

# Lecture 14

## Heat Pumps, Refrigerators, and Bricks!

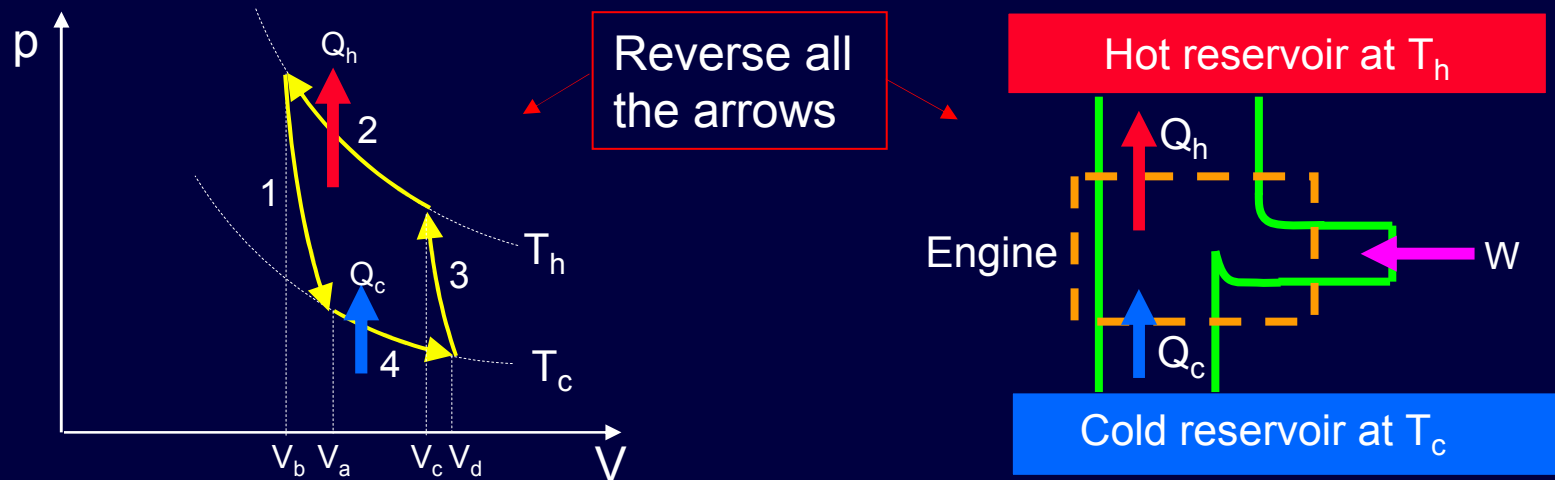
- Pumping Heat: Heat pumps and Refrigerators
- Available Work and Free Energy
- Work from Hot and Cold Bricks

Reading for this Lecture:  
Elements Ch 10

Reading for Lecture 16:  
Elements Ch 11

# Run the Engine in Reverse

The Carnot cycle is reversible (each step is reversible):



When the engine runs in reverse:

Heat is transferred from cold to hot by action of work on the engine.

Note that heat never flows spontaneously from cold to hot;

the cold gas is being heated by adiabatic compression (process 3).

$Q_c / Q_h = T_c / T_h$  is still true. (Note:  $Q_h$ ,  $Q_c$ , and  $W$  are still positive!)

# Refrigerators and Heat Pumps

Refrigerators and heat pumps are heat engines running in reverse.

How do we measure their performance?

It depends on what you want to accomplish.

Refrigerator:

We want to keep the food cold ( $Q_c$ ).

We pay for  $W$  (the electric motor in the fridge).

