We will discuss basic thermodynamics, especially entropy change due to irreversible and mixing processes.

1 [Drinking bird]\(^1\)
Estimate the efficiency of the ‘drinking bird’ toy. Assume that the room temperature is 300 K and the liquid in the bird is dichloromethane CH\(_2\)Cl\(_2\) (boiling point is about 40 °C, density = 1.33 g/cm\(^3\)). The humidity of the room may be around 50%.

![Figure DH6.1: How diligent is the birdy?](image)

Soln.
The upper limit is given by Carnot’s theorem. The bird works between the room temperature \(T_H = 300\) K and the temperature of the cooled head \(T_L\), which may be 10 K lower than the room temperature. Let us assume \(T_L = 290\) K.

\[
\eta \simeq 1 - \frac{290}{300} = \frac{1}{30}.
\]  
(DH6.1)

This is probably too good for the actual bird, because the cooled liquid is mixed with the hot bottom liquid at every drinking (like the Newcomen engine). Thus, the effective heat bath temperatures are perhaps 292 - 298 K:

\[
\eta = 1 - \frac{292}{298} \simeq \frac{1}{50}.
\]  
(DH6.2)

In any case the ‘ideal’ efficiency is of order 1%.

How can we actually measure it? The amount of heat going through the system may be estimated from the amount of water evaporated from the head. The work actually produced may be obtained from the volume of the dichloromethane (1.333 g/cm\(^3\)) liquid column pushed up in one cycle: 2 cm\(^3\) for 1.5 cm per 15 sec (= period). 20 cm\(^3\) of water (\(\Delta H = 2\) J/g) is gone over 12 hrs. This seems to give about 2% (too good, perhaps). If you search a paper, there is at least one relevant, which measured ‘the actual value’ of 10\(^{-2}\)% (but I do not trust it very much).
2 [Explosion in a box] = Q11.2
Inside a thermally insulated (i.e., adiabatic) empty (i.e., vacuum) box of volume $10V$ is a small can of volume $V$ containing one mole of an ideal gas at temperature $T$. The can is punctured and the gas escapes to a larger box and eventually reaches a new equilibrium state (see Fig. DH6.2).

![Figure DH6.2: Initially, the can is filled with a gas (Left) and is inside a vacuum box of volume $10V$. Then, it is punctured and the gas escapes to reach the final equilibrium state (Right).](image)

(1) What is the change of the total internal energy of the system due to puncturing the can?
(2) What is the total entropy change due to puncturing the can?
(3) What happens if the hole in the can is extremely small and only one molecule at a time can escape the can?

**Soln.**
(1) No heat nor work is exchanged with the outside world, so $\Delta E = 0$. Since our gas is ideal, this implies that the temperature (when definable) is invariant.

(2) We may use the equation of state $S = S(E, V)$:

$$S(E, V) = C_V \log E + R \log V + \text{constant.}$$  \hspace{1cm} (DH6.3)

Thus,

$$\Delta S = R \log(V_F/V_0) = R \log 10.$$

(3) No change, because $\Delta E = 0$ does not change, and the final state does not change, so whatever the process is as long as the system is energetically isolated, the result cannot change. However, you might be suspicious. Let us actually compute the entropy change along the extreme-slow leak process.

This is very slow but not a quasistatic process (recall a hot coffee in a thermos). Actually, if we pay attention to a small portion $\delta N'$ of the gas going out from the can into the box, the process is patently an irreversible expansion. The volumes and pressures of the remaining bulk gases change, but the temperatures do not change and the pressure changes are due to reversible mechanical work by the leaking gas, so for the bulk gases as a compound system the net change is adiabatic and reversible; no net entropy changes there. Thus, entropy increases is solely due to this small leakage. This increase may be computed, and after integrating all these infinitesimal increases $\delta S$ of entropy, we could get exactly the same
result (as demonstrated below).

