# Lecture 10
## Chapter 20: **Entropy and the second law of thermodynamics**

**20-1 Second Law of Thermodynamics in terms of Entropy:** $\Delta S \geq 0$

Reversible process: Let's check the change in entropy of the enlarged system consisting of gas and reservoir. We can then calculate separately the entropy changes from the following equations.

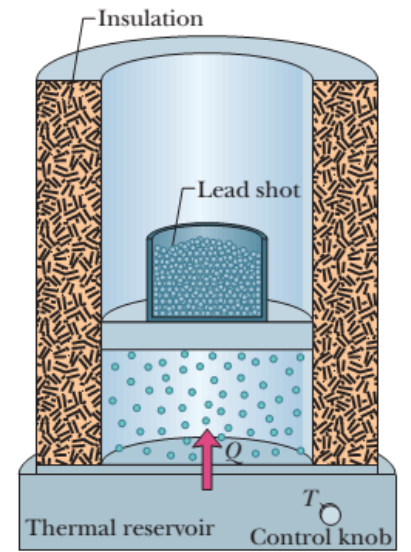$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \frac{1}{T} \int_i^f dQ = \frac{Q}{T} \qquad T = constant$$

$$\Delta S_{gas} = -\frac{Q}{T}$$

$$\Delta S_{res} = +\frac{Q}{T}$$

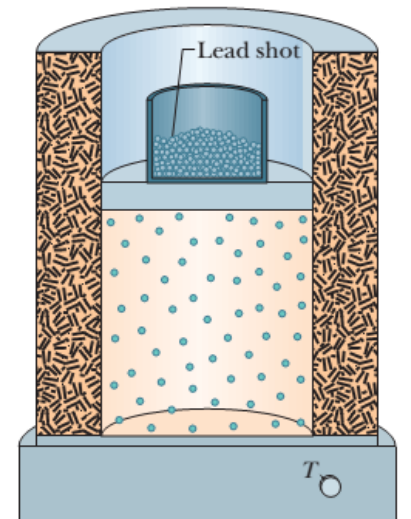$$\Delta S = -\frac{Q}{T} + \frac{Q}{T} = 0$$



Insulation
Lead shot
Q
T
Thermal reservoir    Control knob
(a) Initial state i

Reversible process

Lead shot
T
(b) Final state f

"**If a process occurs in a closed system, the entropy of the system increases for irreversible processes** $(\Delta S > 0)$ **and remains constant for reversible processes** $(\Delta S = 0)$. **It never decreases.**"

That is, $\Delta S \geq 0$

In the **real world almost all processes are irreversible** to some extent because of friction, turbulence, and other factors, so the entropy of real closed systems undergoing real processes always increases. Processes in which the system's entropy remains constant are always idealizations.

## 20-2 Entropy in the Real World: Engines

Heat Engine: A heat engine, or more simply, an engine, is a device that extracts energy from its environment in the form of heat and does useful work. At the heart of every engine is a working substance.

Carnot Engine: Although an ideal gas does not exist, any real gas approaches ideal behavior if its density is low enough. Similarly, we can study real engines by analyzing the behavior of an ideal engine.

"An ideal engine where all processes are reversible and no wasteful energy transfers occur due to, say, friction and turbulence".

# Schematic diagram of a Carnot Engine:

We shall focus on a particular ideal engine called a Carnot engine after the French scientist and engineer N. L. Sadi Carnot (pronounced "cah-no"),who first proposed the engine's concept in 1824.This ideal engine turns out to be the best (in principle) at using energy as heat to do useful work. Surprisingly, Carnot was able to analyze the performance of this engine before the first law of thermodynamics and the concept of entropy had been discovered.

## pV plot of the Carnot cycle:



Schematic of a Carnot engine

Heat is absorbed.

$Q_H$

$T_H$

W

Heat is lost.   $Q_L$

$T_L$

Work is done by the engine.

If we place the cylinder in contact with the high temperature reservoir at temperature $T_H$, heat $Q_H$ is transferred to the working substance from this reservoir as the gas undergoes an isothermal expansion from volume $V_a$ to volume $V_b$.

