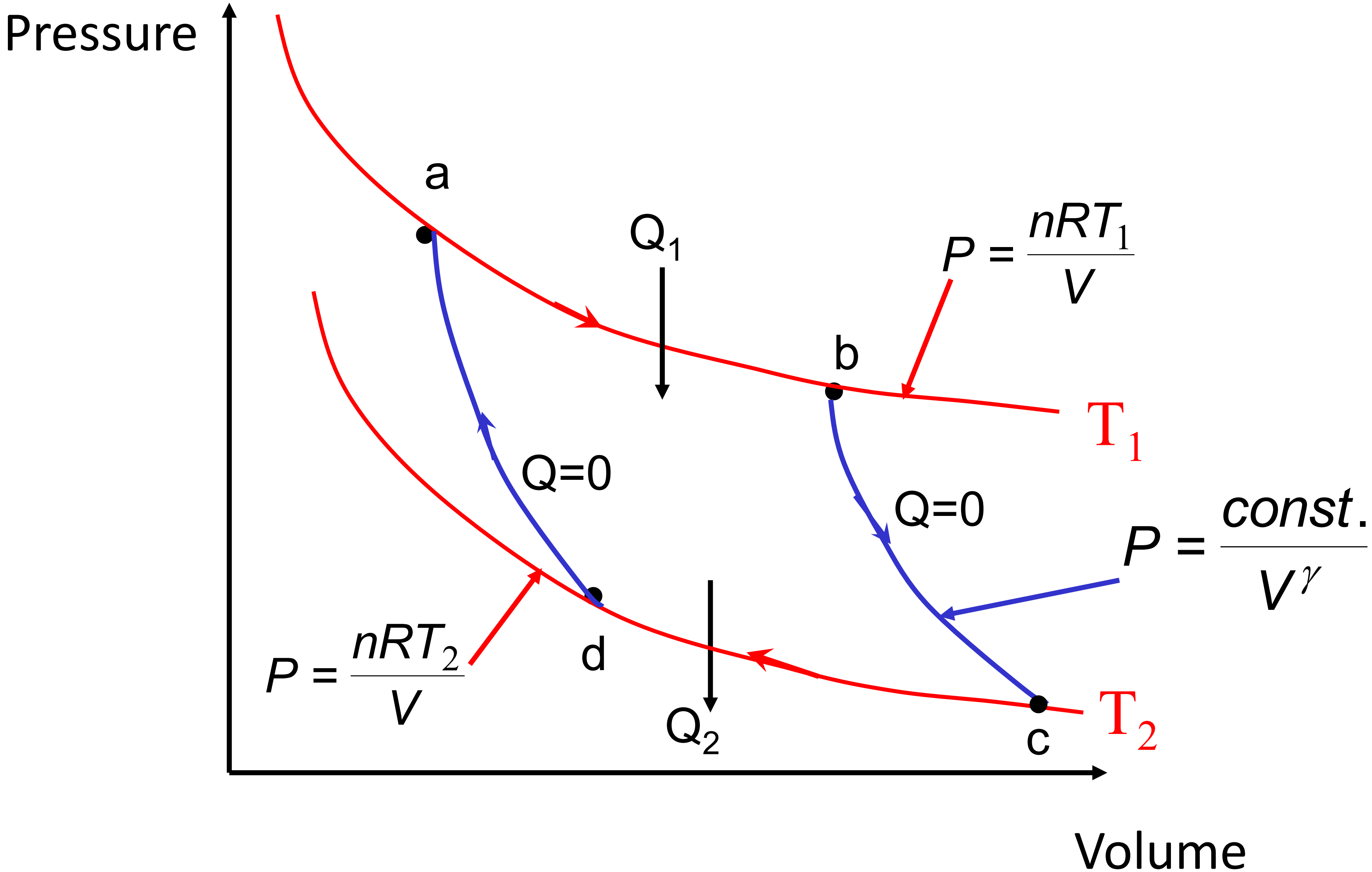
The Clausius Inequality

- Expressions of inequality/equality relating to heat flow at a fixed temperature.

