Chapter 19

The First Law of Thermodynamics

PowerPoint® Lectures for
University Physics, Twelfth Edition
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Topics for Chapter 19

- I. First Law of Thermodynamics

    – Internal energy, concept of state variables

    – Difference between Work and Heat

- II. Examine various types of thermodynamic processes:

    – Constant volume

    – Constant pressure

    – Constant temperature

    – Zero heat transfer - adiabatic process

First Law of Thermodynamics

- 1st Law of Thermodynamics is a statement about **conservation of energy** and it categorizes the method of energy transfer into two basic forms: **work (W) and heat (Q).**

- The "internal" energy of a system (U) (for a container of ideal gas, U =kinetic energy of the molecules) can be changed by transferring heat to and from the environment and/or performing work on or by the environment.

Surroundings
(environment)

$Q > 0$ System $W > 0$

Heat is positive when it *enters* the system, negative when it *leaves* the system.

Work is positive when it is done *by* the system, negative when it is done *on* the system.

Surroundings
(environment)

$Q < 0$ $W < 0$

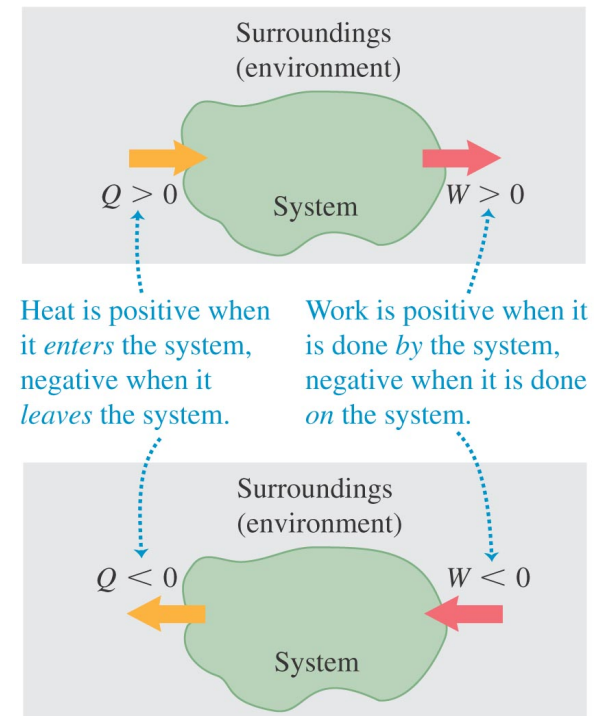System

$$U_f - U_i = \Delta U = Q - W$$

Positive Q $\Rightarrow$ heat input to the system from the environment

Negative Q $\Rightarrow$ heat output from the system to the environment

Positive W $\Rightarrow$ work done by the system on the environment

Negative W $\Rightarrow$ work done on the system by the environment

Note : The combined energy of the system and the environment is conserved; energy merely transferred to and from system and environment.

Internal energy, concept of state variables

- Internal energy = energy of the system with respect to the center of mass reference; we are not concerned with the situation where the entire system is moving.

- Example: The internal energy of n moles of monatomic ideal gas is the kinetic energy of the gas with respect to the center of mass reference frame and it is $U = 3/2nRT = 3/2PV$.

- U is called a "state variable" because once the state of the system is specified, such as the number of moles and the temperature or pressure and volume, U has an unique value, that is U is function $U(n,T)$ or $U(P,V)$. The change of a state variable does not depend on how the system goes from the initial to the final state.

- For example, you can add heat or do work to change the system's from T_i to T_f, then $\Delta U = 3/2nRT_f - 3/2nRT_i$ no matter what methods was used.

Work = pressure x change of volume

- Consider the work done by the system (e.g. a gas) on the environment.

System   dx

pA

A

load

Force that system
exerts on piston
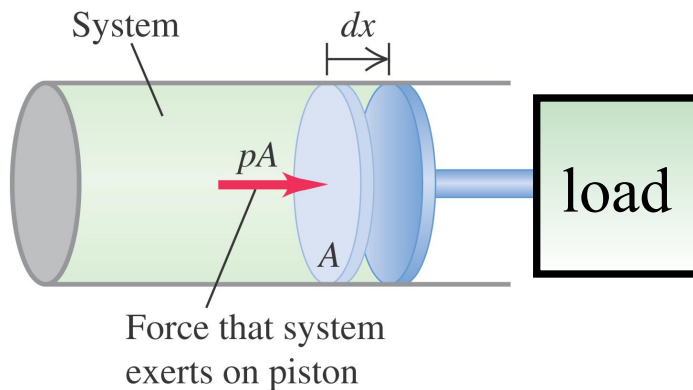
$W = Fdx = PAdx = PdV$

