Temperature, Energy, Heat and Work – What's the Difference?

We have defined the absolute temperature in Kelvin in the last lecture as a measure of the kinetic energy of particles in an ideal gas. This concept needs to be generalized to all systems. We shall define **temperature** for now to be a measure of the tendency of an object to spontaneously give up energy. What is energy? It is a fundamental dynamical quantity that is conserved in all processes. **Energy** comes in many forms, including linear kinetic, rotational kinetic, gravitational potential, electrostatic potential, electromagnetic, nuclear, chemical, etc. Energy can never be created or destroyed, it can only change form. Things get interesting when energy changes form. However, the total energy of the universe, when summed up over its many forms, always remains constant. This important principle will now be applied to thermodynamics.

In thermodynamics, the energy of a system can only change due to two processes:
1) **Heat**
2) **Work**

The definition of **heat** is: The <u>spontaneous</u> flow of energy from object to another due to a difference in temperature. Spontaneous means that no "agent" has to intervene to accomplish the energy transfer. The definition of **work** (in thermodynamics) is the set of all other processes that transfer energy between two objects by all means *other than* heat. Work requires the action of an "agent" to accomplish the energy transfer. Examples of work include "heating up your hands" by rubbing them together (agent: your muscles applying a force to overcome friction), "heating up water" in a microwave oven (agent: the magnetron that creates the 2.45 GHz electric field). Our everyday notion of "heat" has to be adjusted to the thermodynamic definition.

Heat can flow by means of conduction, convection and radiation.

Heat and work refer to energy in transit. As such they are fleeting and ephemeral. There is no point in keeping track of the heat content or work content of an object. It only makes sense to keep track of the energy that arrived or left due to these two processes. Hence it *does* make sense to keep track of the energy content of an object. Because of this, the internal energy U is a thermodynamic state variable. It is a function of other state variables such as temperature, particle number, volume, etc. $U = U(T, P, V, N, \dots)$. However there is no thermodynamic state variable associated with heat, or with work. In other words, *there is no quantity* $Q(T, P, V, N, \dots)$ *or* $W(T, P, V, N, \dots)$ *that represent the* heat content or work content of an object.

We can now state the **first law of thermodynamics** (which is just energy conservation) in the unique language of thermodynamics:

$$dU = \dbar Q + \dbar W,$$

where "$\dbar$" or "d-bar" should be read as a pseudo-differential. It reminds us that Q and W are not continuous differentiable state functions of other state variables. This equation simple states that the energy of a system changes when heat flows in or out, or when work is done on or by the system.

We considered compressive work on a substance and showed that it can be calculated as $W = -\int_{V_i}^{V_f} P(V, T, N, \dots) dV$, where V_i is the initial volume and V_f is the final volume. We considered compression of an ideal gas in two cases, isothermal and adiabatic.

Isothermal compression of an ideal gas. Consider attaching a cylinder of gas to a thermodynamic reservoir at temperature T. A reservoir is an object at fixed temperature with large thermal inertia. One can extract (or inject) a large amount of heat from (into) this object but not change its temperature. The gas is compressed slowly with a piston to keep its temperature constant (iso-thermal) during the process. The work done is $W = -\int_{V_i}^{V_f} P(V) dV = -Nk_B T \int_{V_i}^{V_f} \frac{dV}{V} = Nk_B T \ln\left(\frac{V_i}{V_f}\right).$

In compression, we expect $V_f < V_i$, the logarithm will be positive, and the work done on the gas will be positive. The first law of thermodynamics says that $\Delta U = Q + W$. As we saw in the last lecture, the internal energy of the gas is proportional to temperature, hence the internal energy of the gas is unchanged in an isothermal process. This means that $0 = Q + W$, or $Q = -W$. Whatever work is done on the system is balanced by heat *leaving* the system. In the case of isothermal compression of an ideal gas, the work done on the gas is accompanied by a flow of heat to the reservoir. The amount of heat leaving is equal to the work done on the gas.

Adiabatic compression of an ideal gas. Imagine the gas being held an insulated cylinder, and the piston is moved inward very quickly such that no heat has time to enter or leave the system. The first law now says $\Delta U = 0 + W$, so the work done in compression shows up as a change in energy of the gas. We stated that the energy of a substance can be written (equipartition theorem) as $U = \frac{f}{2}Nk_BT$, where f is the number of "degrees of freedom" of each particle in the substance. For an ideal gas, each particle has energy only in the form of kinetic energy. The Hamiltonian of monatomic ideal gas particle is simply $H = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$, where m is the mass of the atom and v_x is the x-component of velocity, etc. The number of degrees of freedom is the number of terms in the particle's Hamiltonian that are quadratic in the coordinate or velocity of the particle. In this case the number of degrees of freedom is 3. Hence for a monatomic ideal gas, the internal energy is $U = \frac{3}{2}Nk_BT$. During an adiabatic compression we can now use the first law to say $\Delta U = -P\Delta V$. Hence $\frac{3}{2}Nk_B\Delta T = -P\Delta V$, so a change in volume will be accompanied by a change in temperature. Using the ideal gas law to express P in terms of V and T, we have $\frac{3}{2}\frac{\Delta T}{T} = -\frac{\Delta V}{V}$. In the differential limit we can integrate both sides of the equation between the initial condition (T_i, V_i) and the final state (T_f, V_f) and arrive at $V_iT_i^{3/2} = V_fT_f^{3/2}$. In other words the product of $VT^{3/2}$ remains constant in am adiabatic process. Using the ideal gas law to replace temperature with pressure results in $PV^\gamma = constant$, where $\gamma = (f+2)/f$ is called the adiabatic exponent.

Heat capacity is defined as the amount of heat required to change the temperature of a substance by one degree Celsius or Kelvin. It is an extensive quantity. One can define it as $C = Q/\Delta T$, where Q is the heat added and ΔT is the resulting temperature change. The intensive version of heat capacity is called the specific heat, and is defined as the heat capacity per unit mass, $c = C/m$, where m is the mass of the substance. The specific heat of water at room temperature is $c = 4.2\frac{J}{^\circ C}/g$.

Using the first law, the heat capacity can be written as $C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}$. If we consider compressive work, $W = -P\Delta V$, then the heat capacity can be written as $C = \frac{\Delta U + P\Delta V}{\Delta T}$. Consider what happens if we hold the volume of the substance fixed while heat is added to it. This results in the heat capacity at constant volume: $C_V = \frac{\Delta U + 0}{\Delta T}$, which becomes $C_V = \left.\frac{\partial U}{\partial T}\right|_V$. It turns out that this is a difficult quantity to measure experimentally. It is much easier to add heat to a substance at constant pressure. In this case the heat capacity acquires a term due to work done on the system while heat is added: $C_P = \left.\frac{\partial U}{\partial T}\right|_P + P\left.\frac{\partial V}{\partial T}\right|_P$. For an ideal gas, one finds that $C_P = C_V + Nk_B$.

Latent Heat. In some cases you can add heat to a substance without changing its temperature. This happens at a phase transformation. For example the transition from ice to liquid water, or from liquid water to steam. Consider a solid object of mass m at its melting temperature. The latent heat is the heat that must be supplied to this object to complete the phase transformation from solid to liquid, all at the melting temperature, divided by the mass of the object, $L = Q/m$. The concept generalizes to other phase transformations, such as vaporization. For water the latent heat of fusion (solid $\leftrightarrow$ liquid) is $L_f = 333\,J/g$, while the latent heat of vaporization (liquid $\leftrightarrow$ vapor) is $L_v = 2260\,J/g$.