

CH365 Chemical Engineering Thermodynamics

Lesson 22 Statements of the Second Law and Derivation of Entropy

Professor Andrew Biaglow
14 October 2022

Axioms and Postulates

An axiom is an unprovable statement accepted as true because it is self-evident or particularly useful. For example, for any three numbers a , b , and c in a collection of numbers, $a \cdot (b \cdot c) = (a \cdot b) \cdot c$. In other words, the multiplication operation is associative.

An axiom is generally considered to be true but without a clearly defined proof. You just “know that it is true.” Nobody can prove that it is correct or disprove that it is incorrect. An axiom is a proposition which is self-evidently true.

A postulate is the same as an axiom but is a statement with higher significance and relates to a specific field. For example, a postulate of Euclidean geometry is that a straight line can be drawn between two points.

Axioms and postulates are the same and have the same definition.

They differ based on the context they are used or interpreted. The term axiom is used to refer to a statement which is always true in a broad range. A postulate is used in a very limited subject area.

Axiom is an older term while postulate is relatively modern in usage.

Postulates (Axioms) of the 1st Law

There exists a form of energy, known as internal energy U , which is an intrinsic property of a system.

Internal energy is functionally related to the measurable variables that characterize the system (T , V , P , and composition).

For a closed system, changes in internal energy are given by:

$$\Delta U = Q + W$$

Chapter 2, page 28

(First Law) The total energy of any system and its surrounding is conserved.

The macroscopic properties of a homogeneous PVT (fluid) system at equilibrium can be expressed as a function of temperature, pressure, molar volume, and composition.

Postulates (Axioms) of the 2nd Law

Entropy S is an intrinsic property of any system at equilibrium.

Entropy is functionally related to the measurable state variables that characterize the system (T , V , P , and composition).

Differential changes in the total system entropy S^t are given by:

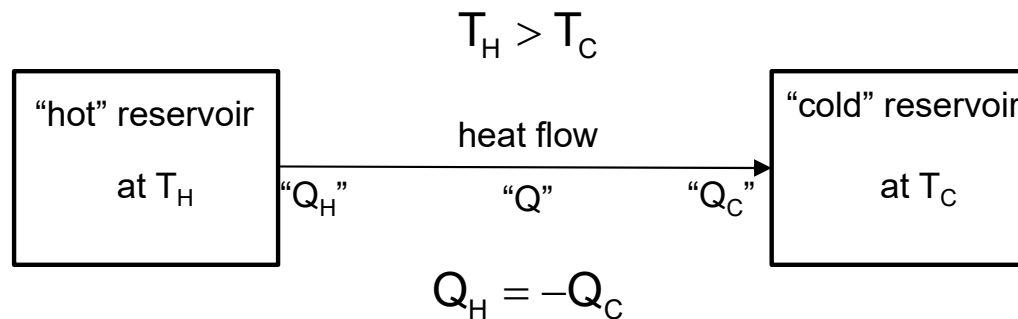
$$dS^t = \frac{dQ_{\text{rev}}}{T} \quad \text{Eq. 5.1, p. 178}$$

The entropy change of any system and its surroundings, considered together, and resulting from any real process, is positive, approaching zero only when the process approaches reversibility.

$$\Delta S_{\text{total}} \geq 0 \quad \text{Eq. 5.2, p. 178}$$

No process is possible which consists solely in the transfer of heat from one temperature level to a higher one.

Application to Simple Heat Transfer



A “reservoir” is capable of absorbing or rejecting an unlimited quantity of heat without changing temperature.

from Eq. 5.1: $dS^t = \frac{dQ_{\text{rev}}}{T} \xrightarrow{\int} \Delta S = \frac{Q}{T} \quad (\text{constant } T)$

$$\Delta S_H^t = \frac{Q_H}{T_H} = \frac{-Q_C}{T_H} \quad \text{and} \quad \Delta S_C^t = \frac{-Q_C}{T_C}$$

$$\Delta S_{\text{total}} = \Delta S_H^t + \Delta S_C^t = \frac{-Q_C}{T_H} + \frac{Q_C}{T_C} = Q_C \left(\frac{T_H - T_C}{T_H \cdot T_C} \right)$$

$$\left. \begin{array}{l} \Delta S_{\text{total}} > 0 \\ T_H > 0 \\ T_C > 0 \end{array} \right\} Q_C (T_H - T_C) > 0 \xrightarrow{\quad} Q_C > 0 \quad T_H > T_C$$

