

Reif Problem 4.1 Assignment 7

28.1

(a) 1 kg of water at 0°C brought into contact with large heat reservoir at 100°C . For the small system, we have

$$dS = \frac{dQ}{T}$$

Integration yields

$$\Delta S = \int \frac{dQ}{T} = \int_{T_i}^{T_f} \left(\frac{\partial Q}{\partial T} \right)_P \frac{dT}{T}$$

we assume that the process occurs at constant pressure. Then we have

$$\Delta S = \int_{T_i}^{T_f} c_p M \frac{dT}{T}, \quad K = ^\circ\text{C} + 273.15$$

where $M = 1 \text{ kg}$ and $c_p = \frac{1 \text{ cal}}{\text{g} \cdot \text{deg}}$, $1 \text{ cal} = 4.184 \text{ joule}$

$$\Delta S = c_p M \ln\left(\frac{T_f}{T_i}\right) = 1305 \frac{\text{joule}}{\text{deg}}$$

$$\Rightarrow \boxed{\Delta S = 1305 \frac{\text{joule}}{\text{deg}}}$$

The heat transferred to the small system is

$$\Delta Q = \int dQ = \int \left(\frac{\partial Q}{\partial T} \right)_P dT = c_p M \int_{T_i}^{T_f} dT$$

This yields

$$\Delta Q = c_p M (T_f - T_i)$$

or

$$\Delta Q = 4.184 \times 10^5 \text{ joule}$$

The heat reservoir satisfies the macroscopic relation

$$\Delta S_{\text{res}} = \frac{\Delta Q_{\text{res}}}{T_{\text{res}}}$$

since T_{res} is constant. The energy transferred to the reservoir is

$$\Delta Q_{\text{res}} = -\Delta Q = -4.184 \times 10^5 \text{ joule}$$

since the combined system is isolated,

We therefore obtain

$$\Delta S_{\text{res}} = \frac{-4.184 \times 10^5 \text{ joule}}{373.15 \text{ K}}$$

$$\Delta S_{\text{res}} = -1121 \frac{\text{joule}}{\text{deg}}$$

The entropy change for the combined system is

$$\Delta S^{(1)} = \Delta S + \Delta S_{\text{res}} = 184 \frac{\text{joule}}{\text{deg}}$$

Hence the entropy of the combined

system increases as it must.

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(b) Next consider a two-step process:

1. place small system in contact with 50°C heat reservoir
2. then place small system in contact with 100°C heat reservoir

We have, using results from part (a), for step 1

$$\Delta S_1 = c_p M \ln\left(\frac{323.15}{273.15}\right) = 703 \frac{\text{joule}}{\text{deg}}$$

$$\Delta Q_1 = c_p M (323.15 - 273.15) = 2.1 \times 10^5 \text{ joule}$$

$$\Delta S_{\text{res}1} = \frac{-2.1 \times 10^5 \text{ joule}}{323.15 \text{ K}} = -647 \frac{\text{joule}}{\text{deg}}$$

and for step 2

$$\Delta S_2 = c_p M \ln\left(\frac{373.15}{323.15}\right) = 601 \frac{\text{joule}}{\text{deg}}$$

$$\Delta Q_2 = c_p M (373.15 - 323.15) = 2.1 \times 10^5 \text{ joule}$$

$$\Delta S_{\text{res}2} = \frac{-2.1 \times 10^5 \text{ joule}}{373.15 \text{ K}} = -560 \frac{\text{joule}}{\text{deg}}$$

For the combined system we therefore obtain

$$\Delta S^{(0)} = \Delta S_1 + \Delta S_{\text{res}1} + \Delta S_2 + \Delta S_{\text{res}2}$$

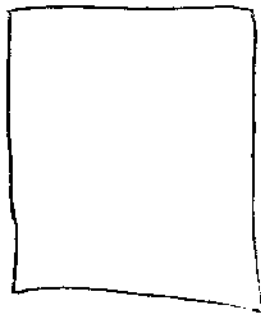
$$\Rightarrow \boxed{\Delta S^{(0)} = 97 \frac{\text{joule}}{\text{deg}}}$$

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(c) How might ~~the~~ 1 kg of water be heated from 0°C to 100°C with no change in entropy of ~~the~~ entire system?

