3 - 1st Law of Thermodynamics

Thermodynamic Systems

We must define clearly what is and is not included in the thermodynamic system. The state of the thermodynamic system changes when it goes through a thermodynamic process.
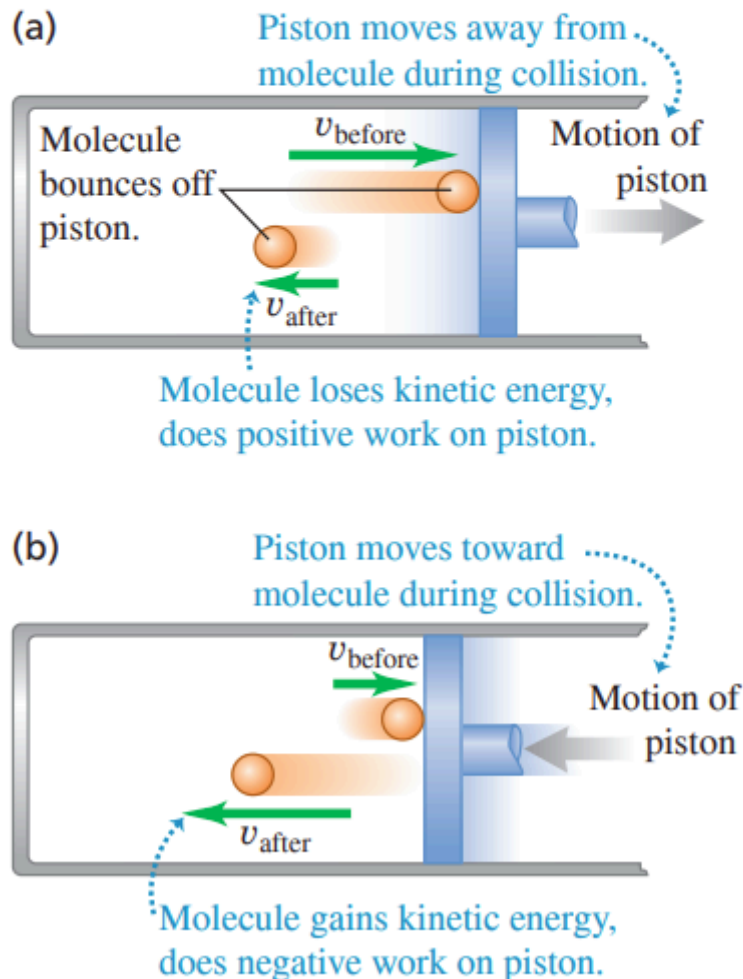

1st Law of Thermodynamics

$$\Delta U = Q - W$$

where U refers to the internal energy, Q is heat, and W is work done by the system.

Work Done During Volume Changes

Consider the work done by the system during a volume change.

Figure **19.4** A molecule striking a piston (a) does positive work if the piston is moving away from the molecule and (b) does negative work if the piston is moving toward the molecule. Hence a gas does positive work when it expands as in (a) but does negative work when it compresses as in (b).

(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.

When a gas expands, it pushes outward on its boundary surfaces as they move outward. An expanding gas always does positive work.

Let
A: Cross sectional area of the cylinder
p: pressure exerted by the system at the piston face
$F = pA$: is the total force exerted by the system on the piston

When the piston moves a distance dx, then the work dW by this force is:

$$dW = F\,dx = pA\,dx$$

But remember that

$$A\,dx = dV \qquad \text{(infinitesimal change in volume)}$$

The work done by the system in this small volume change:

$$dW = p\,dV$$

In a finite volume change from V_1 to V_2:

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

In general, the pressure of the system may vary during the volume change. Let us try to find how the pressure varies as a function of volume using a pV-diagram (i.e. use the work formula to find the area under the pV curve):

Figure **19.6** The work done equals the area under the curve on a pV-diagram.