Let us follow the very slow process just described. Suppose $N'$ molecules have already leaked out from the can (assume that the leakage is very slow, so the can and the box are almost in equilibrium separately\(^1\)). Then, the can pressure is $P = (N - N')k_B T/V$. Let $\delta N'$ be the further small amount of leak from the can. Before going out of the can, this portion $\delta N'$ occupies the volume (note that $N - N'$ molecules still occupy the volume $V$ of the can)

\[
\delta V_i = \frac{\delta N'}{N - N'} V
\]

in the can. The pressure in the outer box is $P = N'k_B T/9V$, so the escaping molecules $\delta N'$ occupy the volume

\[
\delta V_f = \frac{\delta N'}{N'} 9V.
\]

That is, the leaked $\delta N'$ changes its volume from $\delta V_i$ to $\delta V_f$. Therefore, the entropy increase due to this escape is (notice that the amount of molecules going out is $\delta N'$)

\[
\delta S = k_B \delta N' \log \frac{\delta V_f}{\delta V_i} = k_B \delta N' \log \frac{9(N - N')}{N'}.
\]

We should integrate this from 0 to $9N/10$ ($N/10$ remaining in the can):

\[
\Delta S = \int_0^{9N/10} dN' k_B \log \frac{9(N - N')}{N'} = Nk_B \log 10,
\]

the same answer.

3 [Irreversible expansion]
A rigid cylinder is initially separated by a piston held at location P initially as in Fig. DH6.3. Both the compartments contain one mole of identical ideal gases.

![Figure DH6.3](image_url)

Figure DH6.3: Left: the initial state; Right: the final state.

In the following no numerical calculation is required.
(1) Assume that the cylinder and the piston is diathermal, and the ambient temperature is

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\(^1\)Remember that a quasistatic process is a chain of equilibrium states. If only the can or the box is considered, the process for each system is quasistatic, but as a compound system it is never in equilibrium, so it is not a quasistatic process for the whole system.
held at $T$. You may assume $T_1 = T_2 = T$. The piston is suddenly allowed to move freely.

(i) What is the final state of the system (That is, what are $V'$ and $P'$ in terms of $T$)?

(ii) What is the entropy change?

Soln.
Notice that thanks to the constraint holding the piston at $P$, the whole system is in equilibrium (as a compound system) initially. When this constraint is removed, the system is no more in equilibrium, so no thermodynamic quantities are well defined, but eventually the system reaches a new equilibrium and all the thermodynamic quantities are again well defined. To calculate the change in any state function, you can use any path connecting the initial and the final states in the thermodynamic space.

(i) Obviously $V' = 5V/2$. Therefore,

$$V'P' = RT$$  \hfill (DH6.8)

implies

$$P' = \frac{RT}{V'} = \frac{2RT}{5V}.$$  \hfill (DH6.9)

(ii) On the left-hand side the volume is changed from $4V$ to $5V/2$, but $E$ does not change, because there is no $T$ change. On the right-hand side the volume is changed from $V$ to $5V/2$.

Since entropy is a state function, we may apply

$$\Delta S = S(E_2, V_2) - S(E_1, V_1) = nC_V \log \frac{E_2}{E_1} + nR \log \frac{V_2}{V_1}$$  \hfill (DH6.10)

to each side separately. We have

$$\Delta S_L = R \log (5/8), \quad \Delta S_R = R \log (5/2).$$  \hfill (DH6.11)

Therefore,

$$\Delta S = \Delta S_L + \Delta S_R = R \log (25/16).$$  \hfill (DH6.12)

(2) Assume that the cylinder is adiabatic and the piston is diathermal. The temperatures are initially different, $T_1$ on the left-hand side and $T_2$ on the right-hand side. The piston is suddenly allowed to move freely as in (1).

(i) What is the final state of the system (That is, what are $V'$ and $P'$ in terms of $T_1$, $T_2$ and $V$)? You may assume the gas is a monatomic gas.

