

Ch 19. The First Law of Thermodynamics

19-1. Thermodynamic Systems

Thermodynamic system:

A system that can interact (and exchange energy) with its surroundings

Thermodynamic process:

A process in which there are changes in the state of a thermodynamic system

Heat Q

added to the system

$$Q > 0$$

taken away from the system

$$Q < 0$$

(through conduction, convection, radiation)

Work

done by the system onto its surroundings $W > 0$

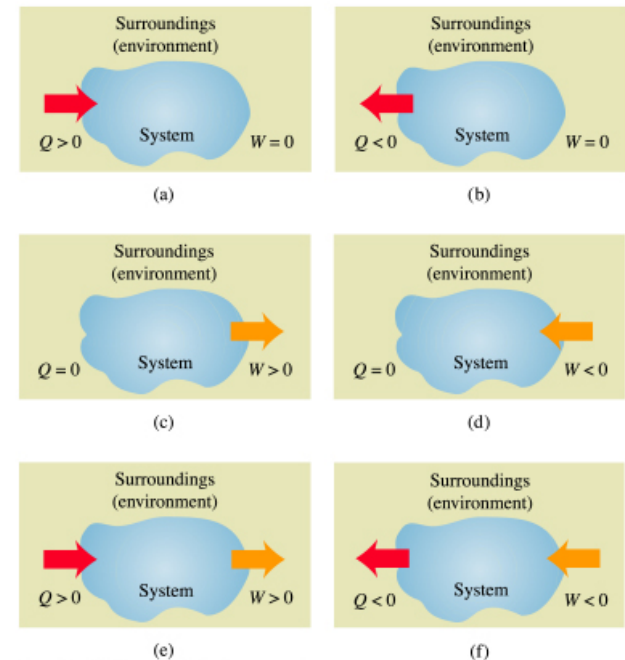
done by the surrounding onto the system $W < 0$

Energy change of the system is

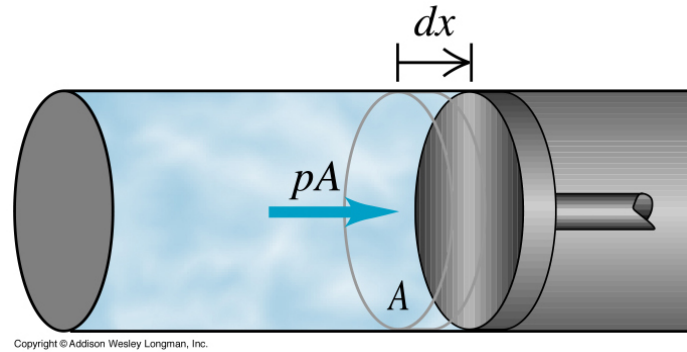
$$Q + (-W) \text{ or } Q - W$$

Gaining energy: +;

Losing energy: -



19-2. Work Done During Volume Changes



Area: A
Pressure: p

Force exerted on the piston:

$$F = pA$$

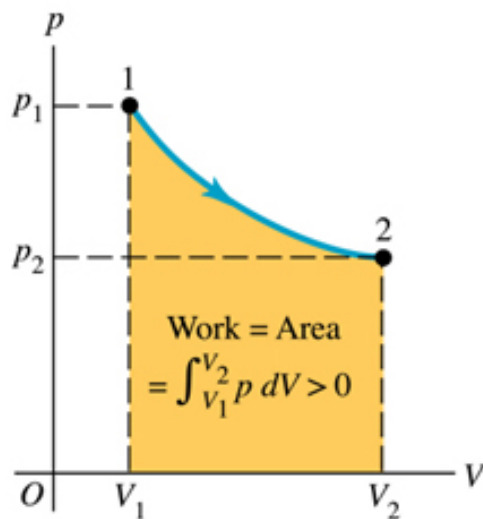
Infinitesimal work done by system

$$dW = F dx = p A dx = p dV$$

Work done in a finite volume change

$$W = \int_{V_{initial}}^{V_{final}} p dV$$

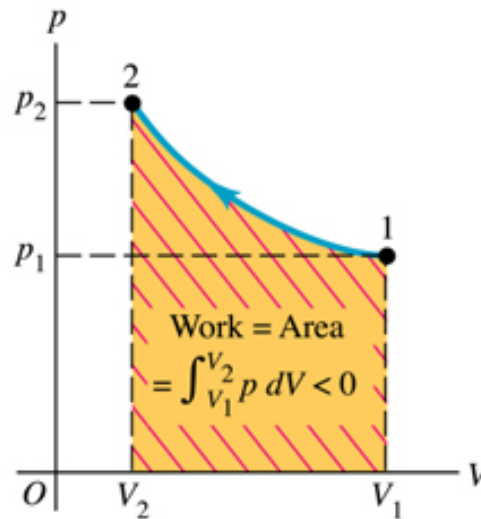
Graphical View of Work



(a)