Similarly, with the working substance in contact with the low-temperature reservoir at temperature $T_L$, heat $Q_L$ is transferred from the working substance to the low-temperature reservoir as the gas undergoes an isothermal compression from volume $V_c$ to volume $V_d$ .

Thus the heat transfers to or from the working substance only during the isothermal processes $ab$ and $cd$.
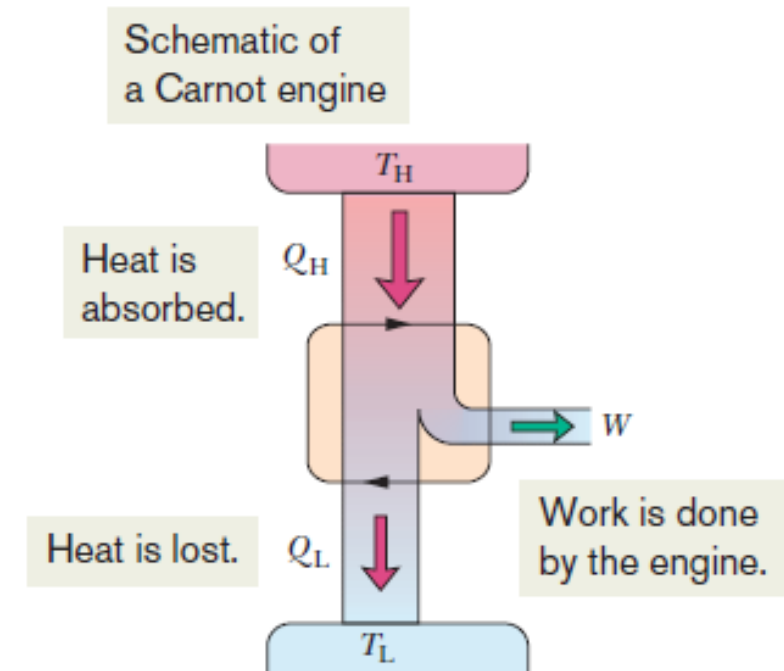
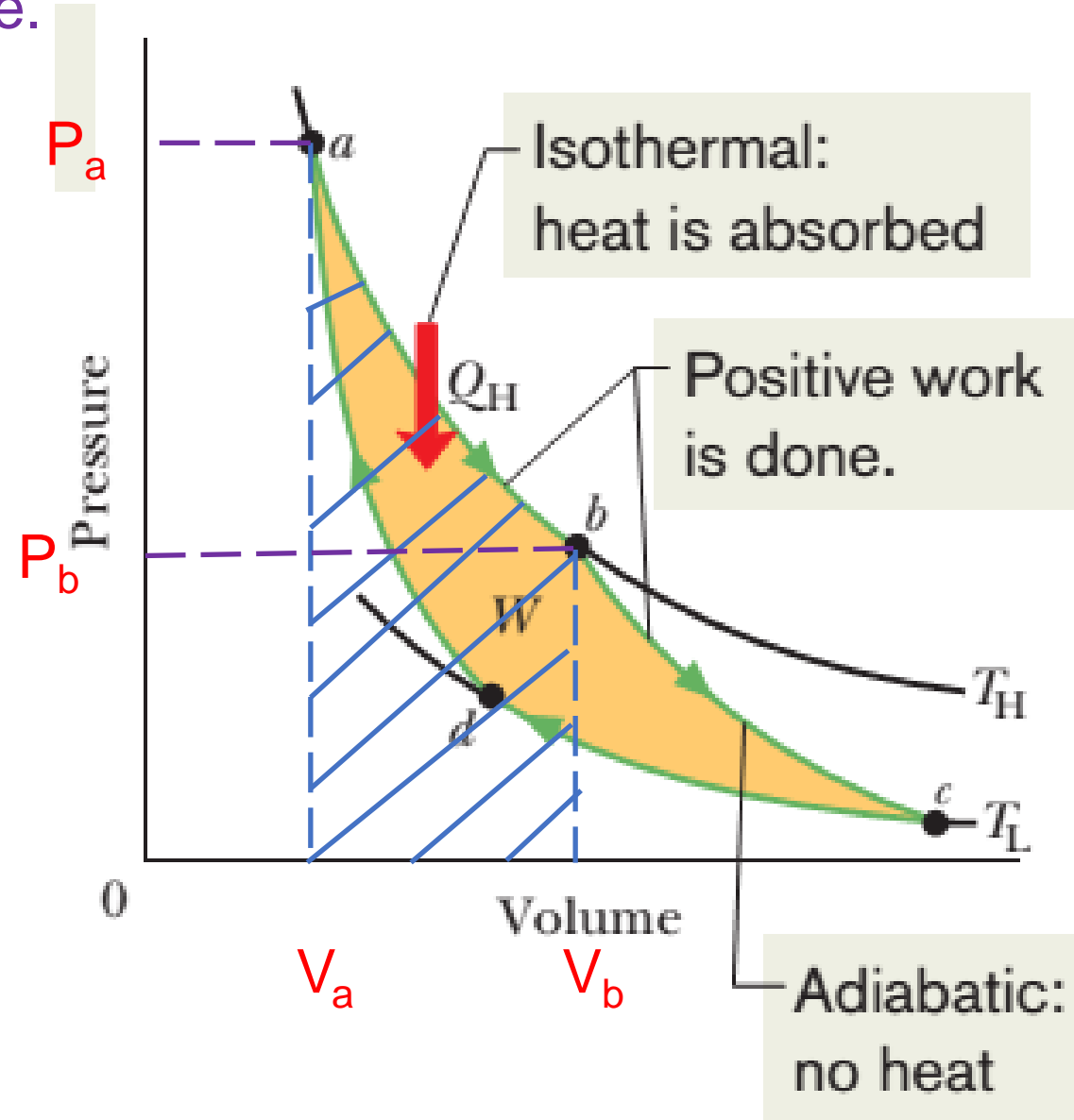**Isothermal expansion** at constant $T_H$ from a to b states:

Heat $Q_H$ is absorbed by the working substance.

Pressure decreases from $P_a$ to $P_b$

Volume increases from $V_a$ to $V_b$

$$W = nRT_H \ln\frac{V_b}{V_a} \qquad \text{[positive]}$$

**During the processes ab and bc, the working substance is expanding and thus doing positive work as it raises the weighted piston. This work is represented by the area under curve abc.**
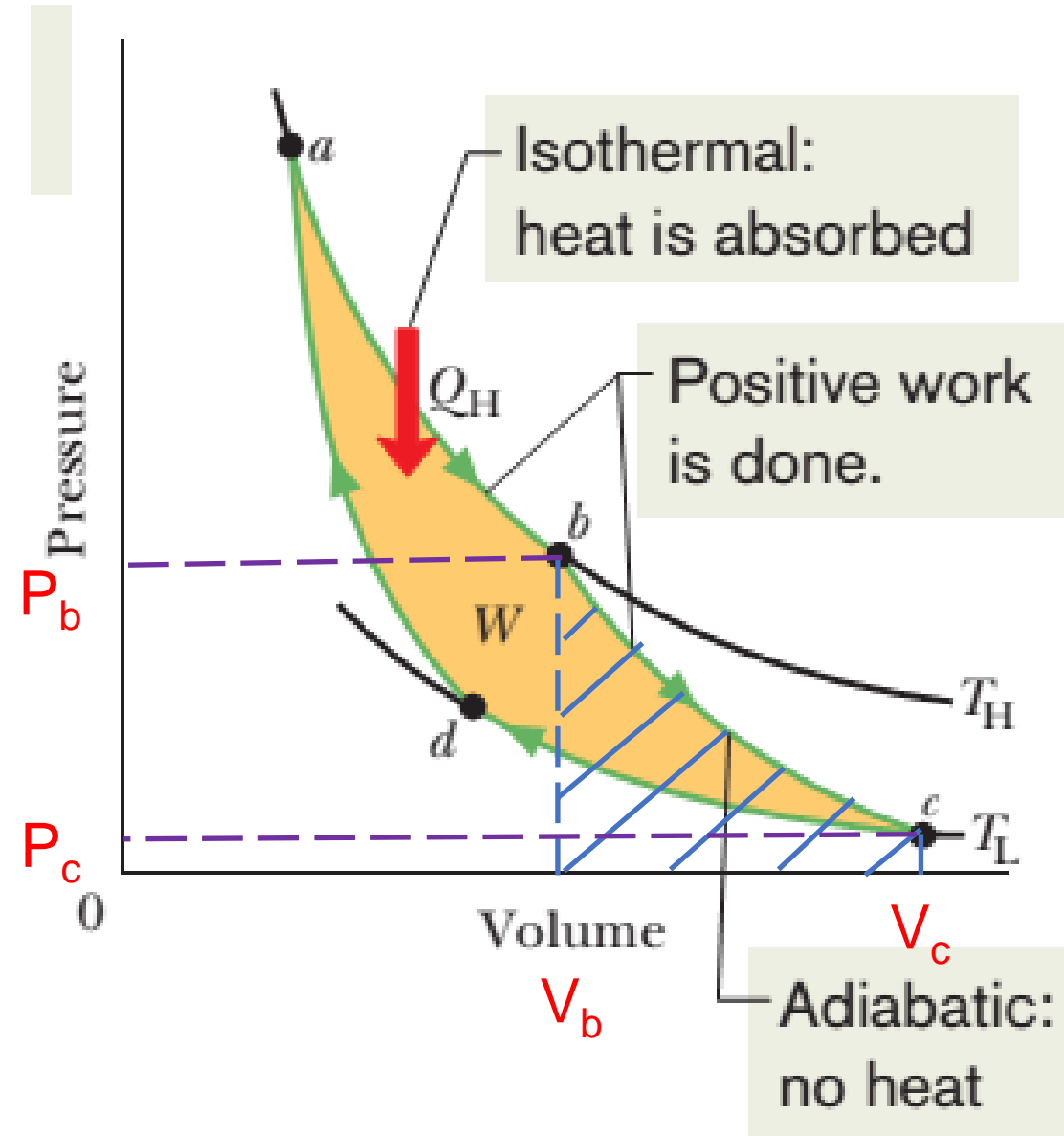


Isothermal:
heat is absorbed

Positive work
is done.

$T_H$

$T_L$

Adiabatic:
no heat

**Adiabatic expansion** from b to c states:

Heat Q is zero.

Pressure decreases from $P_b$ to $P_c$

Volume increases from $V_b$ to $V_c$

$$W = \frac{P_b V_b - P_c V_c}{\gamma - 1} \qquad \text{[positive]}$$



Isothermal: heat is absorbed

Positive work is done.

$Q_H$

$W$

$P_b$

$P_c$

$0$

$V_b$

$V_c$

Volume

Pressure

$T_H$

$T_L$

Adiabatic: no heat

Isothermal compression at constant $T_L$ from c to d states:

Heat $Q_L$ is released.

