Problem 1.   Phase Space and Entropy of a MAIG

The phase space volume is a measure of the total number of possible ways for N of particles to *share* (or partition) the total energy and volume. For instance one particle could have almost all the available energy and the remaining $N-1$ particles could have very little. Such configurations are unlikely since they occupy only a small portion of the available phase space volume.

Consider a single particle in three dimensions in a box

$$0 < x, y, z < L \tag{1}$$

The three momenta components are sharing (or partitioning) the total energy which lies between E and $E + \delta E$, i.e.

$$E < \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} < E + \delta E \,, \tag{2}$$

The particle is free to move around in phase space but the energy must lie in this range. $\delta E/E$ is the precision in the energy and should be considered small, say 10^{-4}. Your should realize that this means that the momentum is confined to a spherical shell between $p \equiv \sqrt{2mE}$ and $p_{\max} = \sqrt{2m(E + \delta E)}$.

(a) Show that the accessible phase space volume is

$$V_{\text{ps}} = \int_{[E, E+\delta E]} \mathrm{d}^3\boldsymbol{r}\mathrm{d}^3\boldsymbol{p} = V \left[4\pi \, (2mE)^{3/2} \frac{\delta E}{2E} \right] \tag{3}$$

Hint: Show that the thickness of the shell in momentum space is

$$\delta p \equiv p_{\max} - p \simeq p \frac{\delta E}{2E} \tag{4}$$

To count the number of configurations, divide up the phase space volume into cells of (arbitrary) small size $h = \Delta x \Delta p_x$, or in three dimensions cells of size[1]

$$h^3 = (\Delta x \Delta y \Delta z)(\Delta p_x \Delta p_y \Delta p_z) \tag{5}$$

The "number of ways" for p_x, p_y, p_z and to share (or partition) the available energy is denoted by $\Omega(E, V)$ and it is phase space volume divided by the cell size

$$\Omega(E, V) = \frac{1}{h^3} \int_{[E, E+\delta E]} \mathrm{d}^3\boldsymbol{r}\mathrm{d}^3\boldsymbol{p} \tag{6}$$

$$= V \left(\frac{2mE}{h^2} \right)^{3/2} 4\pi \frac{\delta E}{2E} \tag{7}$$

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[1]Classically this cell size was arbitrary. With the advent of quantum mechanics, it was realized that a natural choice for the cell size is Plank's constant h. But here let's understand it from a classical perspective first, choosing the cell size to be h somewhat arbitrarily.

$\Omega(E, V)$ is the number of accessible states for a single particle with energy between E and $E + \delta E$.

The number of accessible configurations for two particles sharing the available energy between E and $E + \delta E$ is

$$\Omega(E, V) = \frac{1}{2!} \int_{[E, E+\delta E]} \frac{\mathrm{d}^3 r_1 \mathrm{d}^3 p_1}{h^3} \frac{\mathrm{d}^3 r_2 \mathrm{d}^3 p_2}{h^3} . \tag{8}$$

The 2! is inserted because if I simply exchange what I call particle 1 and particle 2, that is not to be considered a new configuration.

(b) Show that for two particles in three dimensions the number of accessible configurations is

$$\Omega(E, V) = V^2 \left(\frac{2mE}{h^2} \right)^3 \pi^3 \frac{\delta E}{4E} . \tag{9}$$

Hint: It is helpful to recall that the area of a sphere in d dimensions is given by a general formula

$$A_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1} . \tag{10}$$

In class we showed that for N particles with total energy E and volume V, the total the number of configurations and corresponding entropy of the system are given by

$$\Omega(E, V) = C(N) V^N E^{3N/2} \tag{11}$$

$$S(E, V) = k_B \ln \Omega = \frac{3}{2} N k_B \log E + N k_B \log V + \text{const} . \tag{12}$$

In the remainder of the exercise we will keep track of the constant $C(N)$.

