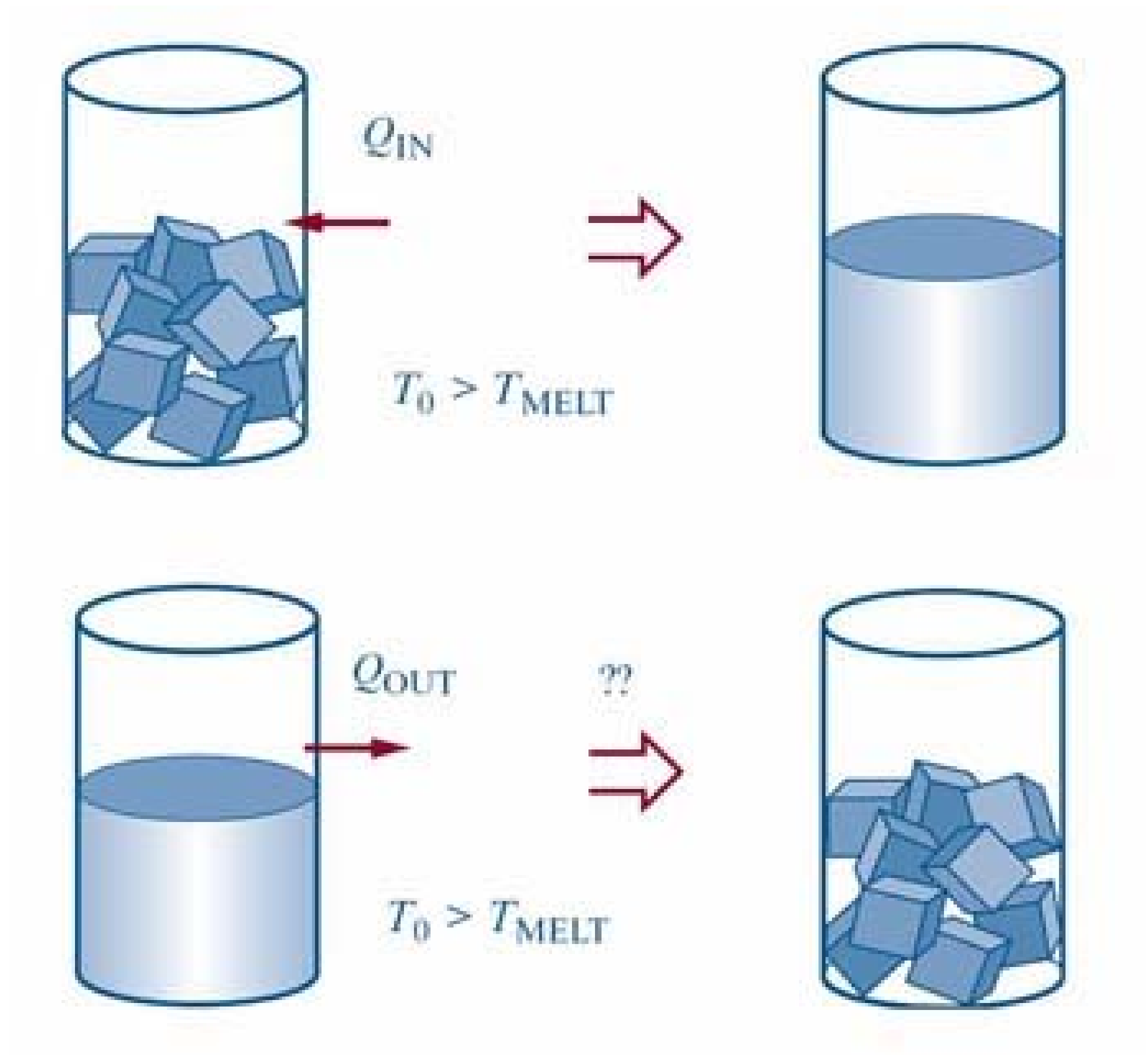
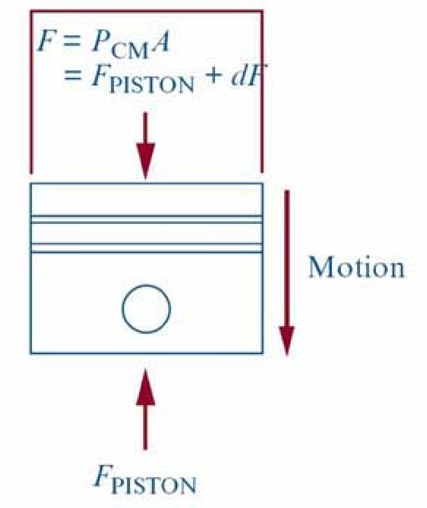
The Second Law of Thermodynamics

