

## Topic 4F - Entropy

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### Isothermal vs. Adiabatic Gas Processes

#### Isothermal Processes

For an isothermal expansion of an ideal gas,  $\Delta U = 0$  (since  $\Delta T = 0$ ). If the expansion is reversible ( $P \approx P_{\text{ext}}$ ), then

$$w = - \int_{V_1}^{V_2} P dV = - nRT \int_{V_1}^{V_2} \frac{dV}{V} = - nRT \ln \left( \frac{V_2}{V_1} \right) = nRT \ln \left( \frac{V_1}{V_2} \right)$$

Since  $\Delta U = q + w = 0$ , then

$$q = -w = -nRT \ln \left( \frac{V_1}{V_2} \right) = nRT \ln \left( \frac{P_1}{P_2} \right)$$

#### Adiabatic Processes

For an adiabatic, reversible expansion of an ideal gas,  $q = 0$  and  $\Delta U = w$ .

For an infinitesimal change in volume,  $dV$ , the temperature changes by  $dT$ , and  $dU = dw$ :

$$dU = nC_v dT = -P_{\text{ext}} dV = -\frac{nRT}{V} dV$$

Dividing both sides by  $nT$  gives

$$\frac{C_v}{T} dT = -\frac{R}{V} dV$$

For an infinite number of such infinitesimal volume changes:

$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

or

$$C_v \ln\left(\frac{T_2}{T_1}\right) = -R \ln\left(\frac{V_2}{V_1}\right)$$

Taking anti-logs of both sides gives:

$$\left(\frac{T_2}{T_1}\right)^{C_v} = \left(\frac{V_1}{V_2}\right)^R = \left(\frac{V_1}{V_2}\right)^{C_p - C_v}$$

since  $R = C_p - C_v$ .

Thus,

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{C_p}{C_v} - 1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

where  $\gamma = C_p/C_v$ . Rearranging gives

$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}$$

And since

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

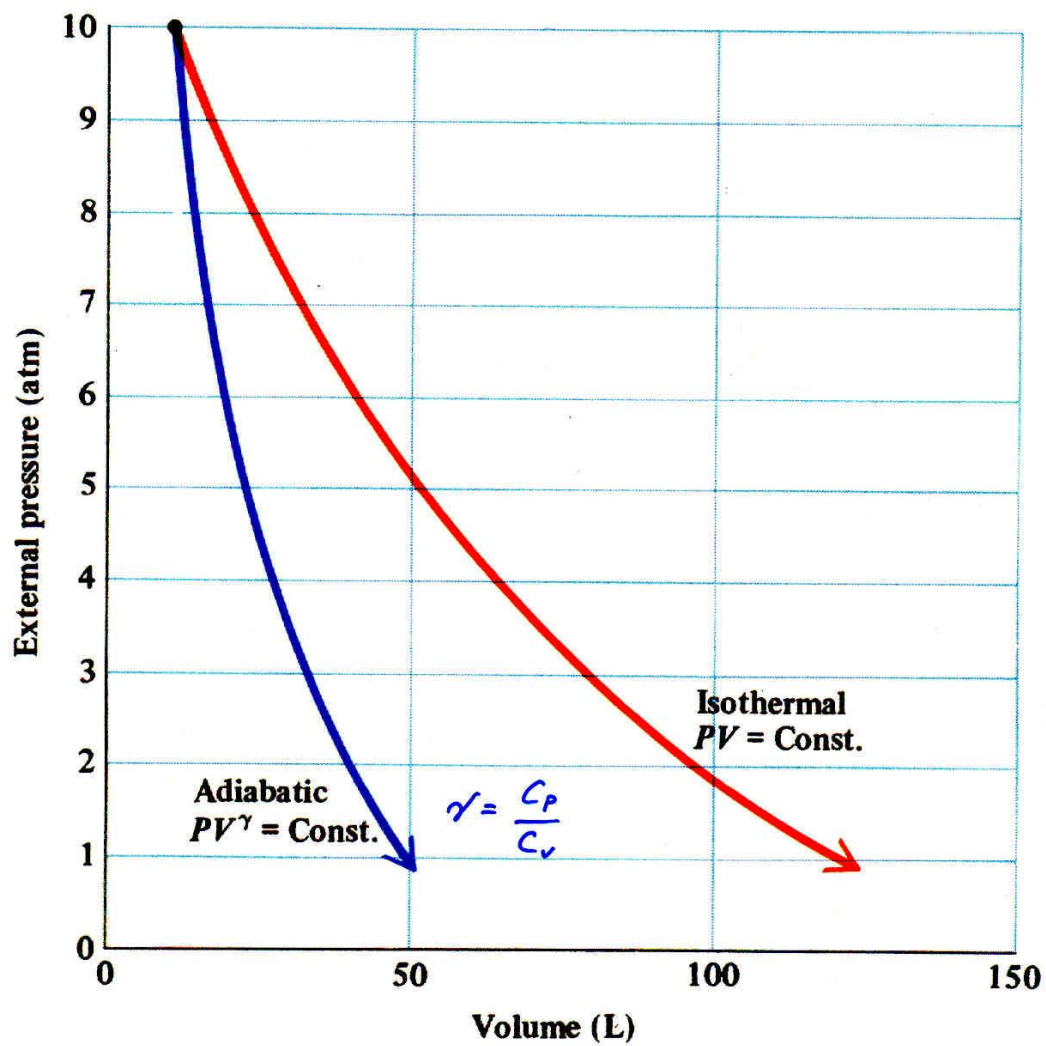
multiplying the latter two equations gives

