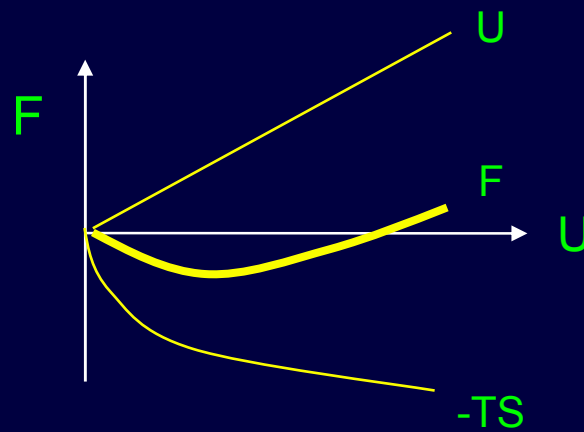


Lecture 15

Available Work and Free Energy



Helpful Hints in Dealing with Engines and Fridges

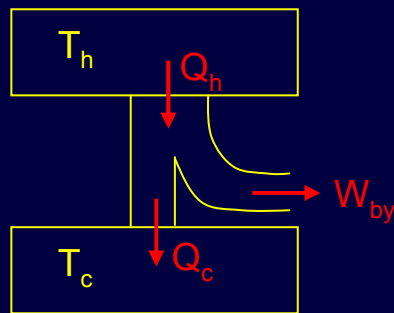
Sketch the process (see figures below).

Define Q_h and Q_c and W_{by} (or W_{on}) as positive and show directions of flow.

Determine which Q is given.

Write the First Law of Thermodynamics (FLT).

We considered three configurations of Carnot cycles:



Engine:

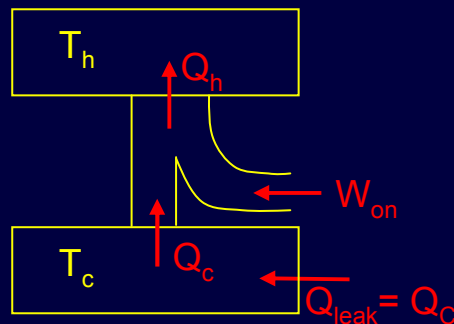
We pay for Q_h ,

we want W_{by} .

$$W_{by} = Q_h - Q_c = \varepsilon Q_h$$

$$\text{Carnot: } \varepsilon = 1 - T_c/T_h$$

This has large ε
when $T_h - T_c$ is large.



Refrigerator:

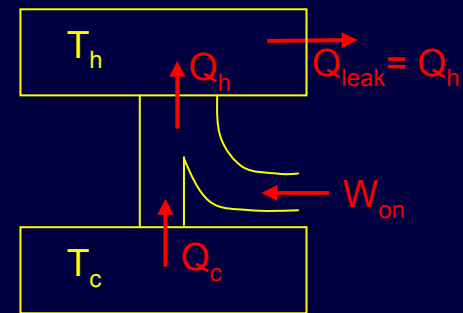
We pay for W_{on} ,

we want Q_c .

$$Q_c = Q_h - W_{on} = KW_{on}$$

$$\text{Carnot: } K = T_c/(T_h - T_c)$$

These both have large K when $T_h - T_c$ is small.



Heat pump:

We pay for W_{on} ,

we want Q_h .

$$Q_h = Q_c + W_{on} = KW_{on}$$

$$\text{Carnot: } K = T_h/(T_h - T_c)$$

ACT 1:

Entropy Change in Heat Pump

Consider a Carnot heat pump.

1) What is the sign of the entropy change of the hot reservoir during one cycle?

