law of Thermodynamics.”

We define the efficiency of a heat engine as the ratio of the work done per cycle to the thermal energy from the hot reservoir per cycle, usually expressed as a percentage. The second law of thermodynamics says that the efficiency is always less than 100%.

Heat engines and heat pumps based on the Carnot cycle have the maximum possible theoretical efficiency for any engine operating between any given temperature extremes.

This is because the Carnot cycle involves thermal energy *input* that comes entirely *from* a single reservoir at the highest temperature encountered and thermal energy *output* that goes entirely *to* a single reservoir at the lowest temperature encountered. In the Carnot cycle *all* thermal energy *input* occurs during a high temperature isothermal expansion and *all* thermal energy *output* occurs during a low temperature isothermal compression. An adiabatic expansion links the high temperature expansion to the low temperature compression and an adiabatic compression links the low temperature compression back to the high temperature expansion.