Chapter 18: Heat, Work, the First Law of Thermodynamics

Thermodynamic systems

- Thermodynamic system
  
  Thermodynamic system is any collection of objects that is convenient to regard as a unit, and that may have the potential to exchange energy with its surroundings.
  
  A process in which there are changes in the state of a thermodynamic system is called a thermodynamic process.

- Signs for heat and work in thermodynamics
  
  \( Q \)  
  \( W \)

  \( Q \) is + if heat is added to system
  
  \( Q \) is − if heat is lost by system
  
  \( W \) is + if work is done by the system.
  
  \( W \) is − if work is done on the system.
Work done during volume changes

- **Work done**

Piston in a cylinder moves by $dl$ due to expansion of gas at pressure $p$

Force on piston: $F = p \cdot A$

Incremental work done:

$$dW = F \cdot dl = p \cdot A \cdot dl = p \cdot dV$$

Total work done:

$$W = \int_{V_i}^{V_f} pdV$$
Work done during volume changes (cont’d)

Work and pV diagram

- Process A → B: If $V_B > V_A$, $W > 0$
- Process B → A: If $V_B > V_A$, $W < 0$
- Process A ↔ B: If $V_A = V_B$, $W = 0$

Work done depends on the path taken.

$$W = \int_{V_A}^{V_B} p\,dV = \text{area under p - V curve}$$
Work done during volume changes (cont’d)

Work and pV diagram (cont’d)

Work done depends on the path taken.

- \( A \rightarrow C \) : \( W = 0 \)
- \( C \rightarrow B \) : \( W = p_B(V_B - V_A) \)
- \( B \rightarrow C \) : \( W = p_B(V_A - V_B) \)
- \( A \rightarrow C \rightarrow B \) : \( W = p_B(V_B - V_A) \)
- \( A \rightarrow D \) : \( W = p_A(V_B - V_A) \)
- \( D \rightarrow B \) : \( W = 0 \)
- \( A \rightarrow D \rightarrow B \) : \( W = p_A(V_B - V_A) \)
Internal energy and the first law of thermodynamics

Internal energy

Tentative definition:
The internal energy $U$ of a system is the sum of the kinetic energies of all of its constituent particles, plus the sum of all the potential energies of interactions among these particles.

The first law of thermodynamics

$$U_2 - U_1 = \Delta U = Q - W$$

Now define the change in internal energy using the first law of thermodynamics.

It is known from experiments that while $Q$ and $W$ depend on the path, $\Delta U$ does not depend on the path.
A cyclic process

: is a process in which the initial and final states are the same.

\[ W_{A \rightarrow B}^{\text{lower}} > 0, \quad W_{B \rightarrow A}^{\text{upper}} < 0, \quad \left| W_{A \rightarrow B}^{\text{lower}} \right| < \left| W_{B \rightarrow A}^{\text{upper}} \right| \]

If the directions of the arrows are reversed, then

\[ W_{A \rightarrow B \rightarrow A} = W_{A \rightarrow B}^{\text{lower}} + W_{B \rightarrow A}^{\text{upper}} < 0 \]

\[ W_{A \rightarrow B \rightarrow A} = W_{A \rightarrow B}^{\text{upper}} + W_{B \rightarrow A}^{\text{lower}} > 0 \]
Internal energy and the first law of thermodynamics

- Infinitesimal changes in state
  
  The first law of thermodynamics:

  \[ dU = dQ - dW \]

  For the system we will discuss, the work \( dW \) is given by \( pdV \)

  \[ dU = dQ - pdV \]
Kinds of thermodynamics process

- **Adiabatic process**
  
  An adiabatic process is defined as one with no heat transfer into or out of a system.
  
  \[ \Delta U = -W, \, Q=0 \]

- **Isobaric process**
  
  An isobaric process is a constant-pressure process.
  
  \[ W = p(V_2-V_1) \, , \, p = \text{constant} \]

- **Isothermal process**
  
  An isothermal process is a constant-temperature process. For a process to be isothermal, any heat flow into or out of the system must occur slowly enough that thermal equilibrium is maintained.
  
  \[ T = \text{constant} \]
Kinds of thermodynamics process (cont’d)

Work done by a gas depends on the path taken in pV space!

