The laws of Thermodynamics

The work done on a gas in a cylinder is directly proportional to the force and the displacement.

\[ W = -F\Delta y = -PA\Delta y \]

It can be also expressed in terms of the pressure exerted by the piston and the variation in volume.

\[ W = -P\Delta V \]

Compression: work is positive
Expansion: work is negative
Work: questions

A monoatomic gas is expanded from an initial state with volume \( V = 1 \text{ L} \) to a final state \( 4V \). This process happens at constant pressure \( P = 1 \text{ atm} \). Next, the pressure on the gas is increased at constant volume \( 4V \) to \( 2 \text{ atm} \).

1) The work done during the first process is:
   a) positive, b) negative c) zero

2) The work done during the second process is:
   a) positive, b) negative c) zero

3) What is the net work and sketch the processes in a graph of \( P \) versus \( V \).

PV diagrams

The work done on a gas when taking it from an initial thermodynamic state (I) to a final thermodynamic state (f) can be determined by the area below the PV diagram.
PV diagrams

Isobaric process: constant pressure
Isovolumetric process: constant volume

The work depends not only on the initial and final state but also on the path taken.

PV diagrams: question time

In which case if there more work done on the system:

a) A
b) B
c) Both the same
**First law of thermodynamics**

The change in internal energy of the system is the sum of the heat transferred to the system and the work done on the system

\[ \Delta U \equiv U_f - U_i = Q + W \]

---

**First law of Thermodynamics**

**Isolated systems:** \( W=0 \) and \( Q=0 \) \( U_f = U_i \)

**Cyclic processes:** if the process ends up in the same thermodynamics state as it started there will be no change in its internal energy

\[ U_f = U_i \rightarrow W = -Q \]
First law of Thermodynamics

**Isothermal processes**: if the temperature is constant over the process

\[ U = \frac{3}{2} nRT \leftrightarrow U_f = U_i \rightarrow W = -Q \]

\[ W_{\text{env}} = nRT \ln \frac{V_f}{V_i} \]

**Adiabatic processes (Q=0)**: if the energy transferred by heat in a process is zero then

\[ \Delta U = W \]

First law of thermodynamics: question

Which of the following processes correspond to
1. Isobaric
2. Isothermal
3. Isovolumetric
4. Adiabatic
First law of thermodynamics: example

An ideal mono-atomic gas is confined in a cylinder by a movable piston. The gas starts at P=1.00atm, V=5.00L and T=300K. An isovolumetric process raises the pressure to 3 atm. Then an isothermal expansion brings the system back to 1atm. Finally an isobaric compression at 1atm completes the cycle and return the gas to its original state. (R=8.31 J/mol/K=0.0821 atm L/mol/K)

1) Find the number of moles, the temperature B, and the volume of the gas at C.

First law of Thermodynamics: example

2) Find the internal energy of the gas (in kJ), at A, B, and C. List P,V,T, U for the points A,B and C.
3) Consider the process A to B, B to C and C to A. For each case determine the sign of W and Q.
4) Calculate Q, W and ΔU for each transition
5) Tabulate W,Q and ΔU for each transition and calculate the net effect of each.
Heat engines

**The heat engine** is a device that converts internal energy into other useful forms of energy (electrical, mechanical, etc).

In general, it carries a working substance (ex: water) through cycles:
1) Energy is transferred from a hot reservoir
2) Work is done by the engine
3) Energy is expelled into a cold reservoir

Because the substance goes through a cycle its initial internal energy is the same as the final:

\[
W_{\text{engine}} = -Q_{\text{net}}
\]

\[
W_{\text{engine}} = |Q_{\text{hot}}| - |Q_{\text{cold}}|
\]

The work done by an engine for a cyclic process is the area enclosed in the curve of a PV diagram.
Thermal efficiency of Heat engines

Thermal efficiency of the heat engine is the ratio of the work done by the engine to the energy absorbed from the hot reservoir in a cycle:

\[ \varepsilon = \frac{W_{\text{eng}}}{|Q_{\text{hot}}|} \]

\[ \varepsilon = \frac{|Q_{\text{hot}}| - |Q_{\text{cold}}|}{|Q_{\text{hot}}|} = 1 - \frac{|Q_{\text{cold}}|}{|Q_{\text{hot}}|} \]

Second law of thermodynamics: It is impossible to construct a heat engine with 100% efficiency!

Reversible and Irreversible processes

Reversible process: the system is taken through a path of states in equilibrium and can be returned to the original state along the same path.

Most natural processes are Irreversible!
Carnot engine

No real engine operating between two energy reservoirs can be made more efficient than a Carnot engine operating between the same reservoirs

\[ \varepsilon = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} \]

All real engines operate irreversibly (friction and cycles are short)
Carnot engine: question time

Three engines operate between reservoirs separated in temperature by 300 K. The reservoir temperatures are:
Engine A operates between 1000K and 700K
Engine B operates between 800K and 500K
Engine C operates between 600K and 300K

1) Which one has the highest efficiency?
2) Which one has the lowest efficiency?

Heat engines: example

A car engine delivers 8.2 KJ of work per cycle.
a) Before tune-up the efficiency is 25%. Calculate, per cycle, the heat absorbed from combustion of fuel and the energy lost by the engine
b) After a tune-up the efficiency is 31%. What are the new values of the quantities calculated in a) when 8.2 KJ of work is delivered per cycle.