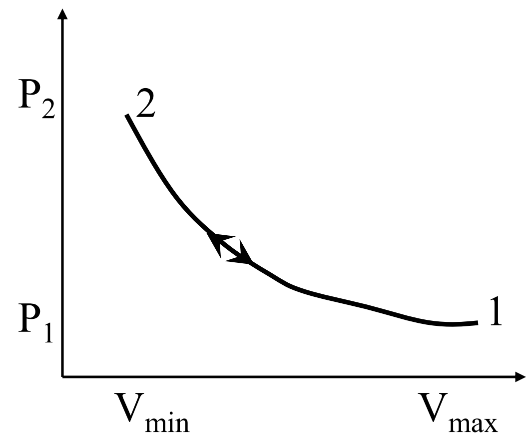
A reversible process

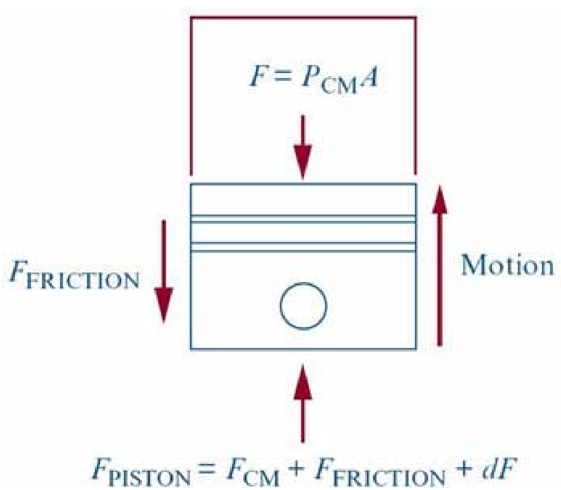


A reversible process …

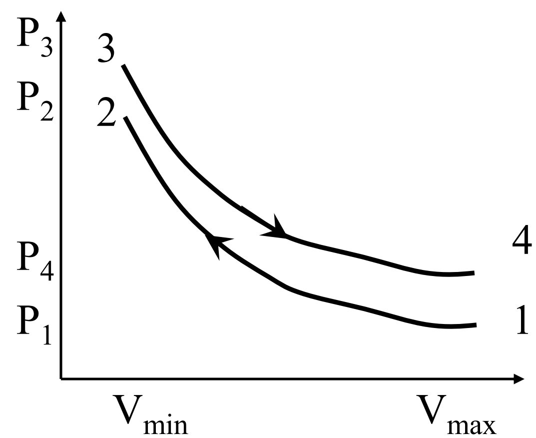


reversible





irreversible



A reversible process …

- proceeds slowly through equilibrium states.
- could be reversed with no change in heat or work output.

All real processes …

- are irreversible and have additional heat losses (e.g. due to friction).
- have efficiency $\varepsilon < \varepsilon_{ideal}$

Second Law of Thermodynamics

Heat flows spontaneously from a hot object to a cold object, but **will not** flow spontaneously from a cold object to a hot object.