So, the coefficient of performance,  $K$  is:

It's not called "efficiency".

$$K \equiv \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} = \frac{T_c}{T_h - T_c}$$

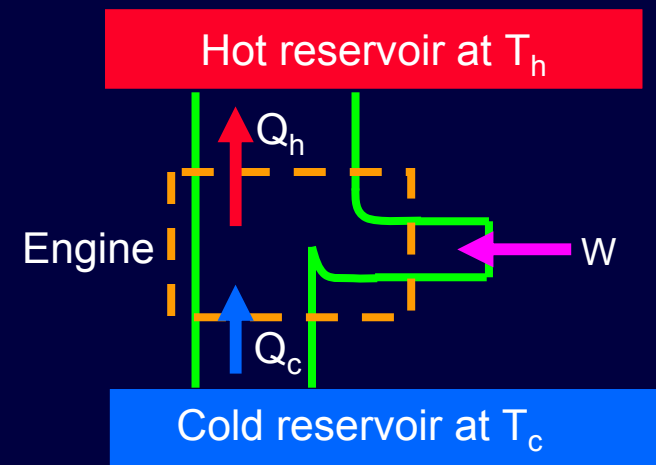
Heat pump:

We want to keep the house warm ( $Q_h$ ).

We pay for  $W$  (the electric motor in the garden).

The coefficient of performance,  $K$  is:

$$K \equiv \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c} = \frac{T_h}{T_h - T_c}$$



# Helpful Hints in Dealing with Engines and Fridges

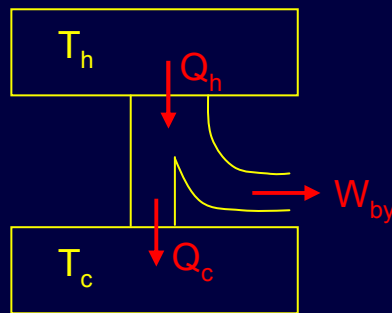
Sketch the process (see figures below).

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:

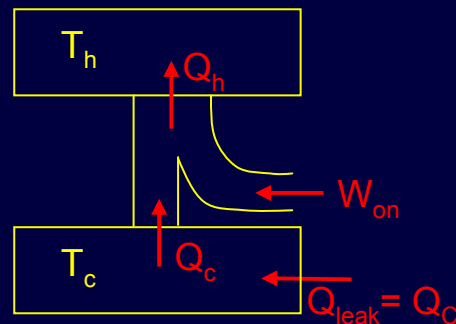
We pay for  $Q_h$ ,

we want  $W_{by}$ .

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

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

This has large  $\varepsilon$   
when  $T_h - T_c$  is large.



Refrigerator:

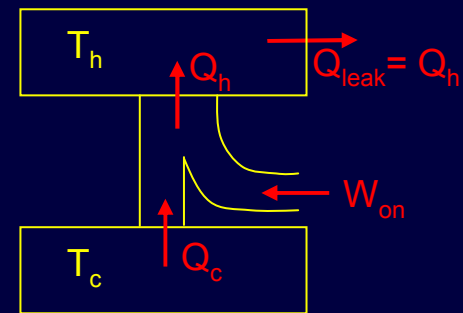
We pay for  $W_{on}$ ,

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: Refrigerator

There is a 70 W heat leak (the insulation is not perfect) from a room at temperature  $22^\circ\text{C}$  into an ideal refrigerator. How much electrical power is needed to keep the refrigerator at  $-10^\circ\text{C}$ ? Assume Carnot performance.

a)  $< 70\text{ W}$

b)  $= 70\text{ W}$

c)  $> 70\text{ W}$

# Act 1: Refrigerator

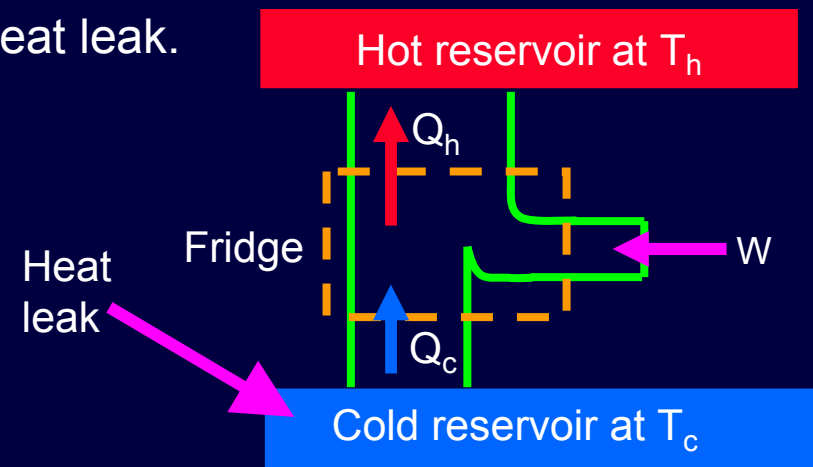
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Hint:  $Q_c$  must exactly compensate for the heat leak.