(c) Show that the total number of ways for N particles to share the energy E (i.e. total number of accessible configurations with energy between E and $E + \delta E$) is

$$\Omega(E, V) = \frac{1}{N!} \int \frac{\mathrm{d}^3 r_1 \mathrm{d}^3 p_1}{h^3} \cdots \frac{\mathrm{d}^3 r_N \mathrm{d}^3 p_N}{h^3} , \tag{13}$$

$$= \frac{1}{N!} V^N \left(\frac{2\pi mE}{h^2} \right)^{3N/2} \frac{1}{\Gamma(3N/2)} \frac{\delta E}{E} . \tag{14}$$

N is large and is of order Avogadro's number.

(d) Use the Stirling approximation to show that[2]

$$\Omega(E, V) \simeq e^{5N/2} \left(\frac{V}{N} \right)^N \left(\frac{4\pi m}{3h^2} \frac{E}{N} \right)^{3N/2} , \tag{16}$$

$$\tag{17}$$

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[2]For large n

$$\Gamma(n) \equiv (n-1)! \simeq n! \simeq (n/e)^n \tag{15}$$

Note the Stirling approximation works for n not integer, if $n!$ is understood as $\Gamma(n+1)$.

and that the entropy is

$$S(E,V) = Nk_B \log \left[\left(\frac{V}{N} \right) \left(\frac{4\pi m}{3h^2} \frac{E}{N} \right)^{3/2} \right] + \frac{5}{2} Nk_B , \qquad (18)$$

$$= Nk_B \left[\log \left(\frac{v_N}{\lambda_{\text{th}}^3} \right) + \frac{5}{2} \right] . \qquad (19)$$

Here $v_N = V/N$ is the volume per particle and

$$\lambda_{\text{th}} = \frac{h}{\sqrt{2\pi m k_B T}} = \frac{h}{\sqrt{4\pi m E/(3N)}} , \qquad (20)$$

is the typical de Broglie wavelength at temperature T. The temperature is determined by the energy per particle for a monoatomic gas, $E/N = \frac{3}{2} k_B T$.

Hint: The $\delta E/E$ term is not exponentially large in contrast to the other terms. Thus $\delta E/E$ can be set to one via the following approximation:

$$e^{5N/2} \left(\frac{\delta E}{E} \right) = e^{5N/2 + \log(\delta E/E)} \simeq e^{5N/2} . \qquad (21)$$

Convince yourself of this step by taking $\delta E/E = 10^{-6}$ (or whatever you like). How big is $\log(\delta E/E)$ compared to $5N/2$? Something is exponentially large if its logarithm is of order Avogadro's number.

Discussion: The result for S in Eq. (**??**) is known as the Sackur Tetrode equation and is fundamental. The Sackur-Tetrode equation says that the entropy per particle S/Nk_B is of order the logarithm of the accessible phase space per particle in units of h^3. Roughly speaking each particle has volume $v_N = V/N$. The *typical* momentum of a particle is of order $p_{\text{typ}} \sim \sqrt{m k_B T}$. The phase space per particle is the coordinate space volume v_N times the momentum space volume $\sim p_{\text{typ}}^3$ and is of order

$$V_{\text{ps}} \sim v_N \, p_{\text{typ}}^3 . \qquad (22)$$

The entropy per particle (divided k_B) is the logarithm of this phase space in units of h^3 and is of order

$$\frac{S}{Nk_B} \sim \log \left(\frac{v_N \, p_{\text{typ}}^3}{h^3} \right) \sim \log \left(\frac{v_N}{\lambda_{\text{th}}^3} \right) . \qquad (23)$$

This logarithm is never very large (at most 10), and in practice the entropy per particle is an order one number.

(e) Recall that "Normal Temperature and Pressure" (NTP) is a temperature of $T^\ominus \equiv 298\,^\circ\text{K}$ and $p^\ominus \equiv 1\,\text{bar}$. Show that the entropy per particle is

$$\frac{S}{Nk_B} \simeq 13.1 - \ln(p/p^\ominus) + \frac{5}{2} \ln(T/T^\ominus) + \frac{3}{2} \ln(m/m_H) \qquad (24)$$

Here m_H is the mass of a hydrogen atom and $13.1 = 10.6 + 5/2$. *Hint:* What is the entropy of Hydrogen gas at NTP?

