1. **Entropy**

First law: \( dU = dQ - dW \)

\[
\frac{dW}{P} = dV
\]

\[
\frac{dQ}{T} = dS
\]

\[
\begin{align*}
\text{(Exact)} & \quad \text{total differential} \\
\left(\frac{dQ}{T}\right) & \equiv dS \\
\text{(Clausius)} & \quad \text{To be shown later}
\end{align*}
\]

\[
\begin{align*}
dU & = TdS - PdV
\end{align*}
\]

2. **The Second Law of Thermodynamics**

**Clausius:** It is impossible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a cold body to a hotter body.

\[
\text{Heat} \quad \begin{array}{c}
\text{Lo} \\
\text{Hi}
\end{array}
\]

**Kelvin-Planck:** It is impossible to construct a device that operates in a cycle and produces no other effect than the performance of work and the exchange of heat with a single reservoir.

\[
\text{Heat} \quad \begin{array}{c}
\text{Lo} \\
\text{Hi}
\end{array}
\]
Carnot theorem: No engine operating between two reservoirs can be more efficient than a Carnot engine.

Proof: We consider two engines, M (Carnot) and M' (hypothetical).

We assume: $q' > q_c$

Since Carnot engine is reversible, we reverse its operation.

We conclude that the composite engine does not work but extract that $|q_1| - |q_1'|$ from the cold reservoir.

The machine violates the Clausius statement of the
2nd law: $\Rightarrow \eta' < \eta_c$ and $|q_1'| > |q_1|$

Now let the hypothetical machine be reversible. We can prove $\eta' \geq \eta_c$. For both conditions to be satisfied, we obtain

$$\eta' = \eta_c = 1 - \frac{T_1}{T_2}$$
(4) **The Clausius Inequality.**

- For Carnot engine, \( \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \); i.e. \( \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0 \)

\[ \Rightarrow S \text{ is a state variable?} \]

We consider an arbitrary reversible cycle, e.g., a P-V diagram. The cycle is divided into infinitesimal Carnot cycles. Thus:

\[ \sum \frac{\delta Q_1}{T} = \int \frac{\delta Q}{T} = 0 \]

Integrates over the entire contour of the cycle.

\[ \therefore \oint dS = 0 \Rightarrow S \text{ is a state variable!} \]

\[ dS \text{ is a total differential} \]

- **Irreversible processes:**

  Examples: 1. Exhaust gases leaving a combustor.
  2. Mixing of gases inside a vessel.
  3. Free expansion ( Joule process).
  4. Heat flows from a high temperature object to a low temperature reservoir.

For an irreversible process, we find \( \frac{|Q^e|}{|Q_e|} > \frac{|Q^r|}{|Q_r|} \)

or

\[ \frac{Q_1'}{Q_2'} < \frac{Q_1}{Q_2} = -\frac{T_1}{T_2} \]

\[ \Rightarrow \frac{\delta Q_1'}{T_1} + \frac{\delta Q_2'}{T_2} < 0 \]

\[ \oint \frac{\delta Q'}{T} < 0 \]

Clausius inequality
Consider an irreversible process from \( 1 \rightarrow 2 \).

What is the change of entropy? 

\[
\Delta S = \int_{1}^{2} \frac{\delta Q}{T}
\]

Now consider a closed process from \( 1 \rightarrow 2 \) and from \( 2 \rightarrow 1 \), where \( 2 \rightarrow 1 \) is a reversible process.

\[
\int_{1}^{2} \frac{\delta Q}{T} = \int_{1}^{2} \frac{\delta Q}{T} + \int_{2}^{1} \frac{\delta Q}{T} \leq 0
\]

\[
\int_{1}^{2} \frac{\delta Q}{T} \leq -\int_{2}^{1} \frac{\delta Q}{T} = -\int_{1}^{2} \frac{\delta Q}{T} = S_{2} - S_{1}
\]

\[
\Delta S = S_{2} - S_{1} \geq \int_{1}^{2} \frac{\delta Q}{T} \quad \text{or} \quad \Delta S \geq \frac{\delta Q}{T}
\]

For an isolated system, \( \delta Q = 0 \), we find \( \Delta S \geq 0 \).

The entropy of an isolated system increases in any irreversible process, and is unaltered in any reversible process.

(6) Absolute Temperature

We consider a Carnot engine operating between two scaled temperatures \( \Theta_{1} \) and \( \Theta_{2} \).

\[
\frac{\Theta_{1}}{\Theta_{2}} = f(\Theta_{1}, \Theta_{2})
\]

The heat flow depends only on temperature alone!