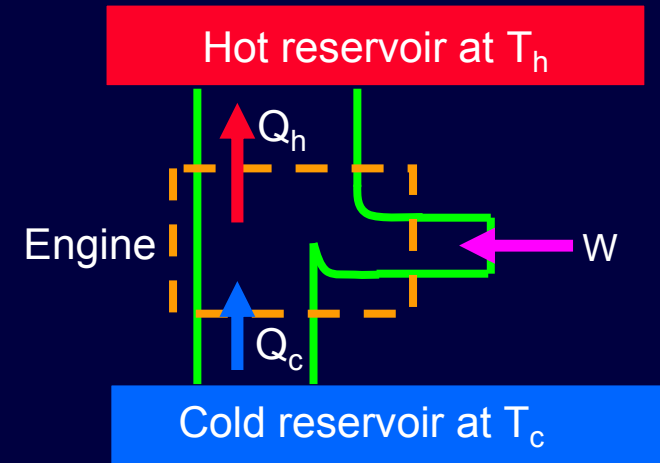
- a) $\Delta S_h < 0$ b) $\Delta S_h = 0$ c) $\Delta S_h > 0$

2) What is the sign of the entropy change of the cold reservoir?

- a) $\Delta S_c < 0$ b) $\Delta S_c = 0$ c) $\Delta S_c > 0$

3) Compare the magnitudes of the two changes.

- a) $|\Delta S_c| < |\Delta S_h|$ b) $|\Delta S_c| = |\Delta S_h|$ c) $|\Delta S_c| > |\Delta S_h|$



Solution

Consider a Carnot heat pump.

1) What is the sign of the entropy change of the hot reservoir during one cycle?

a) $\Delta S_h < 0$

b) $\Delta S_h = 0$

c) $\Delta S_h > 0$

Energy (heat) is entering the hot reservoir, so the number of available microstates is increasing.

2) What is the sign of the entropy change of the cold reservoir?

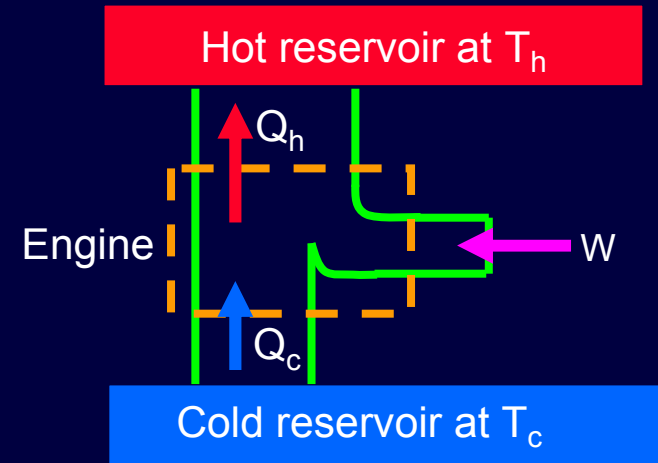
a) $\Delta S_c < 0$

b) $\Delta S_c = 0$

c) $\Delta S_c > 0$

3) Compare the magnitudes of the two changes.

a) $|\Delta S_c| < |\Delta S_h|$ b) $|\Delta S_c| = |\Delta S_h|$ c) $|\Delta S_c| > |\Delta S_h|$



Solution

Consider a Carnot heat pump.

1) What is the sign of the entropy change of the hot reservoir during one cycle?

a) $\Delta S_h < 0$

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c) $\Delta S_h > 0$

Energy (heat) is entering the hot reservoir, so the number of available microstates is increasing.

2) What is the sign of the entropy change of the cold reservoir?

a) $\Delta S_c < 0$

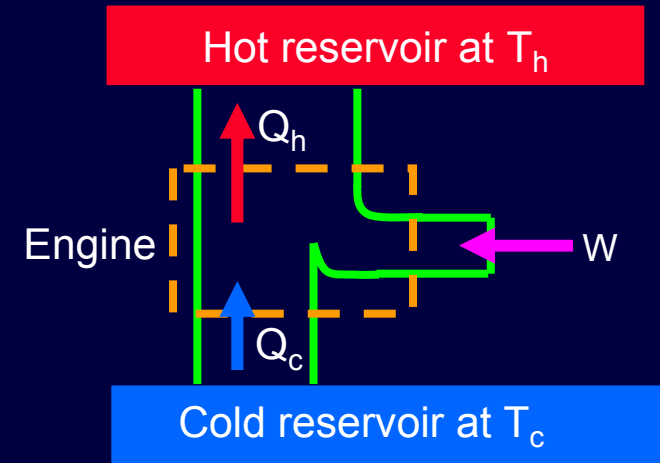
b) $\Delta S_c = 0$

c) $\Delta S_c > 0$

Energy (heat) is leaving the cold reservoir.

