Adiabatic Expansion \((\Delta Q = 0)\)

Occurs if:
- change is made sufficiently quickly
- and/or with good thermal isolation.

Governing formula:

\[
P V^{\gamma} = \text{constant}
\]

where \(\gamma = \frac{C_p}{C_v}\)

Because \(PV/T\) is constant (ideal gas):

\[
V^{\gamma-1} T = \text{constant} \quad \text{(for adiabatic)}
\]
Proof of $PV = \text{constant}$
(for adiabatic process)

1) Adiabatic: $dQ = 0 \Rightarrow dU + dW = dU + PdV$

2) $U$ only depends on $T$:

$$dU = n C_V \, dT$$ (derived for constant volume, but true in general)

3) Ideal gas: $T = \frac{PV}{nR}$

$$dT = \frac{[(dP)V + P(dV)]}{nR}$$

Plug into 2): $dU = \left(\frac{C_V}{R}\right)[VdP + PdV]$

Plug into 1): $0 = \left(\frac{C_V}{R}\right)[VdP + PdV] + PdV$
Rearrange:

\[
\frac{dP}{P} = - \frac{(C_V + R)}{C_V} \frac{dV}{V}
\]

where \( \boxed{g} = \frac{(C_V + R)}{C_V} = \frac{C_p}{C_V} \)

Integrate both sides:

\[
\ln(P) = - \boxed{g} \ln(V) + \text{constant}
\]

or

\[
\ln(PV^{\boxed{g}}) = \text{constant}
\]

or

\[
P^{\boxed{g}}V = \text{constant}
\]

QED
Irreversible Processes

Examples:

• Block sliding on table comes to rest due to friction: KE converted to heat.

• Heat flows from hot object to cold object.

• Air flows into an evacuated chamber.

Reverse process allowed by energy conservation, yet it does not occur.

→ arrow of time

Why?

2nd Law of Thermodynamics (entropy)
Heat Engines

Heat engine: a cyclic device designed to convert heat into work.

Hot Reservoir, $T_H$

---

$Q_H$

---

Work, $W$

---

$Q_C$

---

Cold Reservoir, $T_C$

$2^{nd}$ Law of TD (Kelvin form):

It is impossible for a cyclic process to remove thermal energy from a system at a single temperature and convert it to mechanical work without changing the system or surroundings in some other way.
For a cyclic engine $\sum U = 0$,

So work done is equal to
heat in minus heat out:

$$ W = Q_H - Q_C $$

Define the Efficiency of the engine:

$$ e = \frac{W}{Q_H} = \frac{(Q_H - Q_C)}{Q_H} = 1 - \frac{Q_C}{Q_H} $$

Corollary of the 2nd Law of TD:

It is impossible to make a heat engine whose efficiency is 100%.
Refrigerators

Refrigerator: a cyclic device which uses work to transfer heat from a cold reservoir to hot reservoir.

2nd Law of TD (Clausius form):

It is impossible for a cyclic process to have no other effect than to transfer thermal energy from a cold object to a hot object.
A measure of refrigerator performance is the ratio:

\[ K = \frac{Q_c}{W} \]

"Coefficient of performance"
(The larger the better.)

Corollary of the 2\(^{nd}\) Law of TD:

It is impossible for the coefficient of performance to be infinite.
Equivalence of Kelvin and Clausius Statements

For example:

You could combine an ordinary refrigerator with a perfect engine (impossible)...

to obtain a perfect refrigerator (also impossible).
The Carnot Engine

2\textsuperscript{nd} Law of TD says:
100\% efficient Heat Engine is impossible.

What is the maximum possible efficiency?

No engine working between 2 heat reservoirs can be more efficient than an ideal engine acting in a Carnot cycle.
(Sadi Carnot, 1824)

Properties of the Carnot cycle:

1. It is reversible: no friction or other dissipative forces.
2. Heat conduction only occurs isothermally at the temperatures of the two reservoirs.
Derivation of Carnot Efficiency

1-2: Isothermal ($Q_{\text{in}}$ at $T_H$)
2-3: Adiabatic expansion
3-4: Isothermal ($Q_{\text{out}}$ at $T_C$)
4-1: Adiabatic compression

$$e = 1 - \frac{T_C}{T_H}$$
The Stirling Engine

Invented by Robert Stirling in 1816. Its operating cycle is:

The two temperature-changing steps are performed at constant volume; A heat transfer occurs at these steps also.