If $dx > 0 \Rightarrow dV > 0 \Rightarrow$ volume expands

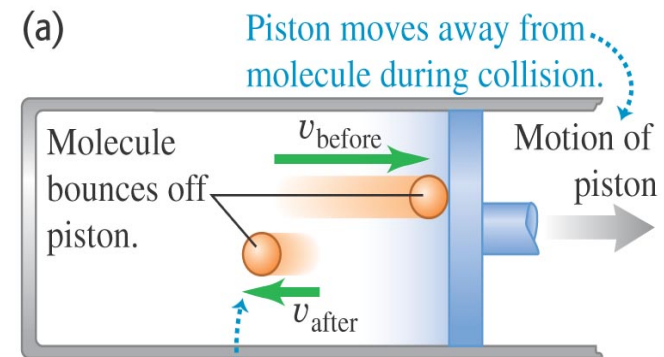$\Rightarrow$ system does positive work on the enviroment

According to the first Law :

$\Delta U = Q - W \Rightarrow$ positive work on the evironment
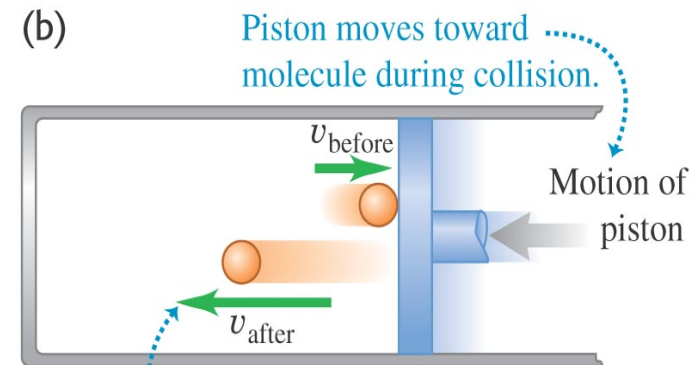
lowers the internal energy of the system

If $dx < 0 \Rightarrow$ compression, then $W < 0$ and the

internal energy increases.

(see picture to the right)

(a)

Piston moves away from
molecule during collision.

Molecule
bounces off
piston.

v_{before} Motion of
piston

v_{after}

Molecule loses kinetic energy,
does positive work on piston.

(b)

Piston moves toward
molecule during collision.

v_{before}

Motion of
piston

v_{after}

Molecule gains kinetic energy,
does negative work on piston.

Work done by a varying pressure is given by integration

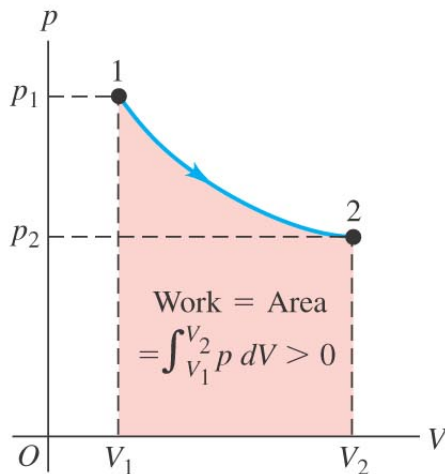$$W = \int_{V_i}^{V_f} P(V)\,dV$$

Note :

(1) The direction of the path (indicated by an arrow) determines whether W is positive or negative.

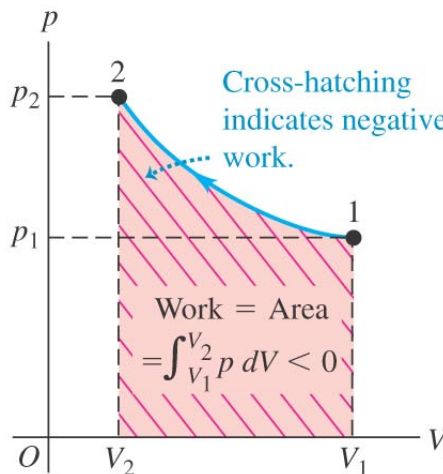(2) W depends on the path going from initial to final state (see next slide)