- **Isochoric process**

  An isochoric process is a constant-volume process.

\[ W_{A\rightarrow D\rightarrow B} < W_{A\rightarrow B} \]
Kinds of thermodynamics process (cont’d)

- Isothermal vs. adiabatic process

![Diagram showing isochoic, isobaric, and isothermal processes](Image)

- Isochoic: $T_2 < T_a$
- Isobaric: $T_3 > T_a$
- Isothermal: $T_4 = T_a$
- Adiabatic: $T_1 < T_a$

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Work done by expanding gases: path dependence

\[ W = \int_{V_1}^{V_2} p \, dV, \quad p = \frac{nRT}{V} \]

\[ \Rightarrow W = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \left( \frac{V_2}{V_1} \right) \]

Isothermal expansion (1 → 2 on pV diagram) for ideal gas:

\[ W = nRT \ln \left( \frac{V_2}{V_1} \right) \]
Work done by expanding gases: path dependence

Expression for the work done in an *isobaric expansion* of an ideal gas (3 → 2 on pV diagram).

\[ W = p_2(V_2 - V_1) \]
Internal energy of an ideal gas

- **Free expansion**
  - the same initial state
  - the same final state

Controlled expansion
(The temperature is kept constant and the expansion process is done very slowly)
- Work done
- Heat exchanged

Uncontrolled expansion
- = Free expansion
- No work done
- No heat exchanged

Different paths
Internal energy of an ideal gas

Another property of an ideal gas

From experiments it was found that the internal energy of an ideal gas depends only on its temperature, not on its pressure or volume.

However, for non-ideal gas some temperature change occur. The internal energy $U$ is the sum of the kinetic and potential energies for all the particles that make up the system. Non-ideal gas have attractive intermolecular forces. So if the internal energy is constant, the kinetic energies must decrease. Therefore as the temperature is directly related to molecular kinetic energy, for a non-ideal gas a free expansion results in a drop in temperature.
Heat capacities of an ideal gas

- Two kinds of heat capacities
  - $C_V$: molar heat capacity at constant volume  
    easier to measure
  - $C_p$: molar heat capacity at constant pressure

But why is there a difference between these two capacities?

- For a given temperature increase, the internal energy change $\Delta U$ of an ideal gas has the same value no matter what the process.

\[
\begin{align*}
\text{constant-volume (no work)} & : \quad dQ = nC_VdT = dU + dW = dU \quad \Rightarrow \quad dU = nC_VdT \\
\text{constant-pressure} & : \quad dQ = nC_pdT = dU + dW = dU + pdV \\
& \quad \quad \quad \quad \quad \quad pV = nRT \quad \Rightarrow \quad pdV = nRdT; \quad dU = nC_VdT \\
& \quad \quad \quad \quad \quad \quad \Rightarrow \quad nC_pdT = nC_VdT + nRdT
\end{align*}
\]

$C_p = C_V + R$

For an ideal gas
Heat capacities of an ideal gas

- Ratio of heat capacities
  \[ \gamma = \frac{C_p}{C_v} \]

**Example**

\[ C_p = C_v + R = \frac{3}{2} R + R = \frac{5}{2} R \]

\[ \Rightarrow \gamma = \frac{5}{3} = 1.67 \quad \text{for an ideal monatomic gas} \]

\[ C_p = C_v + R = \frac{5}{2} R + R = \frac{7}{2} R \]

\[ \Rightarrow \gamma = \frac{7}{5} = 1.40 \quad \text{for most diatomic gas} \]
Adiabatic processes of an ideal gas