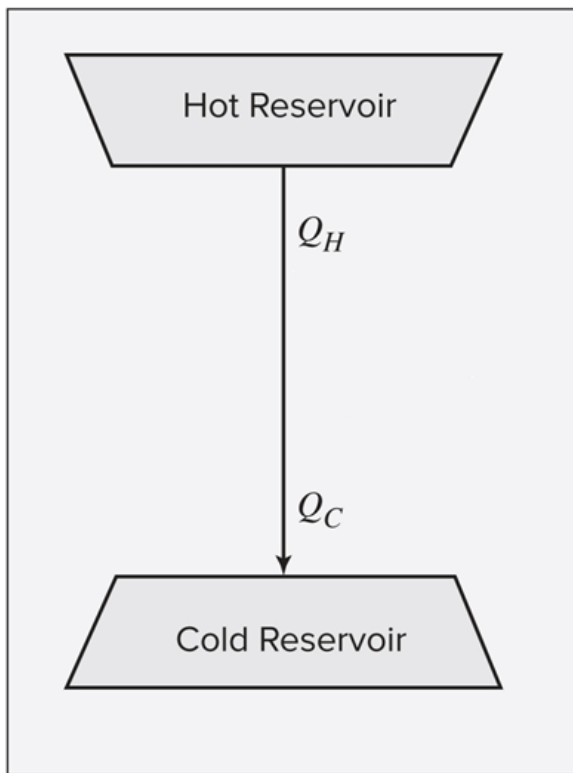
Since Q_C is positive, heat flows into the cold reservoir. That is, **heat must flow from higher to lower T**

No process is possible which consists solely in the transfer of heat from one temperature level to a higher one.

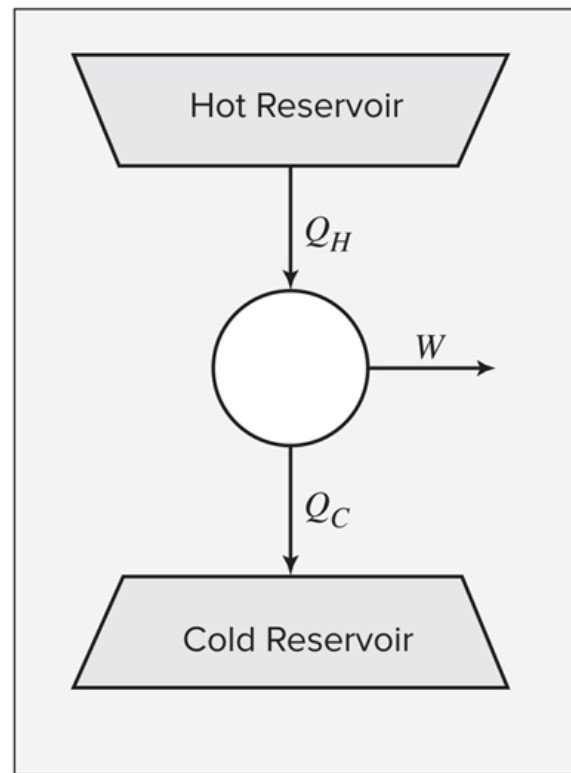
Application to Heat Engines

Slide 6

The simple heat transfer model can be modified by adding a device to draw out work from the flowing heat.