This can be accomplished by placing the small system in contact with an infinite sequence of heat reservoirs with closely-spaced temperatures. Although there will be no increase in the entropy of ~~the~~ combined system, that entropy is infinite.

Problem 4.2



750 g Cu Calorimeter }
+ } 20°C
200 g H₂O }
+ }
30 g ice at 0°C }

(a) it takes heat $\Delta Q = 333 \frac{\text{joule}}{\text{g}} \cdot 30 \text{g}$

$\therefore \Delta Q = 9990 \text{ joule}$

to melt the ice.

If this heat comes from the 200 g of water, then its new temperature is calculated using

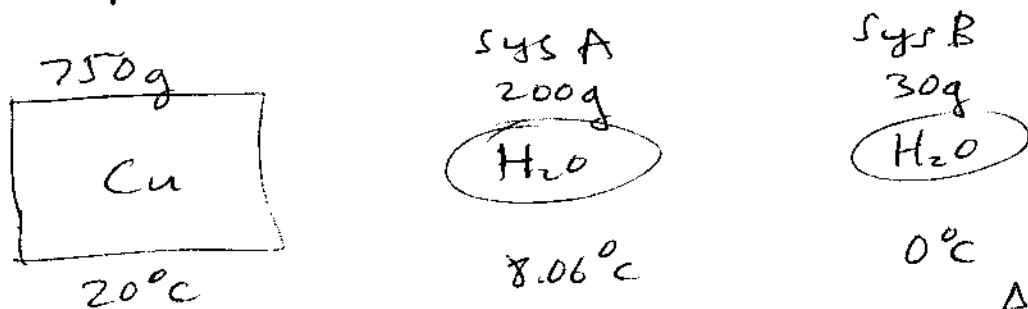
$$\Delta Q = \int_{T_i}^{T_f} \left(\frac{\partial Q}{\partial T} \right)_p dT = c_p M \Delta T$$

$$\Rightarrow \Delta T = \frac{\Delta Q}{c_p M} = \frac{-9990 \text{ joules}}{\frac{4.184 \text{ joules}}{\text{g deg}} \cdot 200 \text{ g}} = -11.94^\circ \text{C}$$

Hence the post-melt temperature of the 200 g of water is

$$20^\circ \text{C} - 11.94^\circ \text{C} = 8.06^\circ \text{C}$$

To determine the final equilibrium temperature of the combined system, we write



$$\Delta Q_B = c_p M (T_{eq} - 0^\circ \text{C})$$

$$\Delta Q_{Cu} = c_p M (T_{eq} - 20^\circ \text{C})$$

$$\Delta Q_A = c_p M (T_{eq} - 8.06^\circ \text{C})$$

Energy conservation gives

$$\Delta Q_{Cu} + \Delta Q_A + \Delta Q_B = 0$$

Hence we obtain

$$0.418 \frac{\text{joule}}{\text{g}} \cdot 750\text{g} (T_{\text{eq}} - 20^\circ\text{C}) \\ + \frac{4.184 \text{ joule}}{\text{g}} \cdot 200\text{g} (T_{\text{eq}} - 8.06^\circ\text{C}) \\ + \frac{4.184 \text{ joule}}{\text{g}} \cdot 30\text{g} (T_{\text{eq}} - 0^\circ\text{C}) = 0$$

or

$$1275.82 T_{\text{eq}} - 13014.61 = 0$$

$$\Rightarrow \boxed{T_{\text{eq}} = 10.2^\circ\text{C}}$$

(b) compute ~~total~~ entropy change.