$\Rightarrow$ W is NOT a state variable;
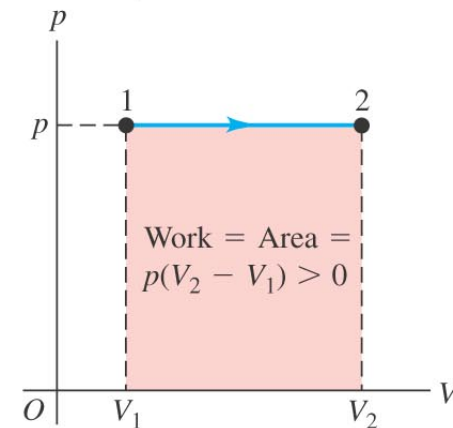
there is NO such thing as $\Delta W = W_f - W_i$

(a) pV-diagram for a system undergoing an expansion with varying pressure

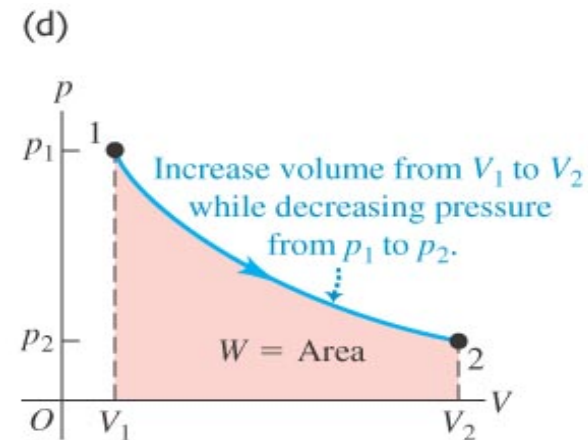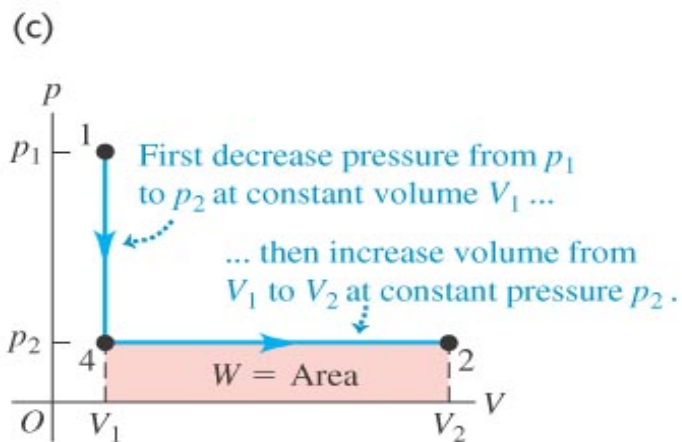(b) pV-diagram for a system undergoing a compression with varying pressure
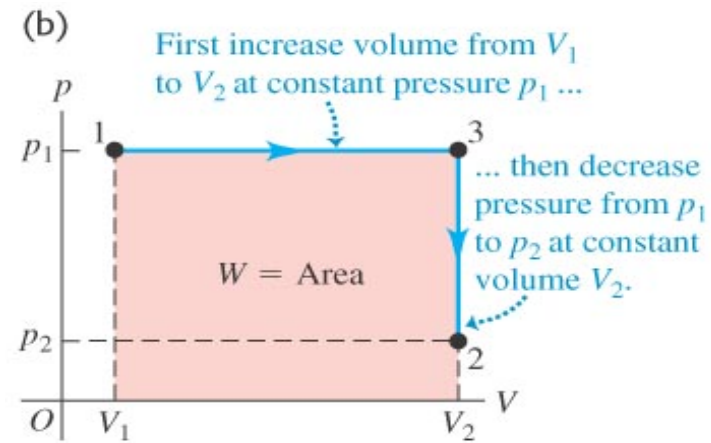
(c) pV-diagram for a system undergoing an expansion with constant pressure

Cross-hatching indicates negative work.

Work = Area $= \int_{V_1}^{V_2} p\,dV > 0$

Work = Area $= \int_{V_1}^{V_2} p\,dV < 0$

Work = Area = $p(V_2 - V_1) > 0$

Work done depends on the path.

