Lecture 6

The first law of thermodynamics

Pre-reading: §19.1

1st law of thermodynamics

A *thermodynamic system* is a collection of objects we can regard as a unit, that can exchange energy with its surroundings.

We can now think about energy transfers into and out of these systems; through

– heat transfer Q and

– work W

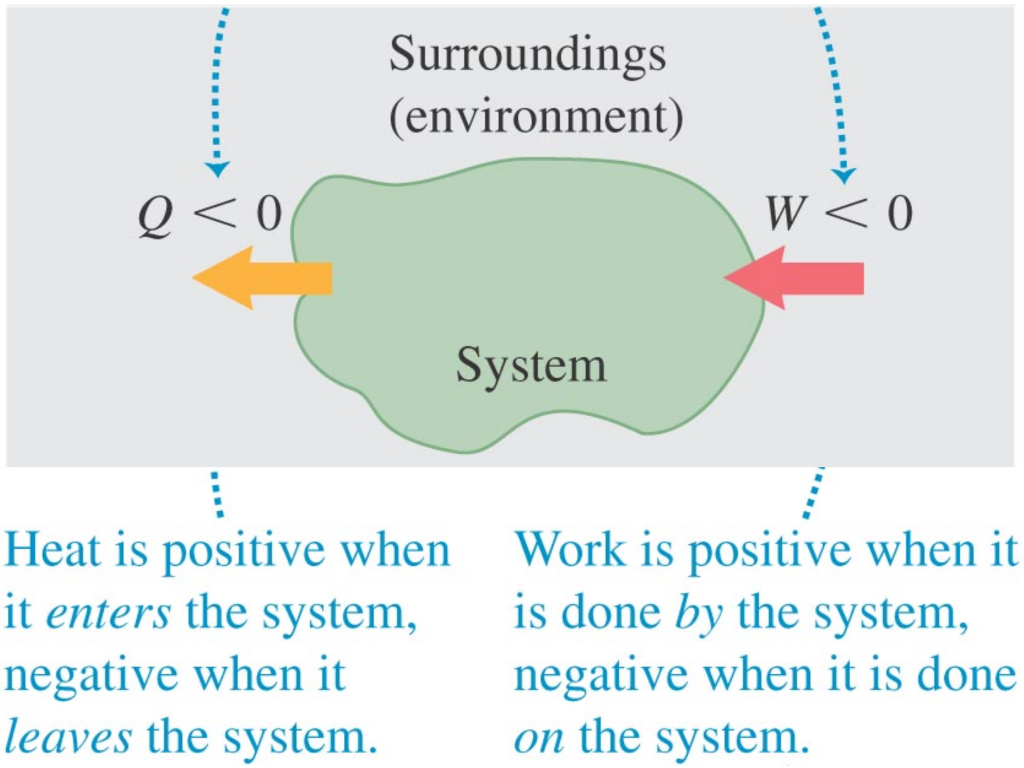
YF §19.1

Sign convention

We need to be careful about signs:

Q_{in} is positive
Q_{out} is negative

W done *by* the system is positive
W done *on* the system is negative



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

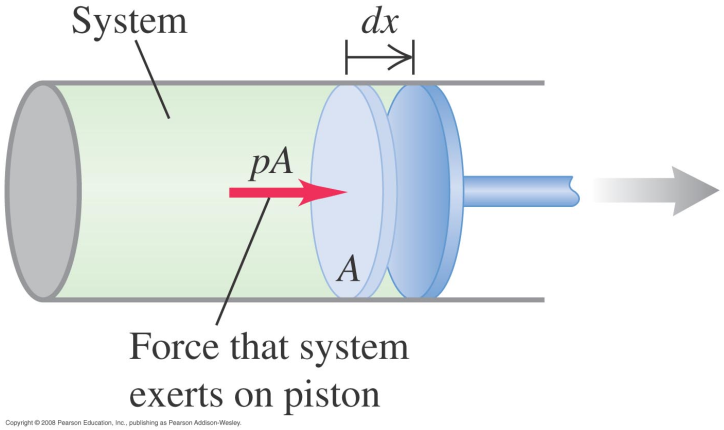
Work is positive when it is done *by* the system, negative when it is done *on* the system.

YF §19.1

Work *W*

Let's look at work done during volume changes.