(ii) What is the entropy change?

(iii)* Which entropy change is larger, case (1) or case (2)? Is the answer obvious?

Soln.
(i) The initial total internal energy is ($C_V = 3R/2$)

$$E = C_V T_1 + C_V T_2.$$  \hfill (DH6.13)
Notice that this is invariant, because no work nor heat is added to or extracted from the system. Therefore, we get the final temperature \( T' \) as

\[
T' = \frac{T_1 + T_2}{2}. \tag{DH6.14}
\]

This should be obvious from symmetry.

After equilibration the pressures of the compartments are identical \( P' \). Also the temperatures must be identical, so the volumes are both \( 5V/2 \). Therefore,

\[
(5/2)VP' = RT' \tag{DH6.15}
\]

or

\[
P' = \frac{2RT'}{5V} = \frac{R(T_1 + T_2)}{5V}. \tag{DH6.16}
\]

(ii) The entropy change may be calculated just as in (1), but we must pay attention to the temperature change that causes the change in \( E \).

On the left-hand side the internal energy changes from \( T_1C_V \) to \( T'C_V \). Thus,

\[
\frac{E'_1}{E_1} = \frac{T'}{T_1} = \frac{T_1 + T_2}{2T_1}. \tag{DH6.17}
\]

Therefore,

\[
\Delta S_L = C_V \log \frac{T_1 + T_2}{2T_1} + R \log(5/8). \tag{DH6.18}
\]

Analogously, we have

\[
\Delta S_R = C_V \log \frac{T_1 + T_2}{2T_2} + R \log(5/2). \tag{DH6.19}
\]

Therefore,

\[
\Delta S = \Delta S_L + \Delta S_R = 2C_V \log \frac{T_1 + T_2}{2\sqrt{T_1T_2}} + R \log(25/16). \tag{DH6.20}
\]

(cf 10.10 for the temperature contribution to \( \Delta S \) or the significance of \( \sqrt{T_1T_2} \).)

(iii) \( \Delta S \) for (2) is always larger than that for (1) as long as \( T_1 \neq T_2 \), because \((x + y)/2 \geq \sqrt{xy}\) (for nonnegative \( x \) and \( y \); prove it\(^2\)). It should be obvious without any calculation, since more difference is eliminated in (2) than in (1).

(3)* The same as (2) but this time the piston is also adiabatic. What can you say about the final state?

**Soln.**

To determine the final state, we can use the conservation of \( E \), (DH6.13). Thus we have

\[
T_1 + T_2 = T'_1 + T'_2 \tag{DH6.21}
\]

\(^2\)Using the convexity of \(-\log x\) is the best as shown in Fig. 10.10.
The final pressures must be identical on both sides. Thus,

\[ P'V' = RT_1', \quad P'(5V - V') = RT_2' \]  

(DH6.22)

or

\[ 5VP = R(T_1 + T_2). \]  

(DH6.23)

Thus, \( P \) is determined, but, unfortunately, we cannot claim \( V' = 5V/2 \), because we cannot know \( T_1' \). Thus, we cannot go further, thermodynamically. Thus, thermodynamically there is no definite prediction.

It is not hard to understand that the final outcome depends on the details such as how the heat generated by the friction of the piston against the cylinder wall is distributed to each compartment. That is why we cannot know the final temperatures without further information.

Those who did not really understand thermodynamics wrote papers to remove this ‘defect’ from thermal physics. You must recognize that the conclusion that there is no definite outcome is a prediction of thermodynamics; you must respect it. This uncertainty is NOT the weakness of thermodynamics; on the contrary it reinforces how powerful and reliable thermodynamics is.

4 [Mixing two chemically distinct ideal gases]³

(1) Assume that the system is, as a whole, adiabatic. Initially, the left-hand half (volume \( V \)) contains one mole of a monatomic ideal gas A (red) at temperature \( T \) and the right-hand half (volume \( V \)) contains two moles of monatomic ideal gas B (green) at temperature \( 2T \) (Fig. DH6.4). After the separating wall is removed, eventually, the system reaches a new uniform equilibrium state.

