Entropy and Spontaneity–The Clausius Inequality

$\text{đ}q_{rev} = T\,dS$ How does dq_{rev}/T relate to dq/T?

$dU = \text{đ}q + \text{đ}w = \text{đ}q - P_{ext}\,dV$ (closed, PV work)

$dU = \text{đ}q_{rev} + \text{đ}w_{rev} = \text{đ}q_{rev} - P\,dV$ (reversible, closed, PV work)

Combined First and Second Laws of Thermodynamics:
$dU = T\,dS - P\,dV$ (closed, PV work)

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV$$ (closed, PV work)

$$dS = \frac{\text{đ}q}{T} - \frac{P_{ext}}{T}\,dV + \frac{P}{T}\,dV$$ (closed, PV work)

$$dS = \frac{\text{đ}q}{T} + \left(\frac{P - P_{ext}}{T}\right)dV$$ need a pressure gradient to do work (closed, PV work)

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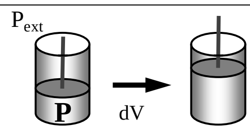
adiabatic: $\text{đ}q = 0$ if $P > P_{ext}$

$\left(\frac{P - P_{ext}}{T}\right) > 0$ system expands: $dV > 0$ so $dS > 0$



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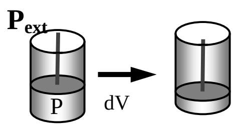
adiabatic: $\text{đ}q = 0$ if $P < P_{ext}$

$\left(\frac{P - P_{ext}}{T}\right) < 0$ system contracts: $dV < 0$ so guarantees $dS > 0$



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reversible process: $P = P_{ext}$, $dw = dw_{max,}$ and then $\left(\frac{P - P_{ext}}{T}\right) dV = 0$ and $dS = 0$

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for a spontaneous expansion $|dw| < |dw_{max}|$ and $\left(\frac{P - P_{ext}}{T}\right) dV > 0$

$\left(\frac{P - P_{ext}}{T}\right) dV$ = "lost work" term energy wasted to increase entropy

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"lost work" term always positive: $dS \geq \frac{\text{đ}q}{T}$ Clausius inequality

\> for irreversible process = for reversible process

$$\frac{\text{đ}q_{rev}}{T} > \frac{\text{đ}q}{T}$$ (irreversible, closed)

$dS \geq 0$ > for irreversible process = for reversible process (isolated)

Entropy always increases for a spontaneous process in an isolated system.