a)  $< 70\text{ W}$

b)  $= 70\text{ W}$

c)  $> 70\text{ W}$



# Solution

There is a 70 W heat leak (the insulation is not perfect) from a room at temperature 22° C into an ideal refrigerator. How much electrical power is needed to keep the refrigerator at -10° C? Assume Carnot performance.

Hint:  $Q_c$  must exactly compensate for the heat leak.

The coefficient of performance is:

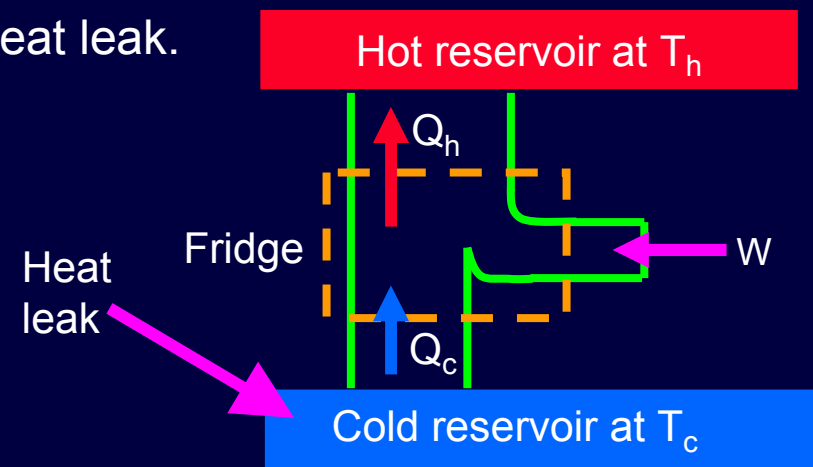
$$W = Q_h - Q_c = Q_c \left( \frac{Q_h}{Q_c} - 1 \right) = Q_c \left( \frac{T_h}{T_c} - 1 \right)$$

We need  $Q_c = 70$  J each second.

Therefore we need  $W \equiv 70 \left( \frac{295}{263} - 1 \right) \text{ J / s}$

The motor power is 8.5 Watts.

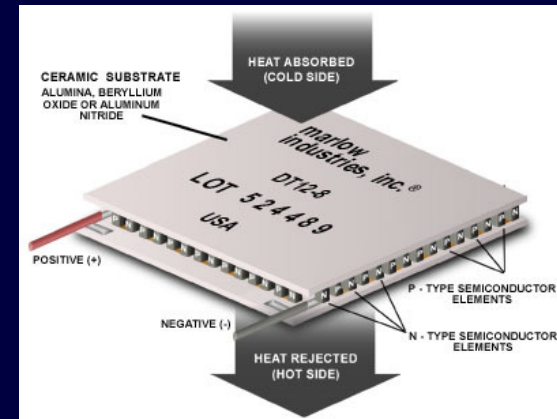
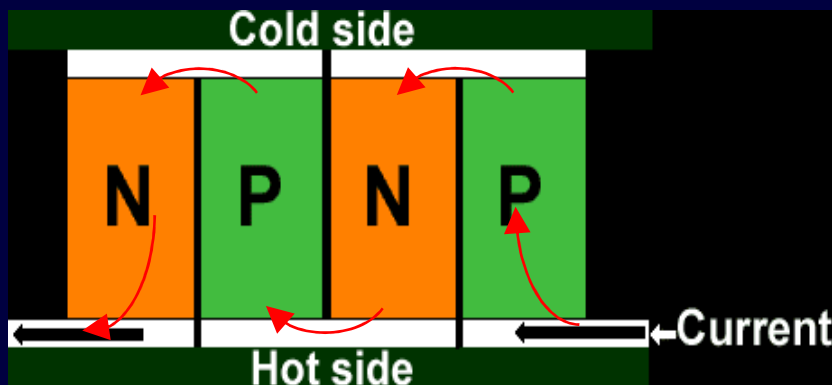
Watt = Joule/second.