 (i) Use the result to evaluate the entropy per particle S/Nk_B of Argon at $200\,^\circ\text{C}$ and two bars of pressure? (Ans: 19.3)
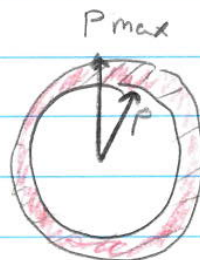
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Phase Space

a) $\qquad V_{PS} = \int d^3r \, d^3p = V \int d^3p$

$\qquad\qquad\qquad\quad [E, E+\delta E] \qquad\qquad$ shell with energy
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ in range $[E, E+\delta E]$

$\qquad\qquad = V \, 4\pi p^2 \, \delta p$

Then

$\qquad\qquad\qquad P = \sqrt{2mE}$

See
lecture! $\qquad P_{max} = \sqrt{2m(E+\delta E)}$

$\delta p = P_{max} - P = \sqrt{2mE}\left(1 + \delta E/E\right)^{1/2} - \sqrt{2mE}$

$\qquad\qquad\qquad \simeq \sqrt{2mE}\left(1 + \dfrac{1}{2}\dfrac{\delta E}{E}\right) - \sqrt{2mE}$

$\qquad\qquad \delta p = P \dfrac{\delta E}{2E} \qquad i.e. \qquad \dfrac{\delta p}{P} = \dfrac{\delta E}{2E}$

So

$$\boxed{V_{PS} = V \, 4\pi p^3 \, \dfrac{\delta E}{2E} = V\left[4\pi (2mE)^{3/2} \, \dfrac{\delta E}{2E}\right]}$$

b) Then

$$\Omega(E,V) = \frac{1}{2!} \int \frac{d^3r_1 \, d^3p_1}{h^3} \frac{d^3r_2 \, d^3p_2}{h^3}$$

$$= \frac{V^2}{2!} \underbrace{\int_{[E, E+\delta E]} \frac{d^3p_1 \, d^3p_2}{h^6}}_{\text{shell volume}/h^6}$$

The momentum integral is a spherical shell in 6 dimensions
The momentum space volume is:

$$\frac{\text{Shell volume}}{h^6} = \frac{2 \pi^{6/2}}{\Gamma(6/2)} p^5 \frac{\delta p}{h^6}$$

As before

$$\delta p = p \frac{\delta E}{2E}$$

So

$$p = \sqrt{2mE}$$

$$\Omega(E,V) = \frac{V^2}{2!} \frac{2\pi^3}{2!} \left(\frac{p}{h}\right)^6 \frac{\delta E}{2E}$$

$$\boxed{\Omega(E,V) = V^2 \pi^3 \left(\frac{2mE}{h^2}\right)^3 \cdot \frac{\delta E}{4E}}$$

c) Now the general case

$$\Omega(E,V) = \frac{1}{N!} \int \frac{d^3r_1 \, d^3p_1}{h^3} \quad \cdots \quad \frac{d^3r_N \, d^3p_N}{h^3}$$

$$= \left(\frac{V^N}{N!}\right) \int_{[E, E+\delta E]} (d^3p_1 \cdots d^3p_N) / h^{3N}$$

↗ coordinate space

momentum space

shell volume / h^{3N}

So this is again a shell of dimension $3N$

$$\frac{\text{Shell volume}}{h^{3N}} = \cancel{2} \frac{\pi^{3N/2}}{\Gamma(3N/2)} \left(\frac{p}{h}\right)^{3N} \frac{\delta E}{\cancel{2} E}$$

Using $\dfrac{p}{h} = \left(\dfrac{2mE}{h^2}\right)^{1/2}$ we get:

momentum space

$$\Omega(E,V) = \left(\frac{V^N}{N!}\right)\left(\frac{1}{\Gamma(3N/2)} \left(\frac{2\pi m E}{h^2}\right)^{3N/2}\right) \frac{\delta E}{E}$$