- Shown below 3 different paths going from state 1 to state 2; the work done are different.
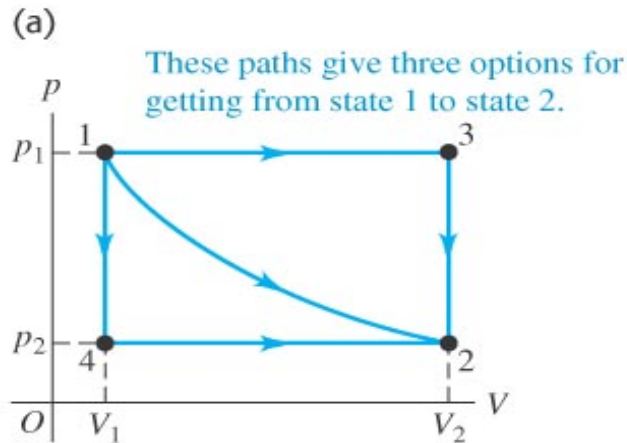
What is energy transfer by heat?

- Imagine heating water with a burner. Energy is transferred from the fast moving molecules in the flame to the slow moving molecules in the pot and then to the slow moving molecules in the water by means of *random* collisions.

- At the microscopic level, the molecules in the flame are doing "work" (force x displacement) on the molecules in the pot which in turns are doing work on the water molecules. At this level, there no different between this method of energy transfer and the one described previously by pushing a piston. However, on the macroscopic level, work done by pushing a piston is done uniformly by changing the volume while heat can be added/ removed without changing the volume.

- The first Law of thermodynamics treat work and heat on equal footing. The second Law of thermodynamics will treat heat differently from work.
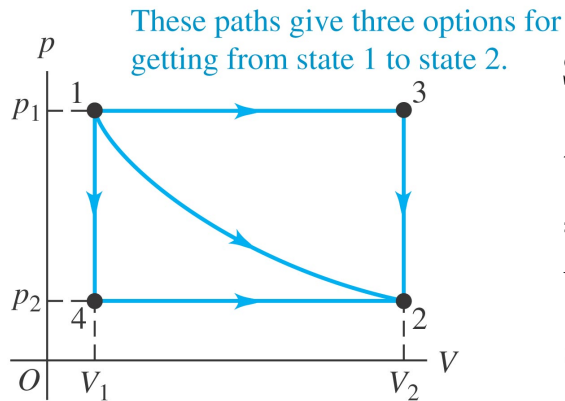
II. Examine various types of thermodynamic processes

- ## Constant volume - "isochoric" process

(a)

These paths give three options for getting from state 1 to state 2.

Process from 1 to 4 is an isochoric process.

Since there is no volume change $\Rightarrow W = \int_{V_1}^{V_1} PdV = 0$

that is why it is called "isochoric".

$\Rightarrow \Delta U = Q$

We won't be able to say anything further unless we know something about the system. Let the system be n moles of monatomic ideal gas, then

Let $P_1 = 3x10^5 \frac{N}{m^2}, P_2 = 1x10^5 \frac{N}{m^2}$

$V_1 = 10^{-2} m^3, n = 2$ moles

Evaluate $\Delta U, W, Q$, and ΔT for the process 1 to 4.

$U = \frac{3}{2} nRT = \frac{3}{2} PV,$

$\Delta U = U_f - U_i = \frac{3}{2} P_2 V_1 - \frac{3}{2} P_1 V_1 = negative = -3kJ$

(*OR* use $\Delta U = U_f - U_i = \frac{3}{2} nRT_4 - \frac{3}{2} nRT_1 = negative; T_4 = 60K, T_1 = 180K$)

$\Rightarrow$ In this process, heat is released at constant volume to lower the pressure of the gas (lower the temperature of the gas)

II. Examine various types of thermodynamic processes

- ## Constant pressure - "isobaric" process

(a)

These paths give three options for getting from state 1 to state 2.

Let $P_1 = 3x10^5 \frac{N}{m^2}, P_2 = 1x10^5 \frac{N}{m^2}$

$V_1 = 10^{-2} m^3, V_2 = 3x10^{-2} m^3,$

$n = 2 \text{ moles}$

Evaluate $\Delta U, W, Q,$ *and* ΔT
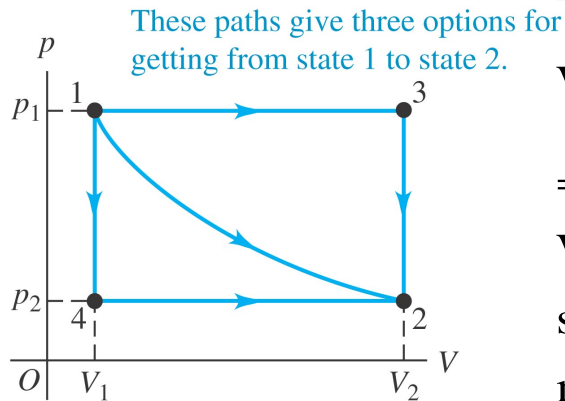
Process from 1 to 3 is an isobaric process.