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad (\text{i.e., } P_1 V_1^\gamma = \text{const.})$$

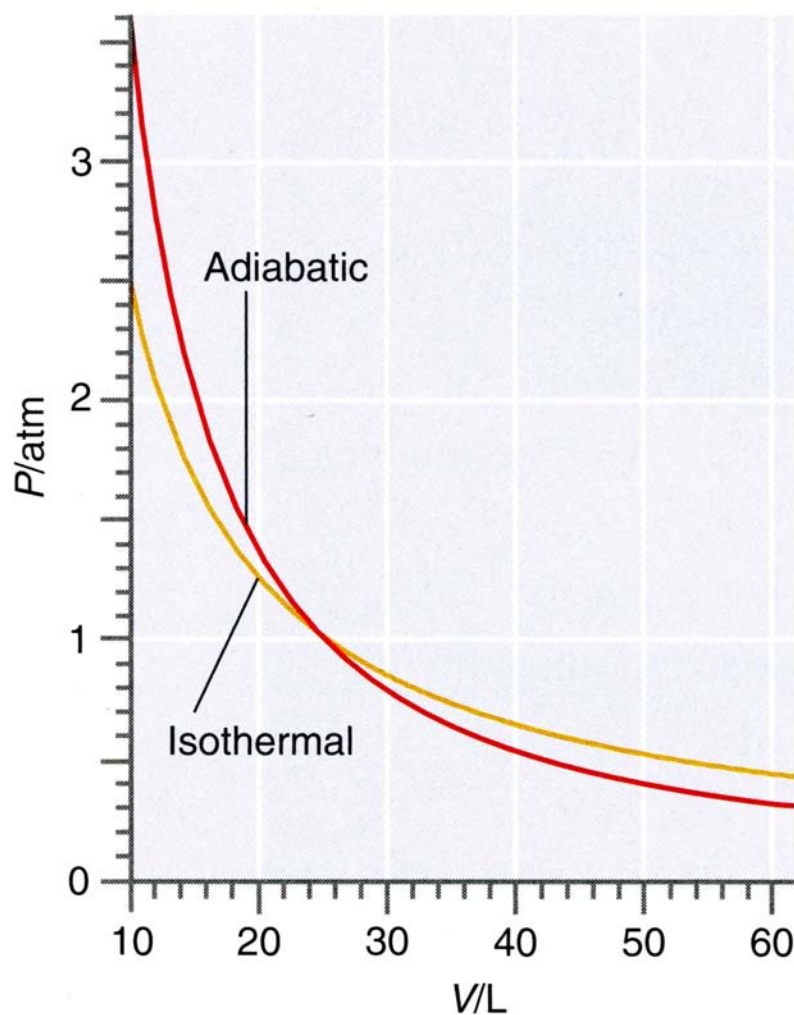
For an isothermal, reversible expansion of an ideal gas:

$$P_1 V_1 = P_2 V_2 \quad (\text{i.e., } P_1 V_1 = \text{const.})$$

Thus, for given values of  $V_1$  and  $V_2$ , less P-V work is performed by a system in an adiabatic expansion than in an isothermal expansion, since no net energy flows into the system as heat.