This result illustrates an unintuitive property of refrigerators and heat pumps: When  $T_h - T_c$  is small, they pump more heat than the work you pay for.

# Supplement: Peltier cooler

- Driving a current (~amps) through generates a temperature difference. 20-50°C typical
- Not so common – they're more costly, take a lot of power, and you still have to get rid of the heat! But....no moving parts to break.
- How's it work...



Electrons pushed from electron-deficit material (p-type) to electron-rich material (n-type); they slow down, cooling the top connector. Similarly, they heat up in going from n to p-type (bottom connector).

Despite the radically different construction, this heat pump must obey exactly the same limits on efficiency as the gas-based pumps, because these limits are based on the 1<sup>st</sup> and 2<sup>nd</sup> laws, not any details.



# The Limits of Cooling

The maximum efficiency is  $\varepsilon = \frac{Q_C}{W} \leq \frac{T_C}{T_H - T_C}$

Refrigerators work less well as  $T_h - T_c$  becomes large.

The colder you try to go, the less efficient the refrigerator gets. The limit as  $T_c$  goes to zero is zero efficiency !

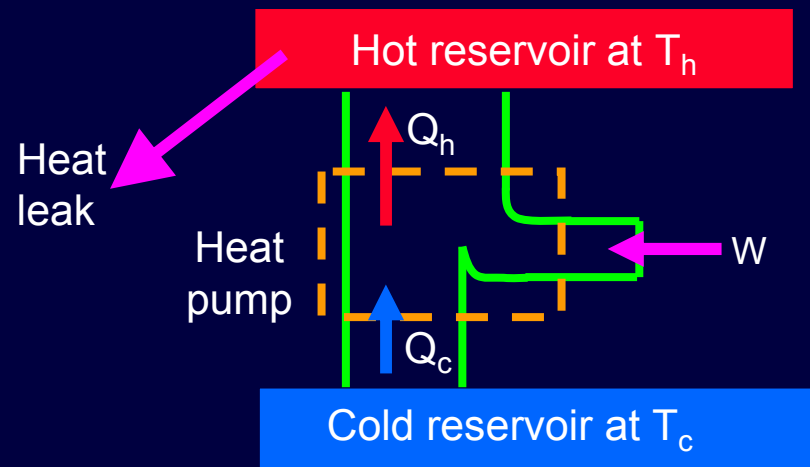
Since heat leaks will not disappear as the object is cooled, you need to supply more work the colder it gets. The integral of the power required diverges as  $T_c \rightarrow 0$ .

Therefore you cannot cool a system to absolute zero.

# Exercise: Heat Pump

Suppose that the heat flow out of your  $20^\circ\text{C}$  home in the winter is  $7\text{ kW}$ . If the temperature outside is  $-15^\circ\text{C}$ , how much power would an ideal heat pump require to maintain a constant inside temperature?

- a)  $W < 7\text{ kW}$
- b)  $W = 7\text{ kW}$
- c)  $W > 7\text{ kW}$



# Solution

Suppose that the heat flow out of your  $20^\circ\text{C}$  home in the winter is  $7\text{ kW}$ . If the temperature outside is  $-15^\circ\text{C}$ , how much power would an ideal heat pump require to maintain a constant inside temperature?

a)  $W < 7\text{ kW}$

b)  $W = 7\text{ kW}$

c)  $W > 7\text{ kW}$

This is what you'd need with an electric blanket or furnace.