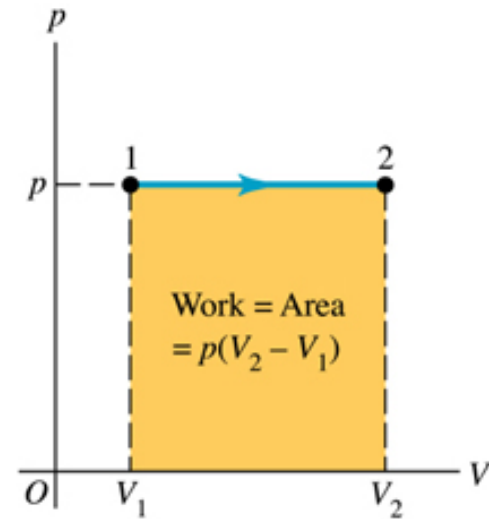
Copyright © Addison Wesley Longman, Inc.

Gas expands
 $dV > 0$, $W > 0$



(b)

Gas compresses
 $dV < 0$, $W < 0$



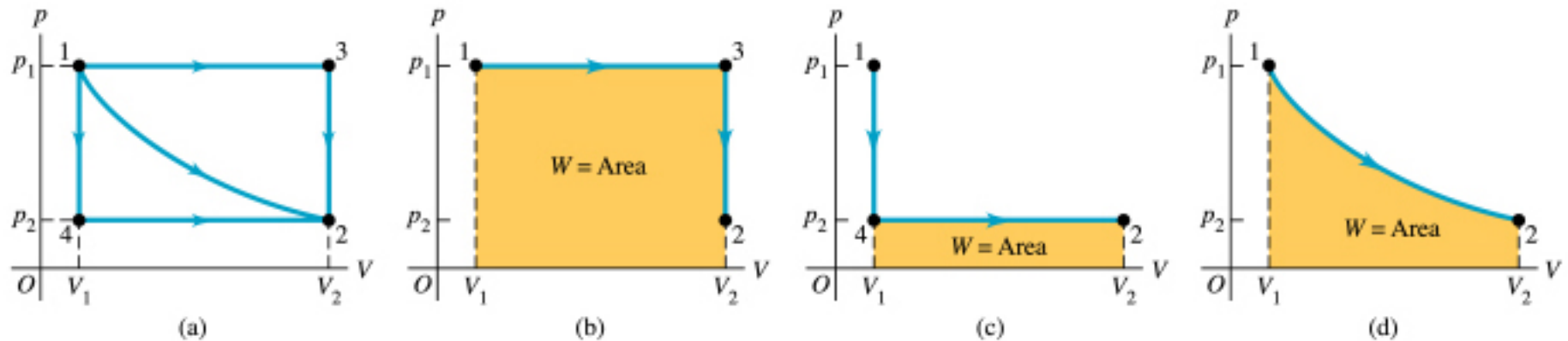
(c)

Constant p
 $W = p(V_2 - V_1)$

19-3. Paths Between Thermodynamic States

Path: a series of intermediate states between initial state (p_1, V_1) and a final state (p_2, V_2)

The path between two states is NOT unique.