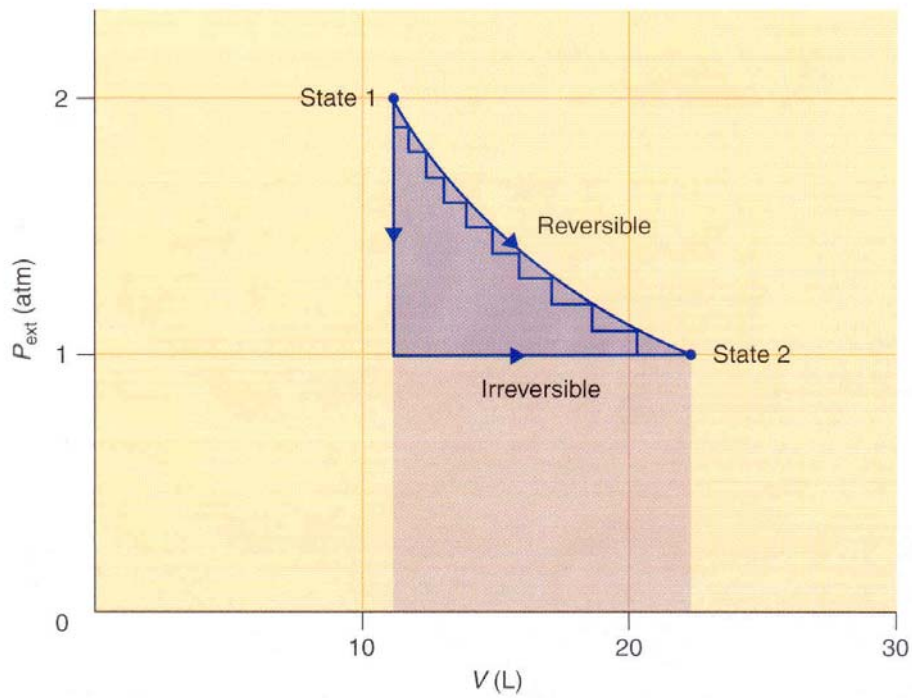
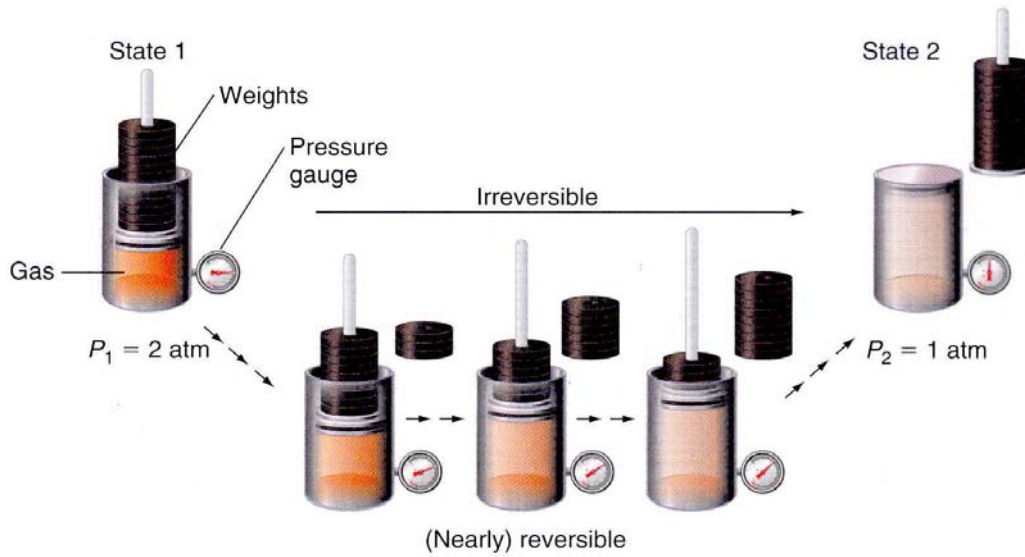
**Figure 8-17**

A comparison of reversible isothermal and adiabatic expansions.

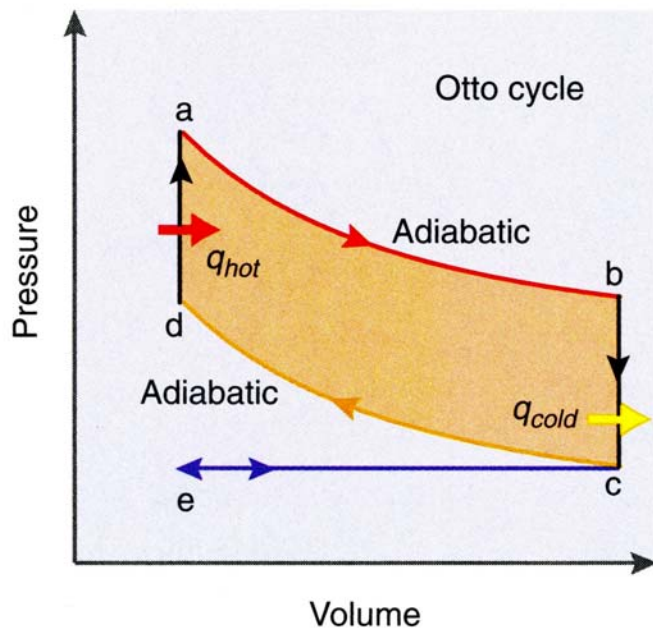
**FIGURE 2.13**

Two systems containing 1 mol of  $\text{N}_2$  have the same  $P$  and  $V$  values at 1 atm. The red curve corresponds to reversible expansion and compression about  $P = 1$  atm under adiabatic conditions. The yellow curve corresponds to reversible expansion and compression about  $P = 1$  atm under isothermal conditions.

