Discussion 6    Feb 26, 2019

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

1 [Drinking bird]’
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)

2 [Explosion in a box] = Q11.2
Inside a thermally insulated (i.e., adiabatic) empty (i.e., vacuum) box of volume 10$V$ 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 10$V$. 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?
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.

\[
\begin{array}{c|c}
4V & V \\
\hline
P_1 & P_2 \\
\hline
T_1 & T_2 \\
\end{array}
\quad \rightarrow \quad
\begin{array}{c|c}
5V' - V' & V' \\
\hline
P' & P' \\
\hline
T' & T' \\
\end{array}
\]

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 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?

(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?

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

4 [Mixing two chemically distinct ideal gases]\(^1\)
(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?

\(^1\)See the figure posted as a supplement to Lect 12 associated with the examples discussed in the lecture.
Suppose the two gases 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?

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).

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:

\[
T = c E^{2/3} / V^{1/2}, \quad \text{(DH6.1)}
\]

\[
P \propto E / V, \quad \text{(DH6.2)}
\]

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 $c$. 

3
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. DH6.6:

\[
\begin{array}{c}
\text{Figure DH6.6: Heat pump operation requires: } Q_L > 0, \ W > 0 \ \text{and } Q_H < 0. \\
\end{array}
\]

\( W \) 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. DH6.7; 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. DH6.7).

(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.\(^2\)

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. DH6.8.

(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.

\(^2\)You will understand (in Section 17) the following simple algebra:

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial(S,T)}{\partial(V,T)} = \frac{\partial(S,T)}{\partial(V,P)} \frac{\partial(V,P)}{\partial(V,T)} = \frac{\partial(V,P)}{\partial(V,T)} = \left(\frac{\partial P}{\partial T}\right)_V.$$