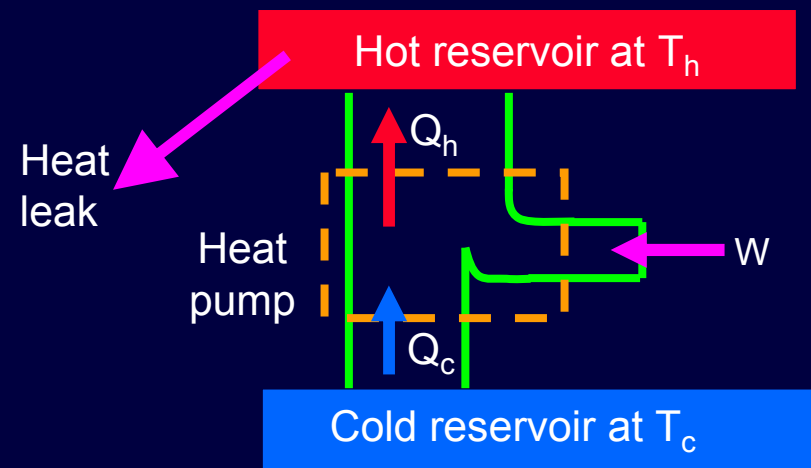
The coefficient of performance is:

$$W = Q_h - Q_c = Q_h \left(1 - \frac{Q_c}{Q_h}\right) = Q_h \left(1 - \frac{T_c}{T_h}\right)$$

We need  $Q_h = 7000\text{ J}$  each second.

Therefore we need  $W \equiv 7000 \left(1 - \frac{258}{293}\right) = 836\text{ J/s}$

The electric company must supply  $836\text{ Watts}$ , much less than the  $7\text{ kW}$  that a furnace would require!



Beware:

Real heat pumps are not nearly ideal, so the advantage is smaller.

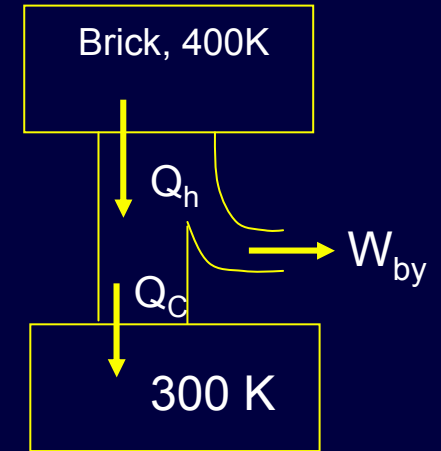
# ACT 2: Work from a hot brick

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

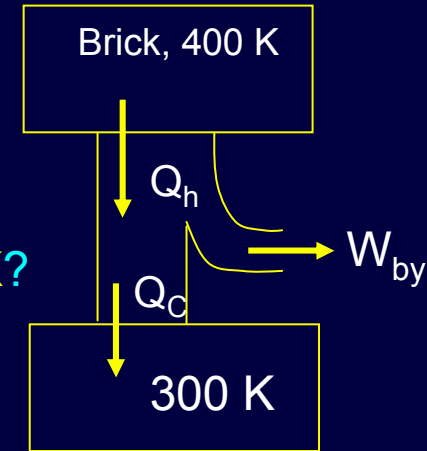
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- a)  $\varepsilon < 25\%$     b)  $\varepsilon = 25\%$     c)  $\varepsilon > 25\%$

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.

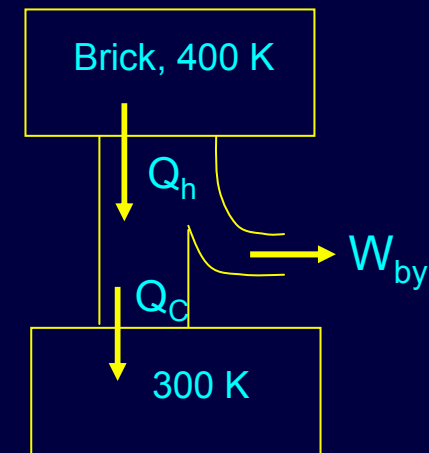
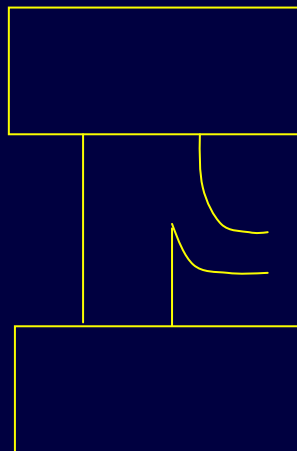
Only the temperature of the environment is important.