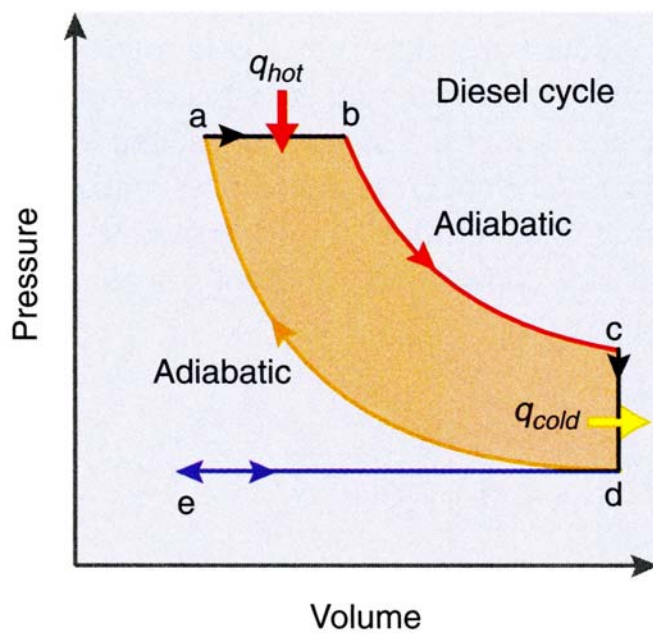
**Figure 11.3: Irreversible and Nearly Reversible Isothermal Expansions**







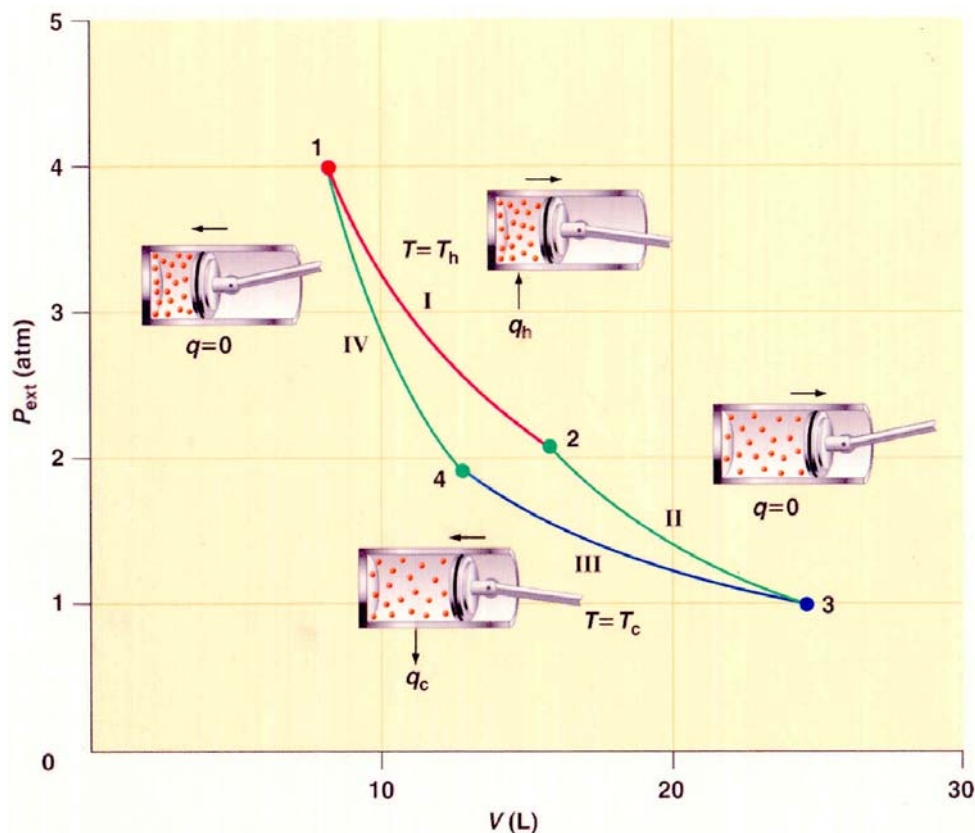
(a)



(b)

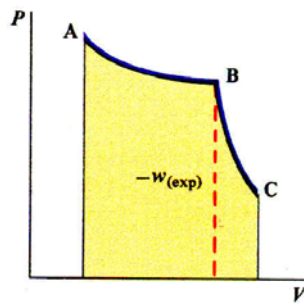
**FIGURE 5.19**

Idealized reversible cycles of the (a) Otto and (b) diesel engines.

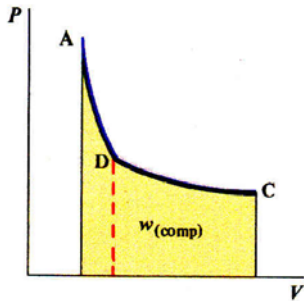


**Figure 11.5**

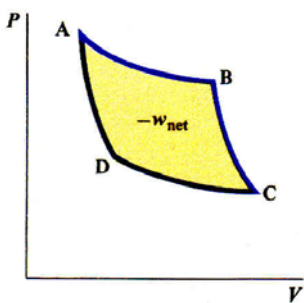
A  $P-V$  diagram for the Carnot cycle. The working substance is an ideal monatomic gas, and all stages, I through IV, are assumed reversible. Stages I and III are isothermal, following Boyle's law,  $PV = \text{const}$ ; whereas stages II and IV are adiabatic, following  $PV^\gamma = \text{const}$ , where  $\gamma = C_p/C_v = 5/3$ . Heat  $q_h$  is taken up from a hot reservoir at temperature  $T_h$  during stage I and  $q_c$  is discharged to a cold reservoir at temperature  $T_c$  during stage III. The cylinders illustrate the expansion and compression stages. The net work done by the engine is the area enclosed by the cycle. (In real cycles the isothermal and adiabatic stages are not cleanly separated.) If you know that 1 mol of gas is involved, can you use the diagram to estimate the temperatures  $T_h$  and  $T_c$  and the efficiency? (Answer: yes; 400 K, 300 K, and 0.25, respectively.)



