Lecture-5

Contents

- The Clausius inequality
- Entropy and Equilibrium
- Molecular interpretation of entropy

The Clausius inequality

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:

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

or, $$dq_{rev} - dq = dw - dw_{rev} \geq 0$$

or , $$dq_{rev} \geq dq$$

or, $$\frac{dq_{rev}}{T} \geq \frac{dq}{T}$$

By using the thermodynamic definition of the entropy ($dS = dq_{rev} /T$) one can write

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

This expression is the **Clausius inequality**.

For an isolated system, $dq = 0$

Therefore, $dS \geq 0$

We conclude that *in an isolated system the entropy cannot decrease when a spontaneous change occurs*.

Entropy Change in Reversible Processes

In a reversible process, any heat flow between system and surroundings must occur with no finite temperature difference; otherwise the heat flow would be irreversible.

Let dq_{rev} be the heat flow into the system from the surroundings during an infinitesimal part of the reversible process. The corresponding heat flow into the surroundings is dq_{rev}. We have

$$dS_{univ} = dS_{syst} + dS_{surr}$$

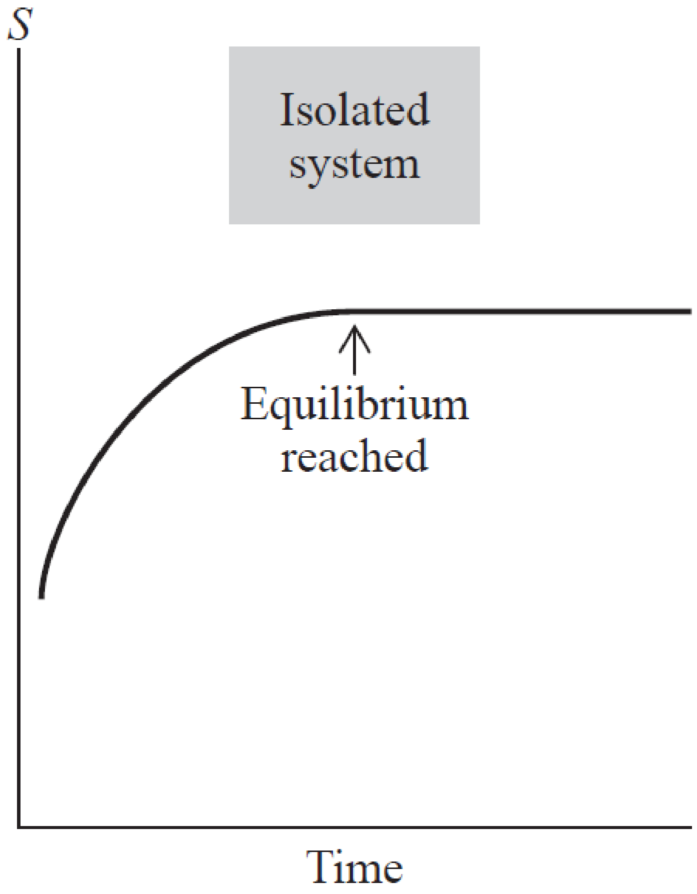
$$= \frac{dq_{rev}}{T_{syst}} + \frac{-dq_{rev}}{T_{surr}} = \frac{dq_{rev}}{T_{syst}} - \frac{dq_{rev}}{T_{syst}} = 0$$

Integration gives,

$\Delta S_{univ} = 0$ for reversible process

Entropy and Equilibrium

- For any irreversible process that occurs in an isolated system, ΔS is positive.
- Since all real processes are irreversible, when processes are occurring in an isolated system, its entropy is increasing.
- Irreversible processes (mixing, chemical reaction, flow of heat from hot to cold bodies, etc.) accompanied by an increase in S will continue to occur in the isolated system until S has reached its maximum possible value.
- When the entropy of the isolated system is maximized, things cease happening on a macroscopic scale, because any further processes can only decrease S, which would violate the second law.
- By definition, the isolated system has reached equilibrium when processes cease occurring.



The entropy of an isolated system is maximized at equilibrium.