3) Compare the magnitudes of the two changes.

a) $|\Delta S_c| < |\Delta S_h|$ b) $|\Delta S_c| = |\Delta S_h|$ c) $|\Delta S_c| > |\Delta S_h|$



Solution

Consider a Carnot heat pump.

1) What is the sign of the entropy change of the hot reservoir during one cycle?

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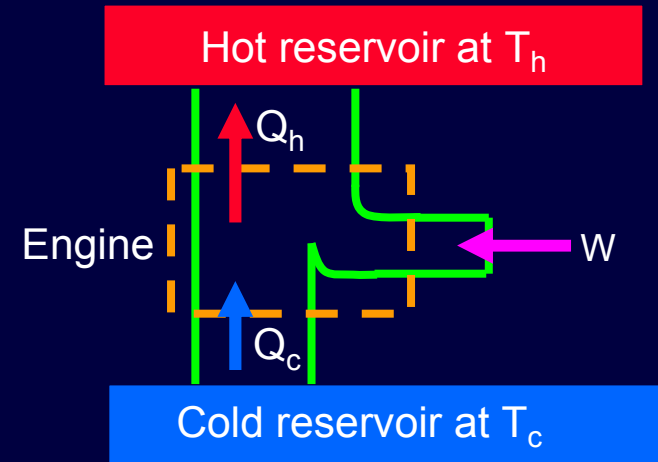
3) Compare the magnitudes of the two changes.

a) $|\Delta S_c| < |\Delta S_h|$

b) $|\Delta S_c| = |\Delta S_h|$

c) $|\Delta S_c| > |\Delta S_h|$

It's a reversible cycle, so $\Delta S_{\text{tot}} = 0$. Therefore, the two entropy changes must cancel. Remember that the entropy of the "engine" itself does not change.



Note: We've neglected the heat leak OUT of the hot reservoir. In fact, this must equal Q_h (why?). If that heat leaks directly into the cold reservoir, this will be irreversible...

Heat Engine Summary

For all cycles:

$$\varepsilon = 1 - \frac{Q_c}{Q_h}$$

Some energy is dumped into the cold reservoir.

For the Carnot cycle:

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

Q_c cannot be reduced to zero.

Carnot (best) efficiency:

$$\varepsilon_{\text{Carnot}} = 1 - \frac{T_c}{T_h}$$

Only for reversible cycles.

Carnot engines are an idealization - impossible to realize.

They require very slow processes, and perfect insulation.

When there's a net entropy increase, the efficiency is reduced:

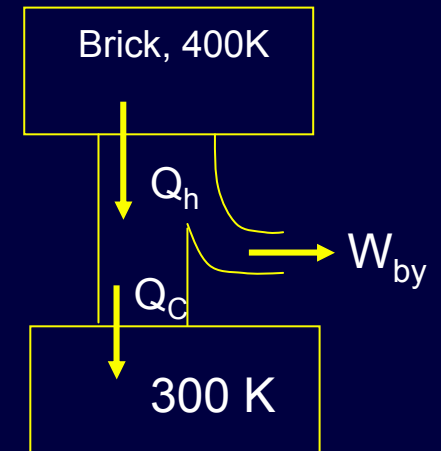
$$\varepsilon = \varepsilon_{\text{Carnot}} - \frac{T_c \Delta S_{\text{tot}}}{Q_H}$$

ACT 2: Work from a hot brick

We saw that the efficiency of *any* heat engine is given by $\varepsilon = 1 - Q_c/Q_h$.

Heat a brick to 400 K. Connect it to a *Carnot Engine*. What is the average efficiency if the cold reservoir is 300 K? The brick has a constant heat capacity of $C = 1 \text{ J/K}$.