(a) Expansion



(b) Compression

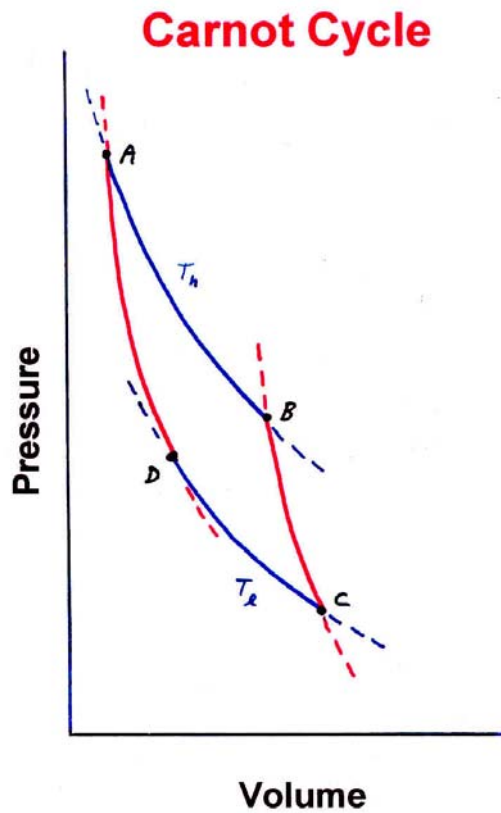


(c) Complete cycle

**Figure 8-18**

Stages of the Carnot cycle. The net work done per cycle is the area enclosed by the curve ABCDA.





**Path AB : Isothermal Expansion :**  $w_{AB} = -q_{AB} = -nRT_h \ln\left(\frac{V_B}{V_A}\right)$

**Path BC : Adiabatic Expansion :**  $w_{BC} = \Delta U_{BC} = -nC_v(T_h - T_l)$

**Path CD : Isothermal Compression :**  $w_{CD} = -q_{CD} = +nRT_l \ln\left(\frac{V_C}{V_D}\right)$

**Path DA : Adiabatic Compression :**  $w_{DA} = \Delta U_{DA} = +nC_v(T_h - T_l)$

$$\begin{aligned}
 w_{\text{net}} &= -nRT_h \ln\left(\frac{V_B}{V_A}\right) - nC_v(T_h - T_l) + nRT_l \ln\left(\frac{V_C}{V_D}\right) + nC_v(T_h - T_l) \\
 &= -nRT_h \ln\left(\frac{V_B}{V_A}\right) + nRT_l \ln\left(\frac{V_C}{V_D}\right)
 \end{aligned}$$

Since  $V_B$  and  $V_C$  lie on one adiabatic path and  $V_A$  and  $V_D$  on another, and since for adiabatic expansions and compressions

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

then

$$\frac{T_h}{T_\ell} = \left( \frac{V_C}{V_B} \right)^{\gamma-1} \quad (\text{for path BC})$$

and

$$\frac{T_h}{T_\ell} = \left( \frac{V_D}{V_A} \right)^{\gamma-1} \quad (\text{for path DA})$$

Equating these two expressions for  $T_h/T_\ell$  gives

$$\left( \frac{V_C}{V_B} \right)^{\gamma-1} = \left( \frac{V_D}{V_A} \right)^{\gamma-1}$$

or

$$\frac{V_C}{V_B} = \frac{V_D}{V_A} \Rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Substituting this equivalence into the expression for  $w_{\text{net}}$  for the Carnot cycle gives:

$$w_{\text{net}} = -nR(T_h - T_\ell) \ln \left( \frac{V_B}{V_A} \right)$$

Thus, the Carnot cycle is an idealized model for a heat engine.

By adding a certain amount of heat ( $q_{AB}$ ) to the system at the higher temperature ( $T_h$ ), a net amount of work ( $-w_{net}$ ) is performed by the system. In addition, some energy ( $q_{CD}$ ) is discharged from the system at the lower temperature ( $T_l$ ) and is irretrievably lost from the system.