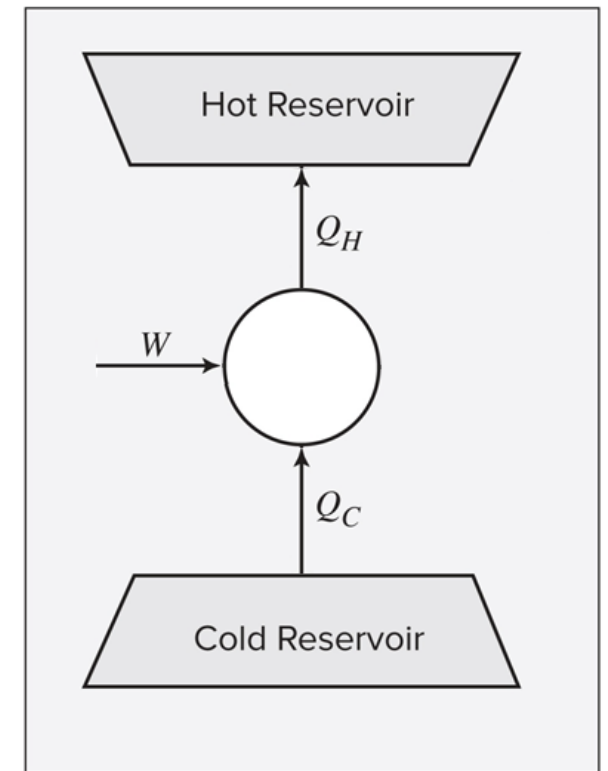


Simple heat transfer



Carnot engine

Even though no process is possible which consists solely in the transfer of heat from one temperature level to a higher one ...



Carnot Refrigerator
(heat pump)

... it turns out that we can do this by adding work to the system.

Derivation of Carnot Equations Slide 7

First Law:

$$\Delta U = Q + W = Q_H + Q_C + W$$

Cyclic processes (engines):

$$\Delta U = 0$$

$$Q_H = -W - Q_C$$

Total entropy change:

$$\Delta S_{\text{total}} = \frac{-Q_H}{T_H} - \frac{Q_C}{T_C}$$

$$Q_H = -T_H \Delta S_{\text{total}} - \frac{Q_C}{T_C} T_H$$

Equate Q_H and solve for W :

$$-W - Q_C = -T_H \Delta S_{\text{total}} - \frac{Q_C}{T_C} T_H$$

$$W = T_H \Delta S_{\text{total}} + Q_C \left(\frac{T_H - T_C}{T_C} \right)$$

Limiting case 1:
(engine is ineffective)
 $W=0$

$$\Delta S_{\text{total}} = -Q_C \left(\frac{T_H - T_C}{T_H T_C} \right)$$

Same as simple heat transfer, slide 5

Limiting case 2:
(completely reversible)

$$\Delta S_{\text{total}} = 0$$

$$W = Q_C \left(\frac{T_H}{T_C} - 1 \right)$$

Eq. 5.3, p. 181

A "Carnot" engine

Entropy:

$$-Q_H - Q_C = Q_C \left(\frac{T_H}{T_C} - 1 \right)$$

$$-Q_H = Q_C \frac{T_H}{T_C}$$

$$\frac{-Q_C}{T_C} = \frac{Q_H}{T_H}$$

Eq. 5.4, p. 182

Efficiency:

$$Q_C = -Q_H \frac{T_C}{T_H}$$

$$W = -Q_H - Q_C$$

$$W = -Q_H + Q_H \frac{T_C}{T_H}$$

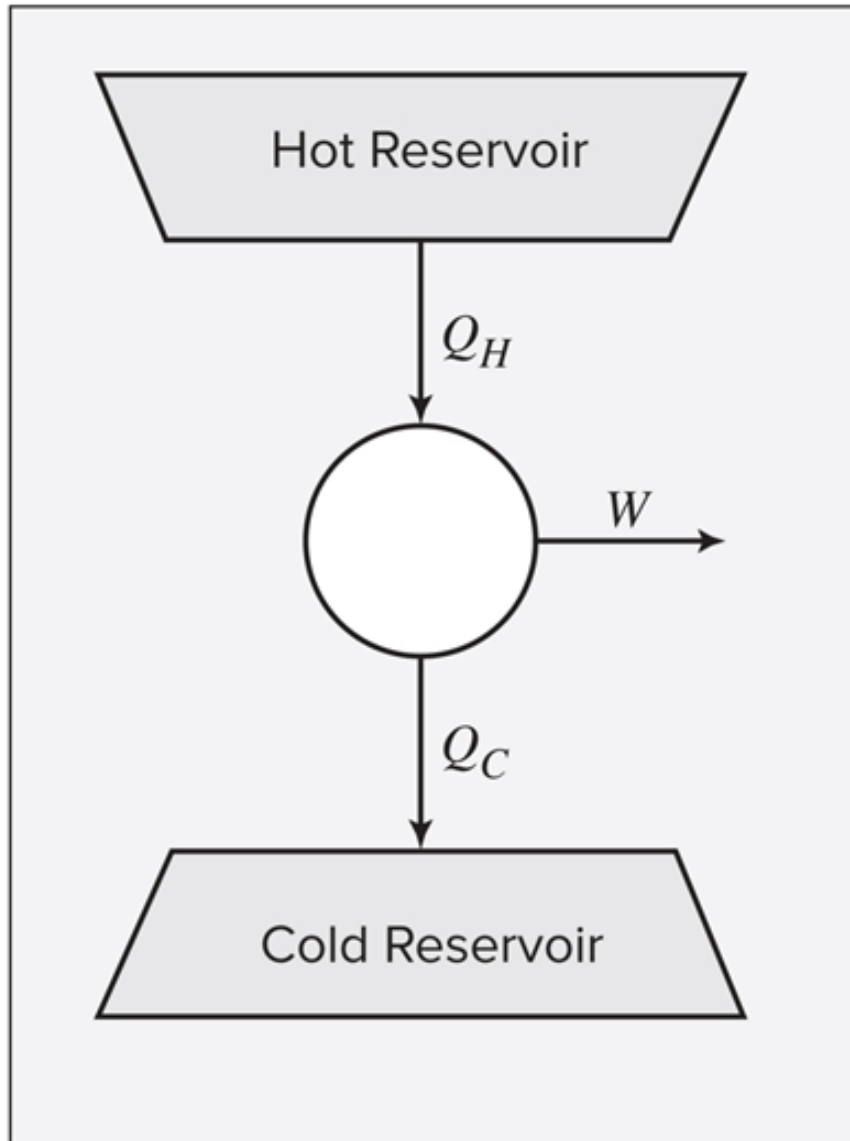
$$W = Q_H \left(\frac{T_C}{T_H} - 1 \right)$$

