Thermodynamic Processes and the 1\textsuperscript{st} Law of Thermodynamics

Physics 116

Tues. 3/7, Thurs. 3/9
Below is a schematic (i.e., highly idealized) presentation of a temperature vs time graph for an experiment in which a sample of solid ice is taken out of a deep freeze at around -75° C and then heated uniformly in a closed container to a final temperature in excess of 100° C. The system is closed (i.e., no material enters or escapes from the system.)

What is happening to the sample during interval: AB? BC? CD? DE? EF?

1. getting warmer
2. freezing
3. melting
4. condensing
5. vaporizing
Recap: Results from Kinetic Theory
Internal energy and the 1st law of thermodynamics

- The average kinetic energy of each particle is:
  \[(KE)_{avg/particle} = \frac{3}{2} kT\]

- Summing up the energy of the particles is the same as multiplying the average energy per particle times the total number of particles. This total energy is called the internal energy of the system:
  \[U_{internal} = \frac{3}{2} NkT\]

- Energy can be added to/removed from the system either by doing work on/by the system or heating/cooling the system. This is the first law of thermodynamics:
  \[\Delta U_{internal} = \frac{3}{2} Nk\Delta T\]
  \[\Delta U_{internal} = W_{onsystem} + Q\]
Changing the system energy

\[ \Delta U_{\text{int}} = W + Q \]

This diagram assumes work done ON the system is positive, that is, when the gas is compressed, positive work is done on the system; when the gas expands, negative work is done on the system.
• In our simple model of an ideal gas, by the 1st law any energy that is added by heating to a closed system can facilitate the gas doing work, increase its internal energy or both:

\[ \Delta U = Q + W_{\text{on system}}, \quad \text{so} \quad Q = \Delta U - W_{\text{on system}}, \] where \( W \) is work done ON the system.

• Work done ON the system is the negative of work done BY the system.

• We can test our model of kinetic theory by predicting what will happen to a gas that is heated in a rigid container (i.e. the volume does not change).

• A small amount of work done by the gas \( W = Fdx = P(Adx) = PdV \), so

if the volume doesn’t change then there is no work done on or by the gas.
Isovolumetric heating

• \( Q = m c_{\text{mass}} \Delta T \)

• Since gas comes in bundles of moles, we’ll use a molar specific heat rather than a mass specific heat (J/mol*K rather than J/kg*K)

• \( Q = n C_n \Delta T \)

• And by the first law: \( \Delta U = Q \) (since no work is done)

• And by the defn. of internal energy (from kinetic theory): \( \Delta U = 3/2 \ N \ k \ \Delta T = 3/2 \ n \ R \ \Delta T \)
Prediction from Kin Theory

- $\Delta U = \frac{3}{2} N k \Delta T = \frac{3}{2} n R \Delta T$
- $\Delta U = Q$
- $Q = nC_n\Delta T$
- So, $\Delta U = nC_n\Delta T$ and $\Delta U = \frac{3}{2} n R \Delta T$
- $nC_n\Delta T = \frac{3}{2} n R \Delta T$
  
  $C_n = \frac{3}{2} R$, this is a constant!

So kinetic theory predicts that the molar specific heat for a monatomic ideal gas, regardless of the gas, will have a value of $\frac{3}{2} R$, or 12.5 J/mol K.
Examples of measured molar specific heats

<table>
<thead>
<tr>
<th>Degrees of freedom</th>
<th>Monoatomic</th>
<th>Diatomic</th>
<th>Polyatomic</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>$C_v = \frac{3}{2} R = 12.5 \frac{J}{mol \cdot K}$</td>
<td>$C_v = \frac{5}{2} R = 20.8 \frac{J}{mol \cdot K}$</td>
<td>$C_v = \frac{6}{2} R = 24.9 \frac{J}{mol \cdot K}$</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>6</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Helium</th>
<th>Argon</th>
<th>Nitrogen (N$_2$)</th>
<th>Oxygen (O$_2$)</th>
<th>Ammonia</th>
<th>Carbon dioxide (CO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12.5</td>
<td>12.6</td>
<td>20.7</td>
<td>20.8</td>
<td>29.0</td>
<td>29.7</td>
</tr>
</tbody>
</table>
Examples of measured molar specific heats

- **Monoatomic**
  \[ C_v = \frac{3}{2} R = 12.5 \frac{J}{mol \cdot K} \]
  - Helium: 12.5
  - Argon: 12.6

- **Diatomis**
  \[ C_v = \frac{5}{2} R = 20.8 \frac{J}{mol \cdot K} \]
  - Nitrogen (N₂): 20.7
  - Oxygen (O₂): 20.8