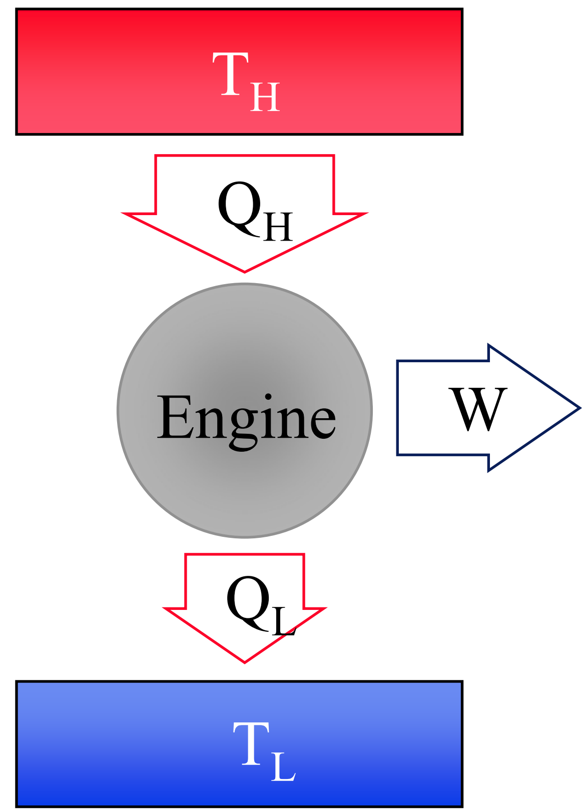
$$\text{Hot Object} \xrightarrow[\textit{heat}]{Q} \text{Cold Object}$$

It is relatively easy to produce thermal energy by doing work (e.g. against friction).

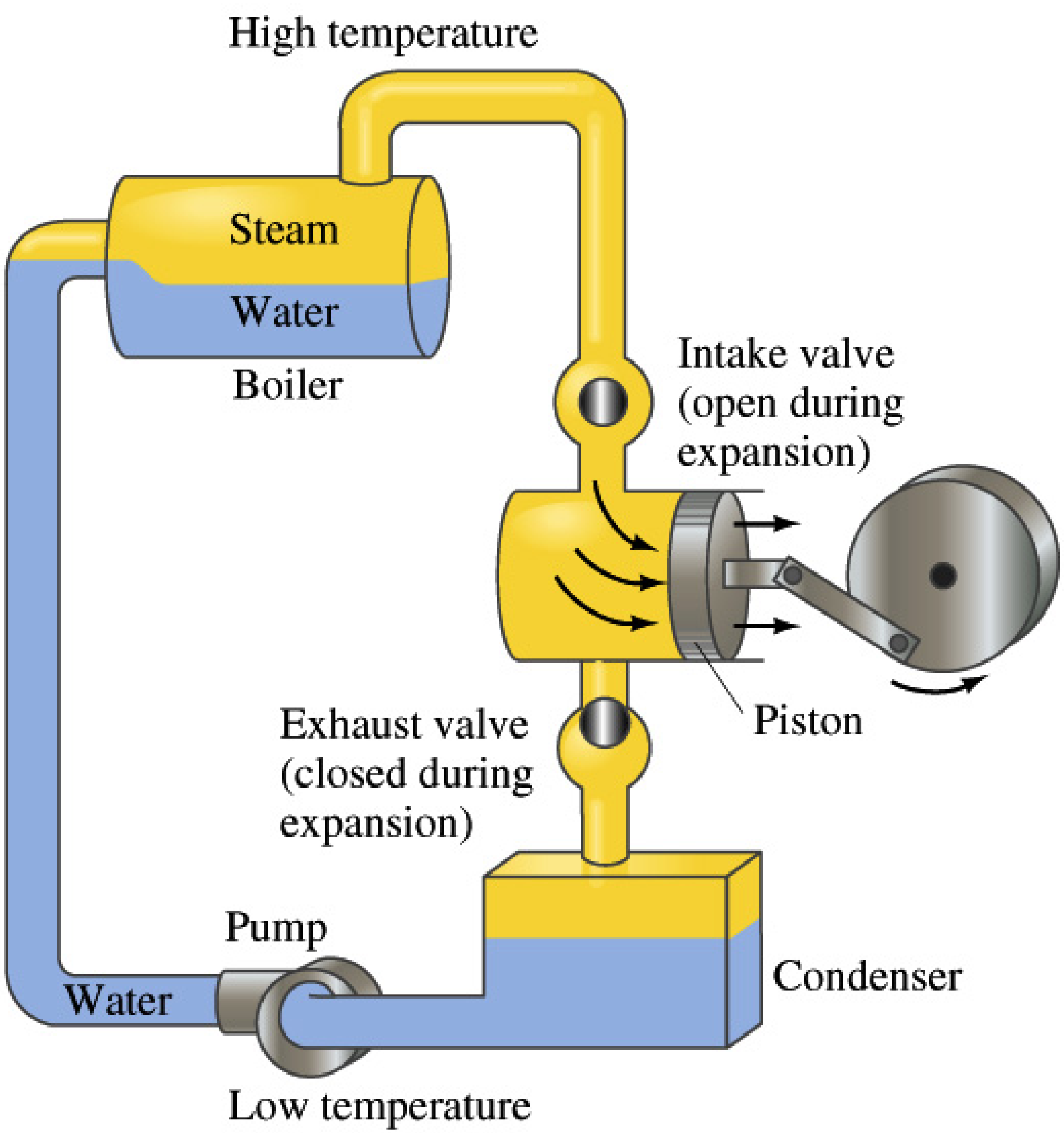
It is also possible to convert internal energy to work.