Pressure exerts a force on the piston, which moves from x_1 to x_2:



$$W = \int_{x_1}^{x_2} F \cdot dx = \int_{x_1}^{x_2} (pA)dx$$

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

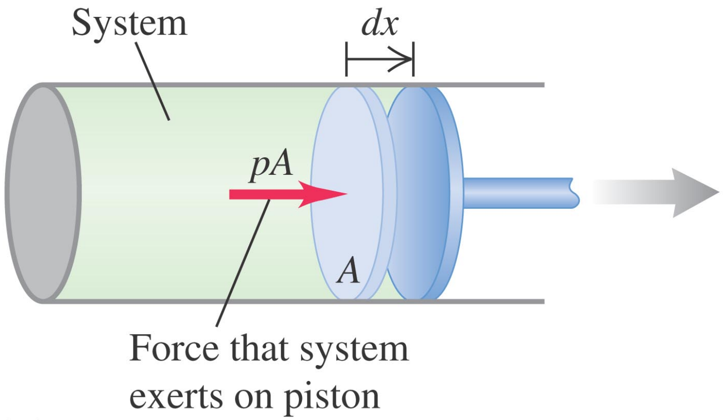
$\boldsymbol{W > 0}$ energy removed from system (work is done by the system against its surroundings) (expansion)

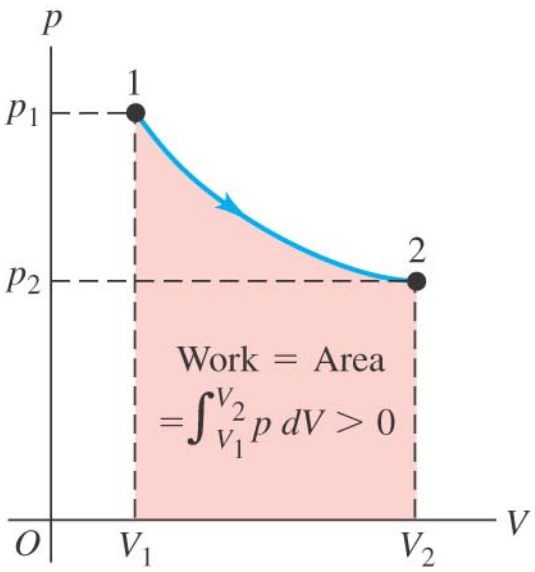
$\boldsymbol{W < 0}$ energy added to system (work is done on the system) (compression)

YF §19.2

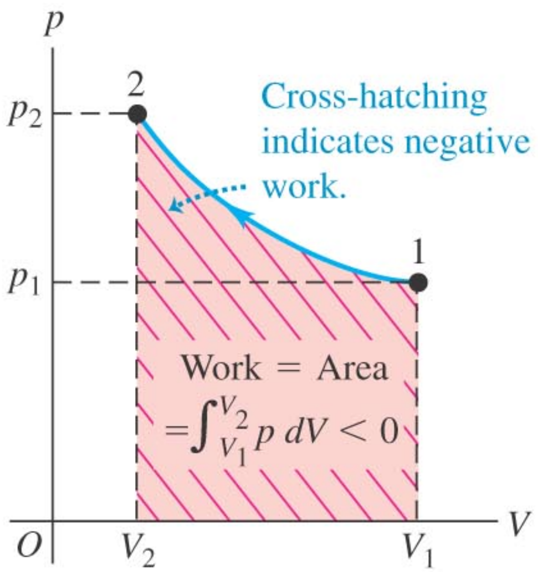
Work *W*

So the *work done* equals the *area* under a pV curve.