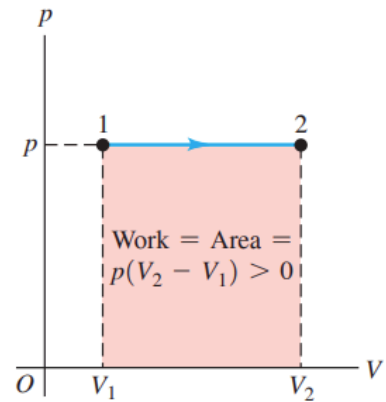(a) pV-diagram for a system undergoing an expansion with varying pressure
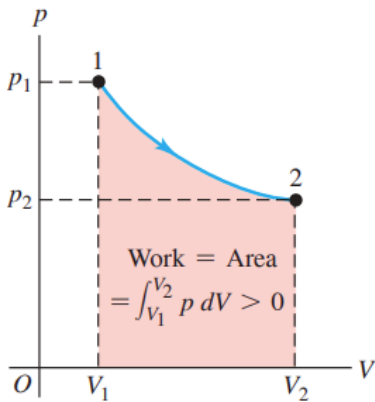
(b) pV-diagram for a system undergoing a compression with varying pressure
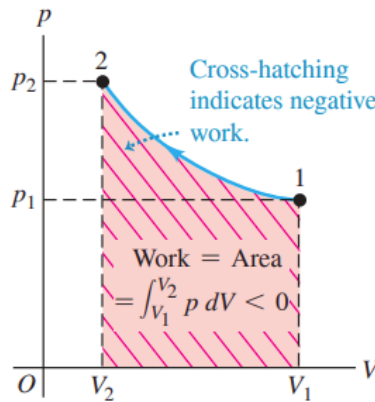
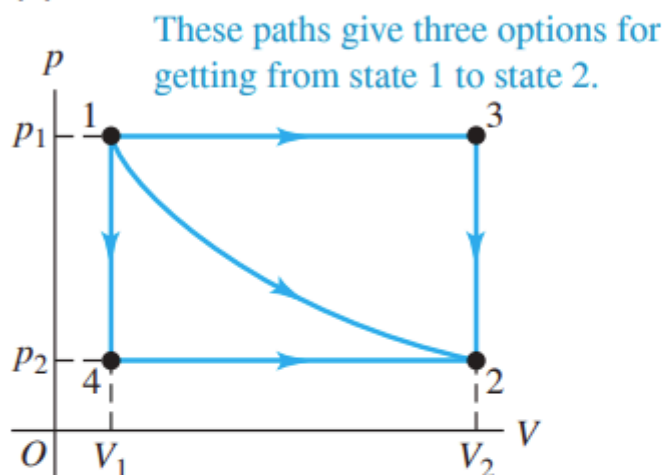(c) pV-diagram for a system undergoing an expansion with constant pressure
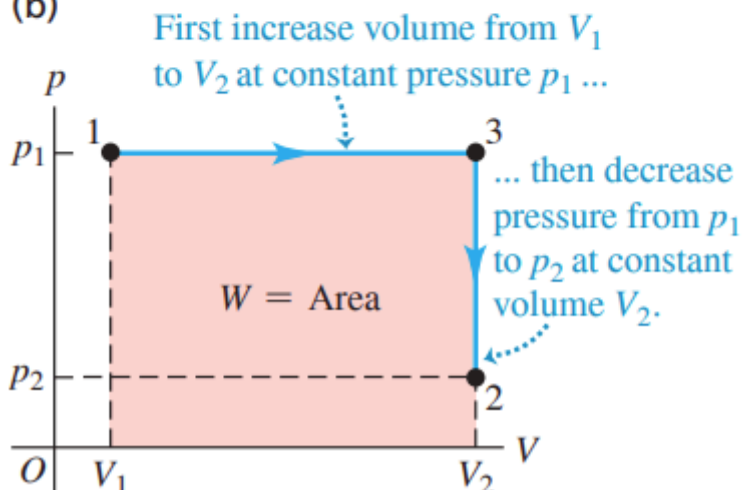
Paths Between Thermodynamic States

When a thermodynamic system changes from an initial state to a final state, it passes through a series of intermediate states (paths).

Figure 19.7 The work done by a system during a transition between two states depends on the path chosen.