(i) Find the final temperature \( T_F \) and pressure \( P_F \).

(ii) What is the entropy increase?

![Figure DH6.4: The mixing process of one + two mole distinct gases.](See the figure posted as a supplement to Lect 12 associated with the examples discussed in the lecture.)

\[ E = C_V T + 2C_V 	imes 2T = 5C_V T = 3C_V T_F. \]  

(DH6.24)

Thus, the final temperature is \( T_F = (5/3)T \). As to the pressure, mixture or not does not matter; what matters is the total number of particles. Thus the final pressure must satisfy

\[ P_F(2V) = 3RT_F = 5RT. \]  

(DH6.25)
That is, \( P_F = \frac{5RT}{2V} \).

(ii) To find the entropy change we must find a quasistatic process that can connect the initial and the final states. Thus, we invent a process illustrated in Fig. DH6.5:

\[
\begin{align*}
\Delta S_{\text{red}} &= C_V \log \frac{5}{3} + R \log 2. \\
\Delta S_{\text{green}} &= 2C_V \log \frac{5}{6} + 2R \log 2.
\end{align*}
\]  

(DH6.26) (DH6.27)

Therefore, the total entropy change is

\[
\Delta S = C_V \log \frac{125}{108} + R \log 8.
\]  

(DH6.28)

(2) Suppose the two gasses are indistinguishable. What is \( \Delta S \)?

That is, on the left-hand side is 1 mole and the right 2 moles of identical gases. Although the volumes are identical \( (V) \), initially, the right-hand side has temperature \( 2T \) and the left \( T \). The membrane is broken and eventually the system reaches a uniform equilibrium state. Assume that the system is, as a whole, adiabatic. What is \( \Delta S \)?

(*) Can you understand the difference in \( \Delta S \) for (1) and (2) intuitively?
Soln.
To find the final state $T$ and $P$, there is no difference from (1): Since the internal energy must be conserved:

$$E = C_V T + 2C_V \times 2T = 5C_V T = 3C_V T_F.$$  \hfill (DH6.29)

Thus, $T_F = (5/3)T$. The final pressure must satisfy

$$P_F (2V) = 3RT_F = 5RT.$$  \hfill (DH6.30)

That is, $P_F = 5RT/2V$.

To find the entropy change we must find a quasistatic process that can connect the initial and the final states. Thus, we invent a process illustrated in Fig. DH6.7:

![Figure DH6.7](image)

Figure DH6.7: From each side we prepare the state with temperature $T_F$ and pressure $P_F$ with the same number densities. The last joining step does not cause any thermodynamic change.

After the processes denoted by the color arrows we prepare the gases with the same temperatures $T_F$ and pressures $P_F$. The mole ratio is 1:2, so the volume ratio of the final states is also 1:2. Then, we join these two. At this final step there is no entropy change, so we have only to compute the entropy change along the colored arrows.

For the left-hand side along the blue arrow the volume changes from $V$ to $2V/3$, and the temperature changes from $T$ to $T_F = 5T/3$. Therefore,

$$\Delta S_L = C_V \log \frac{5}{3} + R \log \frac{2}{3}. \hfill (DH6.31)$$

For the right-hand side along the green arrow the volume changes from $V$ to $4V/3$, and the temperature changes from $2T$ to $T_F = 5T/3$. Therefore, (there are 2 moles!)