$$W = \int_{V_1}^{V_2} PdV = P_1(V_2 - V_1) = +6kJ$$

$$\Rightarrow \Delta U = Q - P_1(V_2 - V_1)$$

We won't be able to say anything further unless we know something about the system. Let the system be n moles of monatomic ideal gas, then

$$U = \frac{3}{2}nRT = \frac{3}{2}PV,$$

$$\Delta U = U_f - U_i = \frac{3}{2}P_1V_2 - \frac{3}{2}P_1V_1 = \frac{3}{2}P_1(V_2 - V_1) = +9kJ$$

$$(OR \text{ use } \Delta U = U_f - U_i = \frac{3}{2}nR(T_3 - T_1))$$

$$\Rightarrow Q = \Delta U + W = \frac{5}{2}P_1(V_2 - V_1) = \frac{5}{2}nR(T_3 - T_1) = 15kJ$$

In this process, heat is must be added to keep the pressure constant while doing work on the environment.

II. Examine various types of thermodynamic processes

- ## Constant temperature - "isothermal" process

(a)

These paths give three options for getting from state 1 to state 2.
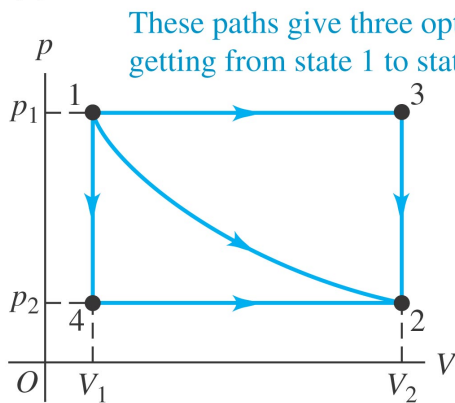
Let process from 1 to 2 be an isothermal process. In this case, we won't be able to say anything at all unless we know something about the system (such as P vs V curve for T = constant). Let the system be n moles of monatomic ideal gas, then

$$P = \frac{nRT}{V}, \ T = constant = T_1 = T_2 = 180K$$

Let $P_1 = 3x10^5 \frac{N}{m^2}, P_2 = 1x10^5 \frac{N}{m^2}$

$V_1 = 10^{-2} m^3, V_2 = 3x10^{-2} m^3,$

$n = 2 \ moles$

Evaluate $\Delta U, W, Q,$ and ΔT

$$W = \int_{V_1}^{V_2} P dV_1 = \int_{V_1}^{V_2} \frac{nRT}{V} dV_1 = nRT \ln \frac{V_2}{V_1} = 3\ln 3 \ (kJ)$$

$$U = \frac{3}{2} nRT \Rightarrow \Delta U = \frac{3}{2} nR\Delta T = 0$$

(Note : isothermal strictly means constant T; for ideal gas it also implies constant U, not true for real gases)

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

In this process, heat is must added to keep the temperature constant while doing work on the environment.

Re-enforce the concept of state variables

(a)

These paths give three options for getting from state 1 to state 2.
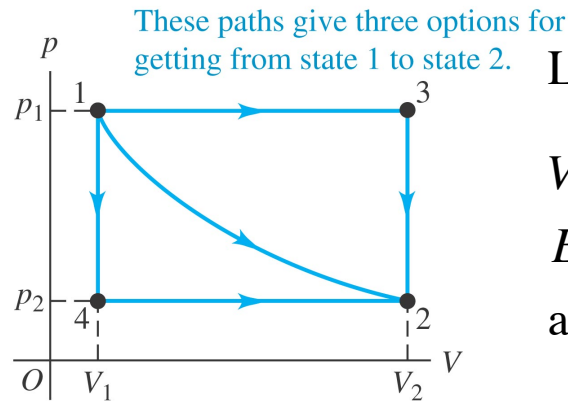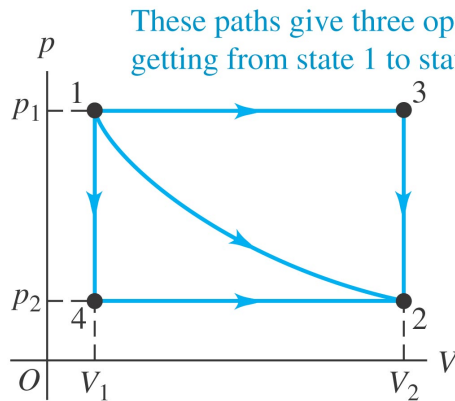
Let $P_1 = 3x10^5 \dfrac{N}{m^2}, P_2 = 1x10^5 \dfrac{N}{m^2}$

$V_1 = 10^{-2} m^3, V_2 = 3x10^{-2} m^3, n = 2 \ moles$ of monatomic ideal gas

Evaluate $\Delta U, W, Q,$ and ΔT for the path $1 -> 3 -> 2$

and compare with the isothermal process $1 -> 2$

II. Examine various types of thermodyanmic processes

- ## No heat transfer (Q=0) - "adiabatic" process

(a)

These paths give three options for getting from state 1 to state 2.