The **efficiency** of such a heat engine is the ratio of the work performed by the system to the amount of heat added along the the high-temperature ( $T_h$ ) isothermal path:

$$\varepsilon = \frac{-w_{net}}{q_{AB}}$$

For an ideal gas as the “working substance” in a Carnot cycle, the efficiency is given by:

$$\begin{aligned}\varepsilon = \frac{-w_{net}}{q_{AB}} &= \frac{nR(T_h - T_l) \ln\left(\frac{V_B}{V_A}\right)}{nRT_h \ln\left(\frac{V_B}{V_A}\right)} \\ &= \frac{T_h - T_l}{T_h} = 1 - \frac{T_l}{T_h}\end{aligned}$$

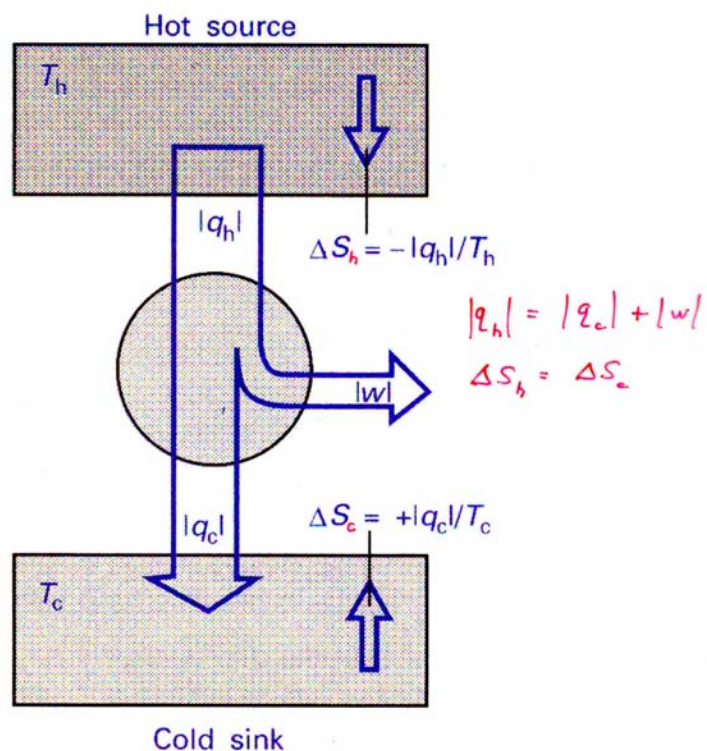
But since  $\Delta U = 0$  for the cyclic process, then  $-w_{net} = q_h + q_l$ .

Thus,

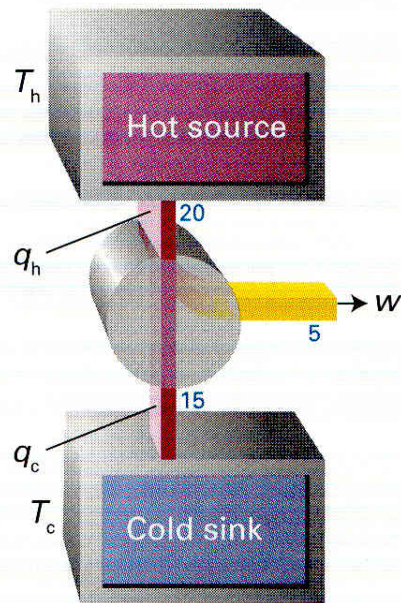
$$\frac{q_h + q_l}{q_h} = \frac{T_h - T_l}{T_h} \Rightarrow \frac{q_h}{T_h} + \frac{q_l}{T_l} = 0$$

Since the net change in the quantity  $\frac{q}{T}$  for the cyclic process is zero, it must be a state function (**entropy**).

$$\Delta S = \frac{q_{rev}}{T}$$

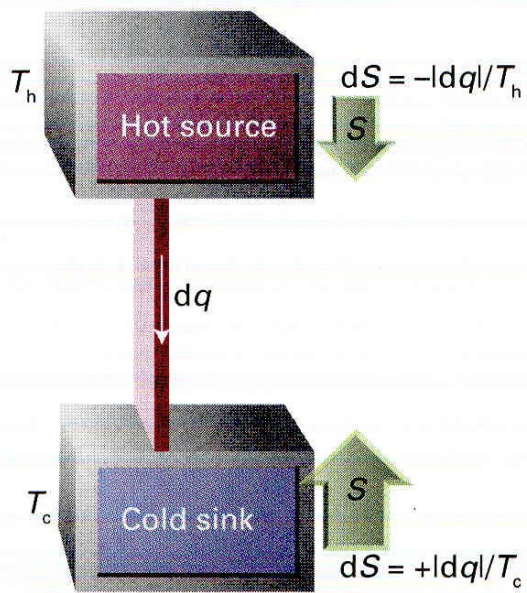


**4.16** When heat leaves a hot source, the source undergoes a decrease in entropy. To achieve a matching increase in entropy, less energy need be transferred as heat to a cold sink. The balance of energy may be extracted as work. This diagram illustrates the energy flow.