- $p$, $V$, and $\gamma$

$$dU = nC_v dT \quad \text{(by definition)}$$
$$dW = pdV$$
$$dU = -dW \quad \text{(adiabatic process)}$$
$$\Rightarrow nC_v dT = -pdV$$
$$\Rightarrow nC_v dT = -\frac{nRT}{V} dV \iff p = \frac{nRT}{V} \quad \text{(ideal gas)}$$

$$\Rightarrow \frac{dT}{T} + \frac{R}{C_v} \frac{dV}{V} = 0$$

$$\Rightarrow \frac{R}{C_v} = \frac{C_p - C_v}{C_v} = \gamma - 1 \Rightarrow \frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0$$

$$\Rightarrow \ln T + (\gamma - 1) \ln V = \text{const}$$

$$\Rightarrow \ln(TV^{\gamma - 1}) = \text{const} \Rightarrow TV^{\gamma - 1} = \text{const}$$
Adiabatic processes of an ideal gas

- $p$, $V$, and $\gamma$ (cont’d)

\[ TV^{\gamma-1} = \text{const} \]

\[ T = \frac{pV}{nR} \quad (\text{ideal gas}) \]

\[ \Rightarrow \frac{pV}{nR} V^{\gamma-1} = \text{const} \Rightarrow pV^{\gamma} = \text{const} \]

\[ Q = 0, W = -\Delta U \quad (\text{adiabatic process}) \]

\[ \Delta U = nC_v(T_2 - T_1) \]

\[ \Rightarrow \]

\[ W = nC_v(T_1 - T_2) \quad \text{For adiabatic process, ideal gas} \]

\[ pV = nRT \quad (\text{ideal gas}) \]

\[ \Rightarrow \]

\[ W = \frac{C_v}{R} (p_1V_1 - p_2V_2) = \frac{1}{\gamma-1} (p_1V_1 - p_2V_2) \]

For adiabatic process, ideal gas
Exercises

Problem 1

Solution

(a) \[ W_{ab} = 0, W_{bc} = p_c (V_c - V_a), \]
\[ W_{dc} = 0, W_{ad} = p_a (V_c - V_a) \]

(b) \[ Q = \Delta U + W \]
\[ Q_{ab} = U_b - U_a, Q_{bc} = U_c - U_b + p_c (V_c - V_a) \]
\[ Q_{dc} = U_c - U_d, Q_{ad} = U_d - U_a + p_a (V_c - V_a) \]

(c) \[ W_{abc} = p_c (V_c - V_a), Q_{abc} = U_b - U_a + (U_c - U_b) + p_c (V_c - V_a) = (U_c - U_a) + p_c (V_c - V_a) \]
\[ W_{adc} = p_a (V_c - V_a), Q_{adc} = U_d - U_a + (U_c - U_d) + p_a (V_c - V_a) = (U_c - U_a) + p_a (V_c - V_a) \]

So assuming \( p_c > p_a \), \( Q_{abc} > Q_{adc} \) and \( W_{abc} > W_{adc} \).
Exercises

Problem 2

Three moles of an ideal gas are taken around the cycle acb shown in the figure. For this gas, \( C_p = 29.1 \) J/(mol K). Process ac is at constant pressure, process ba is at constant volume, and process cb is adiabatic. \( T_a = 300 \) K, \( T_c = 492 \) K, and \( T_b = 600 \) K. Calculate the total work \( W \) for the cycle.

Solution

Path ac is at constant pressure:
\[
W_{ac} = p \Delta V = nR \Delta T = nR(T_c - T_a) = (3 \text{ mol})[8.315 \text{ J}/(\text{mol K})](492 \text{ K} - 300 \text{ K}) = 4.79 \times 10^3 \text{ J}.
\]

Path cb is adiabatic (Q=0):
\[
W_{cb} = Q - \Delta U = -\Delta U = -nC_v \Delta T, \quad C_v = C_p - R
\]
\[
\rightarrow W_{cb} = -n(C_p - R)(T_b - T_c)
\]
\[
= -(3 \text{ mol})[29.1 \text{ J}/(\text{mol K}) - 8.315 \text{ J}/(\text{mol K})]600 \text{ K} - 492 \text{ K}) = -6.74 \times 10^3 \text{ J}.
\]

Path ba is at constant volume: \( W_{ba} = 0 \)

\[
W = W_{ac} + W_{cb} + W_{ba} = -1.95 \times 10^3 \text{ J}.
\]
Exercises

Problem 3

You are designing an engine that runs on compressed air. Air enters the engine at a pressure of \(1.60 \times 10^6\) Pa and leaves at a pressure of \(2.80 \times 10^5\) Pa. What must the temperature of the compressed air be for there to be no possibility of frost forming in the exhaust ports of the engine? Frost will form if the moist air is cooled below \(0^\circ C\).

