

# STATISTICAL MOLECULAR THERMODYNAMICS

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Video 6.8

The Carnot Cycle

## OUR EXPANDING TOOLBOX

$$\delta q_{rev} = TdS, \delta w_{rev} = -PdV, dU = \delta q_{rev} + \delta w_{rev}$$

$$dS = \frac{dU}{T} + \frac{P}{T}dV \quad \rightarrow \quad \begin{array}{l} d\bar{U} = \bar{C}_v dT \\ P\bar{V} = RT \end{array} \quad \rightarrow \quad d\bar{S} = \bar{C}_v \frac{dT}{T} + R \frac{dV}{\bar{V}}$$

If  $C_v$  is independent of  $T$ :

Or, for an ideal gas:

$$\Delta\bar{S} = \bar{C}_v \ln \frac{T_2}{T_1} + R \ln \frac{\bar{V}_2}{\bar{V}_1} \quad \Delta\bar{S} = \bar{C}_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Remember that for a spontaneous irreversible process:  $\Delta\bar{S} > 0$

## SADI CARNOT



At age 28, Carnot wrote *Reflections on the Motive Power of Fire*, a monograph on heat engines and those factors affecting their efficiency.

His work was foundational for Clausius and Lord Kelvin in their development of the Second Law.

Carnot died in a cholera epidemic in 1832 at the age of 36.

# AN IDEAL GAS CARNOT ENGINE

## The Power Cycle

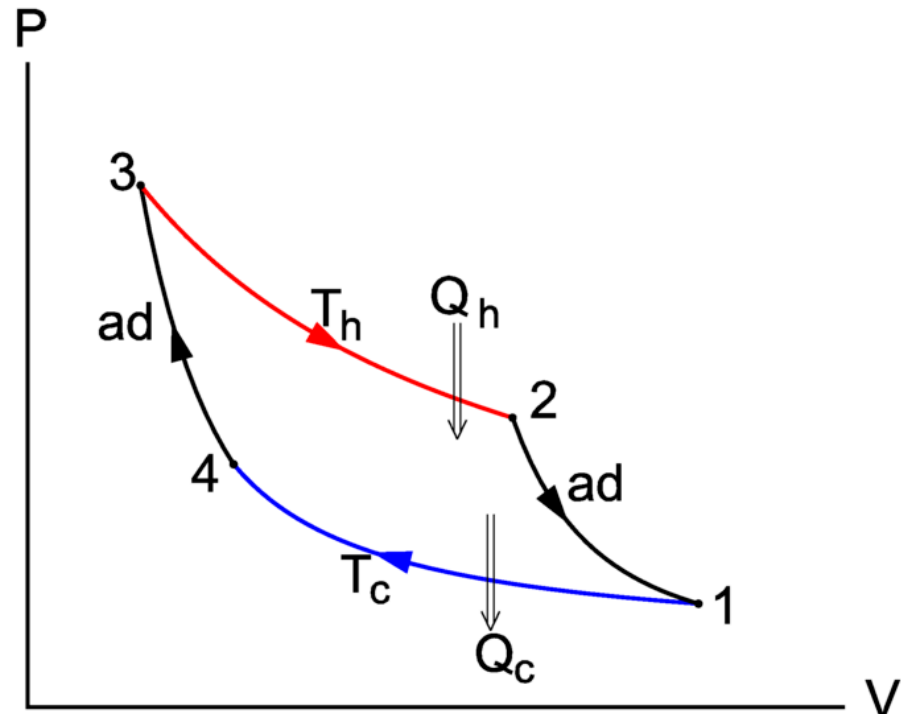
At point 1, in contact with a cold reservoir, isothermally compress gas in a piston

At point 4, continue to compress the gas adiabatically until its temperature rises to that of a hot reservoir

At point 3, in contact with the hot reservoir, permit the gas to expand isothermally, doing work

At point 2, permit the gas to continue to expand adiabatically until its temperature falls to that of the cold reservoir

Net work  $-w$  is area within  $PV$  loop; heat transfers only during isothermal steps



# AN IDEAL GAS CARNOT ENGINE

## Work

Isothermal steps:

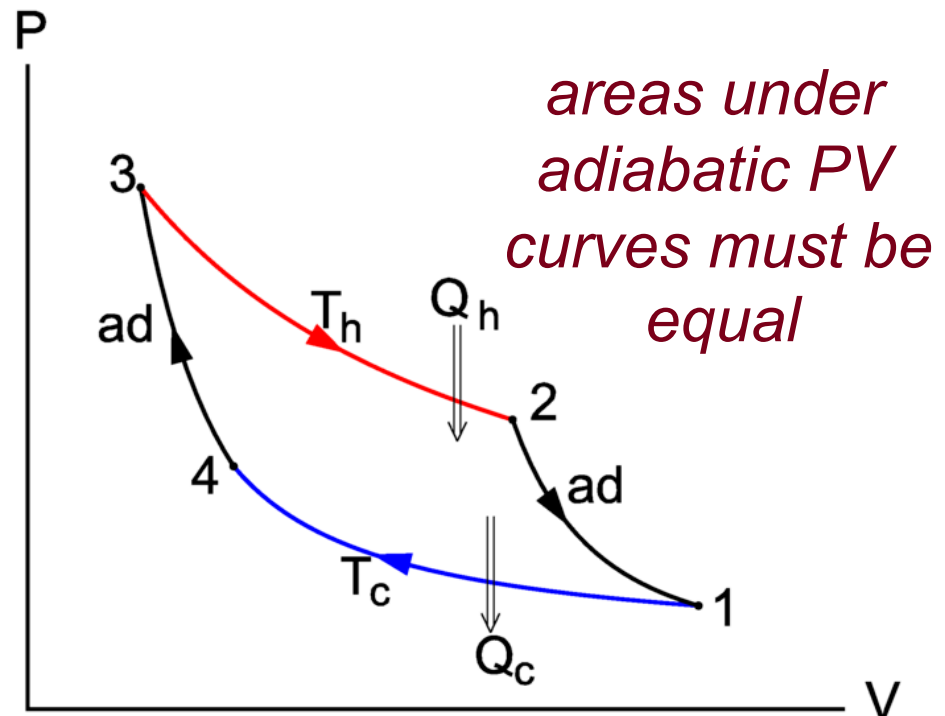
$$w_{rev} = -nRT_j \ln\left(\frac{V_f}{V_i}\right)$$

Adiabatic steps:

$$w = n\bar{C}_v(T_f - T_i)$$

Total:

$$w = -nR \left[ T_h \ln\left(\frac{V_2}{V_3}\right) + T_c \ln\left(\frac{V_4}{V_1}\right) \right]$$

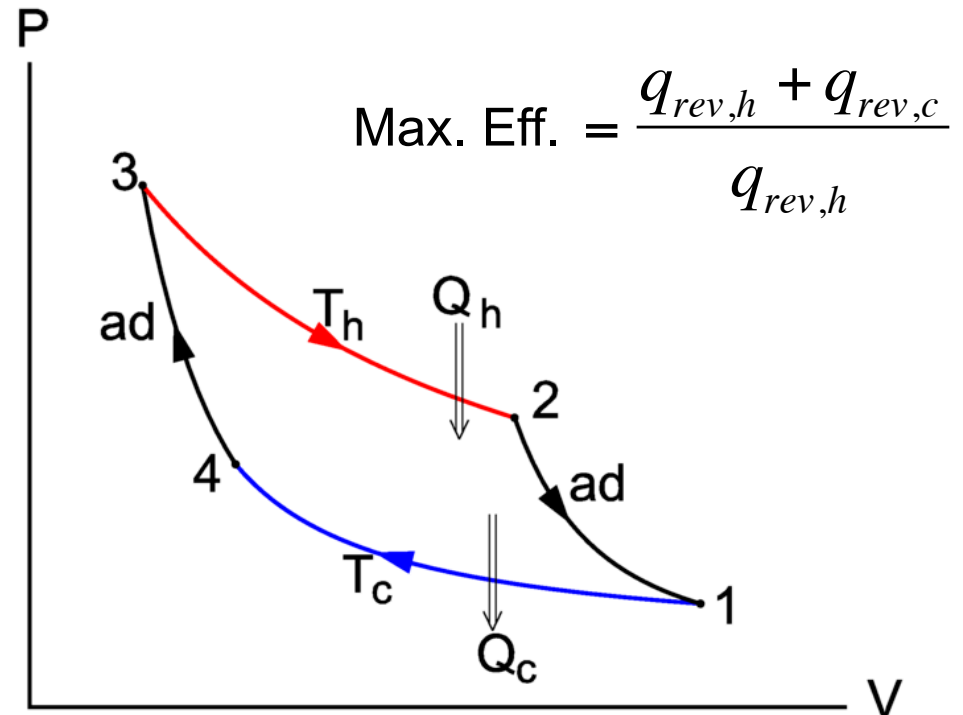


# EFFICIENCY OF THE CARNOT ENGINE

## Efficiency

Defined as work done divided by heat extracted from hot reservoir  $-w / q_{rev,h}$

Question: what is the *maximum possible* efficiency?