- **Polyatomic**
  \[ C_v = \frac{6}{2} R = 24.9 \frac{J}{mol \cdot K} \]
  - Ammonia (NH₃): 29.0
  - Carbon dioxide (CO₂): 29.7
Isovolumetric Process

\[ \Delta U = Q + W_{\text{on system}} \]

In the process depicted above, the internal energy
A. Increases
B. Decreases
C. Stays the same
D. Any of the above
In the process depicted above, the gas is
A. heated
B. cooled
C. either
D. neither

**Why is \( W = 0 \)?**

Area under the PV curve is zero \( \Rightarrow A = (P_B - P_A)(V - V) = 0 \)

From a calculus perspective: \( W_{on\,sys} = -\int_{V_i}^{V_f} PdV \)

\( P \) is independent of \( V \), and \( V_f = V_i \) \( \Rightarrow W_{on\,sys} = -P(V_f - V_i) = 0 \)
Isothermal Process

\[ \Delta U = Q + W_{\text{on system}} \]

In the process depicted above, the internal energy
A. Increases
B. Decreases
C. Stays the same
D. Any of the above
The process depicted above is consistent with
A. A being the initial state and B being the final state
B. A being the final state and B being the initial state
C. either one or the other
D. both are consistent
Isothermal Process

\[ \Delta U = Q + W_{\text{on system}} \]

\[ \Delta U = 0 \]
\[ Q = -W \]

First law of thermodynamics for an isothermal process

\[ \Delta U = \text{internal energy change} \]
\[ Q = \text{heat flow} \]
\[ W = \text{macroscopic work} \]

In the process depicted above, the gas is
A. heated
B. cooled
C. either
D. neither

\[ W \text{ is work done on system: } W_{\text{on sys}} = - \int_{V_i}^{V_f} PdV \]

\[ W_{\text{on sys}} = - \int_{V_B}^{V_A} \frac{nRT}{V} dV = -nRT [\ln(V_A) - \ln(V_B)] = -nRT [\ln \left( \frac{V_A}{V_B} \right)] \]

\[ V_A < V_B, \ W_{\text{on sys}} \to + \text{ so } Q \to - \text{ (flows out) to keep the temperature constant. We “drain” the heat to keep temperature constant. If we didn’t, temperature would increase and it wouldn’t be isothermal.} \]
Isobaric Process

In the process depicted above, the work is done
A. on the gas
B. by the gas
C. either
D. neither

\[ \Delta U = Q + W_{\text{on system}} \]

Work done on system:
\[ W_{\text{on sys}} = -\int_{V_i}^{V_f} P dV \]
\[ W_{\text{on sys}} = -P \int_{V_i}^{V_f} dV \]
\[ W_{\text{on sys}} = -P(V_f - V_i) \]

Work done by system:
\[ W_{\text{by gas}} = \int_{V_i}^{V_f} P dV \]
\[ W_{\text{by gas}} = P \int_{V_i}^{V_f} dV \]
\[ W_{\text{by gas}} = P(V_f - V_i) \]
Isobaric Process

\[ \Delta U = Q + W_{\text{on system}} \]

In the process depicted above, the internal energy

A. Increases
B. Decreases
C. Stays the same
D. Any of the above

1) \( PV = NkT = nRT \) (N is # particles, n is # moles which are constant), if \( P \) is constant and \( V_B > V_A \), then how does \( T_B \) compare to \( T_A \)?

Also, we know **Q is positive** since the burner is supplying heat to the system, **heat flows into the system**. In both ways of reasoning, \( T_B > T_A \)
In the process depicted above, the work is done
A. On the gas
B. By the gas
C. either
D. neither
Adiabatic Process

\[ \Delta U = Q + W \text{ on system} \]

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

First law of thermodynamics for an adiabatic process

\[ Q = \text{heat flow} \]
\[ \Delta U = \text{internal energy change} \]
\[ W = \text{macroscopic work} \]

In an adiabatic process, no heat flow occurs, so internal energy change directly corresponds to the work performed.

In the process depicted above, the internal energy

A. Increases
B. Decreases
C. Stays the same
D. Any of the above
In process depicted above, the gas is

A. heated
B. cooled
C. either
D. neither

All of the work done on the system goes to heating the gas. Alternatively, if the gas expands, the system will cool down (since an expanding gas means negative work done on the gas).
Heat Engine: Putting it all together

Our Engine can work by using heat ($Q_h$) to change $P$, $V$, and $T$ for an ideal gas over a full cycle (we finish how we started).
In one complete cycle depicted above, the change in the internal energy is
A. positive
B. negative
C. zero
D. Any of the above
Guided Problem

Cyclic Process (Ideal Gas)

In one complete cycle depicted above, the gas is
A. heated
B. cooled
C. both
D. neither

Q = ΔU + W_{by gas}
Guided Problem

Cyclic Process

In one complete cycle depicted above
A. the gas does work
B. work is done on the gas
C. neither
D. both

\[ Q = \Delta U + W_{\text{by gas}} \]