Heat Engines

- A *heat engine* converts heat into work.
    - T_H = *temperature of heat source*
    - T_L = *temperature of heat sink*
    - Q_H = *heat supplied*
    - Q_L = *heat released*
    - W = *work produced*

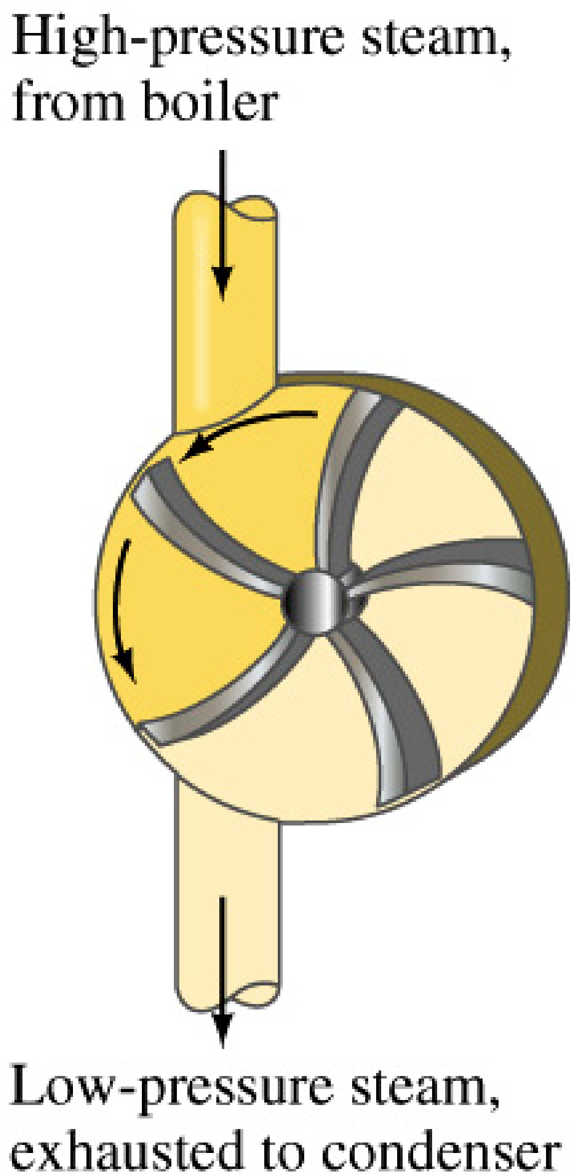


Heat Engines (Steam Engines)



(a) Reciprocating type

Heat Engines (Steam Engines)



Efficiency of Heat Engines

Conservation of Energy (1st Law):