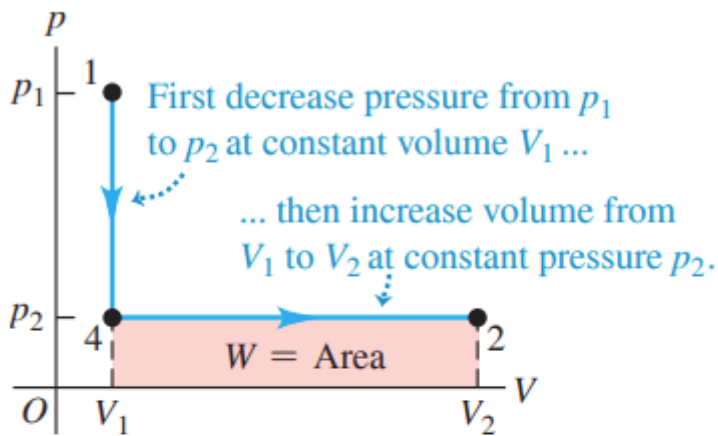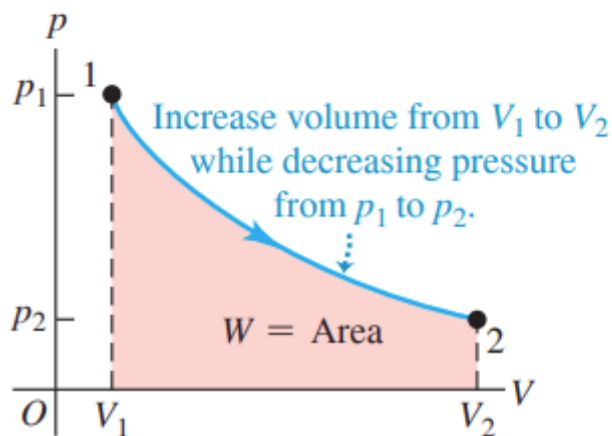**(a)**

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

(b)

First increase volume from V_1 to V_2 at constant pressure p_1 ...

... then decrease pressure from p_1 to p_2 at constant volume V_2.

$W = $ Area

(c)

(d)

This shows us that the work done by the system depends not only on the initial and final states, but also the intermediate states (i.e. the path)

Internal Energy and the First Law of Thermodynamics

Internal energy refers to the sum of the kinetic energies of all the particles in a system, plus the sum of all the potential energy of interaction among particles.

Let U be the internal energy of a thermodynamic system. Then $\Delta = U_2 - U_1$ is the change in internal energy.

There are two possible ways to change the internal energy of a system:

- Add/remove heat from the system
- Let the system do work or do work on the system

Then:

$$\Delta U = Q - W$$

or

$$Q = \Delta U + W$$

(Note that W refers to work done by the system)

The first law of thermodynamics gives us an operational definition of the change in internal energy of a system.

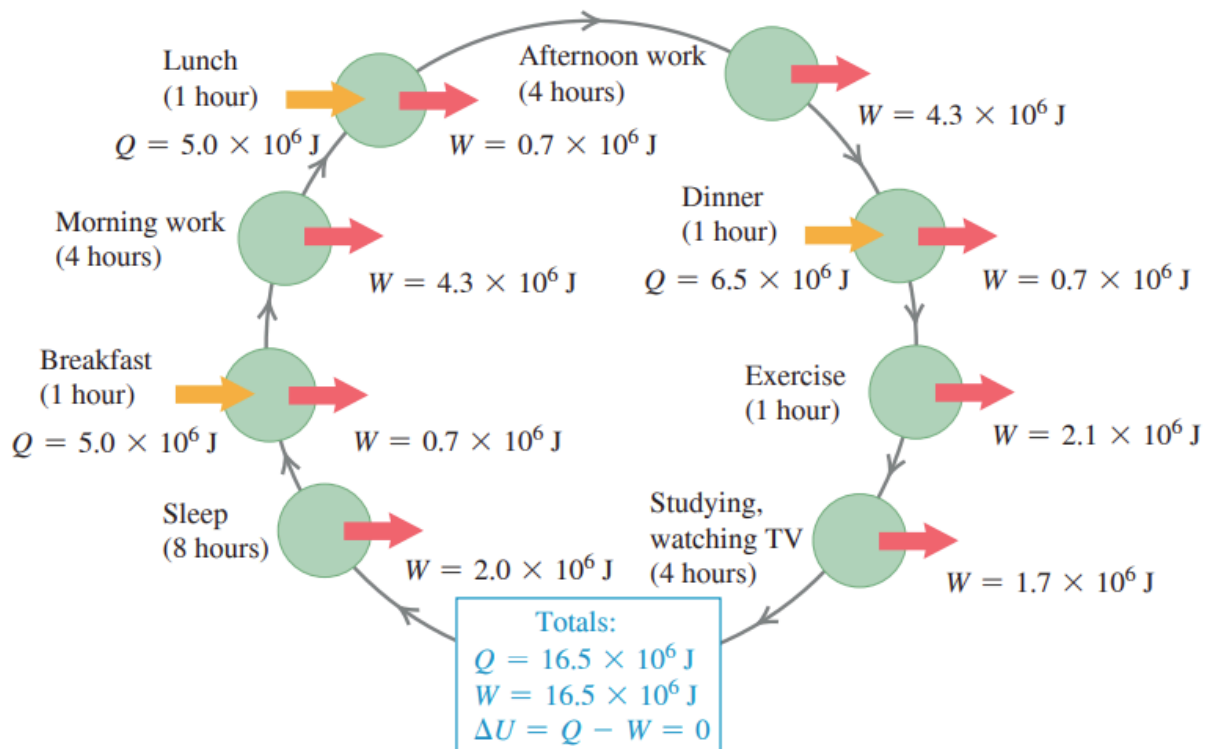In a thermodynamic process, the internal energy may:

- Increase ($\Delta U > 0$)
- Decrease ($\Delta < 0$)
- Remain the same ($\Delta = 0$)

Note that while Q and W are depends on the path, $\Delta U = Q - W$ is independent of the path.

Cyclic Processes and Isolated Systems

A cyclic process is a process that returns the system to its initial state.

Figure **19.11** Every day, your body (a thermodynamic system) goes through a cyclic thermodynamic process like this one. Heat Q is added by metabolizing food, and your body does work W in breathing, walking, and other activities. If you return to the same state at the end of the day, $Q = W$ and the net change in your internal energy is zero.

Lunch
(1 hour)
$Q = 5.0 \times 10^6$ J

Afternoon work
(4 hours)
$W = 0.7 \times 10^6$ J

$W = 4.3 \times 10^6$ J

Morning work
(4 hours)
$W = 4.3 \times 10^6$ J

Dinner
(1 hour)
$Q = 6.5 \times 10^6$ J

$W = 0.7 \times 10^6$ J

Breakfast
(1 hour)
$Q = 5.0 \times 10^6$ J

$W = 0.7 \times 10^6$ J

Exercise
(1 hour)
$W = 2.1 \times 10^6$ J

Sleep
(8 hours)
$W = 2.0 \times 10^6$ J

Studying,
watching TV
(4 hours)

$W = 1.7 \times 10^6$ J

Totals:
$Q = 16.5 \times 10^6$ J
$W = 16.5 \times 10^6$ J
$\Delta U = Q - W = 0$

Types of Thermodynamic Proceses

Adiabatic Process

No heat transfer into or out of a system (such that Q = 0).
This can be accomplished by surrounding the system with thermally insulating material, or carrying out the process very swiftly such that there is not enough time for appreciable heat flow.

$$U_2 - U_1 = \Delta U = -W$$

Isochoric Process

Constant volume process.
When the volume of a system is constant, it does no work on its surroundings (W = 0)

$$U_2 - U_1 = \Delta U = Q$$

Isobaric Process

Constant pressure process.
In this case, ΔU, Q, and W are not zero, but W would then be straightforward:
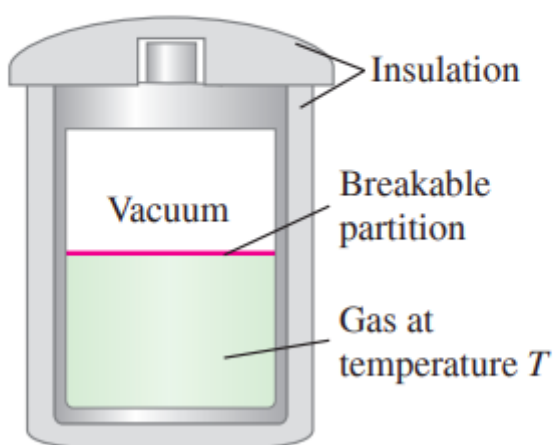
$$W = p(V_2 - V_1)$$

Isothermal Process

Constant temperature process.
For a process to be isothermal, heat flow into or out of a system must occur slowly enough that thermal equilibrium is maintained.