↗ coordinate space

d) Writing

$$N! = \left(\frac{N}{e}\right)^N, \quad \Gamma\left(\frac{3N}{2}\right) = \left(\frac{3N}{2e}\right)^{3N/2}$$

We have

$$\Omega(E,V) = \left[e^N \left(\frac{V}{N} \right)^N \right] \cdot \left[e^{3N/2} \left(\frac{4\pi m E}{3 N h^2} \right)^{3N/2} \right] \frac{\delta E}{E}$$

Taking the log of this expression, and dropping the $\delta E/E$ term, we have

$$S = k \ln \Omega$$

$$S = k \left[\frac{5N}{2} + N \ln \frac{V}{N} + N \ln \left(\frac{4\pi m E}{3 N h^2} \right)^{3/2} \right]$$

The term:
$$\left(\frac{4\pi m E}{N h^2} \right)^{3/2} = \left(\frac{2\pi m kT}{h^2} \right)^{3/2} = \left(\frac{1}{\lambda_{th}^2} \right)^{3/2} = \frac{1}{\lambda_{th}^3}$$

Where we used $\frac{E}{N} = \frac{3}{2} kT$

So finally

$$S = Nk \left[\ln \left(\frac{V_N}{\lambda_{th}^3} \right) + \frac{5}{2} \right]$$

↖ we will derive this in other ways as the course progresses. Here we have derived it from the microcanonical ensemble. Later we will derive it from the canonical ensemble.

Problem 2.   Entropy changes of a MAIG

Find the change in entropy of n_{ml} moles of an ideal monoatomic ideal gas in the following processes:

   (a) the temperature changes from T_1 to T_2 at constant pressure;

   (b) the pressure changes from P_1 to P_2 at constant volume.

Consider the expression for the number of states in a mono-atomic ideal gas

$$\Omega = C(N)V^N E^{3N/2} \,, \tag{25}$$

and the corresponding entropy

$$S = Nk_B \log(V) + \frac{3}{2}Nk_B \log(E) + \mathrm{const} \,. \tag{26}$$

Recall that in an adiabatic expansion of a monoatomic ideal gas no heat enters or exits the system and the entropy remains constant as the volume increases.

   (c)   (i) Using Eq. (??) show that $\Delta S = 0$ for an adiabatic increase in volume from V_1 to V_2. (*Hint:* How does the temperature change during an adiabatic expansion of a mono-atomic ideal gas?)

   (ii) Describe how the particles are redistributed in phase space so that the entropy and total phase space volume remains constant during the expansion.

Ans: (a) $\frac{5}{2}n_{\mathrm{ml}}R\ln(T_2/T_1)$; (b) $\frac{3}{2}n_{\mathrm{ml}}R\ln(P_2/P_1)$.

Entropy Changes of Ideal Gas

This is the entropy of a MAIG, which we derived. We will use this in this problem

(☆) $$S = Nk \ln V + \frac{3Nk}{2} \ln E + const$$

a) $PV = NkT$, so for P const, $\dfrac{V_1}{V_2} = \dfrac{T_1}{T_2} = \dfrac{E_1}{E_2}$

Since $E = \dfrac{3}{2} NkT \propto T$,

So

$$\Delta S = S_2 - S_1$$

$$= Nk \ln \frac{V_2}{V_1} + \frac{3Nk}{2} \ln \frac{E_2}{E_1}$$

$$= Nk \ln \frac{T_2}{T_1} + \frac{3}{2} Nk \ln \frac{T_2}{T_1}$$

$$\boxed{\Delta S = \frac{5}{2} Nk \ln \frac{T_2}{T_1}}$$

b) $$\Delta S = S_2 - S_1$$

constant volum

$$= Nk \ln \frac{V_2}{V_1} + \frac{3}{2} Nk \ln \frac{E_2}{E_1} \quad now \quad PV = NkT$$