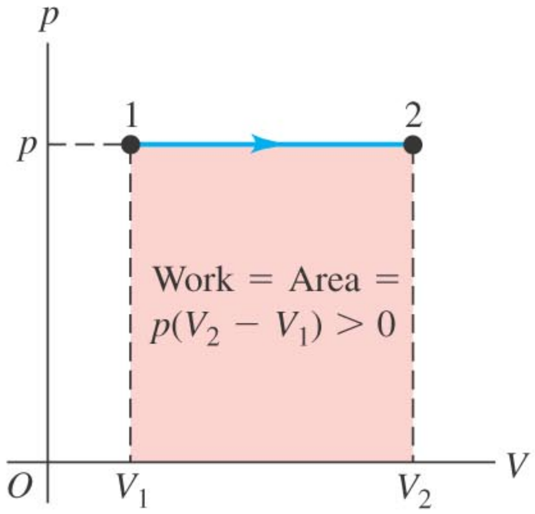




(a) pV-diagram for a system undergoing an expansion with varying pressure



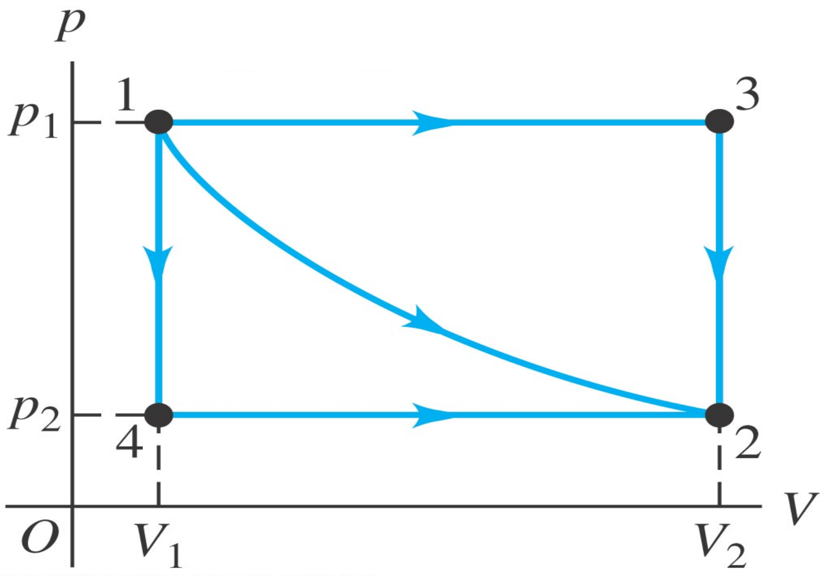
(b) pV-diagram for a system undergoing a compression with varying pressure



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

Work *W*

There can be many different paths from one thermodynamic state to another, so the work done by a system during a transition between two states depends on the path chosen



YF §19.3

Example: Isothermal expansion

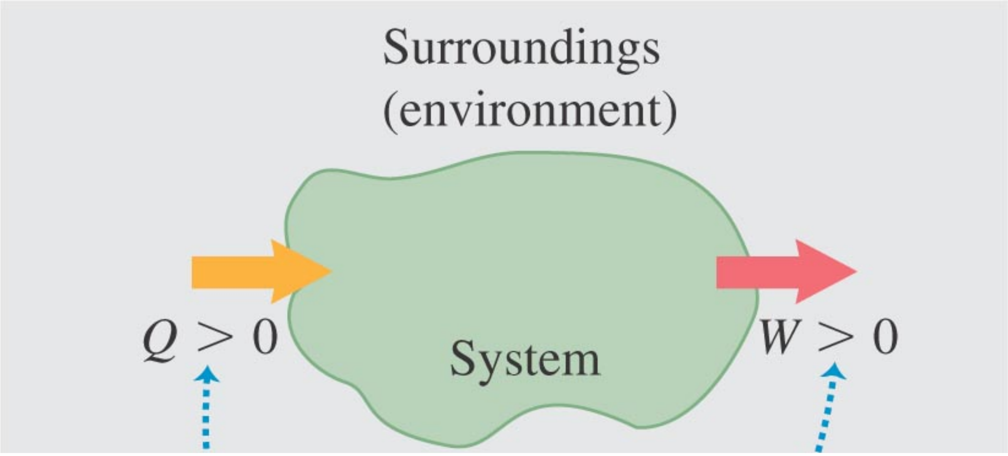
An ideal gas undergoes a constant-temperature expansion at temperature T, so its volume changes from V_1 to V_2. How much work does the gas do?

YF §19.2

Heat transfer Q

A system can interact with its surroundings by doing *work*.

