Thermodynamics

Thermodynamics is the branch of physics that deals with the way in which a system interacts with its surroundings.

**Thermodynamic System** - the substance being manipulated - usually an Ideal Gas

**Surroundings** - everything else

**State of the system** - for a gas, a particular set of $P, V, T, n$

<table>
<thead>
<tr>
<th><strong>Internal energy</strong></th>
<th>total potential energy and random kinetic energy of the molecules of a substance</th>
<th>Symbol: $U$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Units: J</td>
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<thead>
<tr>
<th><strong>Work</strong></th>
<th>product of force and displacement in the direction of the force</th>
<th>Symbol: $W$</th>
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<table>
<thead>
<tr>
<th><strong>Thermal Energy (Heat)</strong></th>
<th>the transfer of energy between two substances by non-mechanical means - conduction, convection and radiation</th>
<th>Symbol: $Q$</th>
</tr>
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**The internal energy of a system can change by . . .**

- **Heating**
  - $Q = +400 \text{ J}$
  - Positive

- **Cooling**
  - $Q = -400 \text{ J}$
  - Negative

- **Expansion**
  - $W = -100 \text{ J}$
  - Negative

- **Compression**
  - $W = +100 \text{ J}$
  - Positive

**Definitions:**
- $Q =$ thermal energy added to the system (positive) or removed from the system (negative)
- $W =$ work done on the system by surroundings (positive) or work done by the system on surroundings (negative)
- $\Delta U =$ change in internal energy of the system

**Note:** Some textbooks define positive work as work done by the system.
1. A sample of gas is heated with a Bunsen burner and allowed to expand. If 400 J of thermal energy are transferred to the gas during heating and the gas does 100 J of work by expanding, what is the resulting change in the internal energy of the gas?

\[ \Delta U = Q + W \]
\[ = (400) + (-100) \]
\[ = 300 \text{ J} \]

2. A sample of gas is warmed by placing it in a bath of hot water, adding 400 J of thermal energy. At the same time, 100 J of work is done compressing the gas manually. What is the resulting change in the internal energy of the gas?

\[ \Delta U = Q + W \]
\[ = (400) + (100) \]
\[ = 500 \text{ J} \]

**First Law of Thermodynamics:** The sum of the heat transferred to a system from its surroundings and the work done on the system by its surroundings is equal to the change in internal energy of the system.

**NOTE:** The First Law is a statement of the principle of conservation of energy when there are no changes in macroscopic kinetic or potential energy.

In each case, determine the change in the internal energy of the gas.

a) A gas gains 1500 J of heat from its surroundings, and expands, doing 2200 J of work on the surroundings.

\[ \Delta U = Q + W \]
\[ = 1500 + (-2200) \]
\[ = -700 \text{ J} \]

b) A substance gas gains 1500 J of heat at the same time as an external force is doing 2200 J of work on it.

\[ \Delta U = 1500 + 2200 \]
\[ = 3700 \text{ J} \]

Internal energy of many substances depends on temperature and intermolecular bonds.

Internal energy of an ideal gas depends on...

1. only temperature since there are no intermolecular bonds

\[ U \propto T \quad \text{so} \quad \Delta U \propto \Delta T \]

\[ U \text{ increases if } T \text{ increases, if } +\Delta T \text{ then } +\Delta U \]

2. the change in internal energy of ideal gas is path independent
Four Common Thermal Processes

1. **An isobaric process** is one that occurs at constant pressure. 
   \[ \Delta P = 0 \]
   \[ W = \text{Weight of brick, piston and atmosphere} \]
   \[ \text{constant} \]

2. **An isochoric (isovolumetric) process** is one that occurs at constant volume. 
   \[ \Delta V = 0 \]
   \[ \Delta W = 0 \]

3. **An isothermal process** is one that occurs at constant temperature. 
   \[ \Delta T = 0 \]
   \[ \Delta U = 0 \]
   \[ Q = 0 \]

4. **An adiabatic process** is one that occurs without transfer of thermal energy. 

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**Isobaric Process**

**Work Involved in a Volume Change at Constant Pressure**

*How is pressure held constant?*

*How is work done by the gas?*

Molecules strike piston and transfer momentum and KE to it causing it to move upward/outward - as KE decreases, so does internal energy and T

*How much work is done by the gas (W) if it expands at constant pressure?*

\[ W = F \cdot \cos \theta \]

\[ = P \cdot A \cdot \cos 0^\circ \]

\[ W = P \Delta V \]

\[ W = -P \Delta V \]
What does an isobaric process look like on a diagram of pressure vs. volume (P-V diagram)?

Expansion of gas

Compression of gas

How can the amount of work done by a gas during a process be determined from a P-V diagram?