The maximum efficiency will be for a *reversible* engine cycle (no irreversible heat loss), in which case

$$\Delta U = w + q_{rev,h} + q_{rev,c} = 0 \quad \Rightarrow \quad -w = q_{rev,h} + q_{rev,c}$$

# EFFICIENCY OF THE CARNOT ENGINE

## Knowledge of Entropy

$$\Delta S = \frac{\delta q_{rev,h}}{T_h} + \frac{\delta q_{rev,c}}{T_c} = 0$$

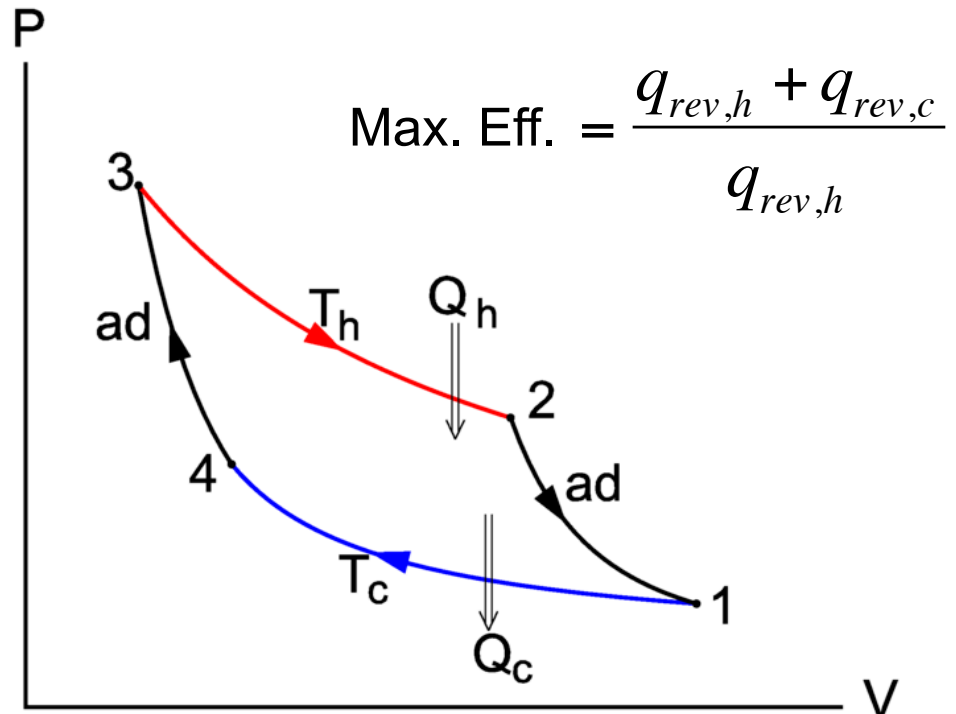
So,

$$q_{rev,c} = -q_{rev,h} \frac{T_c}{T_h}$$

Making this substitution into the expression for

maximum efficiency, we see that the *maximum efficiency depends only on the temperatures of the hot and cold reservoirs*