Internal Energy of an Ideal Gas

Figure **19.17** The partition is broken (or removed) to start the free expansion of gas into the vacuum region.

Many experiments have shown that when a low-density gas undergoes a free expansion, its temperature does not change. This gas is essentially an ideal gas.

The internal energy of an ideal gas depends only on its temperature, not pressure nor volume.

Heat Capacities of an Ideal Gas

Heat capacities may be measured at a constant volume (C_v) or constant pressure (C_p).

Consider: C_v and C_p for an ideal gas.
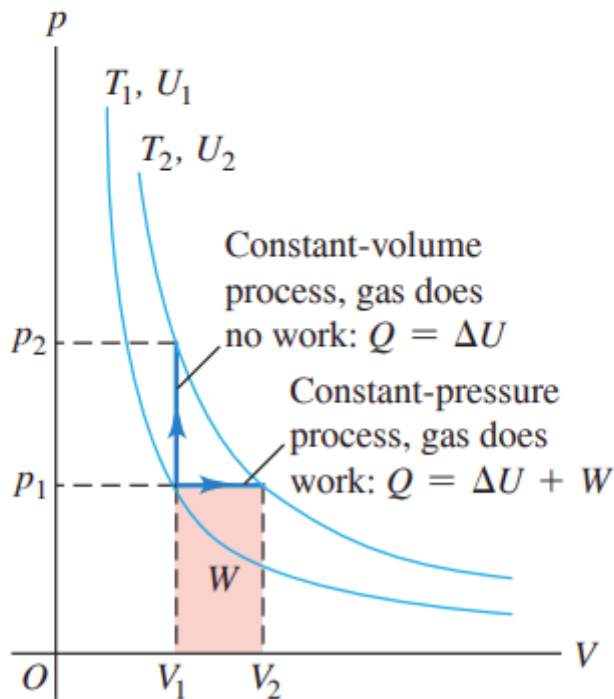
At constant volume: $W = 0$

$$Q = \Delta U$$

At constant pressure:

$$Q = \Delta U + W$$

For a given temperature increase, ΔU of an ideal gas has the same value no matter the process ($U \propto T$ only). Essentially, Q input at a constant pressure > Q input at constant volume.

Figure **19.19** Raising the temperature of an ideal gas from T_1 to T_2 by a constant-volume or a constant-pressure process. For an ideal gas, U depends only on T, so ΔU is the same for both processes. But for the constant-pressure process, more heat Q must be added to both increase U and do work W. Hence $C_p > C_V$.

Raising the temperature of an ideal gas from T_1 to T_2 by a constant-volume or a constant-pressure process. For an ideal gas, U depends only on T, so ΔU is the same for both processes.

But for the constant-pressure process, more heat Q must be added to both increase U and do work U. Hence, $C_p > C_v$ (for air, C_p is 40% greater than C_v).

Relating C_p and C_v for an Ideal Gas

Consider the constant volume process:

$$dQ = nC_v\, dT$$

$dW = 0$ as V is constant.

We can take the first law in a different form:

$$dQ = dU + dW$$

Now consider the constant pressure process:

$$dQ = nC_p\, dT$$

The work dW done on the gas in terms of the ideal gas equation:

Finally, we get the relationship:

$$C_p = C_v + R$$

Ratio of Heat Capacities

$$\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v}$$

e.g. for ideal diatomic gas:

$$C_v = \frac{5}{2} R$$

Thus

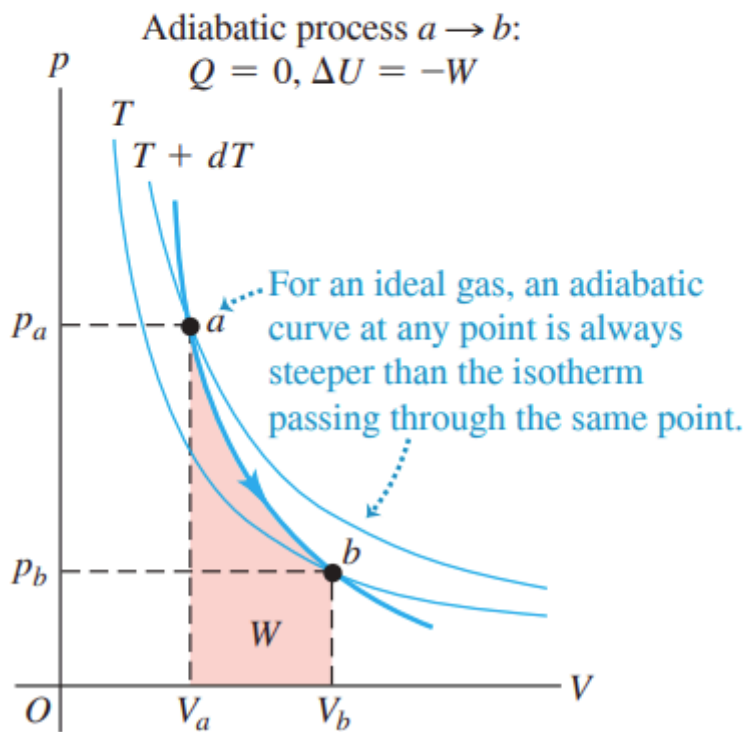$$C_p = C_v + R = \frac{5}{2} R + R = \frac{7}{2} R$$

and

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2} R}{\frac{5}{2} R} = \frac{7}{5} = 1.40$$

Remember that for an ideal gas:

$$\Delta = nC_v \Delta T \qquad \text{(regardless if volume is constant)}$$

Adiabatic Processes for an Ideal Gas

Figure **19.20** A pV-diagram of an adiabatic $(Q = 0)$ process for an ideal gas. As the gas expands from V_a to V_b, it does positive work W on its environment, its internal energy decreases $(\Delta U = -W < 0)$, and its temperature drops from $T + dT$ to T. (An adiabatic process is also shown in Fig. 19.16.)

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

For an ideal gas, an adiabatic curve at any point is always steeper than the isotherm passing through the same point.

As the gas expands from V_a to V_b, it does postivie work W on its environment, its internal energy decreases (as $\Delta = -W < 0$), and its temperature drops from $T + dT$ to T.

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

Note:

- adiabatic heating -> raising the temperature
- adiabatic cooling -> lowering the temperature
- Heat $\neq$ Temperature
- In an adiabatic process, the temperature change is due to work done by or on the system, which means that there is no heat flow at all.

Relating V, T, and p

The change in internal energy of an ideal gas for any process is:

$$dU = nC_v dT$$

And the work done by an ideal gas is

$$dW = pdV$$

Then during an adiabatic process where $dQ = 0$:

$$dU = dQ - dW = -dW$$

Therefore:

$$nC_v dT = -pdV$$
$$n_C vdT = -\frac{nRTdV}{V}$$
$$\frac{dT}{T} + \frac{R}{C_v}\frac{dV}{V} = 0$$

Remember that

$$\frac{R}{C_v} = \frac{C_p - C_v}{C_v} - 1 = \gamma - 1$$

so

$$\frac{dT}{T} + (\gamma - 1)\frac{dV}{V} = 0$$
$$\ln T + (\gamma - 1)\ln V = a \qquad (a \text{ refers to a constant})$$
$$\ln T + \ln V^{\gamma - 1} = a$$
$$\ln(TV^{\gamma - 1}) = a$$
$$TV^{\gamma - 1} = b \qquad (\text{new constant } b)$$

Then, for an initial state of (T_1, V_1) and a final state of (T_2, V_2):

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

Now remember that

$$T = \frac{pV}{nR}$$

so

$$TV^{\gamma - 1} = a$$
$$\frac{pVV^{\gamma - 1}}{nR} = a \$\$Thenwehave$$
$$pV^{\gamma} = b$$

p_1V_1^\gamma = p_2V_2^\gamma

W = nC_v(T_1-T_2)
$$