- Work done on or by the gas: area beneath the curve
- Arrow to right = expansion = negative
- Arrow to left = compression = positive

Isobaric Processes and the First Law of Thermodynamics

**Expansion at constant pressure**

Gas laws:
\[
\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}
\]

\[
P_1 = P_2
\]

\[
\frac{V_1}{T_1} = \frac{V_2}{T_2}
\]

Example: A gas is allowed to expand isobarically by adding 1000 J of thermal energy, causing the gas to increase its internal energy by 200 J. How much work is done by the gas in expanding?

\[
W = \Delta U - Q = 200 - 1000 = -800
\]

**Compression at constant pressure**

Gas laws:
\[
\frac{V_1}{T_1} = \frac{V_2}{T_2}
\]

\[
T \propto V
\]

\[
T \Phi \text{ as } V \Phi
\]

**1st law:**

\[
U = T
\]

So \(\Delta T\) means a \(\Delta U\)

\[
\Delta U = Q + (-W)
\]

\[
(+) = (+) + (-)
\]

\[
|Q| > |W|
\]

More heat added than work done if isobaric.
One mole of an ideal gas is heated at a constant volume of $2.0 \times 10^{-3} \text{ m}^3$ from an initial pressure of $1.0 \times 10^5 \text{ Pa}$ to a final pressure of $5.0 \times 10^5 \text{ Pa}$.

**a)** Determine the initial and final temperatures of the gas.

Initial temperature:

$$T_1 = \frac{PV}{nR} = \left(1.0 \times 10^5 \text{ Pa}\right)\left(2.0 \times 10^{-3} \text{ m}^3\right) \left(\frac{8.31 \text{ J}}{\text{mol} \cdot \text{K}}\right) = 24.1 \text{ K}$$

Final temperature:

$$T_2 = \left(\frac{P_2}{P_1}\right)T_1 = \left(\frac{5.0 \times 10^5}{1.0 \times 10^5}\right)24.1 \text{ K} = 120.5 \text{ K}$$

b) Does the internal energy of the gas increase or decrease? Justify your answer.

Increase $U$ at $T$. As $T$ increases, internal energy increases.

c) Determine the work done by the gas during this process.

$$W = -P\Delta V = 0 \quad \text{(volume does not change)}$$

d) If the change in internal energy of the gas is $1200 \text{ J}$, determine the amount of thermal energy added to the gas.

$$\Delta U = Q + W$$

$$\therefore Q = 1200 \text{ J}$$
2. In each case shown below, an ideal gas at $5.0 \times 10^5$ Pa and $1.0 \times 10^4$ m$^3$ expands to $4.0 \times 10^3$ m$^3$ at a pressure of $1.0 \times 10^3$ Pa by a different process or series of processes.

a) Compare the change in internal energy of the gas as a result of each process. Justify your answer. (i.e. positive or negative, bigger/smaller/the same.)

b) Compare the work done by (or on) the case during each process. Justify your answer.

c) Compare the thermal energy added to or removed from the gas during each process. Justify your answer.

d) If the change in internal energy in each case is 500 J, calculate the work done and thermal energy exchanged in each case.

Conclusions:

1) Change in internal energy does not depend on the path taken – only on the change in temperature – path independent.

2) Work done and thermal energy transferred depend on the path taken between the initial and final states.
Isothermal Process

Heat reservoir: hot or cold water bath that maintains constant temperature of gas by supplying or removing thermal energy.

Gas Law:

\[
P V = nRT
\]

1st Law:

\[
\Delta U = Q + W
\]

If ideal gas, \( \Delta U \propto \Delta T \)

so \( \Delta T = 0 \) means \( \Delta U = 0 \)

so \( Q = -W \)

Expansion: thermal energy flows in at same rate as work is done by gas.

Compression: thermal energy flows out at same rate as work done on the gas.

**Ideal Gas Equation of State**

\[
P V = nRT
\]

\[
P = \frac{nRT}{V}
\]

Isotherm: inverse function of constant temperature

\[
P V = nRT
\]

\[
\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}
\]

\[
P_1 V_1 = P_2 V_2 \text{ on one isotherm}
\]

Conclusions:

1) all states on one isotherm have same \( U \) since they have same \( T \). \( \Delta T \) and \( \Delta U = 0 \) as you move along an isotherm

2) as temperature increases, isotherms move further from origin - higher \( T \) so higher \( U \)

3) \( \Delta U \) between two isotherms is path independent - same \( \Delta U \) since same \( \Delta T \) and \( \Delta U \propto \Delta T \)

Expansion

arrow to right
work done by -
Q added -

Compression

arrow to left
work done on -
Q removed -
Adiabatic Process

**Adiabatic walls**: insulating walls so no thermal energy can enter or leave system.

**NOTE**: Rapid expansion or compression of gas is approximately adiabatic.

\[ \Delta U = 0 + W \]
\[ Q = 0 \]
\[ \Rightarrow \Delta U = W \]

If ideal gas, \( \Delta U \propto \Delta T \)

\[ \Rightarrow W \propto \Delta T \]

**Expansion**: negative work done by gas causes gas to cool down as it loses internal energy.

\[ \frac{P}{V} \frac{dT}{T} = \frac{PV}{T} \]

- \( P \) decreases and \( V \) increases and \( T \) decreases.