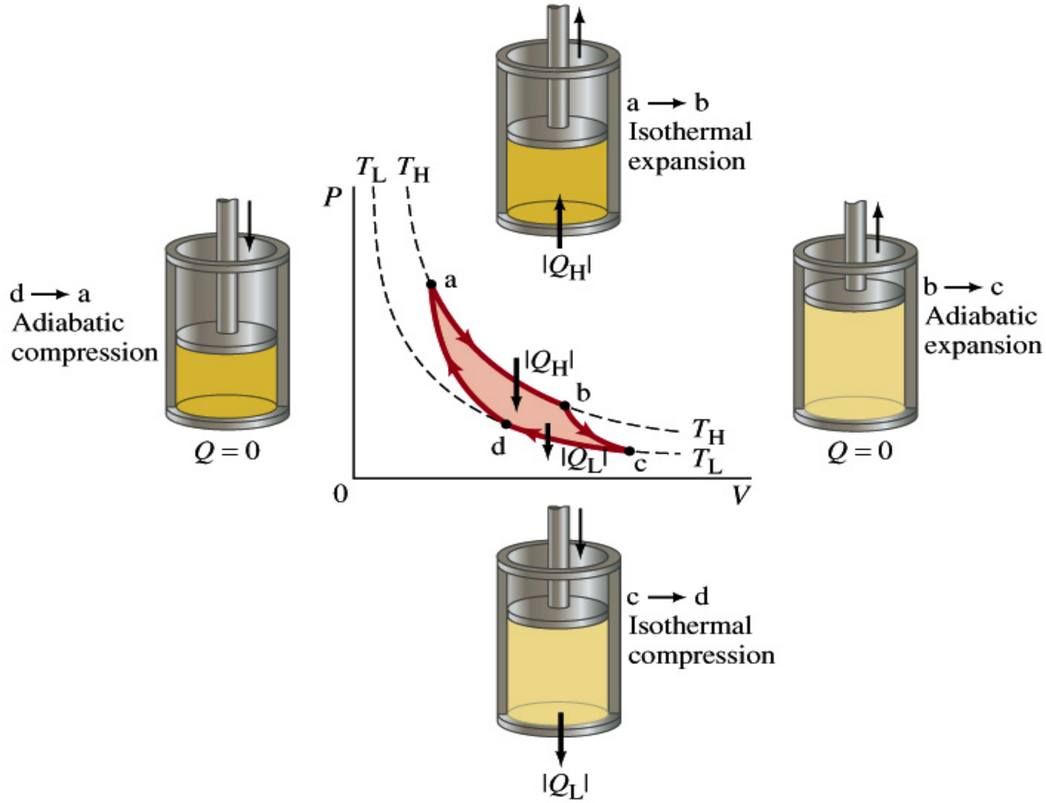
$$0 = \sum Q - \sum W \text{ or } W = Q_H - Q_L$$

An engine operates in a cycle, then efficiency is given by

$$\varepsilon = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

$Q_L > 0$ implies $\varepsilon < 1$

Carnot (Ideal) Heat Engine



<u>Operates in a ***reversible*** cycle</u>:
a–b: isothermal expansion *($\Delta T=0$)*
b–c: adiabatic expansion *($Q=0$)*
c–d: isothermal compression *($\Delta T=0$)*
d–a: adiabatic compression *($Q=0$)*

Ideal (Carnot) Efficiency

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \rightarrow \varepsilon_C = 1 - \frac{T_L}{T_H}$$

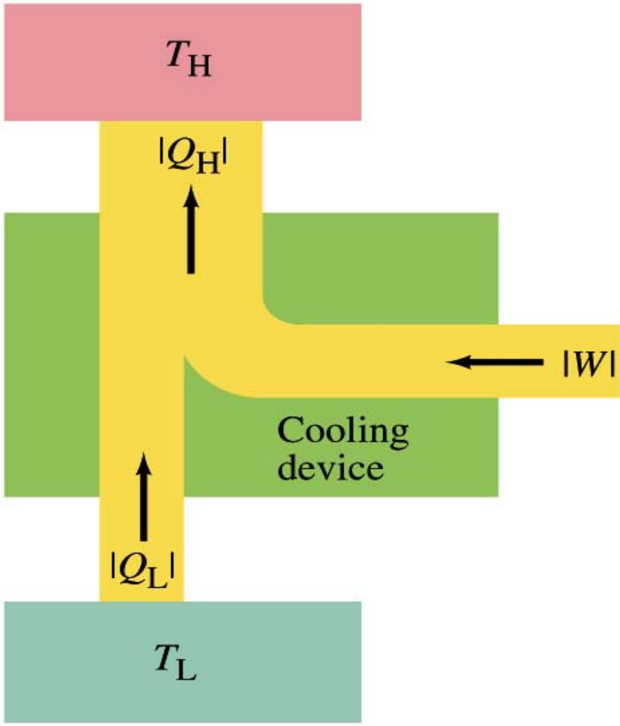
Efficiencies of Real Heat Engines

- No heat engine can ever have an efficiency greater than that of the Carnot (ideal) heat engine.
- All real heat engines have losses (e.g. friction) and are therefore **not reversible**.
- All real heat engines have efficiencies less than that of a Carnot engine operating between the same temperatures T_H and T_L.