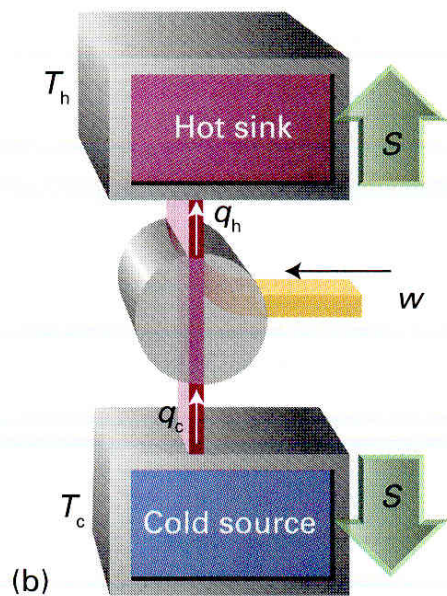
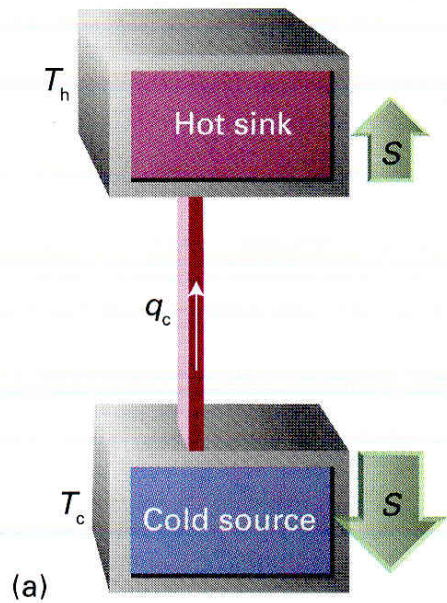


**Fig. 3.7** Suppose an energy  $q_h$  (for example, 20 kJ) is supplied to the engine and  $q_c$  is lost from the engine (for example,  $q_c = -15$  kJ) and discarded into the cold reservoir. The work done by the engine is equal to  $q_h + q_c$  (for example, 20 kJ + (-15 kJ) = 5 kJ). The efficiency is the work done divided by the energy supplied as heat from the hot source.





**Fig. 3.10** When energy leaves a hot reservoir as heat, the entropy of the reservoir decreases. When the same quantity of energy enters a cooler reservoir, the entropy increases by a larger amount. Hence, overall there is an increase in entropy and the process is spontaneous. Relative changes in entropy are indicated by the sizes of the arrows.



**Fig. 3.11** (a) The flow of energy as heat from a cold source to a hot sink is not spontaneous. As shown here, the entropy increase of the hot sink is smaller than the entropy decrease of the cold source, so there is a net decrease in entropy. (b) The process becomes feasible if work is provided to add to the energy stream. Then the increase in entropy of the hot sink can be made to cancel the entropy decrease of the cold source.

## Entropy Changes for Reversible Processes

For isothermal reversible processes, since  $\Delta U = 0$ , then  $q_{\text{rev}} = -w$ . The entropy change for such a process is:

$$\Delta S = \frac{q_{\text{rev}}}{T} \quad (\text{units} = \text{J/K})$$

For the reversible isothermal expansion of an ideal gas:

$$q_{\text{rev}} = -w = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln\left(\frac{V_2}{V_1}\right)$$

Thus, the entropy change for such a process is:

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{nRT \ln\left(\frac{V_2}{V_1}\right)}{T} = nR \ln\left(\frac{V_2}{V_1}\right)$$

Hence, the entropy of a gas always increases during an isothermal expansion.

[Where does the added entropy come from?]

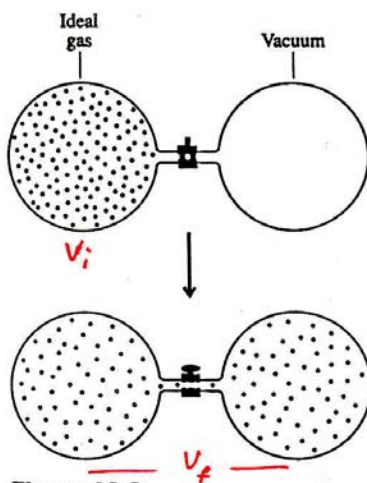
**TABLE 21.1 Number of Equivalent Combinations for Various Types of Poker Hands** (5 CARDS)

Hand	$W$	$\ln W$
Royal flush (AKQJ10 in one suit)	4	1.39
Straight flush (five cards in sequence in one suit)	36	3.58
Four of a kind	624	6.44
Full house (three of a kind plus a pair)	3,744	8.23
Flush (five cards in the same suit)	5,108	8.54
Straight (five cards in sequence)	10,200	9.23
Three of a kind	54,912	10.91
Two pairs	123,552	11.72
One pair	1,098,240	13.91
No pairs	1,302,540	14.08
Total	2,598,960	