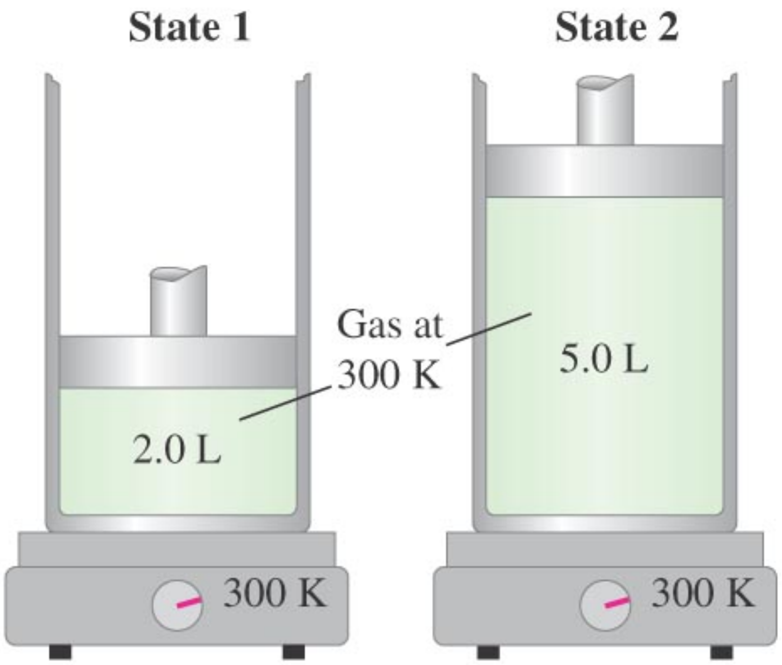
It can also interact with its surroundings by means of *heat transfer*.



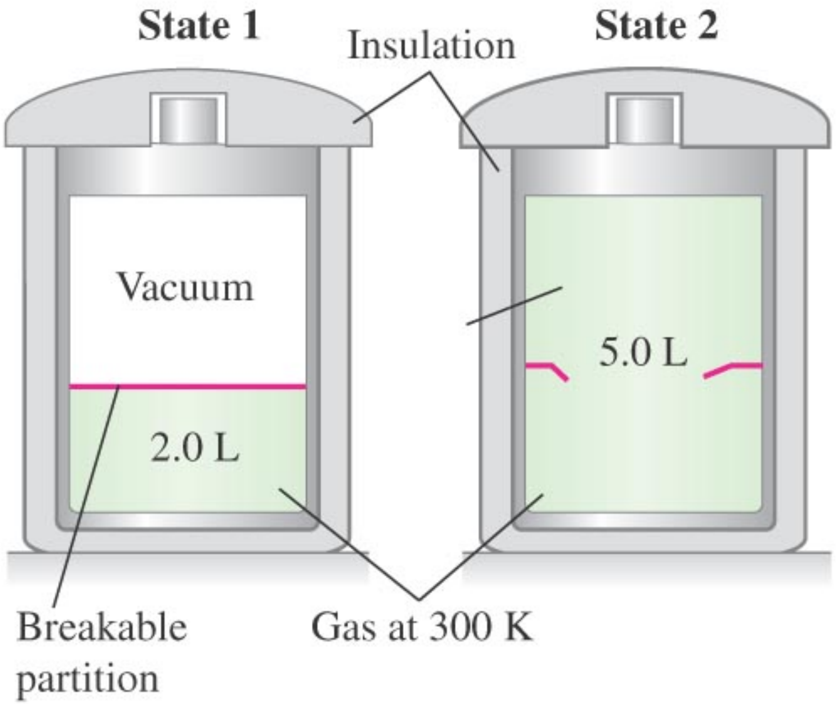
YF §19.3

Heat transfer Q

How much heat is transferred *also* depends on the path taken.



(a) System does work on piston; hot plate adds heat to system ($W > 0$ and $Q > 0$).



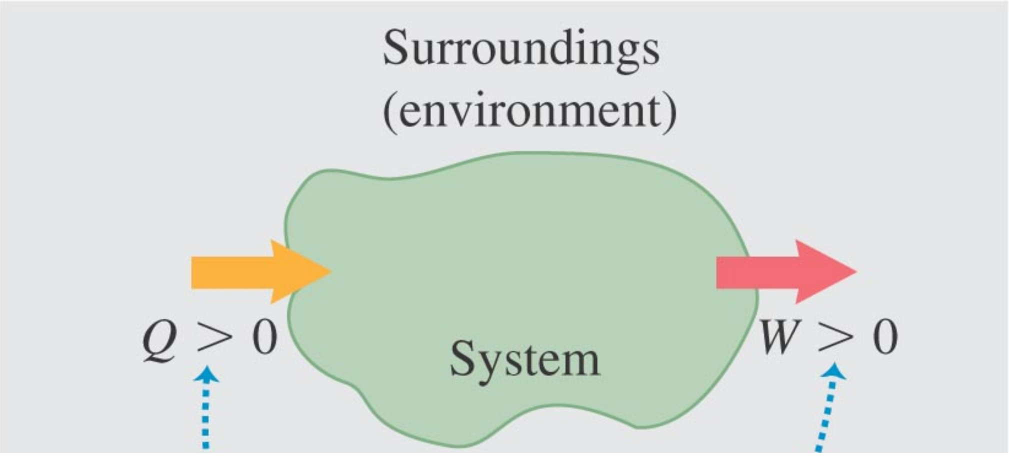
(b) System does no work; no heat enters or leaves system ($W = 0$ and $Q = 0$).