Now consider an intermediate step at \( \Theta_{i} \):

\[
\frac{\Theta_{i}}{\Theta_{1}} = f(\Theta_{i}, \Theta_{1}) \quad \text{and} \quad \frac{\Theta_{i}}{\Theta_{2}} = \frac{\Theta_{i}}{\Theta_{2}}
\]

\[
f(\Theta_{2}, \Theta_{i}) f(\Theta_{i}, \Theta_{1}) = f(\Theta_{2}, \Theta_{1}) \Rightarrow f(\Theta_{i}, \Theta_{1}) = \frac{f(\Theta_{2}, \Theta_{i}) f(\Theta_{i}, \Theta_{1})}{f(\Theta_{2}, \Theta_{1})}
\]
\[ \frac{Q_1}{Q_2} = f(\theta_1, \theta_2) = \frac{\phi(\phi)}{\phi(\theta)} \]

Kelvin suggested:

\[ T = A \phi(\theta) \]

Let \( \phi(\theta) \)?

From (1.15) we found

\[ \frac{\partial u}{\partial v} = T \frac{\partial p}{\partial T} - P \]

Since \( T = A \phi(\theta) \) \( \Rightarrow \) \[ \frac{\partial u}{\partial v} = \frac{\partial u}{\partial \theta} \]

\[ \frac{\partial p}{\partial T} = \frac{\partial p}{\partial \theta} \]

\[ \therefore \]

\[ T \frac{\partial \phi}{\partial T} = P + \frac{\partial u}{\partial \theta} \]

\[ \text{Ideal gas} \]

\[ \text{Now we consider ideal gas:} \]

\[ T \frac{\phi}{\partial T} = \frac{\phi(\phi)}{\phi'(\theta)} = \theta \]

\[ \Rightarrow \]

\[ T = C_\theta \]

\[ T = 273.16 \text{ K} \]

\[ \frac{|Q_1|}{|Q_2|} \]

\[ |Q_1| \text{ is the heat flow for Carnot cycle at } T = 273.16 \text{ K}. \]
Entropy changes in reversible processes

\[
\frac{dq}{T} = ds = \frac{du}{T} + \frac{pdv}{T}
\]

(a) Adiabatic process: \( dq = 0 \)  \( ds = 0 \)  (isentropic process)

(b) Isothermal process: \( s_2 - s_1 = \int ds = \int_1^2 \frac{du}{T} = \frac{1}{T} \left( u_2 - u_1 \right) \)

(c) Isothermal (and isobaric) change of phase

\[
s_2 - s_1 = \frac{1}{T} \Delta q = \frac{1}{T} \left( \Delta L \right) \text{ latent heat}
\]

(d) Isochoric process: \( u = u(v, T) \)  \( ds = 0 \)

\[
s_2 - s_1 = \int ds = \int_1^2 \frac{du}{T} = \int_1^2 \frac{c_v}{T} \frac{dT}{T} \rightarrow c_v \ln \frac{T_2}{T_1}
\]

(e) Isobaric process

\[
h' = u + pv
\]

\[
ds = \frac{dq}{T} = \frac{dh}{T} - \frac{\varepsilon dp}{T} = c_p \frac{dT}{T} + \frac{1}{T} \left( \frac{\partial p}{\partial T} \right)_v dp - \frac{\varepsilon dp}{T}
\]

\[
s_2 - s_1 = \int_1^2 \frac{dq}{T} = \int_1^2 \frac{c_p}{T} \frac{dT}{T} \rightarrow c_p \ln \frac{T_2}{T_1}
\]

(f) A system in thermal contact with a very large reservoir \( T_0 \). A reversible process of the system will result in zero total change of zero entropy.

\[
d_s_{\text{system}} + ds_{\text{reservoir}} = 0
\]

\[
+ \frac{dq}{T} - \frac{dq}{T} = 0
\]
4) Ideal gas
\[ ds = \frac{dq}{T} = c_v \frac{dT}{T} + \frac{P}{V} \, dv \]
\[ S_2 - S_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \]

7) Entropy change in irreversible processes.
Consider the system in thermal contact with a reservoir at \( T_2 \) at a constant pressure.