$$P \propto T \propto E$$

So

$$\Delta S = \frac{3}{2} Nk \ln \left(\frac{P_2}{P_1} \right)$$

c) Now for an adiabatic expansion

$$TV^{\gamma - 1} = \text{const} \qquad \text{this is for a MAIG}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \qquad \text{where} \quad \gamma = \frac{5}{3}$$

or

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{2/3}$$

$$\frac{E_2}{E_1} = \frac{T_2}{T_1} = \left(\frac{V_2}{V_1} \right)^{-2/3}$$

So

$$\Delta S = Nk \ln \frac{V_2}{V_1} + \frac{3}{2} Nk \ln \frac{T_2}{T_1}$$

(i)
$$= Nk \ln \frac{V_2}{V_1} + \frac{3}{2} Nk \ln \left(\frac{V_2}{V_1} \right)^{-2/3} = 0$$

(ii) The coordinate space volume is getting bigger, but the momentum space volume is getting smaller as the temperature drops. We have
$$EV^{3/2} = \text{const} \quad \text{during the adiab expansion of a MAIG.}$$

Problem 3. Ball in lake

In this problem we will explore examine the fundamental formula:

$$\Delta S_{AB} = \int_A^B \frac{dQ_{\text{rev}}}{T} \geq \int_A^B \frac{dQ}{T} . \tag{27}$$

In this equation are considering a system (a ball) placed in contact with a reservoir at temperature T with heat exchange dQ.

(a) A cool ball of iron with initial temperature T_B^0 and constant specific heat C is thrown into a large hot reservoir of water at temperature T, which may be presumed constant. The subsequent equilibration between the system and reservoir is a highly non-equilibrium and irreversible process. How much heat goes from the reservoir to the system as the reservoir and the system equilibrate? What was the change in entropy of the reservoir ?

(b) You can compute the change in entropy of the ball ΔS in the non-equilibrium process by replacing the non-equilibrium process (which actually happened) with an imagined equilibrium process. This replacement is possible because the entropy change depends only on the starting and stopping points and not on the path.

In the imagined process the temperature of the ball T_B is slowly raised from T_B^0 to T by a set of small incremental heat transfers $dQ_{\text{rev}} = CdT_B$ with a sequence of imagined reservoirs with temperatures between T_B^0 and T.

  (i) Find ΔS.

  (ii) Sketch ΔS and Q/T as a function of

$$\frac{\Delta T}{T} \equiv \frac{T - T_B^0}{T}.$$

on the same graph for $\Delta T/T \in [-1, 1]$. Does your graph corroborate the inequality $\Delta S \geq Q/T$?

  (iii) Make a Taylor series of ΔS to show that for small $\Delta T/T$

$$\Delta S = \frac{Q}{T} + \frac{C\Delta T^2}{2T^2} > \frac{Q}{T} \tag{28}$$

What is the change in entropy of the ball, reservoir, and the universe for small ΔT?

Discussion: From this problem we see that $\Delta S = Q/T + \mathcal{O}((\Delta T)^2)$. Thus we find that $dS = dQ/T$ is valid in equilibrium and to linear order in temperature gradients. Correction arise at quadratic order in ΔT.