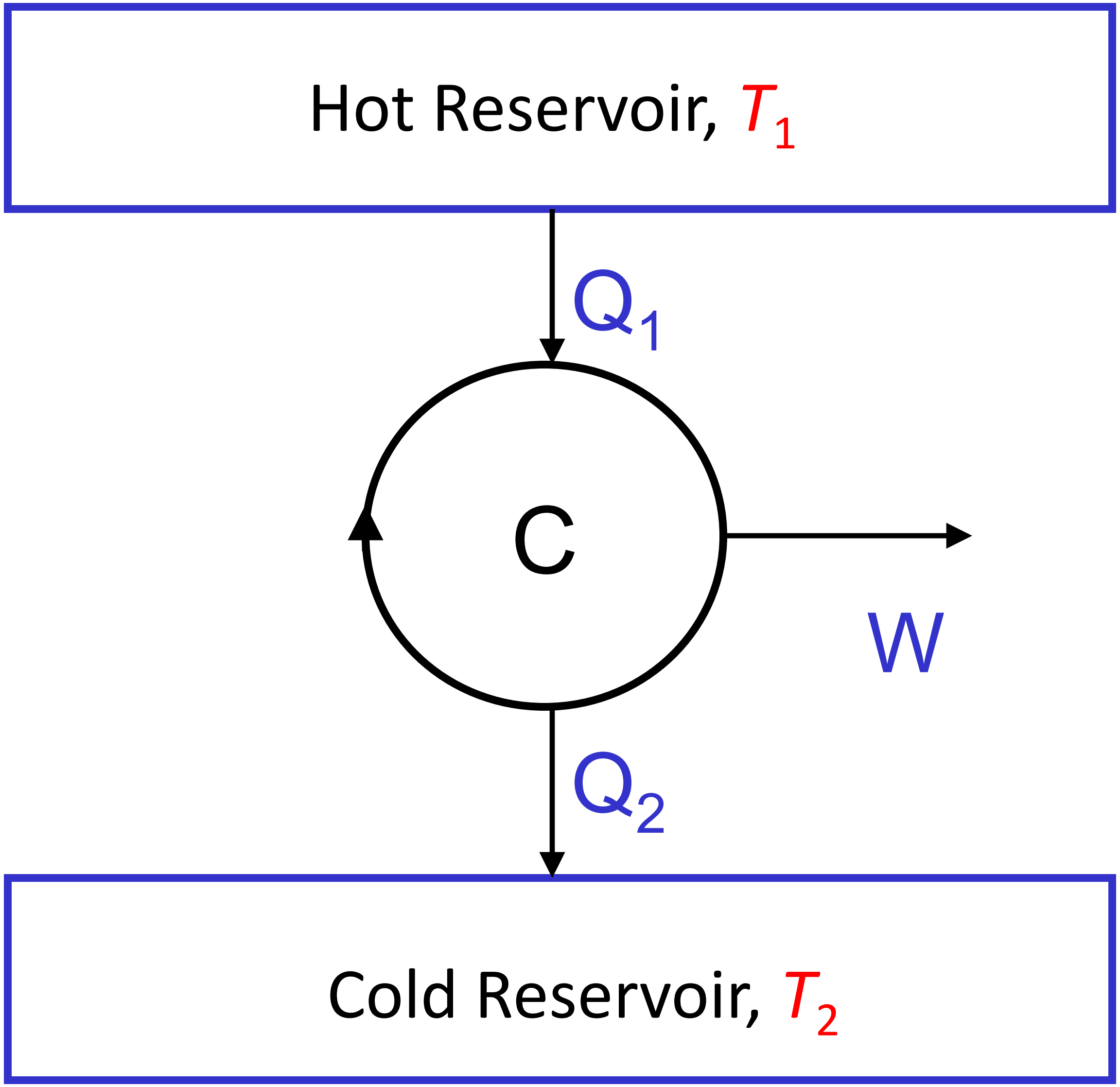
- The expression is required for the derivation of an equation for entropy – which is our next main topic.

- Derived from a “thought experiment” using Carnot engines acting in a series.