\[ dq = c_p \, dt - v \, dp \]

\[ ds = \frac{dq}{T} = c_p \frac{dt}{T} \]

\[
\begin{align*}
(\Delta S)_{\text{system}} &= c_p \ln \frac{T_2}{T_1} \\
(\Delta S)_{\text{reservoir}} &= -\frac{q}{T_2} = -c_p \left( \frac{T_2 - T_1}{T_2} \right) \\
\Delta S_{\text{universe}} &= (\Delta S)_{\text{system}} + (\Delta S)_{\text{reservoir}} \\
&= c_p \left( \ln \frac{T_2}{T_1} - \frac{T_2 - T_1}{T_2} \right) \\
&= c_p \left( x - 1 + \frac{1}{x} \right) > 0
\end{align*}
\]

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<th>( x = \frac{T_2}{T_1} )</th>
<th>( \ln x - 1 + \frac{1}{x} )</th>
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<tr>
<td>1.3</td>
<td>0.0316</td>
</tr>
</tbody>
</table>

\[ \frac{\Delta S}{c_p} \]
The $T$-dS equation

\[ T \Delta s = dU + P dV \]

\[ = C_v \Delta T + T \left( \frac{\partial P}{\partial T} \right)_V dV = C_v \Delta T + \frac{T \Delta S}{\kappa} \]

\[ = \frac{C_p}{P} \Delta T - T \left( \frac{\partial V}{\partial T} \right)_P dP = \frac{C_p}{P} \Delta T - T \nu \beta dP \quad s = s(T, P) \]

\[ = \frac{C_v \Delta T}{P} dV + C_v \left( \frac{\partial T}{\partial P} \right)_V dP = C_v \Delta T + \frac{C_p - C_v}{\beta \nu} dP \quad s = s(P, V) \]

\[ \Rightarrow \frac{C_p}{P} \Delta T - T \nu \beta dP = C_v \Delta T + \frac{T \Delta S}{\kappa} \]

\[ dT = \frac{T \beta}{(C_v - C_p) \nu} dV + \frac{T \nu \beta}{C_v - C_p} dP = \left( \frac{\partial T}{\partial V} \right)_P dV + \left( \frac{\partial T}{\partial P} \right)_V dP \]

\[ \left( \frac{\partial T}{\partial V} \right)_P = \frac{T \beta}{(C_v - C_p) \nu} \quad \rightarrow \quad C_v - C_p = \frac{T \nu \beta^2}{\kappa} > 0 \]

--- Applications:

\( C_p \) can easily be measured in lab: \( \Rightarrow C_v \)

Data: Copper East

\( C_p = 2.9 \text{ J/mol K} \quad \beta = 6.5 \times 10^{-6} \text{ K}^{-1} \quad \kappa = 1.5 \times 10^{-12} \text{ Pa} \)

\( \beta \) in molar K

\( u = \frac{V}{n} = \frac{m}{n \rho} = \frac{63.6 \text{ g/mol}}{8.96 \text{ g/cm}^3} = 7.1 \times 10^{-6} \text{ cm}^3 \text{ molecule}^{-1} \)

\( C_v = C_p - \frac{T \nu \beta^2}{\kappa} = 29 \text{ J/mol} \quad \nu = \frac{(6.5 \times 10^{-5}) (2 \times 10^6) (9.5 \times 10^{12})}{26 \text{ J/mol K}} = 26 \text{ J/mol K} \)
Adiabatic process \( ds = 0 \)
\[
\frac{C_p}{\beta T} \frac{dv}{dt} = -\frac{C_v}{\beta} \alpha \frac{dP}{dt}
\]
\[
K_s = -\frac{1}{\nu} \frac{\partial (\beta v)}{\partial P} = \frac{\nu}{\alpha} \frac{C_v}{C_p} = \frac{\nu}{\alpha} \frac{K}{Y} < K
\]
\[
Y = \frac{C_p}{C_v} = \frac{\alpha}{\nu}
\]

The speed of sound is \( c = \sqrt{\frac{1}{\nu K_s}} = \sqrt{\frac{\nu}{\alpha}} \).

The sound speed is fast, and so the process is adiabatic.

\[
C_{air} = \sqrt{\frac{\nu}{\alpha}} = \sqrt{1.4 \frac{1}{1.01e10} \left(\frac{1}{1.01e10} \right)} \approx 340 \text{ m/s}
\]

\[
K = \frac{\nu}{\alpha} = 10^{-5} \text{ Pa}^{-1}
\]

\[
\rho_{air} = 1.29 \text{ kg/m}^3
\]