Pressure increases from $P_c$ to $P_d$

Volume decreases from $V_c$ to $V_d$

$$W = nRT_L \ln \frac{V_d}{V_c} \qquad \text{[negative]}$$

**During the processes cd and da, the working substance is being compressed, which means that it is doing negative work on its environment. This work is represented by the area under curve cda.**
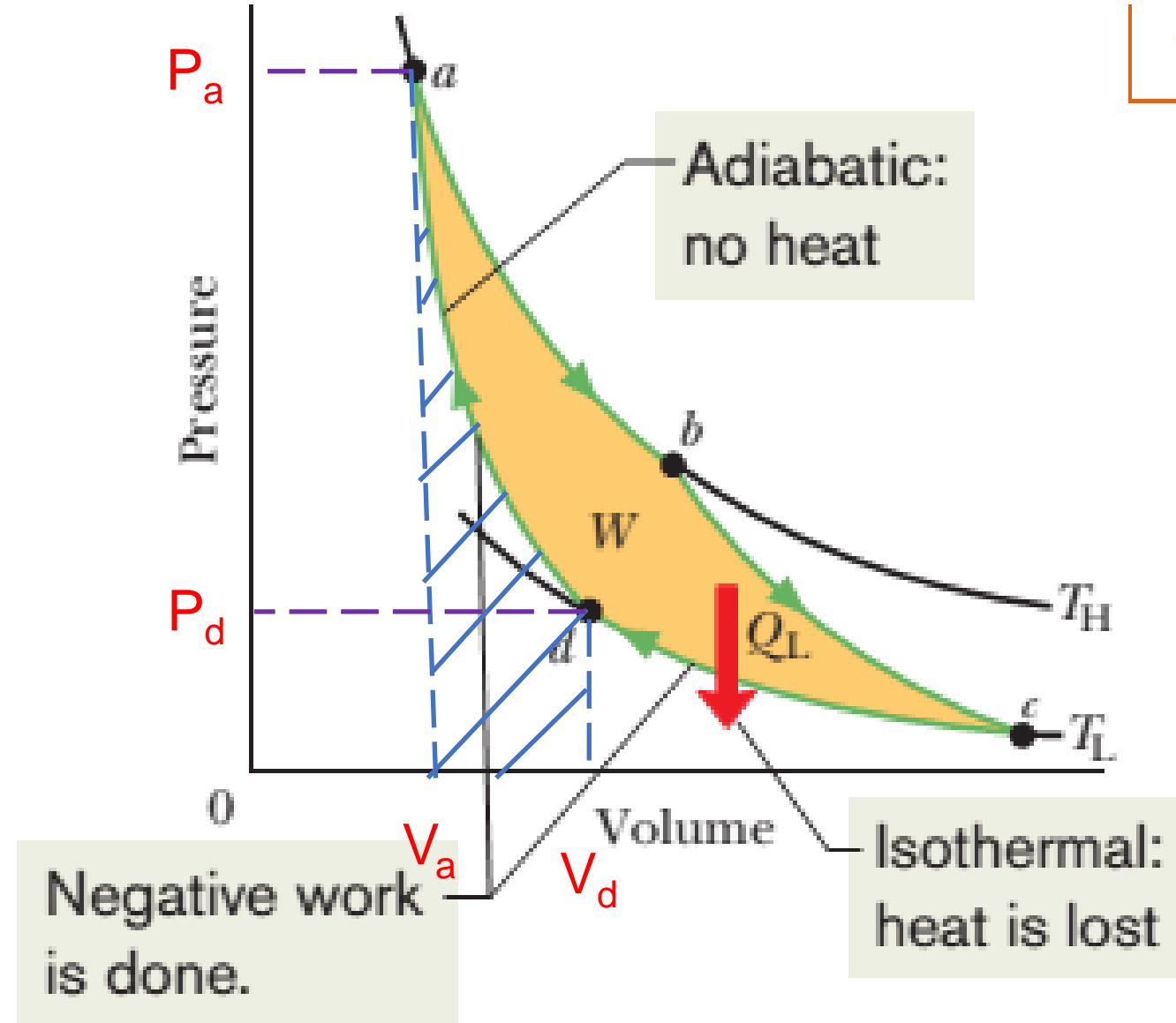