$$\text{Maximum Efficiency} = 1 - T_c / T_h$$

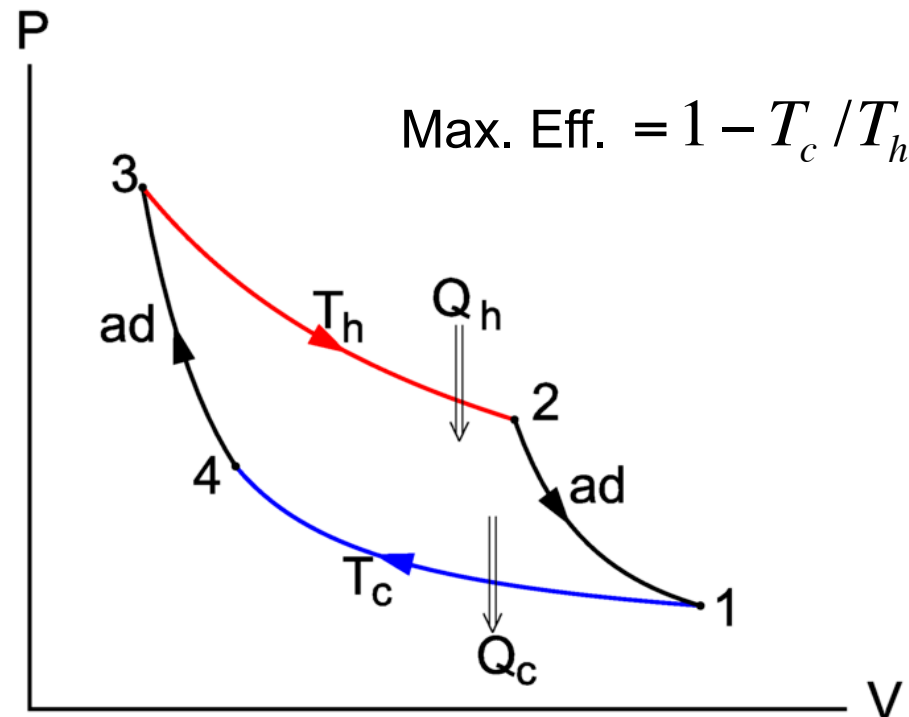


# A FINAL STATEMENT OF THE SECOND LAW

Lord Kelvin



William Thomson  
1824-1907



No net work can be  
obtained from an  
isothermal process

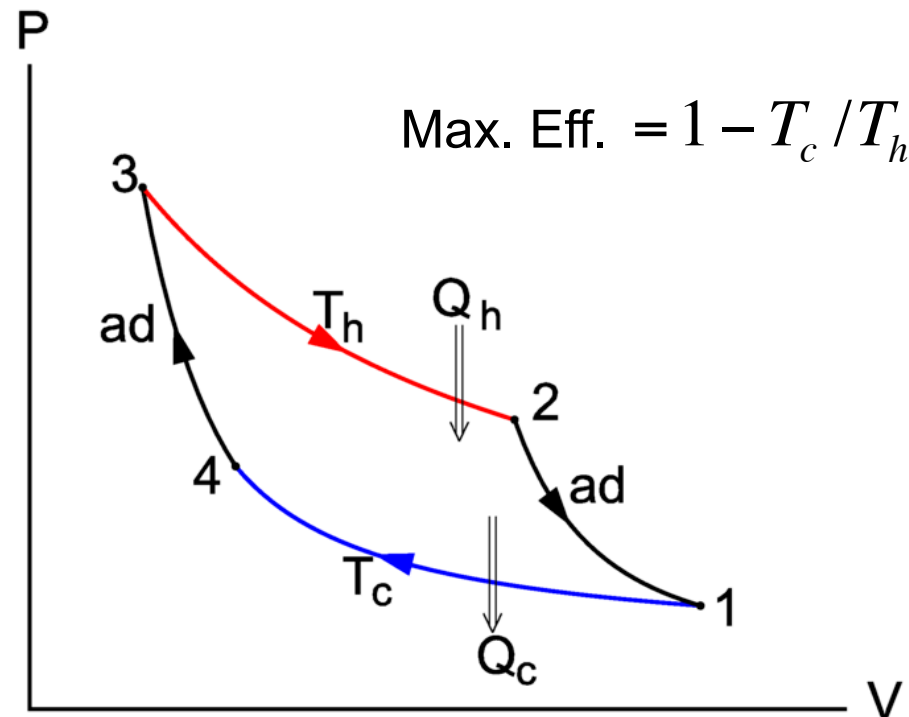


# A FINAL STATEMENT OF THE SECOND LAW

Lord Kelvin

No net work can be obtained from an isothermal process

*19<sup>th</sup> century practical take-away? If you want a better steam engine, use superheated steam*



Note that the above analysis holds for *any* engine converting heat to work, as we could always place such an engine in (reversible) equilibrium contact with a hypothetical ideal gas engine and thereby derive identical results. That's why ideal gases are so useful! They're easy to work with and provide general insights.