Carnot Cycle



Heat Flows in a Carnot Cycle



$$\frac{T_1}{T_2} = \frac{Q_1}{Q_2}$$

$$Q_1 = Q_2 \frac{T_1}{T_2}$$

For a Carnot cycle, some of the heat into the cycle is converted to work so that $Q_1 > Q_2$. We also know that

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Such that

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

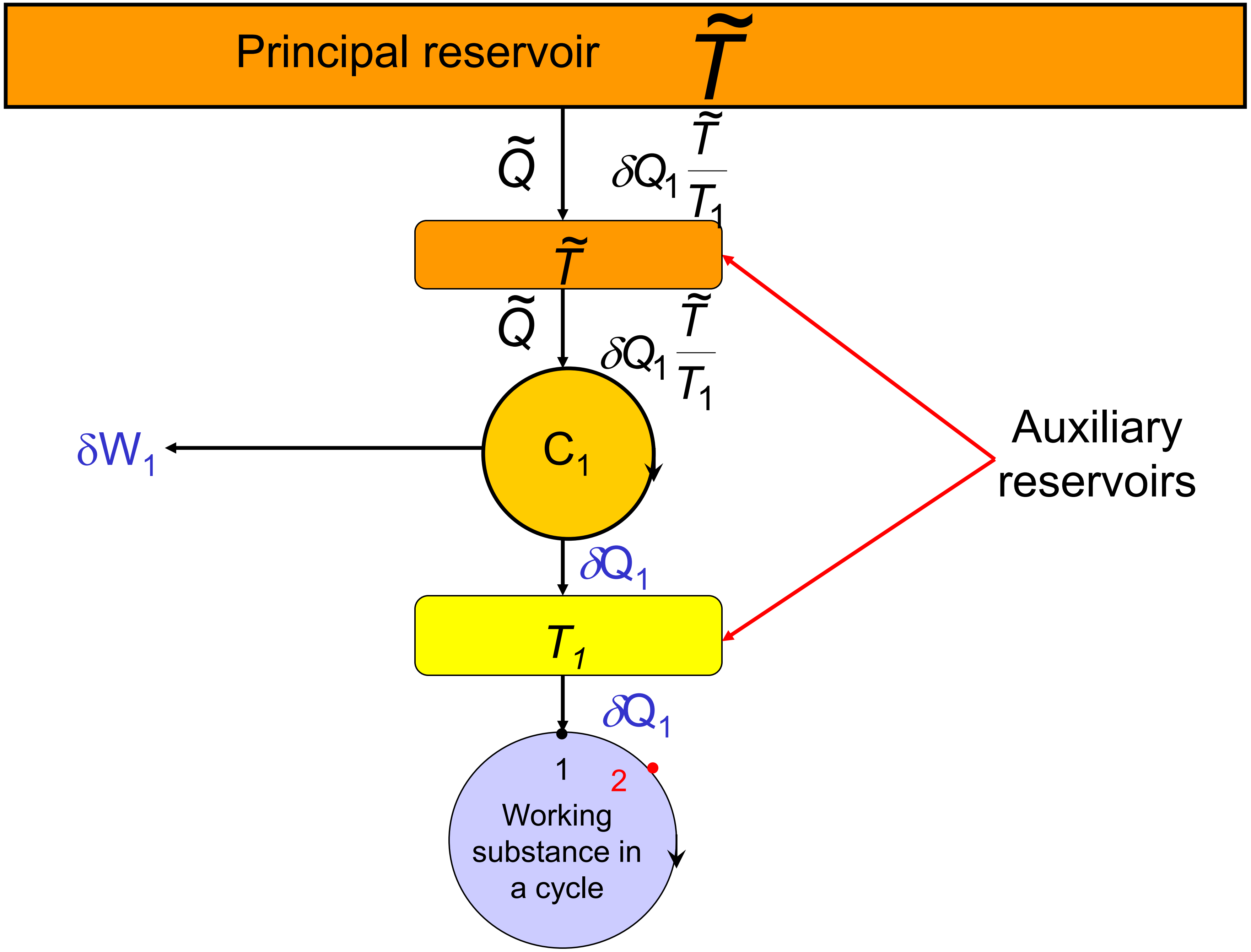
One could also consider the small amount of reversible heat flow δQ^{rev} that flows at a temperature T at each point in the cycle. The net heat flow is equal to the sum of the differential flows:

$$\sum_{cycle} \frac{\partial Q^{rev}}{T} = \frac{Q_1}{T_1} + \frac{-Q_2}{T_2} = 0$$