FOR REVERSIBLE, ISOTHERMAL GAS EXPANSION,  $\Delta U = 0$  AND

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

$$V_f = 2V_i$$



**Figure 10.3**  
The expansion of an ideal gas into an evacuated bulb.

BUT WHEN  $P_{\text{ext}} = 0$  :

$$\Delta T = 0, \Delta U = 0, \underline{w = 0}$$

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$$

$$= R \ln \frac{V_f}{V_i} = R \ln 2$$

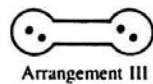
$$\Delta S_{\text{surr}} = 0$$



Arrangement I



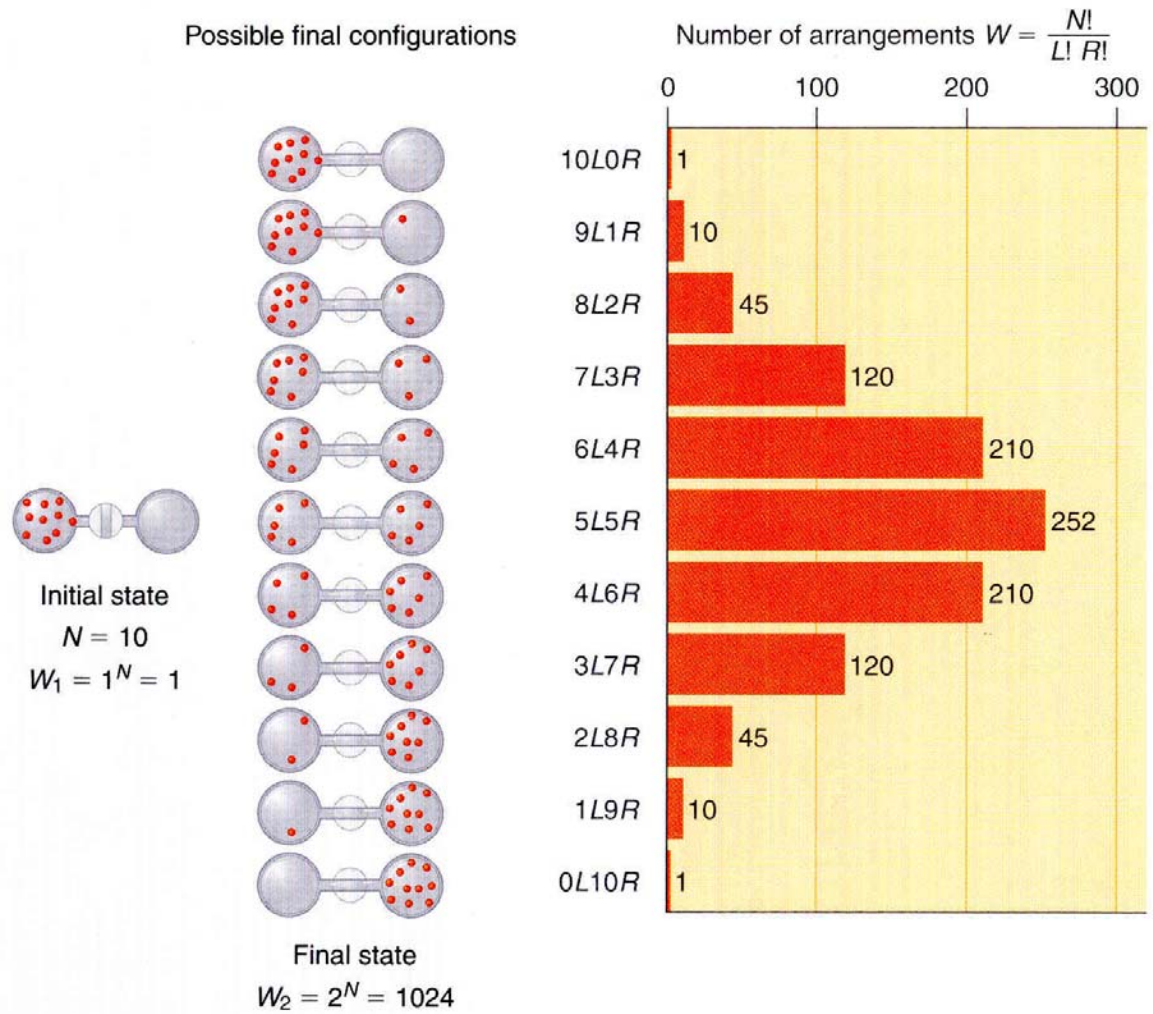
Arrangement II



Arrangement III

**Figure 10.4**  
Three possible arrangements (states) of four molecules in a two-bulbed flask.



**Figure 11.7: 10-Molecule Simulation of the Joule Experiment**

↑

MICROSTATES AVAILABLE =  $W$

**TABLE 10.2 Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules**

<u>Number of Molecules</u>	<u>Relative Probability of Finding All Molecules in the Left Bulb</u>
1	$\frac{1}{2}$
2	$\frac{1}{2} \times \frac{1}{2} = \frac{1}{2^2} = \frac{1}{4}$
3	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^3} = \frac{1}{8}$
5	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^5} = \frac{1}{32}$
10	$\frac{1}{2^{10}} = \frac{1}{1024}$
$n$	$\frac{1}{2^n} = \left(\frac{1}{2}\right)^n$
$6 \times 10^{23}$ (1 mole)	$\left(\frac{1}{2}\right)^{6 \times 10^{23}} = 10^{-(2 \times 10^{23})}$