Let process from 1 to 2 be an adiabtic process.

All we can say is $\Delta U = Q - W = -W$

We won't be able to say anything further unless we know something about the system (such as P vs V curve when $Q = 0$). Let the system be n moles of monatomic ideal gas, then

$$P = \frac{nRT}{V}, \text{ however } T \neq \text{constant}, \quad T_1 = 180K$$

Let $P_1 = 3x10^5 \frac{N}{m^2}, P_2 = ???$

$V_1 = 10^{-2} m^3, V_2 = 3x10^{-2} m^3,$

$n = 2 \text{ moles}$

Evaluate $\Delta U, W, Q,$ and ΔT

$$W = \int_{V_1}^{V_2} PdV_1 = \int_{V_1}^{V_2} \frac{nRT}{V} dV_1 \neq nRT\ln\frac{V_2}{V_1}$$

because T is also a function of V for this path.

Since $W = $ positive (see direction of arrow => expansion)

$\Rightarrow \Delta U = Q - W = -W = $ negative

$\Rightarrow$ T decreases along the path.

For monatomic ideal gas, we can use $\Delta U = \frac{3}{2} nR(T_2 - T_1) = -W$

but need to know $T_2 (see$ next slide)

Adiabatic PV curve for monatomic ideal gas

- In an adiabatic process, no heat is transferred from system and surroundings.

Derive the adiabatic PV curve for an ideal gas.

Use differential form of the 1st Law: $dU=dQ-dW=-dW=-PdV$

Adiabatic process $a \to b$:
$$Q = 0, \Delta U = -W$$

An adiabatic curve at any point is always steeper than the isotherm passing through the same point.

For ideal gas: $U=\dfrac{3}{2}nRT = \dfrac{3}{2}PV \Rightarrow dU = \dfrac{3}{2}PdV + \dfrac{3}{2}VdP$

$$\Rightarrow \frac{3}{2}PdV + \frac{3}{2}VdP = -PdV$$

$$\Rightarrow \frac{5}{2}PdV = -\frac{3}{2}VdP$$

$$\Rightarrow \frac{5}{2}\frac{dV}{V} = -\frac{3}{2}\frac{dP}{P}$$

$$\Rightarrow \frac{5}{2}\ln V\Big|_{V_1}^{V} = -\frac{3}{2}\ln P\Big|_{P_1}^{P}$$

$$\Rightarrow \frac{5}{2}\ln\frac{V}{V_1} = -\frac{3}{2}\ln\frac{P}{P_1}$$

$$\Rightarrow \left(\frac{V}{V_1}\right)^{5/2} = \left(\frac{P}{P_1}\right)^{-3/2} = \left(\frac{P_1}{P}\right)^{3/2}$$

