Statistical Molecular Thermodynamics

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Video 6.3

Spontaneity and the Second Law
Heat Flow in a Special System

Energy as heat flows spontaneously from a region of higher temperature to a region of lower temperature (sometimes called The Zeroth Law of Thermodynamics).

Consider an isolated, rigid two compartment system:

- $U_A + U_B = \text{constant}$
- $V_A = \text{constant}$
- $V_B = \text{constant}$
- $S = S_A + S_B$

Ideal gases in equilibrium, but not with each other when brought into contact.

*Isolated, rigid:* No exchange of energy with surroundings, no work
**Determination of Energy and Entropy**

\[ dV_A = dV_B = 0 \]

\[ \begin{align*}
    dU_A &= \delta q_{\text{rev}} = T_A dS_A \\
    dU_B &= \delta q_{\text{rev}} = T_B dS_B
\end{align*} \]

No work

\[ dS = dS_A + dS_B = \frac{dU_A}{T_A} + \frac{dU_B}{T_B} \]

\[ dU_A = -dU_B \]

Consequence of \( U_A + U_B = \text{constant} \)

\[ dS = dU_B \left( \frac{1}{T_B} - \frac{1}{T_A} \right) \]

\[ \begin{align*}
    T_B > T_A & \quad dU_B < 0 \quad dS > 0 \\
    T_A > T_B & \quad dU_B > 0 \quad dS > 0 \\
    T_A = T_B & \quad dU_B = 0 \quad dS = 0
\end{align*} \]
Spontaneity and Entropy

The spontaneous flow of energy as heat from a body at a higher temperature to a body at a lower temperature is governed by the condition $dS > 0$.

In an isolated system, the energy remains constant, so any spontaneous process must be due to an increase in entropy. Unlike energy, entropy is not conserved; it increases whenever a spontaneous process takes place. The entropy of an isolated system will continue to increase until the system is in equilibrium. An isolated system at equilibrium will have maximal entropy.

$dS > 0$ (spontaneous process in an isolated system)

$dS = 0$ (reversible process in an isolated system)
What about a general situation (non-isolated system)? The change in entropy ($dS$) comes from two “sources”: the entropy produced by an irreversible process itself and the entropy due to the energy as heat exchanged between the system and the surroundings.

\[ dS = dS_{\text{prod}} + dS_{\text{exch}} = dS_{\text{prod}} + \frac{\delta q}{T} \]

Isolated system:
The Second Law

Reversible:

\[ dS = 0 + \frac{\delta q_{rev}}{T} = \frac{\delta q_{rev}}{T} \]

Irreversible:

\[ dS = dS_{prod} + \frac{\delta q_{irr}}{T} > \frac{\delta q_{irr}}{T} \]

There is a thermodynamic function of a system called the entropy, \( S \), such that for any change in the thermodynamic state of the system,

\[ dS \geq \frac{\delta q}{T} \]

\[ \Delta S \geq \int \frac{\delta q}{T} \]

where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage.
**Entropy of irreversible Process**

\[ \Delta S \geq \int \frac{\delta q}{T} \]

system isolated during irreversible step, placed back in contact with surroundings for reversible step

\[ \Delta S_{1 \rightarrow 2 \rightarrow 1} = \oint dS = 0 \]

because entropy is a state function

\[ \Delta S \geq \int_{1}^{2} \frac{\delta q_{\text{irr}}}{T} + \int_{2}^{1} \frac{\delta q_{\text{rev}}}{T} \]

because some step is irreversible

\[ 0 > 0 + S_{1} - S_{2} \]

by definition

system isolated

\[ S_{2} > S_{1} \]

an irreversible process always increases entropy
Restatement of Laws 1 and 2

The energy of the Universe is constant; the entropy is tending to a maximum

\[ \Delta S \geq \int \frac{\delta q}{T} \]

Rudolph Clausius (Entropy, 1865)