CH365 Chemical Engineering Thermodynamics

Lesson 22
Statements of the Second Law and Derivation of Entropy

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:

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

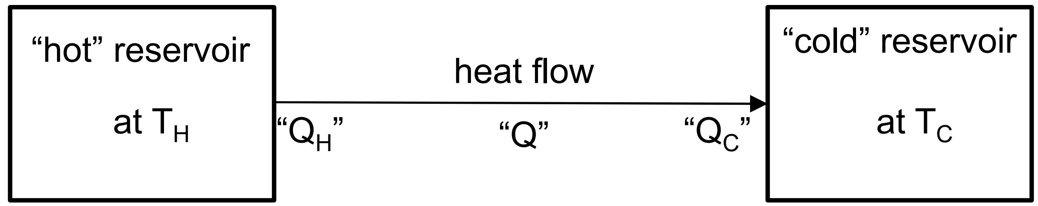
The entropy change of any system and its surroundings, considered together, and resulting from any real process, is positive, approaching zero only when the process approaches reversibility.

$$\Delta S_{total} \geq 0$$ 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

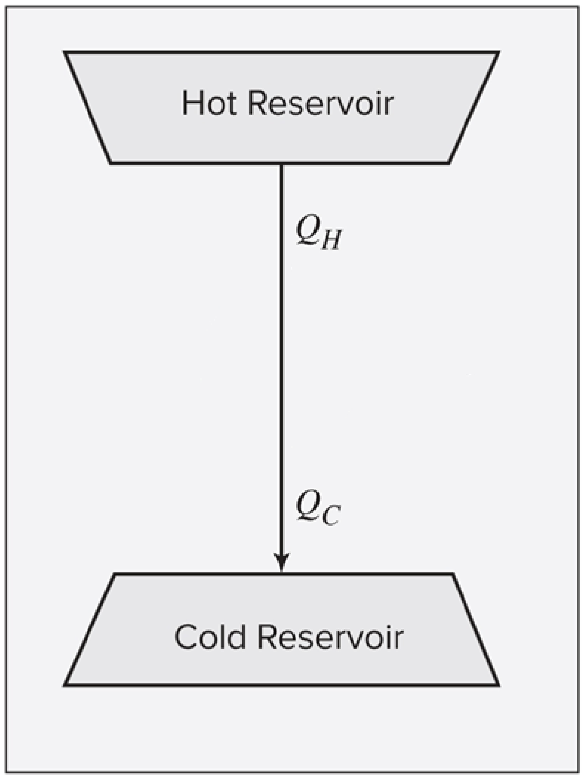
$$T_H > T_C$$



$$Q_H = -Q_C$$

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

Application to Heat Engines



Simple heat transfer

Derivation of Carnot's Equations

First Law (for the engine):

$$\Delta U = Q + W = Q_H + \overset{<0}{Q_C} + \overset{<0}{W}$$

Cyclic processes (engine):

$$\Delta U = 0$$

$$Q_H = -\underset{<0}{W} - \underset{<0}{Q_C}$$

entropy change for "reversible" engine is 0

Total entropy change (reservoirs):