$$\Rightarrow P = P_1\left(\frac{V_1}{V}\right)^{5/3} \quad \text{in particular: } P_2 = P_1\left(\frac{V_1}{V_2}\right)^{5/3} = 3\text{x}10^5\left(\frac{1}{3}\right)^{5/3}\frac{N}{m^2}$$
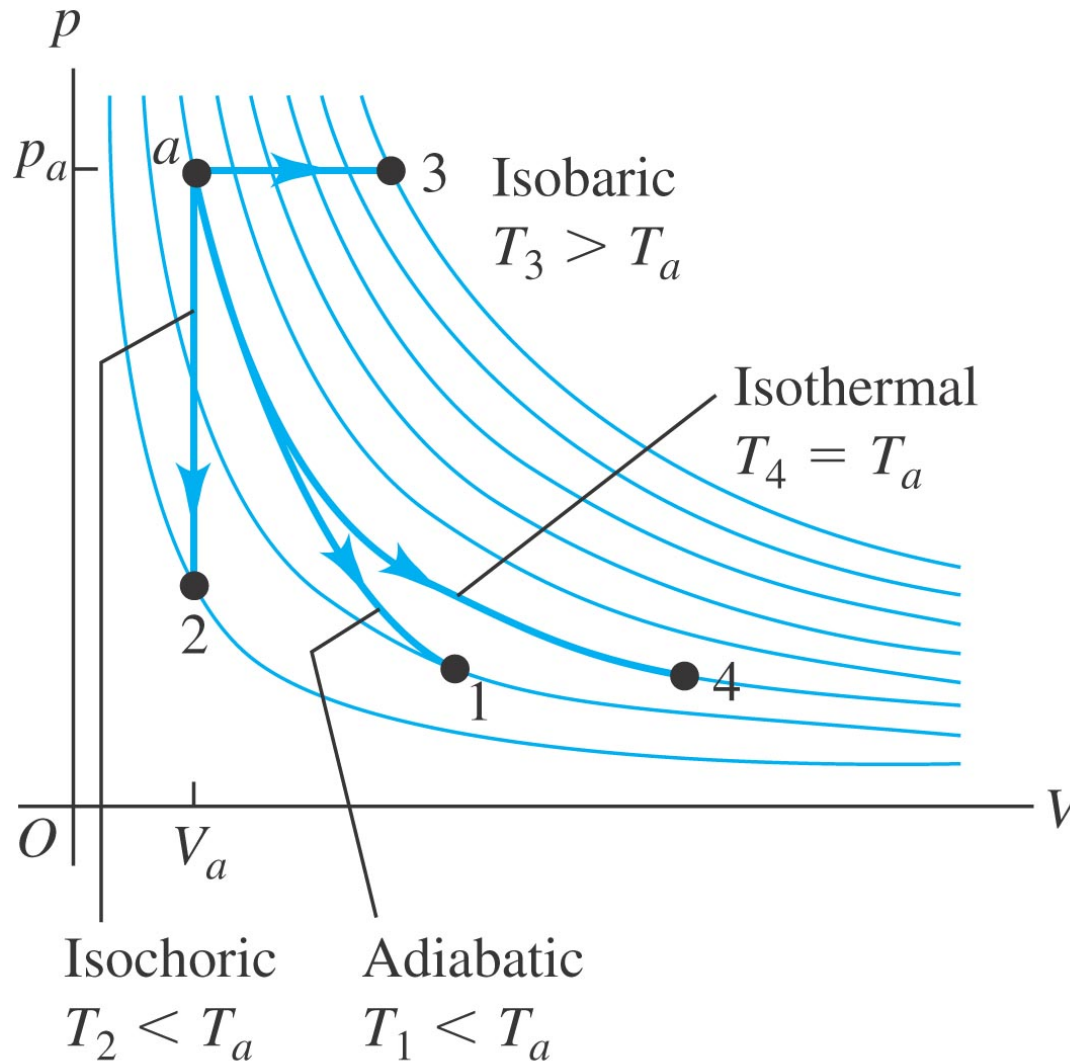
Use $P=\dfrac{nRT}{V} \Rightarrow T=T_1\left(\dfrac{V_1}{V}\right)^{2/3} \Rightarrow T_2 = T_1\left(\dfrac{V_1}{V_2}\right)^{2/3} = 180\left(\dfrac{1}{3}\right)^{2/3}K$

$$W = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} P_1\left(\frac{V_1}{V}\right)^{5/3} dV = P_1V_1^{5/3}\left[-\frac{3}{2}V^{-2/3}\right]_{V_1}^{V_2}$$

$$= \frac{3}{2}P_1V_1\left[1-\left(\frac{V_1}{V_2}\right)^{2/3}\right] = \frac{3}{2}P_1V_1 - \frac{3}{2}P_2V_2 = \frac{3}{2}nR(T_1-T_2) = -\Delta U$$