**Compression**: positive work done on gas causes gas to heat up as it gains internal energy.

\[ \frac{P}{V} \frac{dT}{T} = \frac{PV}{T} \]

- \( P \) increases and \( V \) decreases and \( T \) increases.

---

**Problem**

1. If 410 J of heat energy are added to an ideal gas causing it expand at constant temperature, find:
   a) what is the change in internal energy of the gas?
   b) how much work is done by the gas?
   c) how much work is done on the gas?

2. If an ideal gas is allowed to expand adiabatically, the internal energy of the gas changes by 2500 J. Find:
   a) Does the internal energy of the gas increase or decrease? Justify your answer.
   b) the thermal energy added or removed from the gas.
   c) the work done by the gas.
Cycles

Cycle: a series of processes that returns a gas to its initial state

The cycle shown below represents processes performed on an ideal gas initially at $P_0 = 1.0 \times 10^5 \text{ Pa}$ and $V_0 = 2.0 \times 10^{-3} \text{ m}^3$.

<table>
<thead>
<tr>
<th>Process</th>
<th>$Q$</th>
<th>$\Delta U$</th>
<th>$W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A → B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B → C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C → D</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D → A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycle</td>
<td></td>
<td></td>
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1. Compare the temperatures at each state A, B, C, and D.

2. During process A→B, 600 J of thermal energy were added to the gas. Complete the chart.
Properties of the individual thermal processes

<table>
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<tr>
<th>Process</th>
<th>Description</th>
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<tbody>
<tr>
<td>A → B</td>
<td></td>
</tr>
<tr>
<td>B → C</td>
<td></td>
</tr>
<tr>
<td>C → D</td>
<td></td>
</tr>
<tr>
<td>D → A</td>
<td></td>
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Properties of the entire cycle

1) gas returns to same P, V, and T

2) ΔT = 0 so ΔU = 0 (for all ideal gases)

3) ΔU = 0 so net Q = - (net W)

4) net W = area enclosed by figure; area enclosed means negative net work = work done by gas = net work out

5) net Q = - W so Q = ... so more heat added than removed during cycle = net heat in
An ideal gas is confined in a cylinder with a movable piston. The gas starts at 300 K in state A and proceeds through the cycle shown in the diagram.

a) Find the temperatures at B and at C.

900 K isothermal.

b) State whether $\Delta U$, $W$ and $Q$ are $+$, $-$, or 0 for each of the three processes and for the entire cycle.

\[
\begin{array}{|c|c|c|}
\hline
\text{Process} & Q & \Delta U & W \\
\hline
A \rightarrow B & & & \\
\hline
B \rightarrow C & & & \\
\hline
C \rightarrow A & & & \\
\hline
\text{Cycle} & & & \\
\hline
\end{array}
\]

c) The internal energy of the gas changes by 1520 J during process A to B. 1700 J of heat are added to the gas during process B to C. Find $\Delta U$, $W$, and $Q$ for each process and for the entire cycle.

\[
\begin{array}{|c|c|c|}
\hline
\text{Process} & Q & \Delta U & W \\
\hline
A \rightarrow B & & & \\
\hline
B \rightarrow C & & & \\
\hline
C \rightarrow A & & & \\
\hline
\text{Cycle} & & & \\
\hline
\end{array}
\]
The Second Law of Thermodynamics and Entropy

The Second Law of Thermodynamics implies that thermal energy cannot spontaneously transfer from a region of low temperature to a region of high temperature.

Entropy: a system property that expresses the degree of disorder in the system.

Second Law of Thermodynamics:

1) the overall entropy of the universe is increasing

2) all natural processes increase the entropy of the universe

Although local entropy can decrease, any process will increase the total entropy of a system and its surroundings (the universe).

1. Discuss this statement for the case of a puddle of water freezing into a block of ice.

2. A block of ice is placed in a thermally insulated room initially at room temperature. Discuss any changes in the total energy, total entropy, and temperature of the room.

3. An operating refrigerator with its door open is placed in a thermally insulated room. The refrigerator operates for a long period of time. Discuss any changes in the total energy, total entropy, and temperature of the room.