Adiabatic: no heat

Isothermal: heat is lost

Negative work is done.
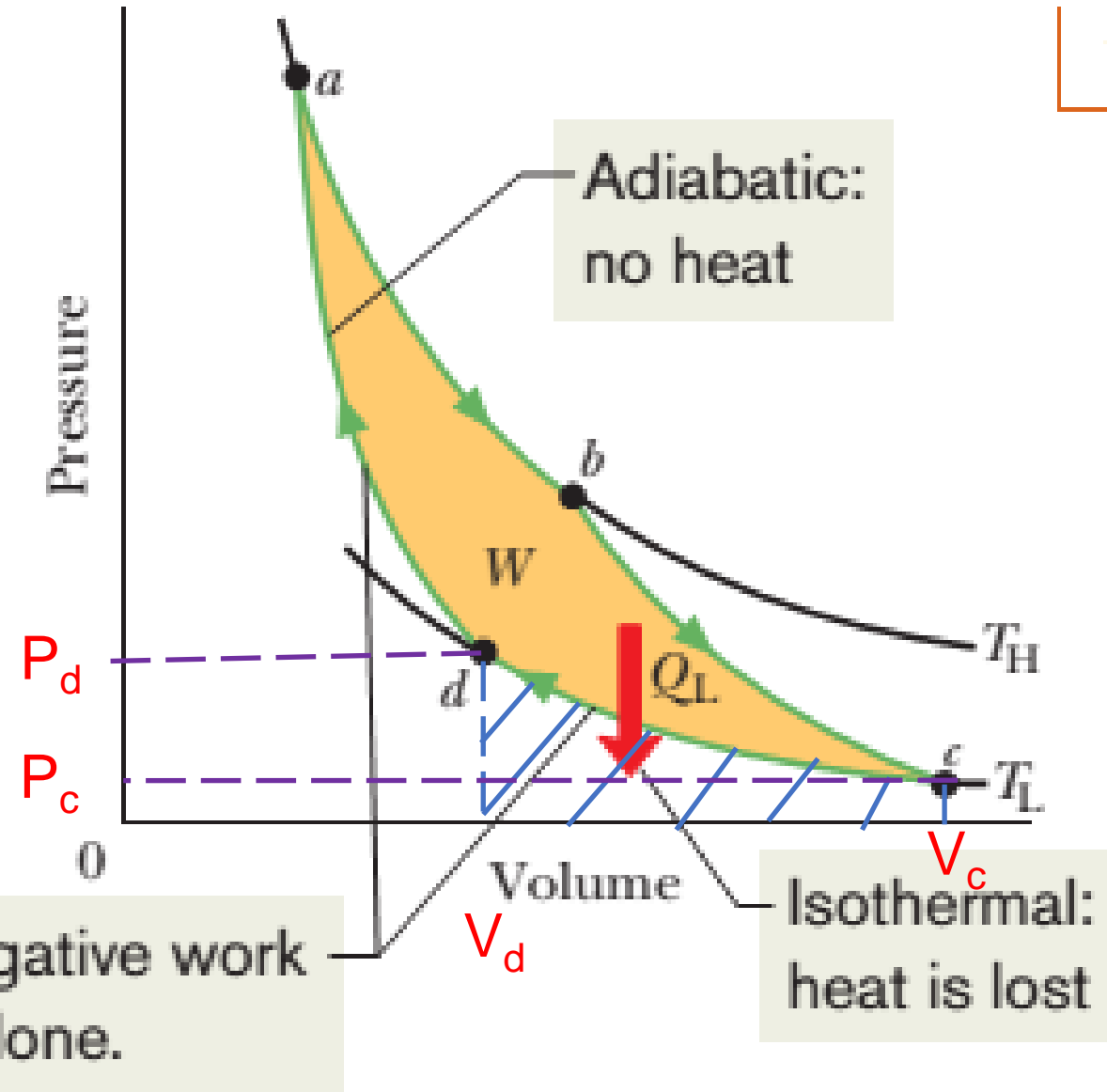
Adiabatic compression from d to a states:

Heat Q is zero.

Pressure increases from $P_d$ to $P_a$

Volume decreases from $V_d$ to $V_a$

$$W = \frac{P_d V_d - P_a V_a}{\gamma - 1}$$   [negative]



$P_a$

$P_d$

$a$

$b$

$W$

$d$

$Q_L$

$T_H$

$c$

$T_L$

Adiabatic: no heat

Isothermal: heat is lost

Negative work is done.

Pressure

Volume

0

$V_a$   $V_d$

Carnot cycle:

W = abcda area inside the curve     [positive]

**The net work per cycle is the difference between these two areas and is a positive quantity equal to the area enclosed by cycle abcda (yellow area).**



Isothermal: heat is absorbed

Positive work is done.