In the first step, the entropy of the ice increases as melts, this increase is given by

$$\Delta S_{\text{melt}} = \frac{\Delta Q}{T} = \frac{9990 \text{ joule}}{273.15 \text{ K}}$$

$$\therefore \Delta S_{\text{melt}} = 36.6 \frac{\text{joule}}{\text{deg}}$$

The 200 g of water loses entropy given by

$$\Delta S_{\text{cool}} = \int \frac{dQ}{T} = c_p M \int_{20^\circ\text{C}}^{8.06^\circ\text{C}} \frac{dT}{T} = c_p M \ln\left(\frac{293.15 \text{ K}}{281.21 \text{ K}}\right)$$

$$\therefore \Delta S_{\text{cool}} = -34.80 \frac{\text{joule}}{\text{deg}}$$

In the second step, the three systems equilibrate to a temperature of $10.2^\circ\text{C} = 283.35\text{K}$. The associated entropy changes are

$$\Delta S_{Ca} = c_p M \ln\left(\frac{283.35\text{K}}{293.15\text{K}}\right) = -10.66 \frac{\text{Joule}}{\text{deg}}$$

$$\Delta S_A = c_p M \ln\left(\frac{283.35\text{K}}{281.21\text{K}}\right) = 6.34 \frac{\text{Joule}}{\text{deg}}$$

$$\Delta S_B = c_p M \ln\left(\frac{283.35\text{K}}{273.15\text{K}}\right) = 4.60 \frac{\text{Joule}}{\text{deg}}$$

Hence the net entropy change for the entire combined system is

$$\text{Step 1: } 36.6 - 34.8 = 1.8 \frac{\text{Joule}}{\text{deg}}$$

$$\text{Step 2: } 6.34 + 4.60 - 10.66 = 0.28 \frac{\text{Joule}}{\text{deg}}$$

Adding these gives for the entire experiment

$$\Delta S^{(0)} = 2.08 \frac{\text{Joule}}{\text{deg}}$$

(c) How much heat must be added to bring the temperature of the combined system back up to 20°C ? There are two ways to look at this.

$$1) \quad \Delta Q_{\text{total}} = \Delta Q_{\text{Cu}} + \Delta Q_A + \Delta Q_B$$

where the change is from the equilibrium temperature $T_{\text{eq}} = 10.2^\circ\text{C}$ up to $T_f = 20^\circ\text{C}$. We have

$$\Delta Q_{\text{total}} = \left(c_p M \Big|_{\text{Cu}} + c_p M \Big|_A + c_p M \Big|_B \right) \Delta T$$

where $\Delta T = T_f - T_{\text{eq}} = 9.8^\circ\text{K}$.

This yields

$$\Delta Q_{\text{total}} = 1276 \Delta T$$

$$\Rightarrow \boxed{\Delta Q = 1.25 \times 10^4 \text{ joules}}$$

2) Suppose we just melted the ice separately from the rest of the system and then heated it to 20°C . The energy required to do this is

$$\Delta Q = 9990 \text{ joules} + c_p M (20^\circ\text{C} - 0^\circ\text{C})$$

$$\Rightarrow \boxed{\Delta Q = 1.25 \times 10^4 \text{ joules}} \quad \text{which agrees with our other result}$$

Problem 4.3

Ideal gas has

$$E = f \frac{kT}{2}$$

where f is the number of degrees of freedom.

The first law gives

$$dE = dQ - PdV$$

$$\therefore dQ = dE + PdV$$

$$= \left(\frac{\partial E}{\partial V} \right)_T dV + \left(\frac{\partial E}{\partial T} \right)_V dT + PdV$$

which can be written as

$$dQ = \left(\frac{\partial Q}{\partial T} \right)_V dT + PdV$$

or

$$dQ = c_v dT + PdV$$

as given in the problem. To obtain the entropy change in going from (T_i, V_i) to (T_f, V_f) , we use

$$\Delta S = \int ds = \int \frac{dQ}{T} = \int \frac{(c_v dT + PdV)}{T}$$

Since we also have the ideal gas equation

of state

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$$P = \frac{RT}{V}$$

this yields

$$\Delta S = \int_{T_i}^{T_f} c_v \frac{dT}{T} + \int_{V_i}^{V_f} \frac{R}{V} dV$$

which gives

$$\Delta S = c_v \ln(T_f/T_i) + R \ln(V_f/V_i)$$

which is path (process) independent.