- a) $\varepsilon < 25\%$ b) $\varepsilon = 25\%$ c) $\varepsilon > 25\%$



Solution

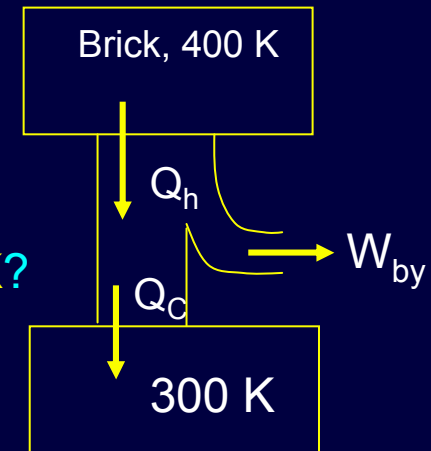
We saw that the efficiency of *any* heat engine is given by

$$\varepsilon = 1 - Q_c/Q_h.$$

Heat a brick to 400 K. Connect it to a *Carnot* Engine.

What is the average efficiency if the cold reservoir is 300 K?

The brick has a constant heat capacity of $C = 1 \text{ J/K}$.



- a) $\varepsilon < 25\%$ b) $\varepsilon = 25\%$ c) $\varepsilon > 25\%$

Did you use: $\varepsilon = 1 - T_c/T_h$?

If so, you missed that the brick is *cooling* (it's not a constant T reservoir).

Therefore, the efficiency (which begins at 25%) drops as the brick cools.

We must integrate: ($dQ_h = -CdT$)

$$W_{by} = \int_{T_h}^{T_c} -C(T) \left(1 - \frac{T_c}{T} \right) dT = C \int_{T_c}^{T_h} \left(1 - \frac{T_c}{T} \right) dT$$

$$= C(T_h - T_c) - T_c C \ln \left(\frac{T_h}{T_c} \right) = -\Delta U + T_c \Delta S$$

This is an interesting result.
Let's discuss it.

Available Work and Free Energy

We just found that the work that the engine can do as the brick cools from its initial temperature to T_c is:

$$W_{by} = -\Delta U_{brick} + T_c \Delta S_{brick}$$

The form of this result is useful enough that we

define a new quantity, the “free energy” of the brick:

$$F_{brick} \equiv U_{brick} - T_{env} S_{brick}$$

In the ACT,
 T_{env} was T_c .

With this definition, $W_{by} = -\Delta F_{brick}$. This is the best we can do.

In general, W_{by} will be smaller: $W_{by} \leq -\Delta F_{brick} = F_i - F_f$

Free energy tells how much work can be extracted.

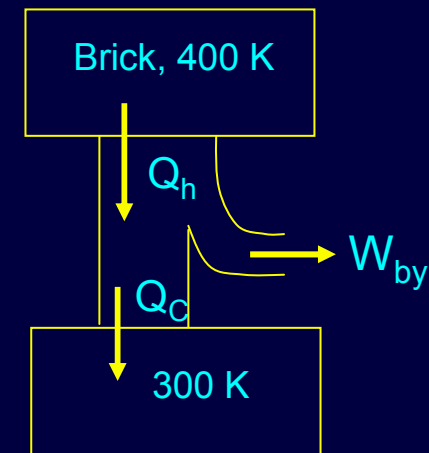
It is useful, because it is almost entirely a property of the brick.

Only the temperature of the environment is important.

ACT 3: Work from a cold brick?

We obtained work from a hot brick, initially at 400K.
If instead the brick were initially at 200K, could we still do work in our 300K environment?

- a) Yes.
- b) No, you can't have $T_h < T_c$.
- c) No, we would have to put work in.



Solution

We obtained work from a hot brick, initially at 400K.
If instead the brick were initially at 200K, could we still do work in our 300K environment?