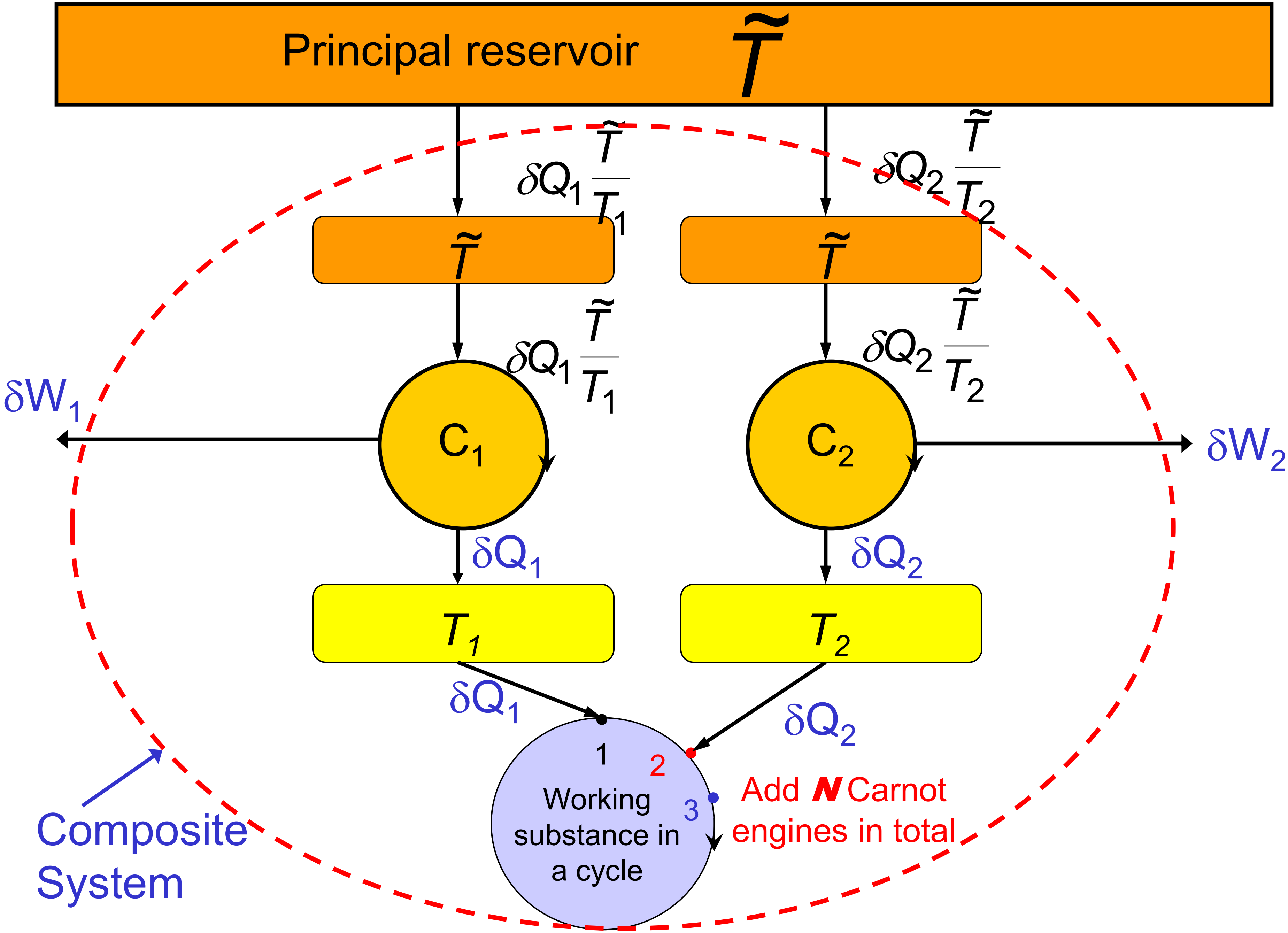
From the definition of an integral, we find for the entire cycle that

$$\oint \frac{\partial Q^{rev}}{T} = 0$$

But is this generally true for ***any*** cycle?



