Lecture 9

**Clausius Inequality, Thermodynamic Potential
and Direction of Spontaneous Change**

- **Can we estimate the change in entropy, ΔS for different processes?**

- Can we use Entropy to determine/predict the following:

  - ✓ the direction of spontaneous change
  - ✓ the condition of equilibrium

- Can we use entropy to explain why the heat engines do not have the ideal efficiency?

The Clausius inequality

We now show that the definition of entropy is consistent with the Second Law. To begin, we recall that more work is done when a change is reversible than when it is irreversible. That is, $|dw_{rev}| \geq |dw|$. Because dw and dw_{rev} are negative when energy leaves the system as work, this expression is the same as $-dw_{rev} \geq -dw$, and hence $dw - dw_{rev} \geq 0$. Because the internal energy is a state function, its change is the same for irreversible and reversible paths between the same two states, so we can also write:

$$dU = dq + dw = dq_{rev} + dw_{rev}$$

It follows that $dq_{rev} - dq = dw - dw_{rev} \geq 0$, or $dq_{rev} \geq dq$, and therefore that $dq_{rev}/T \geq dq/T$. Now we use the thermodynamic definition of the entropy $dS = dq_{rev}/T$) to write

$$dS \geq \frac{dq}{T}$$

Clausius inequality

- **From Clausius inequality**

$$dS > \frac{\eth q_{irrev}}{T}$$

- **In an isolated system, during an irreversible process,**

$$\eth q_{irrev} = 0 \Rightarrow \quad dS > 0$$

- **For a real transformation in an isolated system, upon withdrawal of an internal constraint, the system spontaneously changes towards that direction that increases the entropy.**

Entropy helps determine the direction of spontaneous change

- **Any natural change** within an isolated system is accompanied by **an increase in entropy**

- The entropy continues to increase as long as the changes occur within the system

- When **entropy attains its maximum value,** the system reaches a **new equilibrium state.**

(figure: plot of S vs. Time, labeled "Isolated system", with arrow marking "Equilibrium reached")
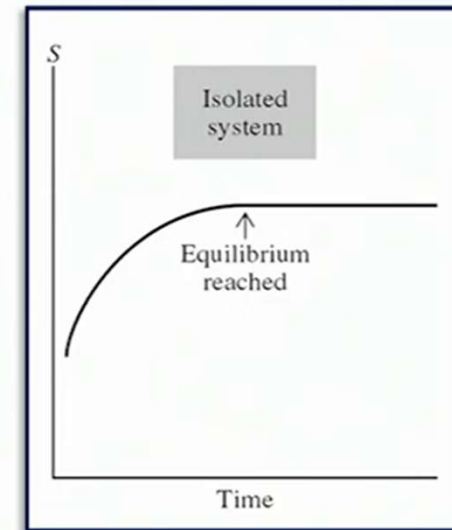
$dS > 0$	**Irreversible and spontaneous change in state**
$dS = 0$	**No further change, a new equilibrium is reached**
$dS < 0$	**Process associated with the change in state is NOT permitted**

**Note that this change is change of mean entropy value. At equilibrium, after reaching the max entropy, it fluctuates around a mean entropy value. At equilibrium, the change of that mean is zero. But, the instantaneous change/fluctuation of entropy (finite ds) still presents.---→ Very important to understand

Initial equilibrium state T V_i N

Final equilibrium state T V_f N

Ideal gas

(U, V_1, N)

Isothermal irreversible **compression**

Isothermal irreversible **expansion**
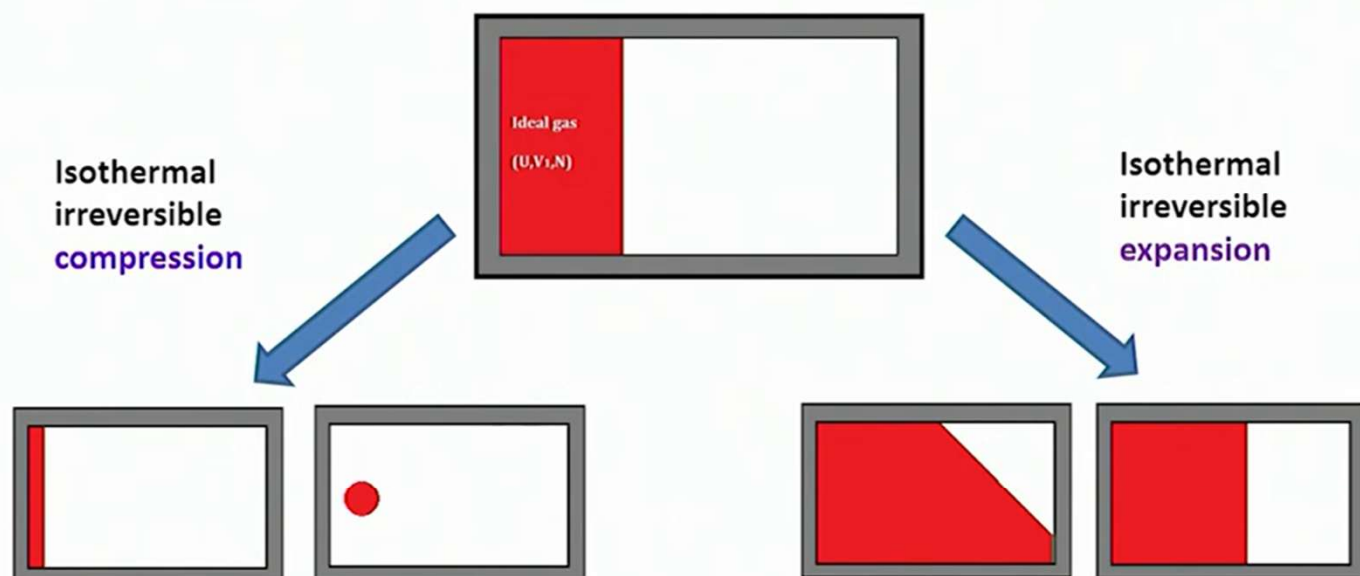
Under what condition does the gas stop expanding any further so that a new equilibrium state is reached?