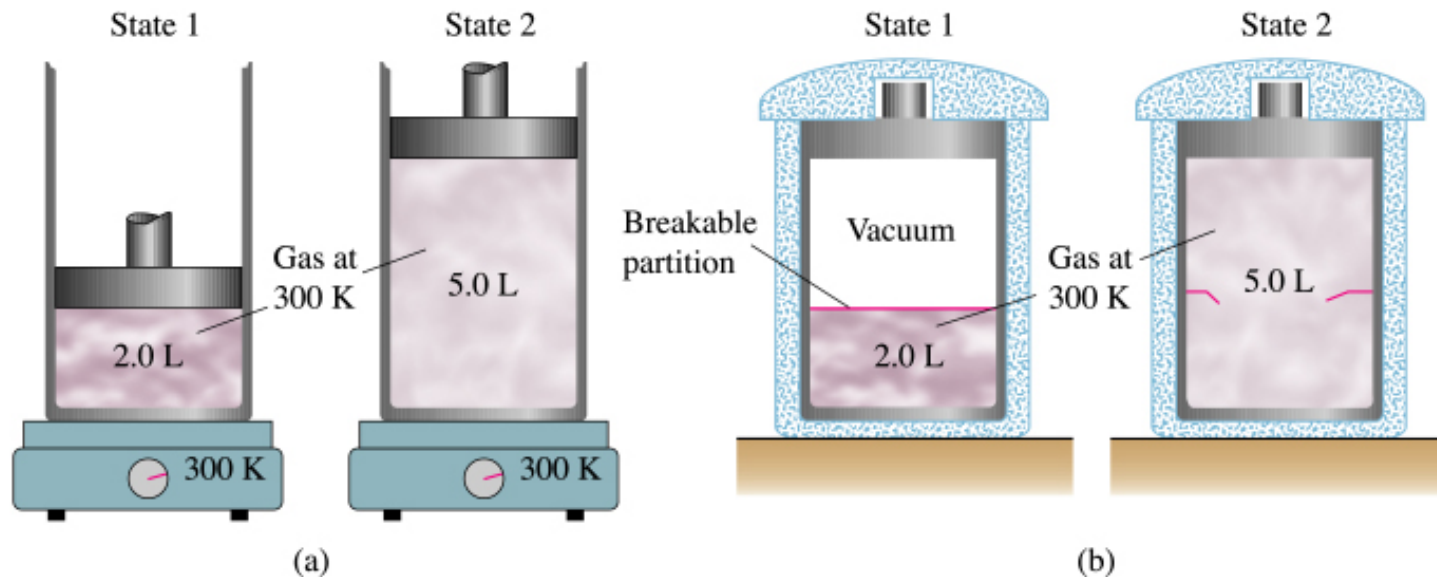
$$W = p_1(V_2 - V_1) + 0$$

$$W = 0 + p_2(V_2 - V_1)$$

$$W = \int_{V_1}^{V_2} p dV$$

Work done by the system is path-dependent.

Path Dependence of Heat Transfer



Isothermal: Keep temperature const.

Insulation +
Free expansion (uncontrolled expansion
of a gas into vacuum)

Heat transfer depends on the initial & final states, also on the path.

19-4. Internal Energy & the First Law of Thermodynamics

Internal energy U : kinetic energies of all constituent particles + potential energies of particle-particle interactions

Recall energy change is $Q-W$

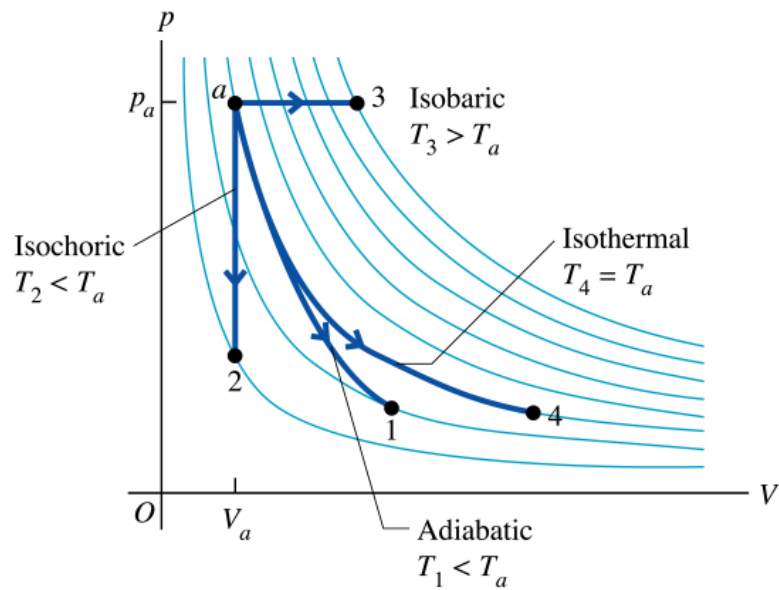
Thus $\Delta U = Q - W$ *First law of thermodynamics*

Although Q & W are path-dependent, experiments found that

ΔU is path-independent

For an isolated system, $W=Q=0$, $\Delta U=0$

19-5. Kinds of Thermodynamic Processes



Copyright © Addison Wesley Longman, Inc.