Area Enclosed = \((P_A-P_C)(V_B-V_D)\)

Gas Expands
Work 1 \(\rightarrow\) 2 = Area 1 \(\rightarrow\) 2 = \(P_A(V_B-V_D)\)

Gas Contracts
Work 3 \(\rightarrow\) 4 = Area 3 \(\rightarrow\) 4 = \(P_C(V_D-V_B)\)

\(W_{\text{by gas}} = \) Area Under PV curve
\[ = P(V_f - V_i) \] [for isobar]

Gas expands \(\rightarrow\) \(W_{\text{by gas}} > 0\), \(W_{\text{on gas}} < 0\)
Gas contracts \(\rightarrow\) \(W_{\text{by gas}} < 0\), \(W_{\text{on gas}} > 0\),
Cyclic Process

- $\Delta U$ is zero for entire process (returns to initial state)
- Net $W$ done by gas in one cycle is the area enclosed.
- By the 1st law ($\Delta U = Q - W_{\text{by gas}}$), since $\Delta U=0$, then $W_{\text{by gas}} = \text{sum of all } Qs$ in one cycle (i.e., $Q_{1\rightarrow2} + Q_{2\rightarrow3} + Q_{3\rightarrow4} + Q_{4\rightarrow1}$)

Guided Problem

For entire cycle:

$$Q = W_{\text{by gas}}$$

since $\Delta U = 0$
Guided Problem

The diagram below describes a cyclic process of one mole of an ideal gas. How much is the net gain in energy from heating in one cycle if $P_o = 8 \times 10^5$ Pa and $V_o = 1.0 \times 10^{-2}$ m$^3$? (think of the energy gained as the available work output of the gas, or the net work done)

\[ Q = \Delta U + W_{by\ gas} \]

1. 8 kJ
2. 16 kJ
3. 32 kJ
4. 64 kJ
5. I have no idea
Guided Problem

The diagram below describes a cyclic process of one mole of an ideal gas. $P_0 = 8 \times 10^5 \text{ Pa}$ and $V_0 = 1.0 \times 10^{-2} \text{ m}^3$

Is net work done on the gas or by the gas for the whole cycle?

How do you know if net work is done on the gas or by the gas?

How much work is done by the gas in each process?
Guided Problem

Q = ΔU + W by gas

The diagram below describes a cyclic process of one mole of an ideal gas. \(P_o = 8 \times 10^5\) Pa and \(V_o = 1.0 \times 10^{-2}\) m\(^3\)

What are the temperatures of each point in the cycle?

What is the change in internal energy (ΔU) of each process?

What is the change in internal energy (ΔU) for the entire cycle?
Guided Problem

The diagram below describes a cyclic process of one mole of an ideal gas. $P_o=8 \times 10^5$ Pa and $V_o = 1.0 \times 10^{-2}$ m$^3$

What is the heat flow ($Q$) for each process? $Q_{1\rightarrow 2}$, $Q_{2\rightarrow 3}$, etc.

For each process, did heat enter or leave the system?

What is the net heat flow $Q_{\text{net}}=(Q_{1\rightarrow 2}+Q_{2\rightarrow 3}+Q_{3\rightarrow 4}+Q_{4\rightarrow 1})$ for the entire cycle?

How do you know? Try using the 1$^{\text{st}}$ law, does the gas change temperature in one cycle? Is there net work done in one cycle?

$Q = \Delta U + W_{\text{by gas}}$
### Summary

<table>
<thead>
<tr>
<th>Name</th>
<th>What is held constant?</th>
<th>Work done by gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobaric</td>
<td>Pressure</td>
<td>( =P(V_f - V_i) )</td>
</tr>
<tr>
<td>Isovolumetric (or Isochoric)</td>
<td>Volume</td>
<td>( =0 )</td>
</tr>
<tr>
<td>Isothermal</td>
<td>Temperature</td>
<td>( =nRT\ln \left( \frac{V_f}{V_i} \right) )</td>
</tr>
<tr>
<td>Adiabatic</td>
<td>No heating or cooling</td>
<td>(-\Delta U)</td>
</tr>
<tr>
<td>Cyclic</td>
<td>( \Delta U=0 ) between initial and final states</td>
<td>area enclosed by cycle on P-V diagram</td>
</tr>
</tbody>
</table>

**1st Law of Thermodynamics:**

\[
\Delta U = Q - W \quad \text{(assuming positive work is work done by the gas)}
\]

\[
\Delta U = Q + W \quad \text{(assuming positive work is work on the gas)}
\]

Your equation sheet is written all in terms of work done BY the gas, i.e., work done by a gas is positive when the gas expands, since \( V_f > V_i \)