Adiabatic: no heat
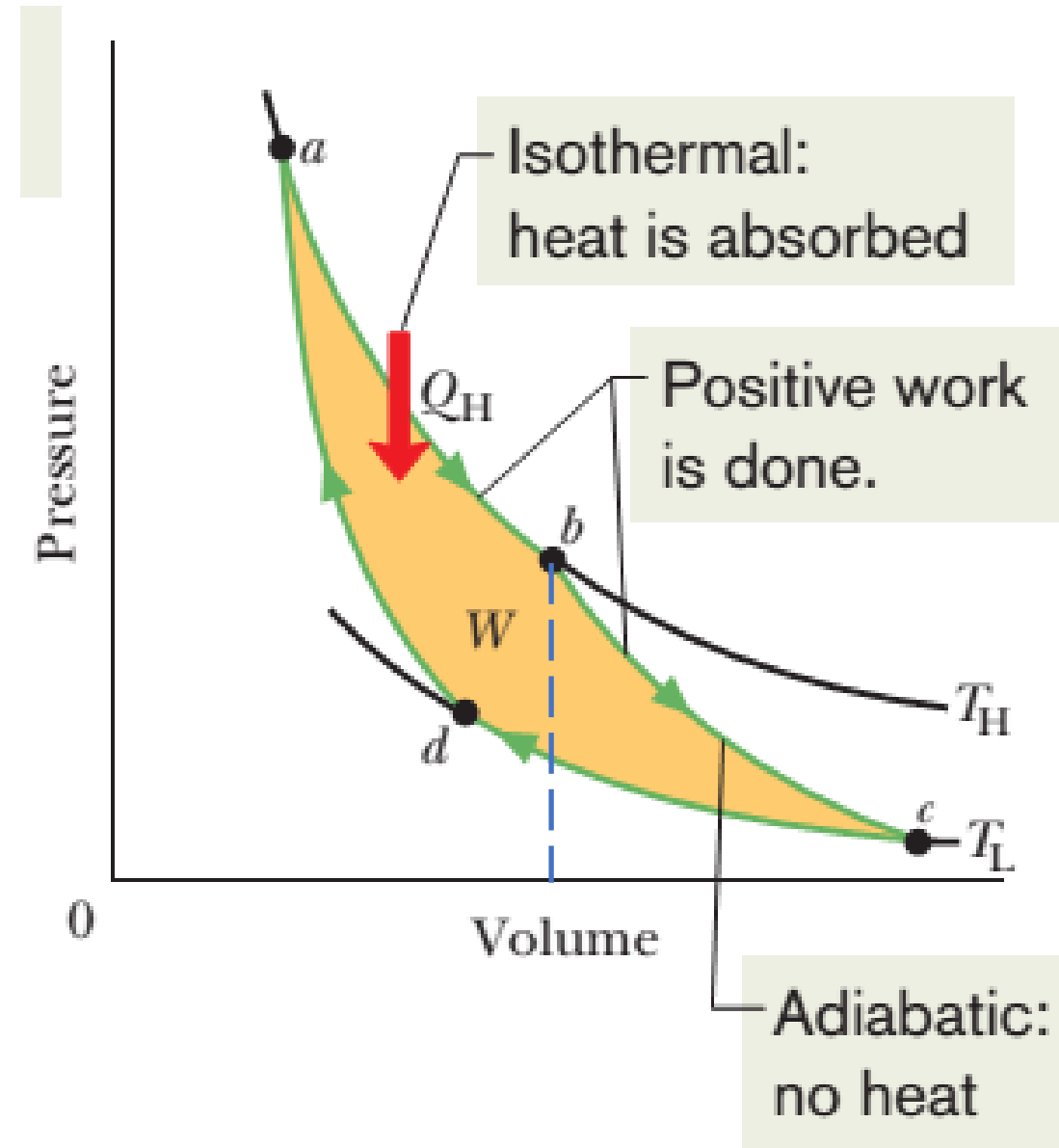
# Carnot cycle on a temperature–entropy diagram

In the temperature–entropy $(T - S)$ diagram the lettered points $a, b, c,$ and $d$ there **correspond** to the lettered points in the $p - V$ diagram for the Carnot cycle.