Let $P_1 = P_a = 3\text{x}10^5 \dfrac{N}{m^2}, P_2 = P_b = ???$

$V_1 = V_a = 10^{-2} m^3, V_2 = V_b = 3\text{x}10^{-2} m^3, n = 2\ moles$

Evaluate $\Delta U, W, Q,$ and ΔT

Compare the four processes on a PV diagram

- Notice the subtle differences for each curve in Figure 19.16.
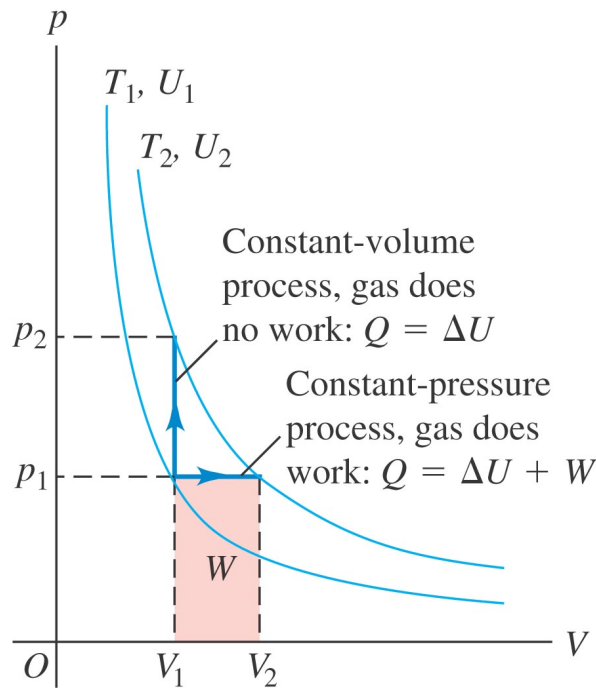
Cyclic process - complete cycle

(a)

These paths give three options for getting from state 1 to state 2.
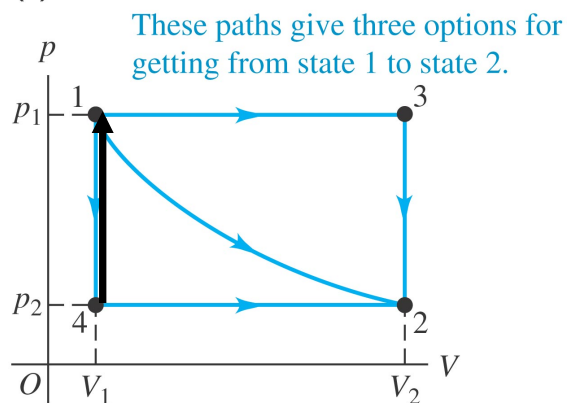
Cyclic process : $1 \rightarrow 3 \rightarrow 2 \rightarrow 4 \rightarrow 1$

No matter what the substance is, $\Delta U_{complete\ cycle} = 0$

because it comes back to the same state

$\Delta U = U_1 - U_1$

Relating heat capacities at constant volume and pressure

Compare molar heat capacities, c_V and c_P, for monatomic ideal gas

Constant volume (W = 0): $Q = \Delta U = \dfrac{3}{2} nR\Delta T \Rightarrow c_V = \dfrac{3}{2} R$

Constant pressure: $W = -P\Delta V \Rightarrow Q = \Delta U + W = \Delta U + P\Delta V$

$PV = nRT \Rightarrow P\Delta V = nR\Delta T$ (for constant P)

$\Rightarrow Q = \dfrac{3}{2} nR\Delta T + nR\Delta T = n(c_v + R)\Delta T$

$\Rightarrow c_p = c_v + R$

It requires more heat to raise the temperature at constant pressure vs constant volume because some of the heat is spent in doing work, expanding the volume.

For solids, $c_p \approx c_v$, because the volume does not expand as easily as a gas. Nonetheless c_p is always greater than c_v.

Heat capacities tabulated for selected gasses

Table 19.1 Molar Heat Capacities of Gases at Low Pressure

Type of Gas	Gas	C_V (J/mol·K)	C_p (J/mol·K)	$C_p - C_V$ (J/mol·K)	$\gamma = C_p/C_V$
Monatomic	He	12.47	20.78	8.31	1.67
	Ar	12.47	20.78	8.31	1.67
Diatomic	H_2	20.42	28.74	8.32	1.41
	N_2	20.76	29.07	8.31	1.40
	O_2	20.85	29.17	8.31	1.40
	CO	20.85	29.16	8.31	1.40
Polyatomic	CO_2	28.46	36.94	8.48	1.30
	SO_2	31.39	40.37	8.98	1.29
	H_2S	25.95	34.60	8.65	1.33

$$c_p = c_v + R; \quad R \sim 8.31\frac{J}{mol \cdot K}$$

$$monatomic : c_v = \frac{3}{2}R \Rightarrow c_p = \frac{5}{2}R \Rightarrow \frac{c_p}{c_v} = \frac{5}{3} \approx 1.67$$

$$diatomic : c_v = \frac{5}{2}R \text{ (without vibration)} \Rightarrow c_p = \frac{7}{2}R \Rightarrow \frac{c_p}{c_v} = \frac{7}{5} \approx 1.4$$