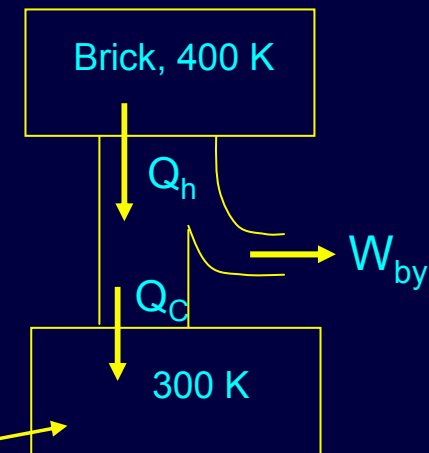
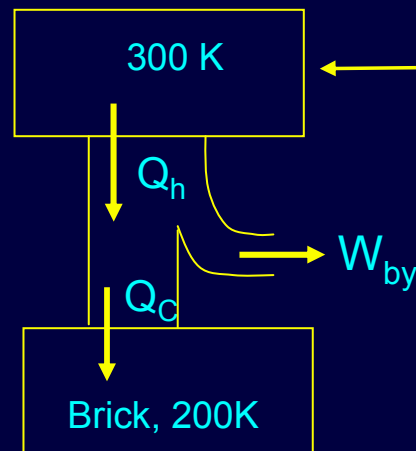
a) Yes.

b) No, you can't have $T_h < T_c$.

c) No, we would have to put work in.

Think outside the box.

Use the brick as the cold reservoir:



Environment

Question:

Can we use free energy to calculate the work?

Exercise: Free Energy and Equilibrium

What is the free energy of an object that is hotter or colder than its environment?

The object is in thermal equilibrium when $T = T_{\text{env}}$, so we will compare the free energy at other temperatures to its value at that temperature, since that is where the object will end up.

1) Heat the brick to 310 K. $\Delta T = +10$ K.

$$\Delta F_B =$$

2) Cool the brick to 290 K. $\Delta T = -10$ K.

$$\Delta F_B =$$

Plot the results:

Useful info:

Heat Capacity of brick: $C = 1 \text{ kJ / K}$

$$\Delta U_B = C \Delta T = C(T_B - 300\text{K})$$

$$\Delta S_B = C \ln (T_B / 300\text{K})$$

$$\Delta F_B = \Delta U_B - (300\text{K}) \Delta S_B$$

Solution

What is the free energy of an object that is hotter or colder than its environment?

The object is in thermal equilibrium when $T = T_{\text{env}}$, so we will compare the free energy at other temperatures to its value at that temperature, since that is where the object will end up.

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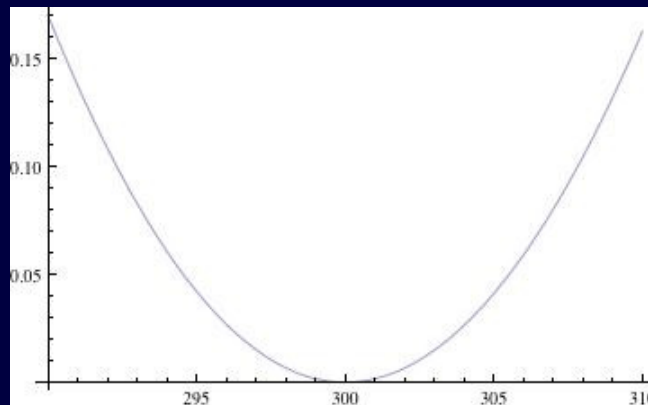
$$\begin{aligned}\Delta F_B &= (1 \text{ kJ/K}) \cdot (10 \text{ K}) - (300 \text{ K}) \cdot (1 \text{ kJ/K}) \cdot \ln(310/300) \\ &= 10 \text{ kJ} - 9.84 \text{ kJ} = 0.16 \text{ kJ}\end{aligned}$$

2) Cool the brick to 290 K. $\Delta T = -10$ K.

$$\begin{aligned}\Delta F_B &= (1 \text{ kJ/K}) \cdot (-10 \text{ K}) - (300 \text{ K}) \cdot (1 \text{ kJ/K}) \cdot \ln(290/300) \\ &= -10 \text{ kJ} + 10.17 \text{ kJ} = 0.17 \text{ kJ}\end{aligned}$$

Plot the results:

You can plot
 $(x-300)-300 \cdot \log(x/300)$
on your calculator.
That's how I got this graph.



