- Recall from last time:

$$\oint \frac{dQ}{T_{ext}} \leq 0.$$

And for a reversible cycle, $T_{ext} = T$, and can reverse to get similar inequality with $dQ \rightarrow -dQ$, so

$$\oint \frac{dQ_R}{T} = 0.$$

So $dQ_R/T = dS$ is a state variable! For any states 1 and 2, we have

$$S_2 - S_1 = \int_1^2 dQ_R/T$$

over **any reversible path**. This defines the entropy difference ΔS between two states even if the process in between is irreversible. The point is that the entropy difference doesn't care about the process in between, only on the endpoints. But it is crucial that ΔS always be computed along a reversible path (even if the process involved isn't itself reversible)!

- Note that, for any process connecting states 1 and 2,

$$\int_{process} \frac{dQ}{T_{ext}} \leq S_2 - S_1,$$

with equality iff the process is reversible. The LHS depends on the process, whereas the RHS depends only on the endpoints, and is some definite value.

- Example: free expansion of an ideal gas, as in the Joule experiment mentioned in class. The volume of the gas increases irreversibly from V_1 to $V_2 > V_1$. No work is done in the process, so $\Delta W = 0$. No heat is transferred in the process, so $dQ = 0$ and $\Delta Q = 0$. Thus $\int_{process} dQ/T_{ext} = 0$. On the other hand, we compute ΔS as discussed in the last lecture: pick to compute it along a reversible isotherm. We get:

$$S_2 - S_1 = \int \frac{dQ_R}{T} = nR\ln\left(\frac{V_2}{V_1}\right).$$

- For a thermally isolated system, we have $dQ = 0$, so $S_f - S_1 \geq 0$. This is the **arrow of time**. A thermally isolated state is in the state of maximum entropy, with external constraints. If not thermally isolated

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0.$$

• Example: consider a cyclic engine, operating between heat baths at temperatures T_1 and T_2, with $T_2 > T_1$. Suppose the engine completes a cycle, consisting of two isotherms, connected by two adiabats. Let Q_2 be the heat absorbed by the engine at T_2, and Q_1 the heat absorbed by the engine at T_1 (with this definition, we should have $Q_1 < 0$). Because the engine completes a full cycle, and S is a state variable, we have $\Delta S_{engine} = 0$. The bath at T_2 has $\Delta S_{bath2} = -Q_2/T_2$ and the bath at T_1 has $\Delta S_{bath1} = -Q_1/T_1$. Note that we computed $\Delta S_{bath} = \int \dbar Q_T/T_{bath} = \Delta Q/T_{bath}$, where we take the bath to be sufficiently large that it has unchanging temperature, so the T_{bath} can be taken out of the integral. We then have

$$\Delta S_{universe} = \Delta S_{bath1} + \Delta S_{bath2} + \Delta S_{engine} = -\frac{Q_1}{T_1} - \frac{Q_2}{T_2} \geq 0.$$

Which we can write as $Q_1/Q_2 \leq T_1/T_2$. Since the engine does work $W = Q_1 + Q_2$, the above entropy condition gives the efficiency $\eta = W/Q_2 \leq 1 - T_1/T_2$, as we've seen before. So the maximum efficiency of engines is just a special case of $\Delta S_{universe} \geq 0$.

• Rewrite the first law as

$$dU = \dbar Q - \dbar W = \dbar Q_R - \dbar W_R = TdS - PdV.$$

Please think deeply about this equation – don't just read it quickly as being obvious. In any process, reversible or not, we have some $\dbar Q$ and $\dbar W$, which depend on the process. For example, for the Joule free expansion, both are zero. The process dependence cancels with their difference, since dU is a state variable. So the difference can be computed for a reversible process. Then we can use $\dbar Q_R = TdS$ and $\dbar W_R = PdV$. Note that, in general, $\dbar Q \leq TdS$ (as we've seen above), and so $\dbar W \leq PdV$, where the inequality becomes an equality iff the process is reversible.

Let's write again the following equation, which is the **most important equation of thermodynamics**

$$dU = TdS - PdV \qquad !$$

Among other uses, we can use this equation as an equation for S:

$$dS = \frac{dU}{T} + \frac{PdV}{T}.$$

For the case of an ideal gas, we can write $dU = C_V dT$, and $P = nRT/V$ to get

$$dS = C_V \frac{dT}{T} + nR\frac{dV}{V}$$

and integrate to get
$$S_2 - S_1 = C_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right).$$
Note that S is an increasing function of both T and V. We'll see later that S is related to molecular disorder, and the system is more disordered when T or V increases.

If we prefer to use P instead of V, we could rewrite this using $PV = nRT$ as
$$S_2 - S_1 = C_P \ln\left(\frac{T_2}{T_1}\right) - nR\ln\left(\frac{P_2}{P_1}\right),$$
where recall $C_P = C_V + nR$. For fixed T, increasing P compresses the gas, so the disorder S decreases.

• Instead of our usual P, V diagrams, we can use T, S diagrams. Plot T on the vertical axis, and S on the horizontal one. Then $\Delta Q = \int_{path} T dS$ is the area under the curve, and for a closed cycle $\Delta Q = \oint T dS$ is the area inside the closed loop. For a cyclic engine, we have $\Delta U = 0$, so $\Delta Q = \Delta W$. Draw the ideal gas Carnot engine as an T, S diagram: it looks like a rectangle in these coordinates, with T_2 the temperature at the top of the rectangle and T_1 that at the bottom. So the rectangle has height $\Delta T = T_2 - T_1$. The width of the rectangle is $S_2 - S_1 = nR\ln(V_b/V_a) = nR\ln(V_c/V_d)$. The area of the rectangle is the product of the height and width, which gives $\Delta W = \Delta Q$, agreeing with what we computed in class before using the P, V diagram.

• Non-ideal gasses, and general case of $C(T)$. If $V_2 = V_1$, have
$$S_2 - S_1 = \int_1^2 \frac{C_V(T)dT}{T},$$
where the integral is a reversible path with constant volume. Similarly, if $P_2 = P_1$, we can compute ΔS using $C_P(T)$ and integrating over a reversible path with constant pressure.

• Back to $\Delta S_{universe} \geq 0$. For a cyclic engine, $\Delta S_{engine} = 0$. We saw for the ideal Carnot engine that the maximum efficiency is when $\Delta S_{universe} = 0$. In general, $\Delta S_{universe}$ is related to wasted energy. For example, in the Joule free expansion of an ideal gas, from volume V_1 to volume V_2, we have $T_2 = T_1 = T$ and
$$\Delta S_{system} = \Delta S_{universe} = nR\ln(V_2/V_1), \qquad \Delta Q = \Delta W = 0.$$
On the other hand, if we considered the reversible expansion of an ideal gas pushing a piston from V_1 to V_2 we would get
$$\Delta S_{system} = -\Delta S_{bath} = nR\ln(V_2/V_1), \qquad \Delta Q = \Delta W = nRT\ln(V_2/V_1).$$
Of course, ΔS_{system} is the same in either case, since it's a state variable. In the irreversible case we have $\Delta S_{universe} > 0$ and in the reversible one we have $\Delta S_{universe} = 0$. These two cases illustrate a general connection between $\Delta S_{universe}$ and wasted work, the degradation of energy from useful to useless form.