The **two horizontal lines** in Fig. correspond to the two **isothermal processes** of the cycle. Process $ab$ is the **isothermal expansion** and process cd is the isothermal **compression** of the cycle.



$$\Delta S = \frac{+Q_H}{TH} \quad Q_H$$

$$\Delta S = S_c - S_b = 10 - 10 = 0$$

$$\Delta S = \frac{-Q_L}{TH} \quad Q_L$$

*Temperature $T$ / Entropy $S$*

As the **working substance** (reversibly) **absorbs energy** $Q_H$ as heat at **constant temperature** $T_H$ during the **expansion**, its **entropy increases**.

$$\Delta S = \frac{+Q}{T}$$

Similarly, during the **isothermal compression** $cd$, the working substance (reversibly) **loses energy** $Q_L$ as heat at **constant temperature** $T_L$, and its **entropy decreases**. $\Delta S = \frac{-Q}{T}$

The **two vertical lines** correspond to the **two adiabatic processes** of the Carnot cycle. Because **no energy is transferred as heat** during the two processes (Q = 0), the **entropy of the working substance is constant** during them. $\Delta S = 0$
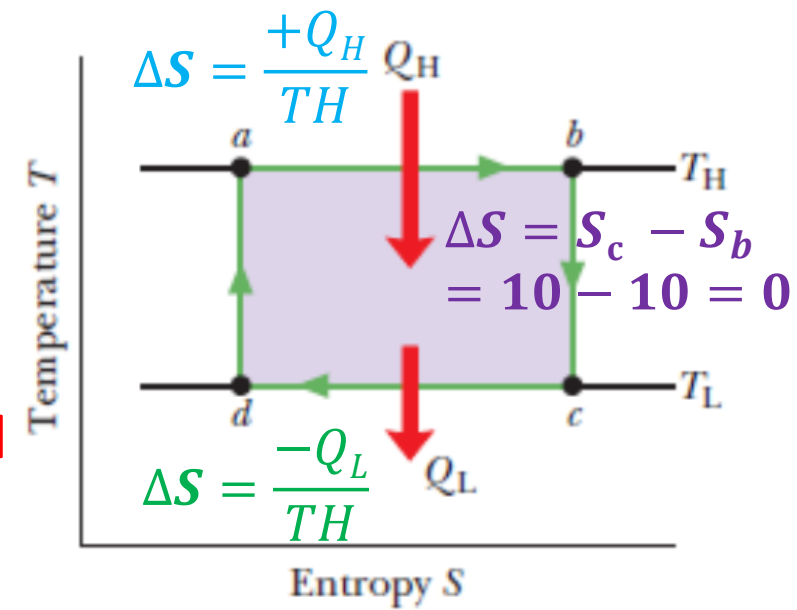
**3. A 2.50 mol sample of an ideal gas expands reversibly and isothermally at 360 K until its volume is doubled. What is the increase in entropy of the gas?**

**Solution:**

$$\Delta S = nRln\frac{V_f}{V_i} + nC_vln\frac{T_f}{T_i}$$

$$\Delta S = nRln\frac{V_f}{V_i} + nC_vln\frac{360}{360}$$

$$\Delta S = nRln\frac{V_f}{V_i} + nC_vln\,1$$

$$\Delta S = nRIn\frac{V_f}{V_i}$$

$$\Delta S = 2.5{\times}8.31{\times}In\frac{2V}{V} = 2.5{\times}8.31{\times}In2$$

$$\Delta S = 14.4\ \text{J/K}\quad\text{(Answer)}$$

**4. How much energy must be transferred as heat for a reversible isothermal expansion of an ideal gas at 132 $^0$C if the entropy of the gas increases by 46.0 J/K?**

Solution:

$$\Delta S = \int_i^f \frac{dQ}{T} = \frac{1}{T} \int_i^f dQ$$

$$\Delta S = \frac{Q}{T}$$

Q = $\Delta S \times$T            [$\Delta S = 46$ J/K]

Q = 46x408            [T = (132 +273) K= 408 K]

Q = 1.88 $\times 10^6$ J      (Answer)