Physics 127a: Class Notes

Lecture 5: Energy, Heat and the Carnot Cycle

Thermodynamic identity

For the entropy of an isolated system $S(E, N, V)$ we can form the differential, evaluating the partials in terms of these expressions for T, μ, and P. This gives the *thermodynamic identity*

$$dS = \frac{1}{T}dE - \frac{\mu}{T}dN + \frac{P}{T}dV \tag{1}$$

telling us how infinitesimal changes of E, N, V change S. Alternatively we could solve $S = S(E, N, V)$ to find $E(S, N.V)$. By rearranging Eq. (1) we have an alternative form of the thermodynamic identity

$$dE = TdS + \mu dN - PdV. \tag{2}$$

This immediately shows us

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V}, \qquad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}, \qquad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N}, \tag{3}$$

which may be more familiar results. In particular the expression for P corresponds to the idea of "virtual work": ask how the energy changes if you change the volume so that the entropy does not change (which, from the microscopic definition we see corresponds to not changing the state of the system, i.e. an adiabatic change).

The thermodynamic identities are the starting point for deducing many results in thermodynamics that are useful in relating different experimental quantities, such as the specific heats at constant volume and pressure.

Extensivity

The energy, entropy, number, and volume are *extensive* quantities—they grow proportional to the volume if identical subsytems are put together. On the other hand temperature, chemical potential and pressure are intensive variables—they do not change when identical subsytems are put together. If we define densities of the energy and entropy $\varepsilon = E/N$, $s = S/N$, $\rho^{-1} = V/N$ ("energy per particle" etc.) then we must have

$$\varepsilon = \varepsilon(s, \rho). \tag{4}$$

Note that 3 extensive variables, or 2 intensive variables (plus the "amount") are sufficient to define the thermodynamic state.

Finally the process of incrementing the size of a system by adding an incremental volume of the same material at the same T, μ, and P (so that the new system remains in equilibrium at these values) can be calculated from Eq. (2). Integrating from zero size (since T, μ, P remain constant in this process) gives

$$E = TS + \mu N - PV \tag{5}$$

Reversible and Irreversible

A process is said to be *reversible* if it can be exactly reversed by infinitesimal changes in the control variables. otherwise it is *irreversible*.

Reversible changes are characterized by: slow, friction free, the balance of forces.

Irreversible changes are often: fast or with friction so that dissipation occurs

In macroscopic systems we associate a reversible change with the quasistatic change of thermodynamic variables so that at each stage of the process the system is equilibrium. In an isolated system a reversible change must be isentropic, since if $dS/dt > 0$ for one direction, then reversibility implies $dS/dt < 0$ for the reverse direction, which violates the second law.

Work and Heat

We will consider a fixed number of particles N in the following.

We have derived the thermodynamic identity

$$dE = TdS - PdV. \tag{6}$$

This relates the changes in thermodynamic variables in equilibrium states in a macroscopic system. For concreteness think of a typical engine-type arrangement of a volume of working fluid held by a movable piston (on which we can do work, or which does work on us, via a force F) and in which may exchange energy (but not N or V) with a thermal reservoir at temperature T. The dotted box in the figure indicates that together, piston plus thermal reservoir, form an isolated system.
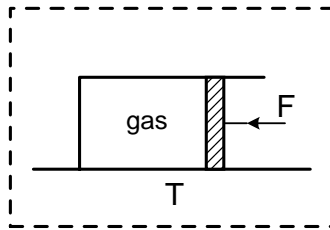
An example of the working fluid might be the ideal gas.

We do work on the system $dW = FAdx$ (x is the position of the piston of area A). In a reversible, quasistatic change $F = PA$ with P the pressure of the fluid, and the work done *on* the gas in a small change of volume is

$$dW = -PdV. \tag{7}$$

In general, there will also be a transfer of energy from the reservoir to the system: we call this heat and write this portion of the energy added to the system as dQ. For a reverisble change we can relate dQ to the change in the entropy of the system dS, for in a reversible change the total change of entropy of system + reservoir is zero

$$0 = dS - \frac{1}{T}dQ. \tag{8}$$

The second term is the change of entropy of the reservoir evaluated as $(\partial S_r/\partial E_r)(-dQ) = -dQ/T$ where T is the temperature of the reservoir.

Thus in general we have (conservation of energy)

$$dE = dQ + dW, \tag{9}$$

a statement of the *first law of thermodynamics*. In the special case of a reversible change

$$dQ = TdS \quad \text{and} \quad dW = -PdV \tag{10}$$

in which case Eq. (9) is consistent with the thermodynamic identity.(the conservation of energy). An important fact is that dQ and dW are *not* differentials of functions of state—there is no "work content" or "heat content"

of a system (I'm using the symbol d, unfortunately not very different from d, to denote this. I used d-slash in class.) However for a reversible change $\mathrm{d}Q/T$ *is* a differential (of the entropy) and so $1/T$ is said to be an integrating factor for the heat.

