Reversible and Irreversible Processes

A process $A \rightarrow B$ is called **reversible** if the system can be brought back to the initial state $A$ from the final state $B$ with no change to any part of the universe.

Consider the following process in a closed, isolated system:

\[
\text{wall is removed} \quad \Delta u = \Delta H + \Delta E = 0 \Rightarrow \Delta T = 0 \text{ (for ideal gases)}
\]

Is this process reversible? We could attempt to reverse it by compressing the gas back to state $A$:

\[
\text{work} \quad \Delta u = Q + w = 0 \Rightarrow w = -Q
\]

Clearly, this "reverse" process results in changes outside the system. However, if we could count all the heat released back into work, the net change would be zero.

Many, many experiments have shown such complete conversion of heat into work to be impossible. The original $A \rightarrow B$ process is **irreversible**. All naturally occurring (spontaneous) processes
are irreversible.
Now consider a different process starting from the same state A, to state C, with \( V_C = V_B \), using a well-lubricated, frictionless piston:

\[
\begin{align*}
\text{State A} & \quad \text{State C}, \quad V_C = V_B \\
\Rightarrow \, W &= - \int PdV < 0 \quad \text{[work produced]} \\
& \quad \text{for the reverse process from C \rightarrow A, exactly as much work is needed as that produced from A \rightarrow C.} \\
& \quad \text{The process is reversible.}
\end{align*}
\]

In general, reversible processes require:
- no internal or external gradients of \( T, P, \mu \)
- \( \mu \equiv \text{chemical potential, to be defined later} \)
- no conversion of mechanical work into heat
- no friction
- infinite time and infinite patience

Irreversibilities in natural processes define a direction in time. Consider the three movies linked from the course web page:
- \( m_1 \): breaking glass
- \( m_2 \): protein-drug interaction
- \( m_3 \): mixing/separation (?) oSILJ fluids

Can you tell when time is running backwards?
Second Law

Makes the notion of spontaneous change rigorous, allowing predictions of processes that can/cannot occur naturally.

Definitions: A "heat reservoir" is a large mass that can exchange heat with no change in $T$.

Heat Engines are devices that exchange heat and work with their surroundings with no internal changes (e.g. a complete cycle of an internal combustion engine).

Kelvin-Planck Postulate (2nd Law)

It is not possible for a heat engine interacting with a single reservoir to convert all the heat transferred from the reservoir into work.

\[
\begin{array}{c}
\text{reservoir} \\
\downarrow Q \\
\begin{array}{c} E \rightarrow W \\
\end{array}
\end{array}
\]

An impossible process

"Perpetual Motion Machine of the 2nd Kind"

[A perpetual motion machine of the 1st kind violates the first law - e.g. $E \rightarrow W$, also impossible]

One of several equivalent statements; cannot be proven but is confirmed by innumerable experiments.
What are the consequences? Consider two engines:

- **A** transfers heat from hot → cold, producing work
- **B** transfers heat from cold → hot, requiring work

Both, in principle, permitted.

But some combinations of the two types could lead us into trouble.

Set $|Q_{ca}| = |Q_{cb}|$ by adjusting the number of cycles or engine size.

Couple A to B

Net process A+B:

$$W = |W_B| - |W_A|$$
$$Q = |Q_{HA}| - |Q_{HB}| = -W$$

If $W < 0$ (work produced) → impossible,

$Q > 0$ (heat absorbed) \{ violates postulate \}

$W > 0$ (work required) \{ for any engines \}

$Q ≤ 0$ (heat produced) \{ $A$ and $B$ \}

Now consider reversible engines $A + B$

$$W = |W_B| - |W_A| ≥ 0 \Rightarrow |W_B| ≥ |W_A|$$

Change labels, run in reverse

$$|W_A| ≥ |W_B| \Rightarrow |Q_{HA}| = |Q_{HA}|$$