Eq. 5.5

$$\frac{-W}{Q_H} = 1 - \frac{T_C}{T_H} \equiv \eta_{\text{Carnot}}$$

Eq. 5.6, 5.7

Carnot Efficiency



$$\eta \equiv \frac{-W}{Q_H} = 1 - \frac{T_C}{T_H}$$

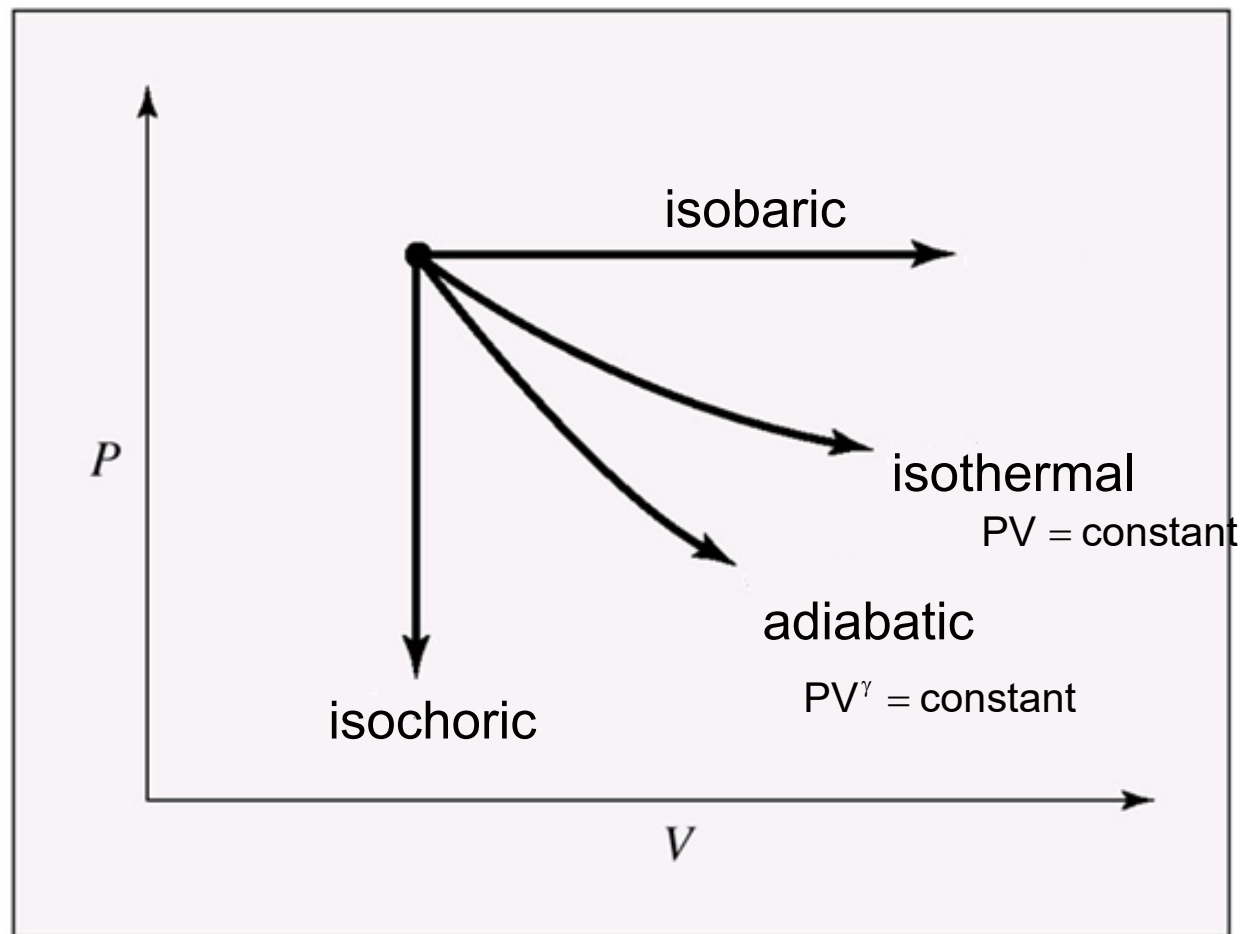
Eqns. 5.6, 5.7

The thermal efficiency of a Carnot engine depends only on the temperature levels and not upon the working substance of the engine.

For two given heat reservoirs, no engine can have a thermal efficiency higher than that of a Carnot engine. The Carnot efficiency is a maximum.

