

Lecture 23

Physics 404

Heat and work both describe the transfer of energy from one system to another. Heat is defined as the transfer of energy by virtue of a difference in temperature between two systems. Heat flows spontaneously. It carries entropy. In fact we define heat in terms of the associated entropy transfer (for a reversible process) as follows: $\delta Q \equiv \tau d\sigma$, where the δ differential denotes the fact that heat Q is not a state function of a system, therefore δQ is not a true differential quantity in the mathematical sense. It makes no sense to talk about the “heat content” of an object. Heat and entropy flow are inseparable.

Work is the transfer of energy between two systems by all means other than a difference in temperature. Reversible work carries no entropy. Work does not occur spontaneously, but requires an ‘agent’ to apply a force through a distance to generate the work. Again, a system does not have a work state function, there is no function W that is a unique function of the variables of a system (temperature, pressure, volume, etc.) that represents the “work content” of an object. Hence energy transfer by means of work δW is another example of a pseudo differential.

We expect conservation of energy to hold in an energy transfer between two systems: $dU = \delta Q + \delta W$. Here dU is a true differential since the energy of a system is a unique and well defined function of the state variables, e.g. $U(N, \tau) = 3N\tau/2$ for the ideal gas. This equation says that energy can be transferred into a system through either heat or work, or both.

Work can be completely converted into heat. Joule did such an experiment when he measured the mechanical equivalent of heat. However heat cannot be completely converted into work. Heat carries entropy, work carries none. Hence the complete conversion of heat to work would require the destruction of entropy. In all processes, entropy either stays the same or increases.

A work-around can be achieved by transferring heat from a hot reservoir to a cold reservoir and stripping off some of the heat and converting it to work in the process. This works because the entropy delivered to the cold reservoir in a reversible process ($\sigma_{Cold} = Q_{Cold}/\tau_{Cold}$) requires less heat than the entropy acquired from the hot reservoir in a reversible process ($\sigma_{Hot} = Q_{Hot}/\tau_{Hot}$), since $\tau_{Cold} < \tau_{Hot}$. (We can’t allow the entropy to accumulate without bound, otherwise the system will quickly become unwieldy and useless.) The difference in heat can, in principle, be converted into work to do useful things. When this process is iterated, it is called a thermodynamic heat engine.

How good can a heat engine be? We know it cannot completely convert heat into work, so just how close can it get? Carnot made the following simple argument. Assuming that the heat engine expels all of the entropy that it acquires from the high temperature reservoir, and does not generate any additional entropy in the cyclic process, we can equate the incoming and outgoing entropy values: $\sigma_{Cold} = \frac{Q_{Cold}}{\tau_{Cold}} = \sigma_{Hot} = \frac{Q_{Hot}}{\tau_{Hot}}$. Also we expect energy to be conserved in the heat engine, so that $W = Q_{Hot} - Q_{Cold}$. Using the entropy equality, we can write the work as $W = Q_{Hot} - \frac{\tau_{Cold}}{\tau_{Hot}} Q_{Hot}$. The Carnot efficiency of the heat engine is the ratio of the work performed to the heat acquired from the high temperature reservoir: $\eta_C = \frac{W}{Q_{Hot}} = \frac{\tau_{Hot} - \tau_{Cold}}{\tau_{Hot}}$. The efficiency should be less than 1 because one

cannot convert all the heat to work. Hence the Carnot efficiency of the heat engine depends on the temperature difference of the hot and cold reservoirs.

We also considered the refrigerator, which is a heat engine run in reverse. It “lifts” heat Q_{Cold} from a cold reservoir and delivers it to a hot reservoir by doing work W . One can define the coefficient of refrigerator performance as the ratio of the heat lifted to the work done as $\gamma_C = \frac{Q_{Cold}}{W} = \frac{\tau_{Cold}}{\tau_{Hot} - \tau_{Cold}}$.