Ball and Lake

a) $Q = C(T - T_B^0)$

b) $\Delta S = \int_{T_B^0}^{T} \dfrac{C \, dT_B}{T_B}$

(i) $\Delta S = C \ln \dfrac{T}{T_B^0}$

(ii) Now

$$\Delta S = C \ln \dfrac{T}{T_B^0} = -C \ln \dfrac{T_B^0}{T} = C \ln \left(1 - \dfrac{T - T_B^0}{T} \right)$$
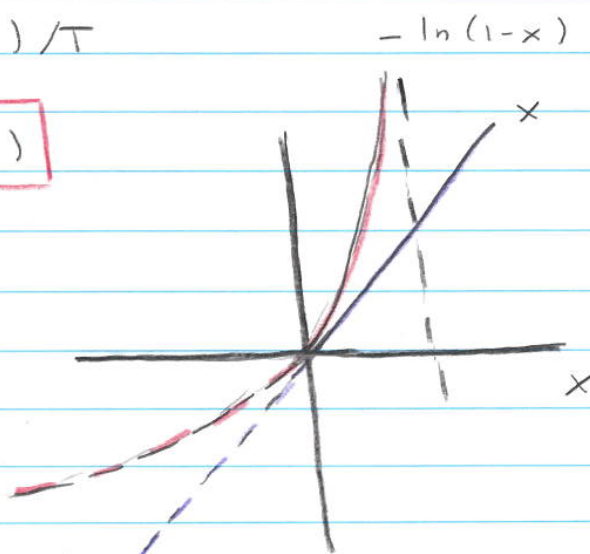
$$\dfrac{Q}{T} = \dfrac{C(T - T_B^0)}{T}$$

So define $x \equiv (T - T_B^0)/T$

$$\boxed{\Delta S = -C \ln(1 - x)}$$

$$\boxed{\dfrac{Q}{T} = C x}$$

So $\Delta S > \dfrac{Q}{T}$

as is clear from graph

iii) For small x

$$-\ln(1-x) \simeq -\left(-x - \frac{(-x)^2}{2}\right)$$

$$\simeq x + \frac{x^2}{2}$$

So

$$\Delta S \simeq C\frac{\Delta T}{T} + \frac{C}{2}\left(\frac{\Delta T}{T}\right)^2 = \frac{Q}{T} + \frac{C\Delta T^2}{2T^2} > \frac{Q}{T}$$

$$\frac{Q}{T} = C\frac{\Delta T}{T}$$

Problem 4. Entropy change in the mixing of hot and cold gasses

$$
\boxed{\begin{array}{c|c} N_1, T_1 & N_2, T_2 \\[1ex] \text{He} & \text{Ar} \end{array}}
$$

Consider two mono-atomic ideal gasses, Helium and Argon, separated by a divider which partitions a container of volume V into two equal parts. There are N_1 Helium atoms on the left of the divider, and N_2 Argon atoms on the right of the divider. The Helium atoms are initially at a temperature of T_1, while the Argon atoms are initially at a temperature of T_2. After the dividing wall is removed, the two gasses mix and ultimately equilibrate.

(a) Determine the final temperature of the system.

(b) Determine the change in entropy of the system resulting from the mixing process in two ways:

   (i) Directly count the number of states at the beginning and end.

   (ii) Calculate the change in entropy by identifying an equilibrium path connecting the state at the beginning and the state at the end and using thermodynamics. Explain how the example illustrates the formula the formula

$$
\Delta S = \int \frac{dQ_{\text{rev}}}{T} > \frac{Q}{T} \tag{29}
$$

Entropy change in the mixing of Hot & Cold Gasses

(a)   Energy is conserved and the gasses ultimately
                                              have the same temperature.

$$E_1 + E_2 = E$$

$$\frac{3}{2} N_1 k T_1 + \frac{3}{2} N_2 k T_2 = \frac{3}{2} (N_1 + N_2) k T$$

$$\frac{N_1 T_1 + N_2 T_2}{(N_1 + N_2)} = T$$

b)   The entropy of Each Gas is

$$S = Nk \ln V + \frac{3}{2} Nk \ln E + cast$$

$$\left.\begin{array}{c}\\\\\end{array}\right\} E \propto T$$

$$S = Nk \ln V + \frac{3}{2} Nk \ln T + const$$

↖ a different constant

So

$$\Delta S = Nk \ln \frac{V_f}{V_i} + \frac{3}{2} Nk \ln T_f / T_i$$

Here we have two gasses :

$$\frac{V_f}{V_i} = \frac{V}{V/2} = 2 \qquad \frac{T_f}{T_i} = \frac{T}{T_1} \quad \text{for gas \#1}$$

$$\frac{T_f}{T_i} = \frac{T}{T_2} \quad \text{for gas \#2}$$

So

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$\Delta S = (N_1 + N_2) k \ln 2 \;+\; \frac{3}{2} N_1 k \ln \frac{T}{T_1} + \frac{3}{2} N_2 k \ln \frac{T}{T_2}$$