Polytropic Processes – Ideal Gases

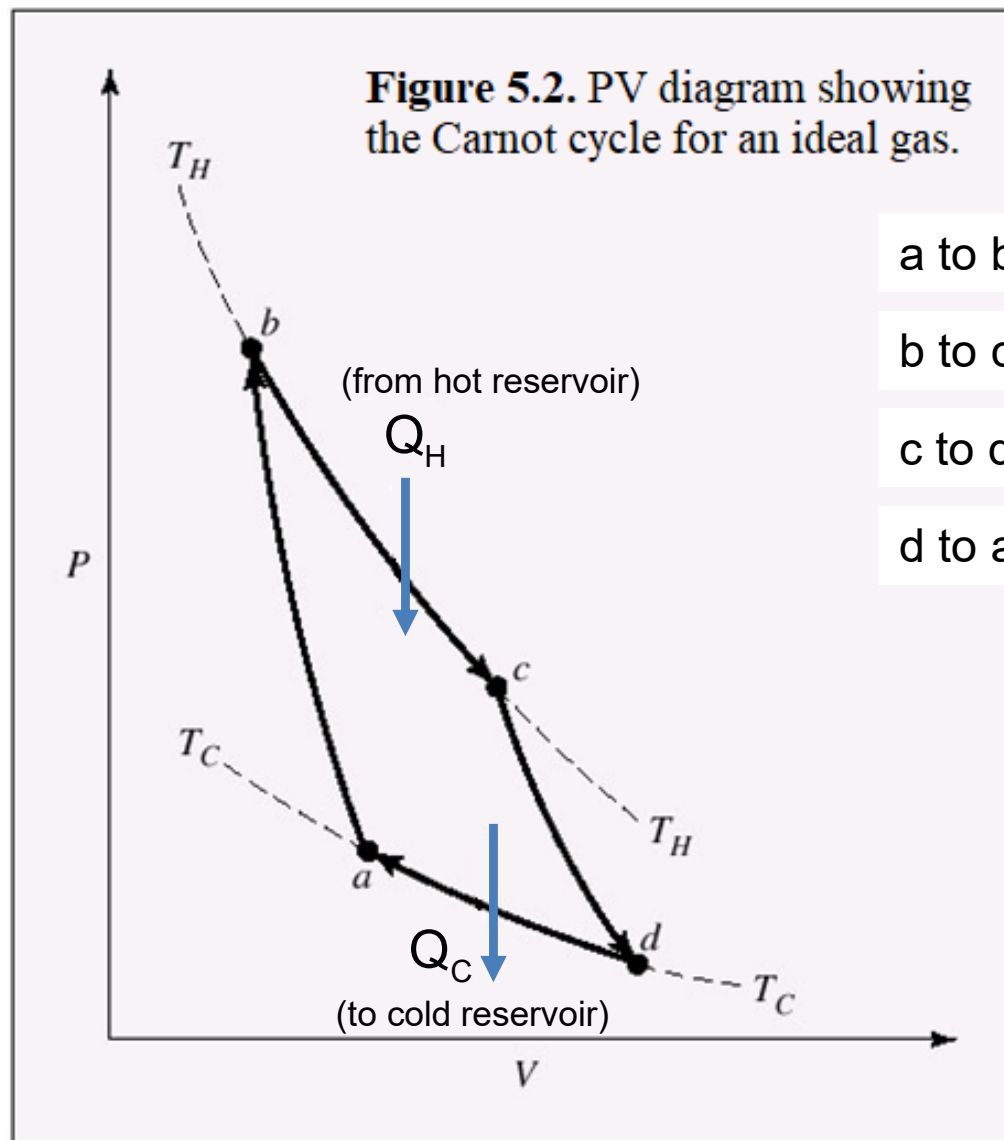
Lesson 11
Slide 12



Paths of polytropic processes

$$\gamma \equiv \frac{C_P}{C_V} > 1$$

Constructing a Carnot Cycle



a to b adiabatic compression T goes from T_C to T_H

b to c isothermal expansion with Q_H added

c to d adiabatic expansion T goes from T_H to T_C

d to a isothermal compression with Q_C ejected

Q , W , ΔH , and ΔU Calculations from L11

$$dQ = C_V dT + RT \frac{dV}{V}$$

(3.16, L11, slide 4, row 2)
(equations for process calcs.)

$$P = \frac{RT}{V} = P(T, V)$$

Lesson 11 Review

Slide 11

Process Calculations, Slide 4

Example:

Using $P = \frac{RT}{V}$, show that $dW = -\frac{RT}{V}dV$ and $dQ = \frac{RT}{V}dV + C_V dT$

(3.17) (3.16)

$$\begin{array}{ccc} & P = \frac{RT}{V} & \\ & \swarrow & \\ dW = -\underbrace{P}dV & \Rightarrow & dW = -\frac{RT}{V}dV \quad \checkmark \\ & 1.3 & \end{array}$$

$$\begin{array}{ccc} dQ + dW = dU & & \\ \swarrow & \searrow & \\ \underbrace{dQ} = C_V dT & dQ = -\underbrace{dW} + C_V dT & \Rightarrow dQ = \frac{RT}{V}dV + C_V dT \\ (3.20a) & & \checkmark \end{array}$$

(Process calculations for ideal gas)

Deriving a Property

Isothermal process, derived from equation 3.16 in lesson 11, slides 4 and 6:

$$Q_H = RT_H \ln\left(\frac{V_c}{V_b}\right) \quad Q_C = RT_C \ln\left(\frac{V_d}{V_a}\right) \quad (\text{Eq. 3.20}) \quad \text{Dividing: } \frac{Q_H}{Q_C} = \frac{RT_H \ln(V_c / V_b)}{RT_C \ln(V_d / V_a)}$$