Derivation of the Clausius Inequality



Derivation of the Clausius Inequality

Analysis of Composite Device

The total heat supplied by the reservoir to the composite device in a cycle with *N* engines is:

$$Q = \sum_{i=1}^{N} \delta Q_i \frac{\tilde{T}}{T_i}$$

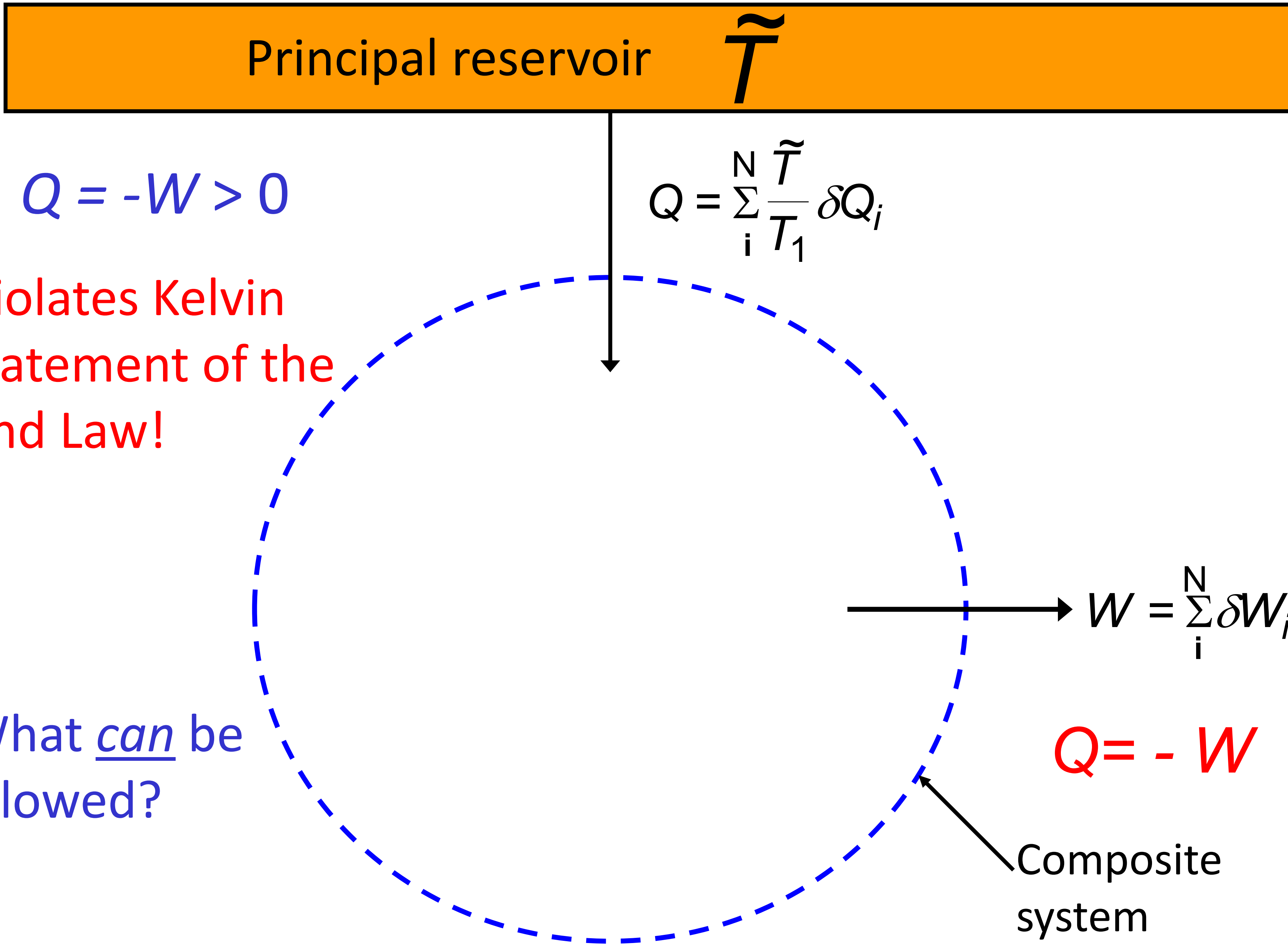
The total work done by the composite device in a cycle is

$$W = \sum_{i=1}^{N} \delta W_i$$

In an entire cycle, ΔU for the working substance and the composite device is 0. Then the First Law says:

$$\Delta U = 0 = W + Q$$

An important conclusion is that $Q = -W$.