The thermodynamic argument for the change in entropy (just found) goes as follows. Take gas 1. It's initial state and final states are

$$(T_1, V_1 = \frac{V}{2}) \to (T_f, V) \tag{30}$$

Since entropy only depends on the state, and not on how you got there, we can pick any convenient equilibrium path to get from the initial state to the final state. The actual system did not follow this path. Then we can evaluate the entropy change using

$$dS = \frac{dQ_{\text{rev}}}{T} . \tag{31}$$

This formula assumes the system is in equilibrium with a reservoir at temperature T, which was not the case here. Here no heat flowed from the environment to the system. The initial and final states of gas 2 are

$$(T_2, V_2 = \frac{V}{2}) \to (T_f, V) \tag{32}$$

A convenient choice of path is: (*Step 1*) first leave the volume constant and increase the temperature; (*Step 2*) then leave the temperature fixed and increase the volume.

Step 1: In the first step the work done is zero since volume is constant. So $dQ_{\text{rev}} = C_V \, dT$ where $C_V = (3/2)N_1 k$ is the specific heat of a MAIG. Thus for gas number 1 in step 1 we have:

$$\Delta S_{1,1} = \int C_V \frac{dT}{T} = C_V \ln(T_f/T_i) = \frac{3}{2} N_1 k \ln(T_f/T_1) \tag{33}$$

Similarly for gas number 2 in step 1 one we have:

$$\Delta S_{2,1} = \frac{3}{2} N_2 k \ln(T_f/T_2) \tag{34}$$

Step 2: Then in the second step the temperature is constant, but the volume increases. The energy is also constant, since for an ideal gas the energy is only a function of temperature, which is constant. So, in the second step $dU = 0$ and $dQ_{\text{rev}} = p_1 \, dV$ by the first law ($dU = dQ - pdV$). Thus we find

$$\Delta S_{1,2} = \int \frac{dQ_{\text{rev}}}{T} = \int_{V_1}^{V} \frac{p_1}{T} dV = N_1 k \ln(2) \tag{35}$$

Similarly, for gas number 2 in step 2

$$\Delta S_{2,2} = N_2 k \ln(2) \tag{36}$$

Putting together the contributions, we find:

$$\Delta S = \Delta S_{1,1} + \Delta S_{2,1} + \Delta S_{1,2} + \Delta S_{2,2} \tag{37}$$

$$= (N_1 + N_2)k \ln(2) + \frac{3}{2} N_1 k \ln(T_f/T_1) + \frac{3}{2} N_2 k \ln(T_f/T_2) \tag{38}$$

which agrees with the previous method.

Discussion: In each step, we assumed that gas 1 and gas 2 were in equilibrated contact with a reservoir at temperature T. This approach is valid (although not reality) because we are using these fictitious reservoir to find the change in entropy of the system, which only depends on the initial and final states, which are in complete equilibrium. But, it must be understood that in reality no heat is exchanged with the environment and $dQ = 0$. In general the change in entropy of the system (which can be computed by assuming a reversible exchange of heat with a reservoir) is larger than the actual heat that flows into the system from a reservoir at temperature T:

$$\Delta S = \int \frac{dQ_{\mathrm{rev}}}{T} > \frac{Q}{T} \tag{39}$$

In this specific problem $Q = 0$ and we found

$$\Delta S = \int \frac{dQ_{\mathrm{rev}}}{T} = (N_1 + N_2)k\ln(2) + \frac{3}{2}N_1 k\ln(T_f/T_1) + \frac{3}{2}N_2 k\ln(T_f/T_2) > 0 \tag{40}$$

Clearly $\Delta S > 0$ and the process is irreversible.