Solution

Physics 213 **Problem 3** **Week 6**

Work and Free Energy

In lecture you have seen that there is a connection between the work that can be extracted from an object and its free energy $F = U - TS$. In this problem, we will review the derivation of free energy and apply it to a problem.

Consider using the energy in a hot brick to drive a Carnot engine. The brick is *initially* at a temperature T_h, and the environment is at temperature T_c. The Carnot efficiency of the engine will decrease as the brick cools, but initially the efficiency is given by:

$$\varepsilon = 1 - T_c/T_h$$

For a small heat flow dQ_h from the brick, the Carnot engine performs work:

$$dW_{by} = \varepsilon dQ_h = (1 - T_c/T_h)\, dQ_h \qquad (dQ_h \text{ is defined to be positive})$$

During this process the energy of the brick decreases by $dU = -dQ_h$ and its entropy decreases by $dS = -dQ_h/T_h$. Therefore the work done is:

$$dW_{by} = -dU + T_c\, dS \equiv -dF \qquad (\text{This is the } \textbf{definition of free energy})$$

Notice the only temperature that appears is that of the environment. All we care about the brick is its internal energy and entropy, not its temperature. When the brick finally reaches T_C, the total work accomplished is:

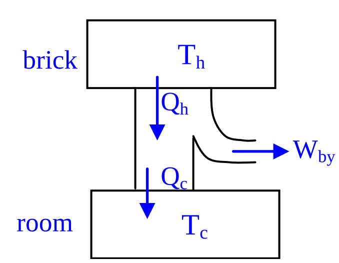
$$\mathbf{W_{by}} = -\Delta U + T_c\, \Delta S = \mathbf{-\Delta F}.$$

The free energy, **F = U - TS**, of an object is referenced to the temperature T of the environment. In this case, $T = T_c$. *The free energy of an object is always defined with reference to the temperature of a reservoir, often the environment.* **Available work = –change in F**.

a) Calculate the work performed by a Carnot engine as the brick cools from 400 K to 300K. Assume the heat capacity of the brick is C = 1 kJ/K. Also assume the environment is at room temperature, 300K. [Hint: Calculate ΔU and ΔS and plug them into the equation above. You must do a simple integral $\Delta S = \int dQ/T = C \int dT/T$.] Does the free energy of the brick *Increase* ___ or *Decrease* _X__ during this process?

$$\Delta U = C\Delta T = C(T_f - T_i) = (1\text{ kJ/K})(300 - 400) = -100\text{ kJ}$$

$$\Delta S = S_f - S_i = \int_{T_i}^{T_f} dQ/T = C\int_{T_i}^{T_f} dT/T = C\ \ln(T_f/T_i)$$
$$= (1\text{ kJ/K})\ \ln(300/400) = -0.288\text{ kJ/K}$$



Label this diagram indicating "brick", "room" , T_h, T_c, Q_h, Q_c, W_{by} and appropriate arrows.

$$T_c\Delta S = (300)\ (-0.288\text{ kJ/K}) = -86\text{ kJ}$$

$$W_{by} = -\Delta U + T_c\, \Delta S = 100\text{ kJ} - 86\text{ kJ} = 13.7\text{ kJ}$$

Free energy change $= \Delta F = -W_{by} = -13.7$ kJ = a decrease in F.

Calculate the free energy change, ΔF, if we start with a **chilled brick** at temperature T_C = 200 K and allow it to warm up to T_h = 300 K? (Note that F = U – TS must be referenced to the temperature of the environment.) Does the free energy of the brick Increase ___or Decrease ___ X___ as the brick warms up to 300 K? Is the amount of work that we could extract from the chilled brick positive _X____or negative ______?

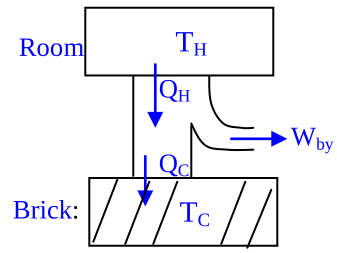
$\Delta U = C\Delta T$ = (1 kJ/K)(300K – 200K) = 100 kJ

ΔS = (1 kJ/K) ln(300/200) = 0.405 kJ/K

$T_h \Delta S$ = (300) (0.405 kJ/K) = 122 kJ

$\Delta F = \Delta U - T_h \Delta S$ = 100 kJ – 122 kJ = -22 kJ **decrease in F**

$W_{by} = -\Delta F$ = 22 kJ = **positive work**.



Label this diagram indicating "brick", "room" , T_h, T_c, Q_h, Q_c, W_{by} and appropriate arrows.

b) Sketch the available work W_{by} for this set of initial brick temperatures: (T_{room} = 300 K)

T_i = {150, 200, 250, 300, 350, 400, 450} Kelvin

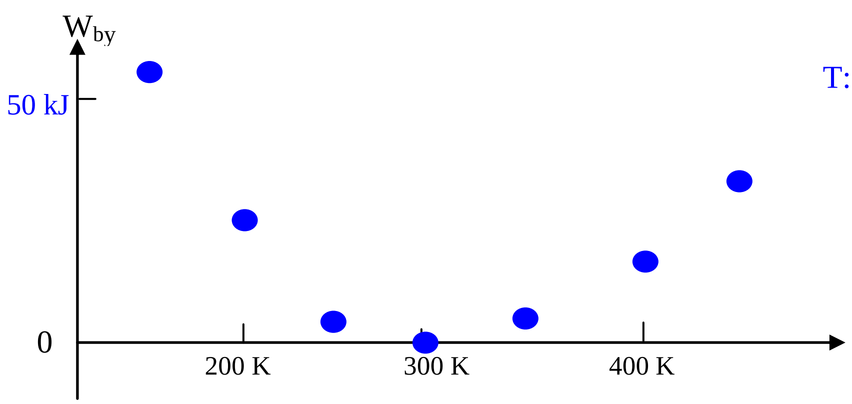
You've already done two of the data points. Fill in a reasonable curve, realizing the value of W_{by} when T_i = 300K.) What can you say about the free energy* of the brick as a function of its temperature?

F_{brick}(relative to room temp)

$= C\Delta T - T_{room}\Delta S$

= 1 kJ/K*[(T-300K) – 300K ln(T/300K)]

T:	F_{brick}:
450 K	28.4 kJ
400	13.7
350	3.8
300	0.0
250	4.7
200	21.6
150	57.9



T_i
(initial temperature of the brick)

d) Consider an object in thermal contact with a reservoir at temperature T. Mark True or False:

T **F** a) The Energy U of the object is a minimum in equilibrium.
T **F** b) The free energy F of the object is a maximum in equilibrium.
T F c) The free energy F of the object is a minimum in equilibrium.
T **F** d) The entropy S of the object is a maximum in equilibrium.
T F e) The entropy of the object plus environment is a maximum in equilibrium.
T F f) The free energy of *liquid* N_2 in the room is greater than N_2 at room temperature.

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* The signs here can be a bit confusing. In part a) we calculated how much the free energy would change as the brick approached room temperature (it decreased, because the capacity of the brick to do work – the free energy! – decreases the closer the brick is to the environmental temperature). In the above table we show F_{brick} as *positive*: for a given temp. of the brick, F_{brick} is the amount of free energy in excess of that if the brick were at room temperature.