$$\Delta S = R \, ln \left(\frac{V_f}{V_i} \right)$$

ΔS reaches a maximum when V_f is maximum

$\Rightarrow$ S_{final} is maximum when $V_f = V_2$

The ideal gas will spontaneously expand till it fills up the entire available volume

Implications of Clausius Inequality under different thermodynamic condition

First, consider heating at constant volume. Then, in the absence of non-expansion work, we can write $dq_V = dU$; consequently

$$dS - \frac{dU}{T} \geq 0 \qquad\qquad (3.28)$$

The importance of the inequality in this form is that it expresses the criterion for spontaneous change solely in terms of the state functions of the system. The inequality is easily rearranged into

$$TdS \geq dU \quad \text{(constant } V, \text{ no additional work)}^5 \qquad\qquad (3.29)$$

At either constant internal energy ($dU = 0$) or constant entropy ($dS = 0$), this expression becomes, respectively,

$$dS_{U,V} \geq 0 \qquad dU_{S,V} \leq 0 \qquad\qquad (3.30)$$

where the subscripts indicate the constant conditions.

➤ The first inequality states that, in a system at constant volume and constant internal energy (such as an isolated system), the entropy increases in a spontaneous change. **That statement is essentially the mathematical expression of the Second Law.**

➤ If the entropy of the system is unchanged, then there must be an increase in entropy of the surroundings, which can be achieved only if the energy of the system decreases as energy flows out as heat.

Condition of Spontaneity and Equilibrium in an Isolated System

$\overline{dS} > 0$	Irreversible and spontaneous change in state	$\overline{dU} < 0$
$\overline{dS} = 0$	No further change, a new equilibrium is reached	$\overline{dU} = 0$
$\overline{dS} < 0$	Process associated with the change in state is **NOT** permitted	$\overline{dU} > 0$

**Note that these changes are changes of mean value. At equilibrium, the mean does not change and is zero. But, at equilibrium the instantaneous change/fluctuation of s or u (ds or du) still presents, though which we measure all the response function, like C_p, C_V , and other.

Implications of Clausius Inequality under different thermodynamic condition
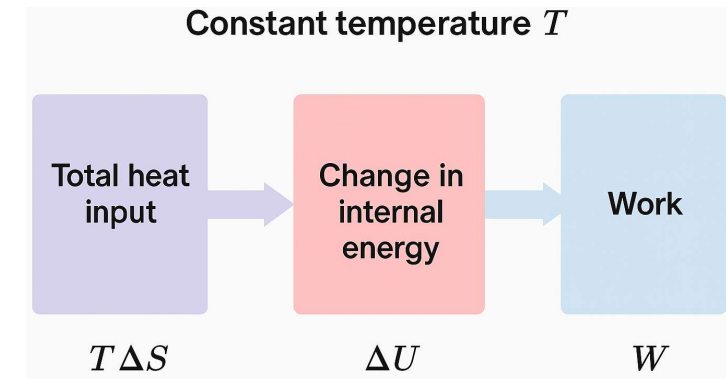
From the **Second Law** (for any process):

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

Now, suppose you want **all** the heat Q to be converted to work, i.e.,

$$W = Q \quad \text{(perfect work extraction)}$$

Then, the First Law says: $\Delta U = Q - W = 0$

Constant temperature T

Total heat input	Change in internal energy	Work
$T\Delta S$	ΔU	W

But then, if no heat is dumped into surroundings, the surroundings gain no entropy: $\Delta S_{\text{surroundings}} = -\dfrac{Q}{T} = -\Delta S_{\text{system}} \Rightarrow \Delta S_{\text{total}} = 0$

So, this is only possible in a **reversible** ideal scenario. In any **real process**, there will be *some* heat loss (some energy dissipated as disordered motion), and:

So now rewrite the First Law again: $W = Q - \Delta U \leq T\Delta S - \Delta U$

$$\boxed{W \leq T\Delta S - \Delta U}$$ ⟶   This amount is available to be extracted as **useful work (maximum work)**.

$$W_{\text{max}} = Q - \Delta U = T\Delta S - \Delta U = -\Delta F$$

A new energy function: Helmholtz Free energy

1st law: $dU = \eth q + \eth w$ **2nd law:** $TdS \geq \eth q$

Thus, $TdS \geq dU - \eth w$

- For an isothermal process (only $p - V$ work)

$$-dU + TdS \geq -\eth w \Rightarrow -d(U - TS) \geq -\eth w$$

Defining $F = U - TS$ Helmholtz free energy,

$$-dF \geq -\eth w$$

$\eth w = 0$ at constant V

$$-dF_{T,V} \geq 0$$

Initial equilibrium state   →   **Final equilibrium state**

Decrease in Helmholtz free energy

Spontaneity and Equilibrium
In
Isolated and non-Isolated Systems

	Thermodynamic state of system	Thermodynamic potential	Direction of spontaneous change in state	Condition of equilibrium
Isolated system	S, V, N U,V,N	U S	Decrease in U **Increase in S**	Minimization of U **Maximization of S**
System + Thermostat	T, V, N	$F = U - TS$	Decrease of F	Minimization of F
System + Thermostat + Barostat	T, p, N	$G = U - TS + pV$	Decrease of G	Minimization of G