$Q = -W > 0$

Violates Kelvin statement of the 2nd Law!

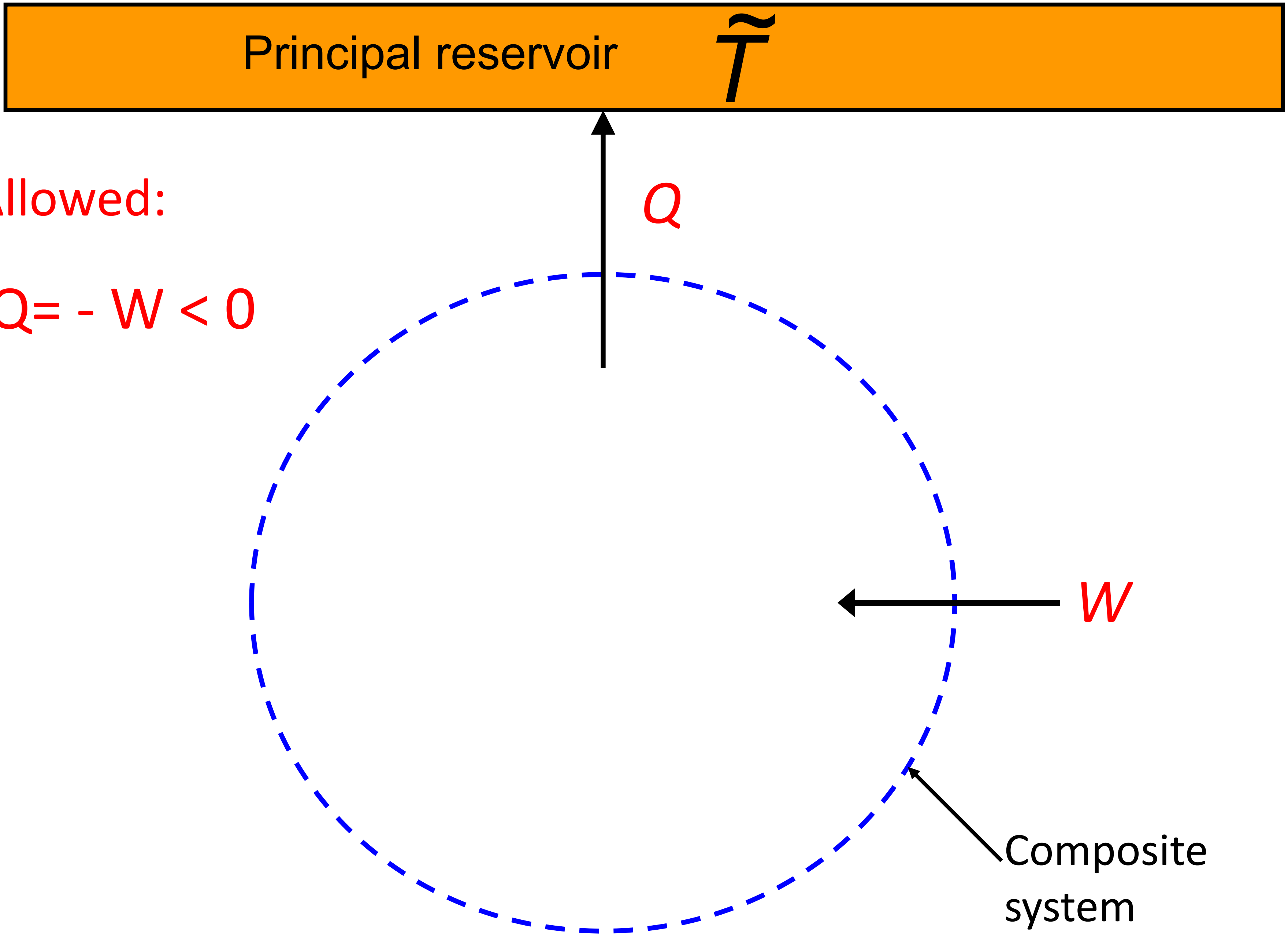
What *can* be allowed?