Adiabatic: No heat transfer in or out, $Q=0$

$$\Delta U = -W$$

Expansion, $W > 0$, $\Delta U < 0$

Compression, $W < 0$, $\Delta U > 0$

Isochoric: constant volume, $W=0$

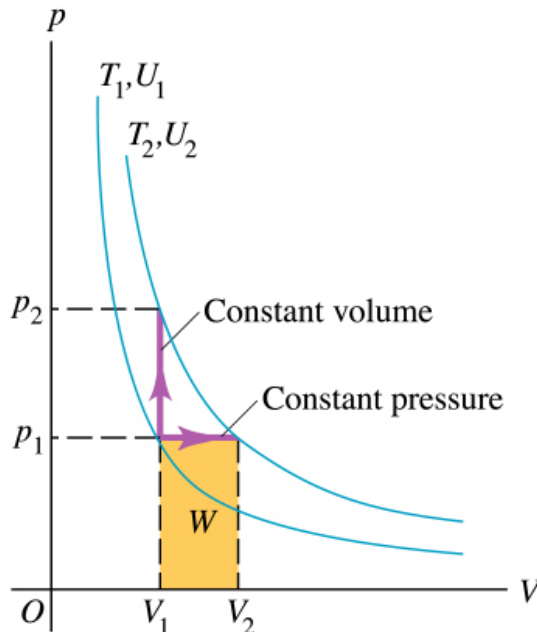
$$\Delta U = Q$$

Isobaric: constant pressure, $W = p(V_2 - V_1)$

Isothermal: constant temperature

19-6 & 7. Internal Energy & Heat Capacities of an Ideal Gas

Ideal gas: U only depends on T



Copyright © Addison Wesley Longman, Inc.

$$Q = nC\Delta T$$

C_V : molar heat capacity at constant volume

C_p : molar heat capacity at constant pressure

Isochoric:

$$W=0, Q=\Delta U=nC_V\Delta T$$

Isobaric:

$$Q=\Delta U+W$$

$$nC_p\Delta T = nC_V\Delta T + W$$

Thus $C_p > C_V$ (opposite if volume reduces during heating)

$$C_p = C_V + R$$

$$\gamma = C_p / C_V > 1$$

Monatomic gas:

$$C_V = 3R/2, \gamma = 5/3$$

Diatomic molecules near RT:

$$C_V = 5R/2, \gamma = 7/5$$

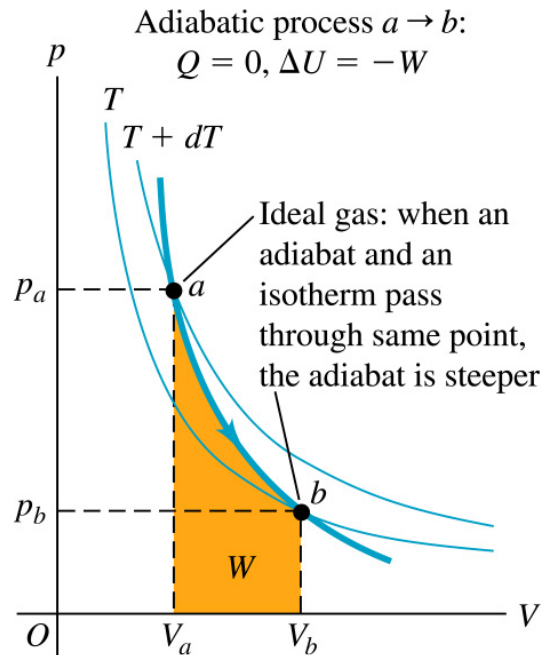
19-8. Adiabatic Processes for an Ideal Gas

$$\Delta U = -W$$

State equations

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \quad \text{or:}$$

$$p_1 V_1^\gamma = p_2 V_2^\gamma$$



Since $\gamma - 1 > 0$,

Adiabatic expansion $dV > 0, dT < 0$, temperature drops

Adiabatic compression, $dV < 0, dT > 0$, temperature rises

Work $W = nC_V(T_1 - T_2)$
 $= C_V(p_1 V_1 - p_2 V_2) / R$
 $= (p_1 V_1 - p_2 V_2) / (\gamma - 1)$

Summary for Ideal Gas

		W	Q	ΔU
		<i>work done by system</i>	<i>heat into system</i>	
Isochoric:	$\Delta V=0$	0	$nC_V\Delta T$	$nC_V\Delta T$
Isobaric:	$\Delta p=0$	$p(V_2-V_1)$	$nC_p\Delta T$	$nC_V\Delta T$
Isothermal:	$\Delta T=0$	$\int_{V_1}^{V_2} pdV$	$\int_{V_1}^{V_2} pdV$	0
Adiabatic:	$Q=0$	$-nC_V\Delta T$	0	$nC_V\Delta T$

Example

A cylinder with a piston contains 0.25 mol of O_2 (treat as ideal gas) at 2.40×10^5 Pa and 355K. The gas first expands isobarically to twice its original volume. It is then compressed isothermally back to its original volume, and finally cooled isochorically to its original pressure.

- A) show the processes in a p-V diagram
- B) T during isothermal process?
- C) maximum pressure?
- D) total ΔU during the cycle?
- E) total work done by the piston on the gas during the processes?

Example

A monatomic ideal gas initially at $p=1.50 \times 10^5$ Pa and $V=0.0800$ m³ is compressed adiabatically to a volume of 0.0400 m³.

- A) final pressure?
- B) Work done by the gas?
- C) $T_{\text{final}}/T_{\text{initial}}$?