Useful info:

Heat Capacity of brick: $C = 1 \text{ kJ / K}$

$$\Delta U_B = C \Delta T = C(T_B - 300 \text{ K})$$

$$\Delta S_B = C \ln(T_B / 300 \text{ K})$$

$$\begin{aligned}\Delta F_B &= \Delta U_B - (300 \text{ K}) \Delta S_B \\ &= C(T - T_e) - CT_e \ln(T/T_e)\end{aligned}$$

Conclusion:

The free energy of the brick is minimum when its temperature is the temperature of the environment.

Equilibrium is found at Free Energy Minimum

The free energy is minimum when the system has the same temperature as the environment. Why is F minimized in thermal equilibrium?

Equilibrium corresponds to a maximum in total entropy:

$$S = S_e + T_e$$

$$S_{\text{tot}} = S + S_e$$

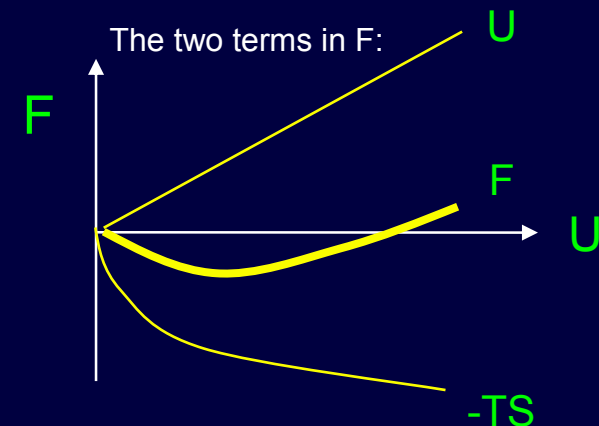
If the system draws dU from the environment, $dS_e = -dU/T_e$. So:

$$\begin{aligned} dS_{\text{tot}} &= dS + dS_e = dS - dU / T_e = 0 \text{ in equilibrium.} \\ &= - (dU - T_e dS) / T_e = - dF / T_e \end{aligned}$$

So, dS_{tot} and dF are proportional to each other with a minus sign (for a given T_e).

Minimizing F is the same as maximizing S_{tot} .

This is not a new physical concept, but F is often a more convenient analysis tool.



Caution...

Maximum S_{tot} Does Not Always Mean Minimum F_{sys}

When we introduced the Helmholtz free energy, F , (see the “hot brick” discussion), we assumed that the volume of the brick was constant. If the volume weren’t constant, then the brick could gain or lose energy (and entropy) by contracting or expanding. That would change the analysis.

It is very common that the pressure, not the volume, is constant (*e.g.*, if our system is a gas at constant atmospheric pressure). In this situation, we use a different form of free energy, called “Gibbs free energy”: $G = U + pV - TS$. The pV term takes into account the work that is done during volume changes.

We won’t use Gibbs free energy in this course, but it is important to be aware that the calculation of free energy depends on the situation.

Free Energy Example

Suppose we have a liter of water at $T = 100^\circ \text{C}$.

What is its free energy, if the environment is $T = 20^\circ \text{C}$?

Verify the result by calculating the amount of work we could obtain.

Remember that $c_{\text{H}_2\text{O}} = 4186 \text{ J/kg}\cdot\text{K}$.

Solution

Suppose we have a liter of water at $T = 100^\circ \text{C}$.

What is its free energy, if the environment is $T = 20^\circ \text{C}$?

Verify the result by calculating the amount of work we could obtain.

Remember that $c_{\text{H}_2\text{O}} = 4186 \text{ J/kg}\cdot\text{K}$.

$\Delta F = \Delta U - T\Delta S$, where T is the temperature of the environment.

$\Delta U = mc\Delta T = 1 \text{ kg} * 4186 \text{ J/kg}\cdot\text{K} * 80 \text{ K} = 3.349 \times 10^5 \text{ J}$.