$Q = -W$

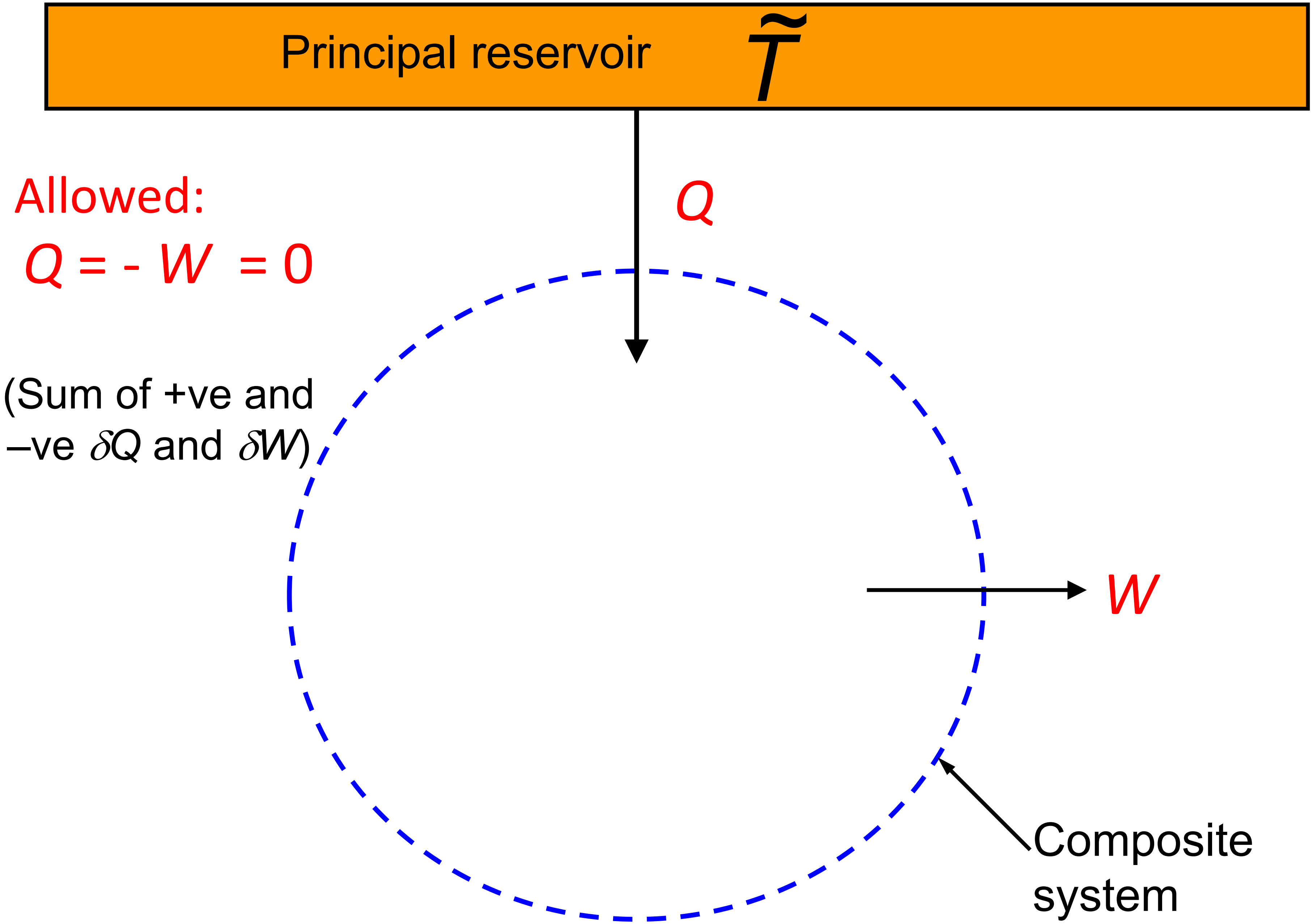
Derivation of the Clausius Inequality

Allowed:

$Q = - W < 0$



Derivation of the Clausius Inequality



Derivation of the Clausius Inequality

Results Allowed by Second Law

Q < *0* or Q = 0, thus $$Q = \tilde{T} \sum_{i=1}^{N} \frac{\delta Q_i}{T_i} \leq 0$$

But $\tilde{T} \neq 0$, so we can divide by $\tilde{T}$

$$\sum_{i=1}^{N} \frac{\delta Q_i}{T_i} \leq 0$$

In the limit of small δQ_i, we can integrate over the entire cycle:

$$\oint \frac{dQ}{T_o} \leq 0$$

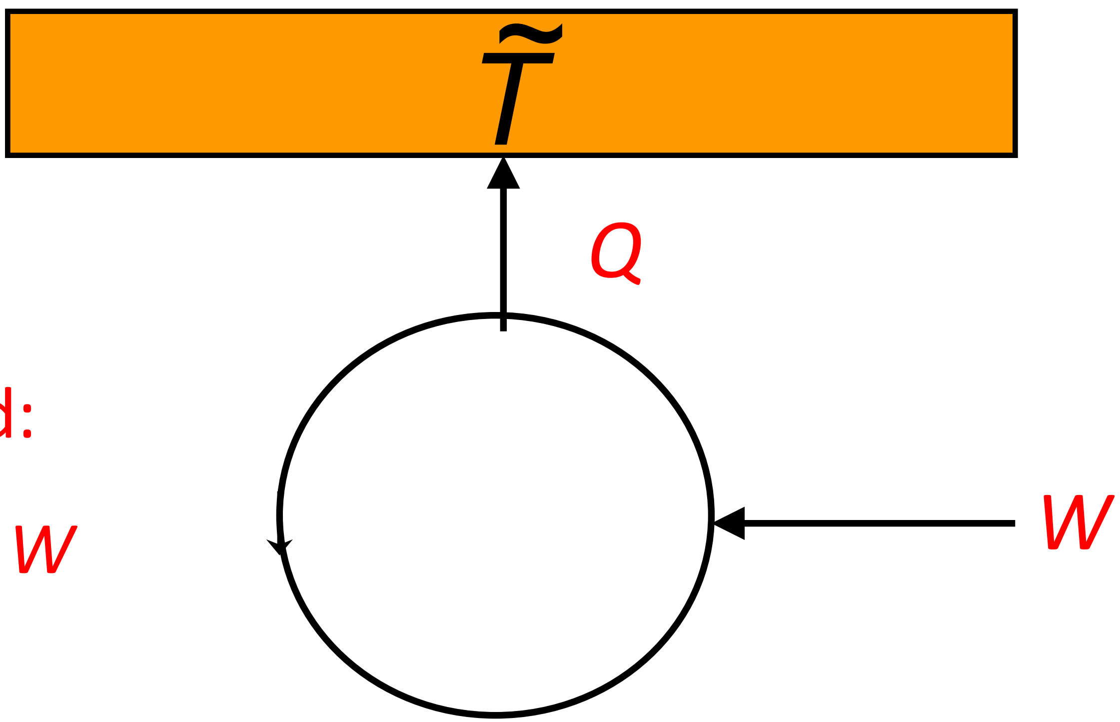
Clausius Inequality

where T_o is the temp. of the reservoir (external heat source) and the circle represents integration over the entire cycle.

Reversible Cycles

If the cycle at the centre of the composite device is *reversible*, then it can be run in reverse.

The opposite result is then obtained. In the composite device, work is done ON the system, and heat is given OFF to the reservoir.



Allowed:

$0 \geq Q = - W$

Reversible Cycles

- Thus, there are restrictions on *Q* when the cycle is operated in reverse.

- But the cycle can still also be operated in the forward direction such that:

$$-W = Q = \tilde{T}\sum_{i=1}^{N}\frac{\delta Q_i}{T_i} \geq 0$$

- Only <u>one</u> solution satisfies both requirements for forward and reverse cycles:

$$Q = \tilde{T}\sum_{i=1}^{N}\frac{\delta Q_i}{T_i} = 0$$

- Integrating:

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

Clausius Equality

In a reversible process, the temperature of the system and reservoir are equal: *T*.