$$\Delta S_R = 2C_V \log \frac{5}{6} + 2R \log \frac{4}{3}. \hfill (DH6.32)$$

Therefore,

$$\Delta S = C_V \log \frac{125}{108} + R \log \frac{32}{27}. \hfill (DH6.33)$$

As you see the energetic contribution is the same as before (since energy is ‘color-blind’). The entropy difference is

$$\Delta S_{mix} - \Delta S_{pure} = R \log \frac{8 \times 27}{32} = R \log \frac{27}{4}. \hfill (DH6.34)$$
Can we understand this intuitively? Yes. The difference is just the mixing entropy we can understand information theoretically: do not forget there are 3 moles of particles.

\[
\Delta S_{\text{inf}} = -3R \times \left( \frac{1}{3} \log \frac{1}{3} + \frac{2}{3} \log \frac{2}{3} \right) = -R \log \frac{1}{3} - 2R \log \frac{2}{3} = R \log \frac{27}{4}.
\] (DH6.35)

5 [Mixing and irreversibility]
Suppose mixing process is reversible. Then, show that we can violate Thomson’s principle (i.e., we can do work with a single heat source).

Soln.
Through isothermally expanding the red and green gases separately (cf. the solution to 4), we can take out work from each process. Now we merge (superpose) the two gases reversibly without any work nor exchange of heat. Then, we can reversibly and adiabatically demix the mixture to go back to the original state. Thus, cyclically the heat taken from a uniform-temperature environment can be converted to work, violating Thomson.

[Comment] The question is often asked in the following manner: Suppose there is no increase of entropy due to mixing. ⋯. Unfortunately thermodynamics cannot tell us whether this process with \( \Delta S = 0 \) can be actually performed or not, so strictly speaking we cannot say anything conclusive. I must hastily add, however, that according to our experience, we can always ingenuously devise such a process. “All the thermodynamically allowed processes are realizable” is, strictly speaking, an extra principle.

6 [Equation of state and entropy]
As we have learned, thermodynamics cannot give you any ‘concrete information’ (e.g., equations of state) for any system. These must be obtained experimentally or by microscopic modeling with the aid of statistical mechanics. Still, after determining the thermodynamic equation of state such as entropy as a function of thermodynamic coordinates, we can know every macroscopic thermal properties of the system. This is the reason why thermodynamics is emphasized in practice.

(1) For one mole of pure substance the following two relations have been empirically obtained:

\[
T = cE^{2/3}/V^{1/2},
\]
\[
P \propto E/V,
\]

where \( c \) is a positive constant.

(i) Write down the corresponding equations for \( N \) moles of the same substance.
(ii) Find the entropy as a function of the thermodynamic coordinates \( E, V, N \) and \( c \).

Soln.
(i) Thermodynamic variables are extensive or intensive (the fourth law), so \( E \) in the above
equation is actually $E/N$, and $V/N$. Therefore,

\[ T = c(E/N)^{2/3}/(V/N)^{1/2} = cE^{2/3}/V^{1/2}N^{1/6}, \quad \text{(DH6.38)} \]
\[ P = aE/V, \quad \text{(DH6.39)} \]

where we write the proportionality relation as an equality with a multiplicative constant $a$, which we must fix eventually. Notice that $T$ is indeed intensive (check this by doubling the system size).

(ii) The Gibbs relation for entropy reads

\[ dS = \frac{1}{T} dE + \frac{P}{T} dV \quad \text{(DH6.40)} \]

Therefore,

\[ dS = \frac{V^{1/2}N^{1/6}}{cE^{2/3}} dE + \frac{aE^{1/3}N^{1/6}}{cV^{1/2}} dV = \frac{1}{c} V^{1/2}N^{1/6} E^{-2/3} dE + \frac{a}{c} E^{1/3}N^{1/6} V^{-1/2} dV. \quad \text{(DH6.41)} \]

Let us integrate this from $(E_0, V_0)$ to $(E, V)$. Since $dS$ is exact, we can choose any integration path. Let us use $(E_0, V_0) \rightarrow (E, V_0) \rightarrow (E, V)$:

\[ S(E,V) - S(E_0,V_0) = \frac{3}{c} V_0^{1/2}N_0^{1/6} (E^{1/3} - E_0^{1/3}) + \frac{2a}{c} E^{1/3}N^{1/6} (V^{1/2} - V_0^{1/2}) \quad \text{(DH6.42)} \]