Alternate Statement of Second Law:

- No device can transform a quantity of heat completely to work.

Heat Pump



- A heat pump is a heat engine operating in reverse.
- Examples of heat pumps are refrigerators and air conditioners.
- Conservation of Energy:

Energy In = Energy Out

$$Q_L + W = Q_H$$

$$CP = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

$$CP_{ideal} = \frac{T_L}{T_H - T_L}$$

Entropy

- Processes that do not violate the first law of thermodynamics (conservation of energy) will never occur spontaneously.
- Entropy *(S)* is a measure of the disorder or randomness in a system, and is a state variable (like P, V, T) that does not depend on the path taken.

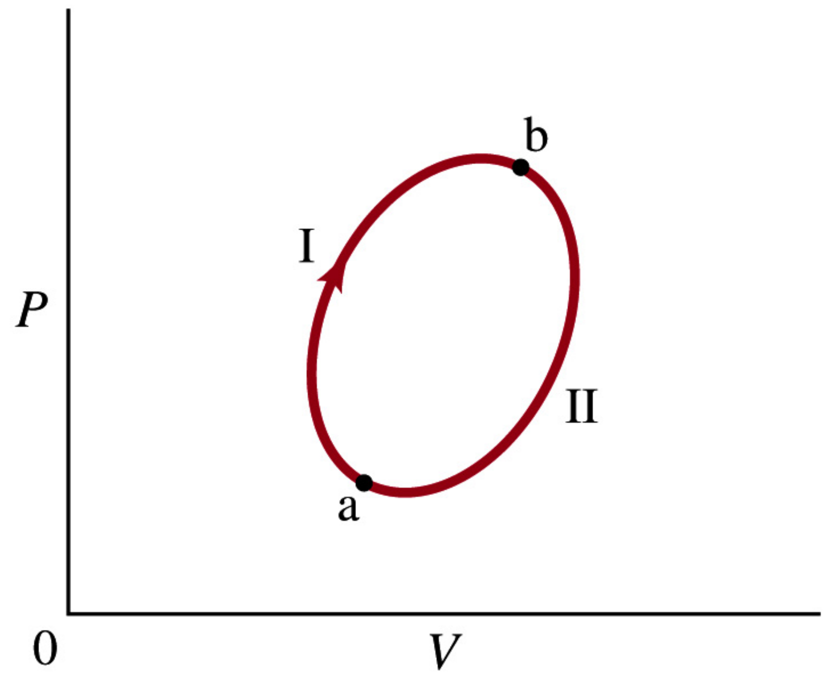
$$dS = \frac{dQ}{T} \text{ (change in entropy S)}$$

where dQ is an infinitesimal heat flow

Entropy and Reversible Processes

For any **reversible process** (e.g. Carnot cycle):

$$\oint \frac{dQ}{T} = 0$$



$$\int_{I\,a}^{b} \frac{dQ}{T} + \int_{II\,b}^{a} \frac{dQ}{T} = 0$$

$$\int_{I\,a}^{b} \frac{dQ}{T} = -\int_{II\,b}^{a} \frac{dQ}{T} = \int_{II\,a}^{b} \frac{dQ}{T}$$

The entropy of a system in a given state is independent of the path taken to get there, and is thus a **state variable**.

Entropy and Equilibrium States

- The entropy difference between two equilibrium states *a* and *b* does not depend on how the system got from *a* to *b*.

$$\Delta S = S_b - S_a = \int_a^b dS = \int_a^b \frac{dQ}{T}$$

Entropy is a **state variable** (like P,V and T)

Second Law in Terms of Entropy

ΔS = 0 reversible process

ΔS > 0 irreversible process

<u>Example</u>: Calorimetry $Q = m\,c\,\Delta T$

For small changes: $dQ = m\,c\,dT$

$$dS = \frac{dQ}{T}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{dQ}{T} = mc\int_{T_i}^{T_f} \frac{dT}{T} = mc\ln\left(\frac{T_f}{T_i}\right)$$