$$\Delta S_{total} = \frac{Q_H}{T_H} + \frac{\overset{<0}{Q_C}}{T_C}$$

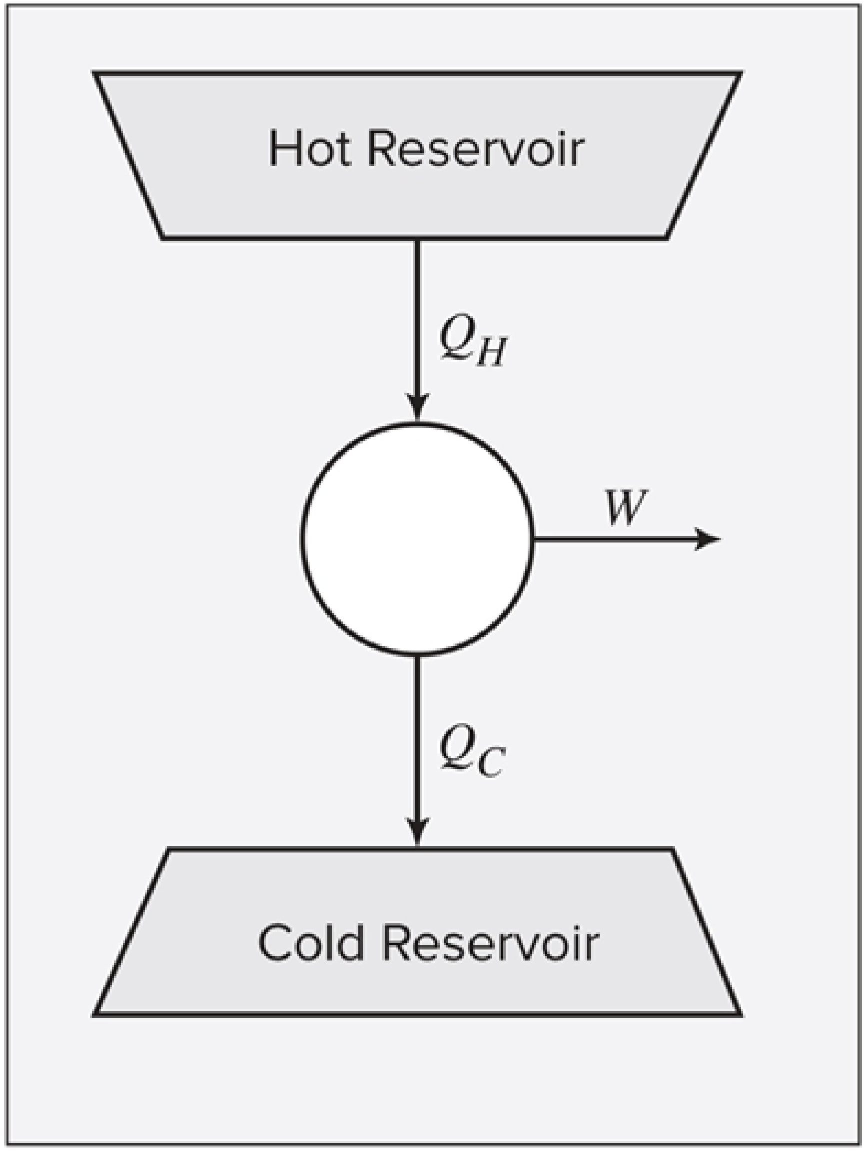
$$Q_H = T_H \Delta S_{total} - \frac{Q_C}{T_C} T_H$$

Equate Q_H and solve for W:

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

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

Carnot Efficiency



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

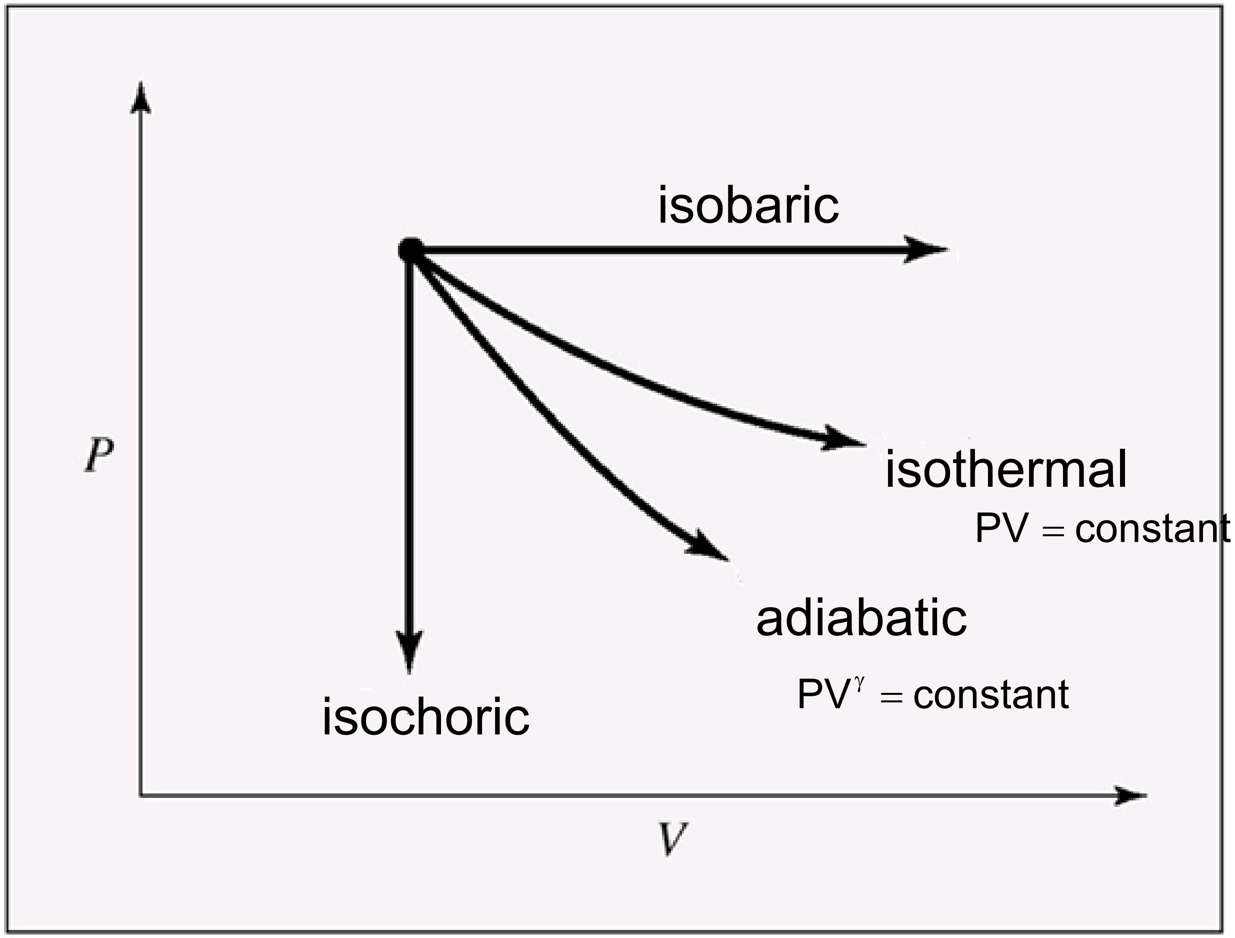
Eqns. 5.6, 5.7

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

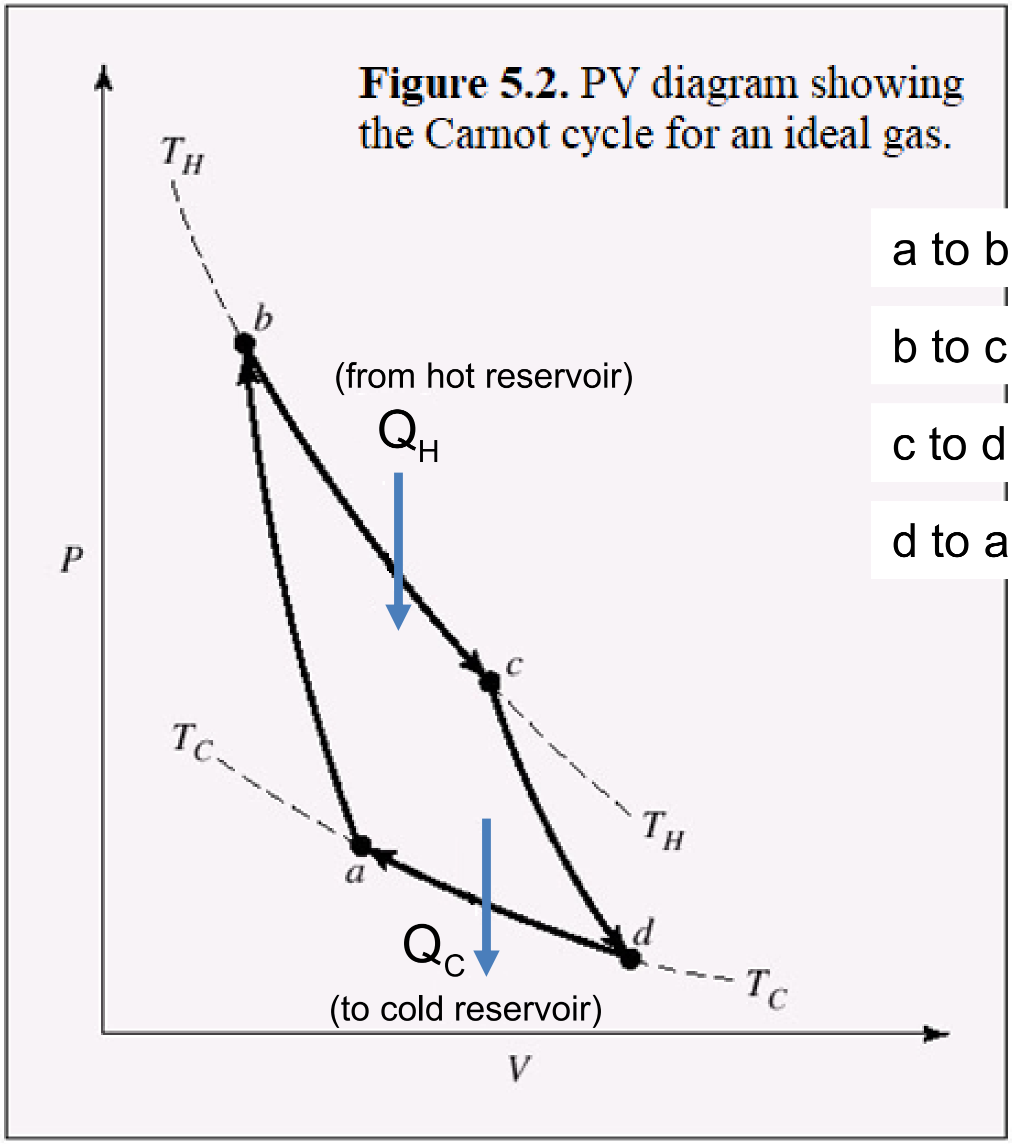
Lesson 11
Slide 12



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

Process Calculations, Slide 4

Example:

Using $P = \dfrac{RT}{V}$, show that $dW = -\dfrac{RT}{V}dV$ (3.17) and $dQ = \dfrac{RT}{V}dV + C_V dT$ (3.16)

$$P = \frac{RT}{V}$$

$$dW = -PdV \quad (1.3) \quad \Rightarrow \quad dW = -\frac{RT}{V}dV \quad ✓$$

$$dQ + dW = dU$$

$$dU = C_V dT \quad (3.20a)$$

$$dQ = -dW + C_V dT \quad \Rightarrow \quad dQ = \frac{RT}{V}dV + C_V dT \quad ✓$$

(Process calculations for ideal gas)

Derivation of Entropy – Ideal Gases

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

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

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

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?

L22 Equation Summary

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

$$W = -Q_H - Q_C$$

Eq. 2.3, p. 27

$$\eta \equiv \frac{-W}{Q_H} = \frac{|W|}{|Q_H|} = \text{thermal efficiency}$$

Eq. 5.6, p. 182

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

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

Eq. 5.4, p. 182

$$\eta = 1 - \frac{T_C}{T_H}$$

Eq. 5.7, p. 182

Questions?