Now consider an irreversible change. Equation (6) just refers to the endpoints, and still applies. However during the process a single P and T may not define the state of the gas, and the force on the piston may not balance $F \neq PA$ so that the work done may not be $-PdV$. In addition, the entropy of the isolated system will increase, so that

$$dS - \frac{\mathrm{d}Q}{T} > 0. \tag{11}$$

Note that here T is the temperature of the reservoir, $\mathrm{d}Q$ is the energy transferred from reservoir to piston, and dS_r is still given by $\mathrm{d}Q/T$ because we suppose changes in the reservoir are quasistatic and reversible. Thus quite generally we have the relationship between the heat added to a system and the entropy change of the system
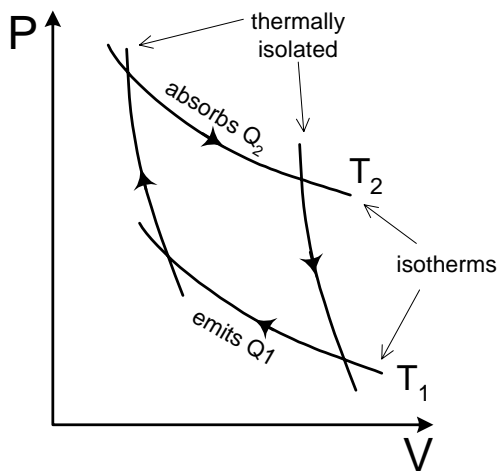
$$\mathrm{d}Q \leq TdS \tag{12}$$

with T the temperature of the reservoir, with the equality only applying for a reversible change. In particular integrating around a closed loop of changes that brings the working fluid back to its initial state

$$\oint \frac{\mathrm{d}Q}{T} \leq 0, \tag{13}$$

again with the equality satisfied only for a completely reversible cycle.

Carnot Cycle

This is a simplified version of an engine converting heat to work that was important in the development of thermodynamics, which tells us the limits to the efficiency of such engines. In the Carnot Cycle a working fluid such as the one we have just investigated is taken through expansion-compression cycle, with portions of the cycle either thermally isolated or in contact with one of two thermal reservoirs at different temperatures. Since the final state of the fluid is unchanged after a cycle, the net result is taking heat Q_2 from the hot reservoir at temperature T_2, and converting part $W = Q_2 - Q_1$ to work done, while rejecting the rest of the energy Q_1 as heat to the lower reservoir at temperature T_1. (Since we have complete expressions for the ideal gas, this is a useful example if you want to calculate everything in detail.)

The work done *by* the gas $W = Q_2 - Q_1$ is the area of the loop ($\oint PdV$ around the loop). On the other hand we have

$$\oint \frac{\mathrm{d}Q}{T} = \frac{Q_2}{T_2} - \frac{Q_1}{T_1} \leq 0, \tag{14}$$

so that the efficiency (work done over heat absorbed) is

$$\eta = \frac{W}{Q_2} = 1 - \frac{Q_1}{Q_2} \leq \frac{T_2 - T_1}{T_2}. \tag{15}$$

Thus the efficiency is limited by the temperature difference that can be reached, and is always less for an irreversible cycle (inequality) than for the ideal reversible one (equality).

We can make a refrigerator by running an engine backwards. Then we do work W taking heat Q_1 out of the colder temperature reservoir at T_1, and dumping both W and Q_1 into the hot reservoir at T_2. A reasonable definition of the efficiency here is

$$\eta_c = \frac{|Q_1|}{|W|} \leq \frac{T_1}{T_2 - T_1}. \tag{16}$$

Note η_c may be greater than one, so that refrigerators (or air conditioners) are quite efficient, but the efficiency decreases reapidly as the desired temperature difference becomes large—turn your thermostat up in when you are using your air conditionner in hot weather! (Of course, we also need work, which is the "expensive" sort of energy.)

Macroscopic Formulations of the Second Law

Considerations of Carnot cycles led to various rigorous macroscopic statements of the second law, that can be shown to be equivalent:

Clausius: It is impossible to devise an engine which, working in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body.

Kelvin: It is impossible to devise an engine which, working in a closed cycle, produces no effect other than the extraction of heat from a reservoir and the performance of an equal amount of mechanical work.

Caratheodory: In the neighborhood of any equilibrium state of a system there are states which are inaccessible by a adiathermal [work only] process.

Reif: An equilibrium macrostate of a system can be characterized by a quantity S called the entropy which has the properties: (a) in any process in which a thermally isolated system goes from one macrostate to another, the entropy tends to increase $\Delta S \geq 0$; (b) if the system is not isolated and undergoes a quasi-static infinitesimal process in which it absorbs heat $\mathrm{d}Q$, then $dS = \mathrm{d}Q/T$ where T is a quantity (called the absolute temperature) characteristic of the macrostate of the system.