$\text{Stirling} < \text{Carnot}$
Entropy

Consider a reversible process for an ideal gas:

\[ dQ = dU + dW = n \, C_v \, dT + P \, dV \]

\[ = n \, C_v \, dT + n \, R \, T \left( \frac{dV}{V} \right) \]

We cannot write a general integral of this, because \( dW \) (and therefore \( dQ \)) depends on the functional form of \( T(V) \) (i.e. the path). However, if we divide by \( T \):

\[ \frac{dQ}{T} = n \, C_v \left( \frac{dT}{T} \right) + n \, R \left( \frac{dV}{V} \right) \]

is integrable independent of path.

This suggests a new state function, **Entropy**, defined by:

\[ \Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} \]

(Valid for any system)
In general, the process may be too complicated to do the integral (particularly if irreversible process):

However, because entropy is a state function, we can choose any convenient path between i and f to integrate.

For an ideal gas:

\[ \Delta S = n \, C_v \, \ln \left( \frac{T_f}{T_i} \right) + n \, R \, \ln \left( \frac{V_f}{V_i} \right) \]

This only depends on the initial state \((V_i, T_i)\) and final state \((V_f, T_f)\), but not the path.
Isothermal Expansion: $T_f = T_i$, $V_f > V_i$

The amount of heat which leaves the reservoir and enters the gas is

$$Q = n \, R \, T \ln(V_f/V_i).$$

The entropy change of the gas is

$$\Delta S_{\text{gas}} = + \frac{Q}{T} = n \, R \, \ln(V_f/V_i).$$

The entropy change of the reservoir is

$$\Delta S_{\text{reservoir}} = - \frac{Q}{T}.$$ 

The net entropy change is

$$\Delta S_{\text{universe}} = \Delta S_{\text{gas}} + \Delta S_{\text{reservoir}} = 0.$$ 

This illustrates a general result:

In a reversible process, the entropy change of the universe (system + surroundings) is zero.
Adiabatic Free Expansion of an Ideal Gas

Two containers connected by stopcock. They are thermally insulated so no heat can flow in or out.

**Initial:** One container is evacuated. Gas is in volume $V_i$ at temperature $T_i$.

**Final:** Stopcock opened, gas rushes into second chamber. Gas does no work (nothing to push against) and there is no heat transfer. So internal energy does not change. Final volume $V_f > V_i$ at temperature $T_f = T_i$. 
Because there is no heat transfer, you might think $\int S = 0$. WRONG! This is an irreversible process. We can’t integrate $\int \frac{dQ}{T}$.

But entropy is a state function, and we do know the initial and final conditions for the **Free Expansion**. They are exactly the same as for an **Isothermal Expansion**. So

$$\Delta S_{\text{gas}} = nR \ln(V_f/V_i).$$

Just as for an isothermal expansion. However, since it is thermally isolated from its surroundings,

$$\Delta S_{\text{surround}} = 0$$

and

$$\Delta S_{\text{universe}} = \Delta S_{\text{gas}} + \Delta S_{\text{surround}} = nR \ln(V_f/V_i) > 0.$$ 

In an irreversible process, the entropy of the universe increases.
Entropy and Heat Engines

For a reversible cycle:

\[ \Delta S = \oint \frac{dQ}{T} \]

This implies that \(dQ\) cannot be strictly positive. There must also be heat released in the cycle.

Carnot cycle: \((Q_{in}/T_H) + (-Q_{out}/T_C) = 0\).

2\textsuperscript{nd} Law of TD (Entropy form):

\[ \Delta S_{universe} \geq 0. \]

(greater-than sign for irreversible processes, and equals sign for reversible processes)