The result should not depend on the mid point location $(E, V_0)$. This implies that $2a = 3$. Thus,

\[ S(E,V) - S(E_0,V_0) = \frac{3}{c} (E^{1/3}N^{1/6} V^{1/2} - V_0^{1/2}N_0^{1/6} E_0^{1/3}). \quad \text{(DH6.43)} \]

$a$ may be determined before integration from the closedness of $dS$ as well:

\[ \frac{1}{2c} V^{-1/2}N^{1/6} E^{-2/3} = \frac{a}{3c} E^{-2/3}N^{1/6} V^{-1/2}. \quad \text{(DH6.44)} \]
Homework 6 due 9 am on Mar 5 (Tu), 2019.
Submit to compass2g

You may discuss with your friends AFTER you have made due efforts of your own to solve the problems. I trust you. I wish you to fully understand the solutions when you submit your homeworks (and get the full credit).

No solution without your justification will get any credit.

1 [Heat pump]
We could import heat from the external world (outdoors) into a room to warm it up. The set up of the analysis is always the same, Fig. DH6.8:

![Heat pump diagram](image)

Figure DH6.8: Heat pump operation requires: $Q_L > 0$, $W > 0$ and $Q_H < 0$.

$W$ is what we invest, and $|Q_H|$ is our gain, so $|Q_H|/W$ is called the coefficient of performance. If the room temperature $T_H = 298$ K and the low-temperature heat source is the $T_L = 288$ K underground device, what is the limit of the coefficient of performance?

2 [Explosion in a cylinder with a piston]
Inside a thermally insulated (i.e., adiabatic) empty (i.e., vacuum) cylinder of volume $10V$ is a small can of volume $V$ containing one mole of an ideal gas at temperature $15T$. The one wall of the cylinder can move outward (see Fig. DH6.9; assume that the piston is frictionless), if the internal pressure is higher than the external one which is $P_{ex} = RT/V$. The can is punctured and the gas escapes and eventually reaches a new equilibrium state (see Fig. DH6.9).

(1) Find the final temperature $T_F$ and the volume $V_F$ of the gas in the cylinder.
(2) What is the total entropy change due to puncturing the can?
3. [General ideal gas]
Experimentally, the internal energy of a gas is volume-independent under constant temperature, and \( PV \) is a function of \( T \) only, say \( PV = \phi(T) \). Show that \( \phi(T) \propto T \). You may use the following Maxwell’s relation
\[
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V,
\]
which we will show in a month.\(^4\)

4 [Mixing diatomic and monatomic gases]
Assume that the system is, as a whole, adiabatic. Initially, the left-hand half (volume \( V \)) contains one mole of a monatomic ideal gas A (red) \( (C_V = 3R/2) \) at temperature \( T \) and the right-hand half (volume \( V \)) contains one mole of diatomic ideal gas B (green) \( (C_V = 5R/2) \) at temperature \( 2T \). After the separating wall is removed, eventually, the system reaches a new uniform equilibrium state as illustrated in Fig. DH6.10.

(1) Find the final temperature \( T_F \) and pressure \( P_F \).
(2) What is the entropy increase? You need not get the numerical answer but may keep \( R \) as a symbol.

\[\text{Figure DH6.10: The mixing process.}\]

\(^4\)You will understand (in Section 17) the following simple algebra:
\[
\left( \frac{\partial S}{\partial V} \right)_T = \frac{\partial(S,T)}{\partial(V,T)} = \frac{\partial(S,T)}{\partial(V,P)} \frac{\partial(V,P)}{\partial(V,T)} = \frac{\partial(V,P)}{\partial(V,T)} = \left( \frac{\partial P}{\partial T} \right)_V.
\]