$\Delta S = mc \ln(T_{\text{H}_2\text{O}}/T_{\text{env}}) = 1011 \text{ J/K}$

$\Delta F = 3.87 \times 10^4 \text{ J}$

Remember to measure temperature in Kelvin.

Otherwise, you'll get the entropy wrong.

Solution

Suppose we have a liter of water at $T = 100^\circ \text{C}$.

What is its free energy, if the environment is $T = 20^\circ \text{C}$?

Verify the result by calculating the amount of work we could obtain.

Remember that $c_{\text{H}_2\text{O}} = 4186 \text{ J/kg}\cdot\text{K}$.

If we run a Carnot engine, the efficiency at a given water temperature is:

$\varepsilon = 1 - T_{\text{cold}}/T_{\text{hot}}$. So, for each small decrease in water temperature, we get this much work out of the engine:

$$dW = \varepsilon Q = -\varepsilon mc \, dT$$

Thus, the total work obtained as T drops from 100°C to 20°C is:

$$\begin{aligned} W &= -mc \int_{373}^{293} \left(1 - \frac{293}{T} \right) dT \\ &= (4186 \text{ J/K}) \left[T - (293 \text{ K}) \ln \left(\frac{373}{293} \right) \right]_{293}^{373} \\ &= 3.87 \times 10^4 \text{ J} \end{aligned}$$

Why is Free Energy important?

- In many situations maximizing total S (sometimes hard to calculate) to reach equilibrium implies minimizing system free energy (sometimes easier to calculate).
- When the system is out of equilibrium, its excess free energy gives the amount of work that an ideal engine could extract from it in a given environment.
- Free energy can be tabulated for many materials (e.g., chemical fuels).

For the rest of the course we will consider important applications of this principle:

Paramagnets (revisited)

The law of atmospheres (revisited)

Solids: defects and impurities

Chemical reactions, especially in gases

Carrier densities in semiconductors

Adsorption of particles on surfaces

Liquid-gas and solid-gas phase transitions

Free Energy Summary

For a Carnot engine: $W_{\text{by}} = -\Delta U + T_e \Delta S = -\Delta F$

where $F = U - TS$ is called the Helmholtz* free energy of the system referenced to the temperature T_e of the environment (or 'reservoir').

The free energy of an object is always defined with reference to the temperature of a reservoir, often the environment. An object's free energy is minimized when its temperature is the same as the environment.

$$F = U - TS = \text{Free energy} \rightarrow \text{Maximum Available Work}$$

- * There are actually several versions of free energy, depending on the particular situation. Helmholtz free energy applies when the system has a constant volume (e.g., a brick). When pressure is constant (e.g., a pot of water open to the air), we use Gibbs Free Energy, $G = U + pV - TS$. We will not study the other versions in this course.

Supplement: Gibbs Free Energy

Most phase transitions are observed under **constant p, T** conditions, not constant-V, T. Unless the stuff is in a closed vessel, it's open to the air (thus, at atmospheric pressure).

In this case, the entropy of the environment changes not only when the system energy changes but also when its volume changes. The reservoir is (by assumption) in equilibrium at fixed T and p. So, as heat flows, the change of the reservoir's entropy is:

$$\Delta S_R = \frac{Q_R}{T} = \frac{\Delta U_R + p\Delta V_R}{T} = \frac{-\Delta U - p\Delta V}{T}$$

$\Delta V_R = -\Delta V$ and $\Delta U_R = -\Delta U$
because total volume and total energy are constant.

The change in the total entropy is thus:

$$\Delta S_{tot} = \Delta S + \Delta S_R = \Delta S - \frac{\Delta U}{T} - \frac{p\Delta V}{T} = \frac{-\Delta(U + pV - TS)}{T} = \frac{-\Delta G}{T}$$

where: $G \equiv U + pV - TS$

Variables U, V, and S are of the system.
Fixed p and T are of the reservoir.

In these conditions, maximizing S_{tot} means minimizing the system's G.

Next Monday

- Free Energy and Chemical Potential
- Simple defects in solids
- Ideal gases, revisited