# 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.

Hint: Fill in the diagram:



# 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?

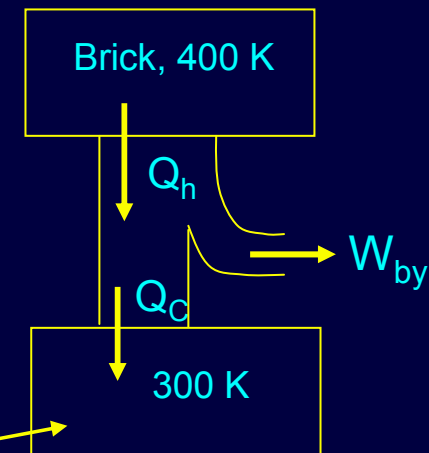
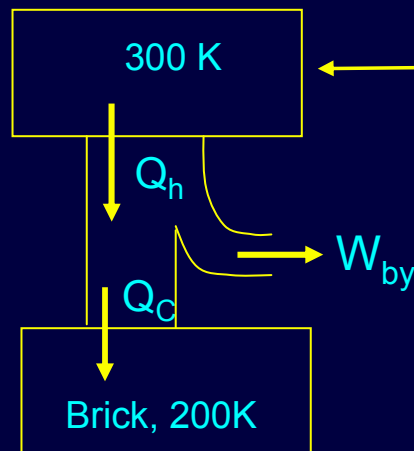
a) Yes.

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:



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:  $C = 1\text{kJ} / \text{K}$

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

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

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

# Solution

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

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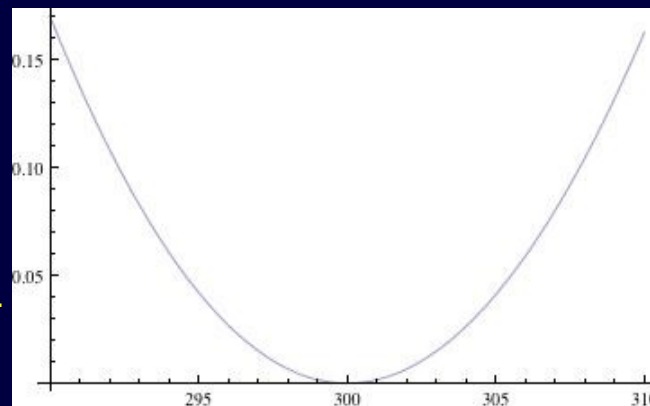
$$\Delta F_B = (1 \text{ kJ/K}) * (10 \text{ K}) - (300 \text{ K}) * (1 \text{ kJ/K}) * \ln(310/300) \\ = 10 \text{ kJ} - 9.84 \text{ kJ} = 0.16 \text{ kJ}$$

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

$$\Delta F_B = (1 \text{ kJ/K}) * (-10 \text{ K}) - (300 \text{ K}) * (1 \text{ kJ/K}) * \ln(290/300) \\ = -10 \text{ kJ} + 10.17 \text{ kJ} = 0.17 \text{ kJ}$$

Plot the results:

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



Useful info:

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

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

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

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

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:

$$S \quad S_e \quad T_e$$

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

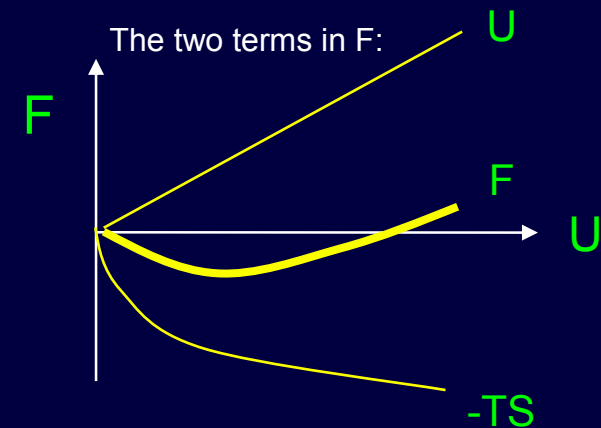
If the system draws  $dU$  from the environment,  $dS_e = -dU/T_e$ . So:

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

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

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

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



# 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.

# Caution...

## Maximum $S_{\text{tot}}$ Does Not Always Mean Minimum $F_{\text{sys}}$

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.

# 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