Solution

\[
TV^{\gamma-1} = \text{const} \rightarrow T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}
\]

\[
pV^{\gamma} = \text{const} \rightarrow p_1V_1^{\gamma} = p_2V_2^{\gamma}
\]

\[
p_1^{\gamma-1}T_1^{\gamma} = p_2^{\gamma-1}T_2^{\gamma} \rightarrow T_1 = T_2\left(\frac{p_1}{p_2}\right)^{\frac{1}{\gamma}}
\]

Using \(\gamma=7/5\) for air,

\[
T_1 = (273.15K)\left(\frac{1.60 \times 10^6}{2.80 \times 10^5}\right)^\frac{2}{7} = 449K = 176^\circ C.
\]
Problem 4

An air pump has a cylinder 0.250 m long with a movable piston. The pump is used to compress air from the atmosphere at absolute pressure 1.01 x 10^5 Pa into a very large tank at 4.20 x 10^5 Pa gauge pressure. For air, $C_v=20.8 \text{ J/(mol K)}$. (a) The piston begins the compression stroke at the open end of the cylinder. How far down the length of the cylinder has the piston moved when air first begins to flow from the cylinder into tank? Assume that the compression is adiabatic. (b) If the air is taken into the pump at 27.0°C, what is the temperature of the compressed air? (c) How much work does the pump do in putting 20.0 mol of air into the tank?

Solution

(a) For constant cross-section area, the volume is proportional to the length, and Eq.19.24 becomes $L_2 = L_1 \left( \frac{p_1}{p_2} \right)^{1/\gamma}$ and the distance the piston has moved is:

$$L_1 - L_2 = L_1 \left[ 1 - \left( \frac{p_1}{p_2} \right)^{1/\gamma} \right] = (0.250m) \left[ 1 - \left( \frac{1.01 \times 10^5 \text{ Pa}}{5.21 \times 10^5 \text{ Pa}} \right)^{1/1.400} \right] = 0.173 \text{ m}.$$

Eq.19.24 $pV^\gamma = \text{const} \rightarrow p_1V_1^\gamma = p_2V_2^\gamma$
Exercises

Problem 5

Solution

(b) Raising both side of Eq. 1 $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$ to the power $\gamma$ and both sides of Eq. 2 $p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$ to power $\gamma-1$, dividing to eliminate the term $V_1^{\gamma(\gamma-1)}$ and $V_2^{\gamma(\gamma-1)}$, solving for the ratio of the temperatures:

$$T_2 = T_1 \left( \frac{p_1}{p_2} \right)^{1-(1/\gamma)} = (300.15K) \left( \frac{5.21 \times 10^5 Pa}{1.01 \times 10^5 Pa} \right)^{1-(1/1.400)} = 480K = 206^\circ C.$$ 

Using the result for part (a) to find $L_2$ and the using Eq. 1 gives the same result.

(c) Of the many possible ways to find the work done, the most straightforward is to use the result of part (b) in Eq. 3 $W=nC_v(T_1-T_2)$:

$$W = nC_v \Delta T = (20.0\text{ mol})[20.8J(\text{ mol } \cdot K)](179.0K) = 7.45 \times 10^4 J.$$ 

where an extra figure was kept for the temperature difference.

Eq. 1 $\quad TV^{\gamma-1} = \text{const} \rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

Eq. 2 $\quad pV^{\gamma} = \text{const} \rightarrow p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$

Eq. 3 $\quad W = nC_v(T_1 - T_2)$