Adiabatic process, equation 3.16, lesson 11, slide 9, with $dQ=0$:

$$-\frac{C_V}{R} \frac{dT}{T} = \frac{dV}{V} \quad (\text{Eq. 3.16})$$

Integrating 3.16 along the adiabatic paths a-b (T_C - T_H) and c-d (T_C - T_H):

$$\begin{aligned} -\int_{T_C}^{T_H} \frac{C_V}{R} \frac{dT}{T} = \ln\left(\frac{V_b}{V_a}\right) &\xrightarrow{\text{Invert the ratio in the natural log term}} \int_{T_C}^{T_H} \frac{C_V}{R} \frac{dT}{T} = \ln\left(\frac{V_a}{V_b}\right) \quad \text{and} \quad -\int_{T_H}^{T_C} \frac{C_V}{R} \frac{dT}{T} = \ln\left(\frac{V_d}{V_c}\right) \\ &\xrightarrow{\text{Switch the limits of integration}} \int_{T_C}^{T_H} \frac{C_V}{R} \frac{dT}{T} = \ln\left(\frac{V_d}{V_c}\right) \end{aligned}$$

These are the same

$$\therefore \ln\left(\frac{V_a}{V_b}\right) = \ln\left(\frac{V_d}{V_c}\right) \Rightarrow \exp\left(\ln\left(\frac{V_a}{V_b}\right)\right) = \exp\left(\ln\left(\frac{V_d}{V_c}\right)\right) \Rightarrow \frac{V_a}{V_b} = \frac{V_d}{V_c} \Rightarrow \frac{V_c}{V_b} = \frac{V_d}{V_a} \Rightarrow \ln\left(\frac{V_c}{V_b}\right) = \ln\left(\frac{V_d}{V_a}\right)$$

$$\frac{Q_H}{Q_C} = \frac{T_H}{T_C} \Rightarrow \frac{Q_H}{T_H} - \frac{-Q_C}{T_C} = 0 \Rightarrow \frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$$

"Entropy" Q/T

Recall that we moved around a cyclic path to return to the same state. Therefore, we must conclude Q/T a state function.
If it looks like a duck and quacks like a duck...

Example 5.1

A central power plant, rated at 800,000 kW, generates steam at 585 K and discards heat to a river at 295 K. If the thermal efficiency of the plant is 70% of the maximum possible value, how much heat is discarded to the river at rated power?

$$\text{Eq. 5.8} \quad \eta_{\max} \equiv \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H} = 1 - \frac{295}{585} = 0.4957$$

$$\eta = 0.7\eta_{\max} = (0.7)(0.4957) = 0.3470$$

$$|W| = 800,000 \text{ kW}$$

$$|Q_H| = \frac{|W|}{\eta} = \frac{800,000}{0.3470} = 2,305,476 \text{ kW}$$

$$|Q_C| = |Q_H| - |W| = 2,305,476 - 800,000 = 1,505,548 \text{ kW}$$

L22 Equation Summary

$$\Delta U = Q + W = Q_H + Q_L + W$$

Eq. 2.3, p. 27

$$W = -Q_H - Q_C$$

$$\eta \equiv \frac{-W}{Q_H} = \frac{|W|}{|Q_H|} = \text{thermal efficiency} \quad \text{Eq. 5.6, p. 182}$$

$$\eta \equiv \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|}$$

$$\frac{-Q_C}{T_C} = \frac{Q_H}{T_H} \quad \Rightarrow \quad \frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \quad \text{Eq. 5.4, p. 182}$$

$$\eta = 1 - \frac{T_C}{T_H} \quad \text{Eq. 5.7, p. 182}$$

Homework

Problem 5.2

A Carnot engine receives 250 kJ s^{-1} of heat from a heat source reservoir at 525°C and rejects heat to a heat-sink reservoir at 50°C . What are the power developed and the heat rejected?

Problem 5.6

Which is the more effective way to increase the thermal efficiency of a Carnot engine: to increase T_H with T_C constant, or to decrease T_C with T_H constant? For a real engine, which would be the more practical way?