Heat and work

So both *heat* and *work* are only recognized as they cross the boundary of a system.

- They are associated with a process, not a state.
- They are both path-dependent functions.
- A system in general does not possess heat or work.

[wrong description:
‘work in a body;
‘heat in a body’]



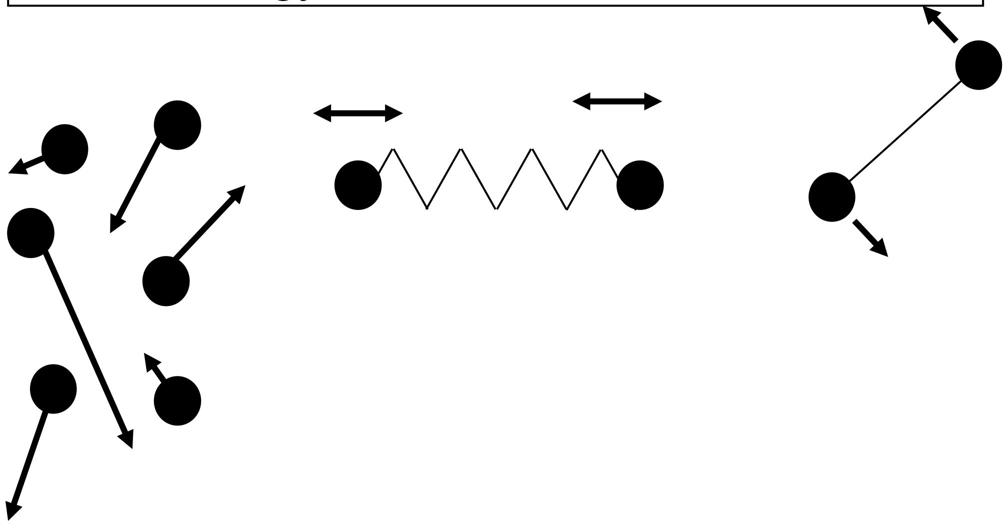
Internal energy *U*

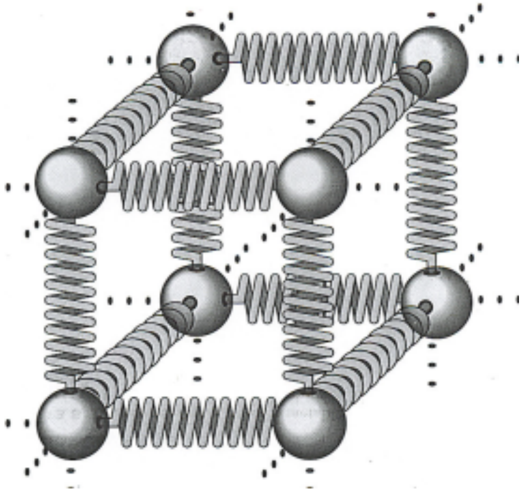
We define the *internal energy* of a system to be the sum of

– the kinetic energy of all its particles

– the potential energy of interactions between particles

Kinetic energy: translation, vibration, rotation





YF §19.4

Internal energy *U*

$$U = \sum KE + \sum PE$$

Random chaotic motion

interaction
between atoms
& molecules

The kinetic and potential energies associated with the random motion of molecules constitute the *internal energy U*.

Value of U not important, ΔU during a thermal process is what matters:

$$\boxed{\Delta U = U_2 - U_1 = U_{final} - U_{initial}}$$

YF §19.4

The first law of thermodynamics

The first law of thermodynamics:

The total change in internal energy of a system is the sum of the heat added to it and the work done on it.

$$\Delta U = Q - W$$

(conservation of energy)

Remember:

Q_{in} is positive	W done *by* the system is positive
Q_{out} is negative	W done *on* the system is negative

YF §19.4

The first law of thermodynamics

While Q and W depend on the path, $\Delta U = Q - W$ does not.

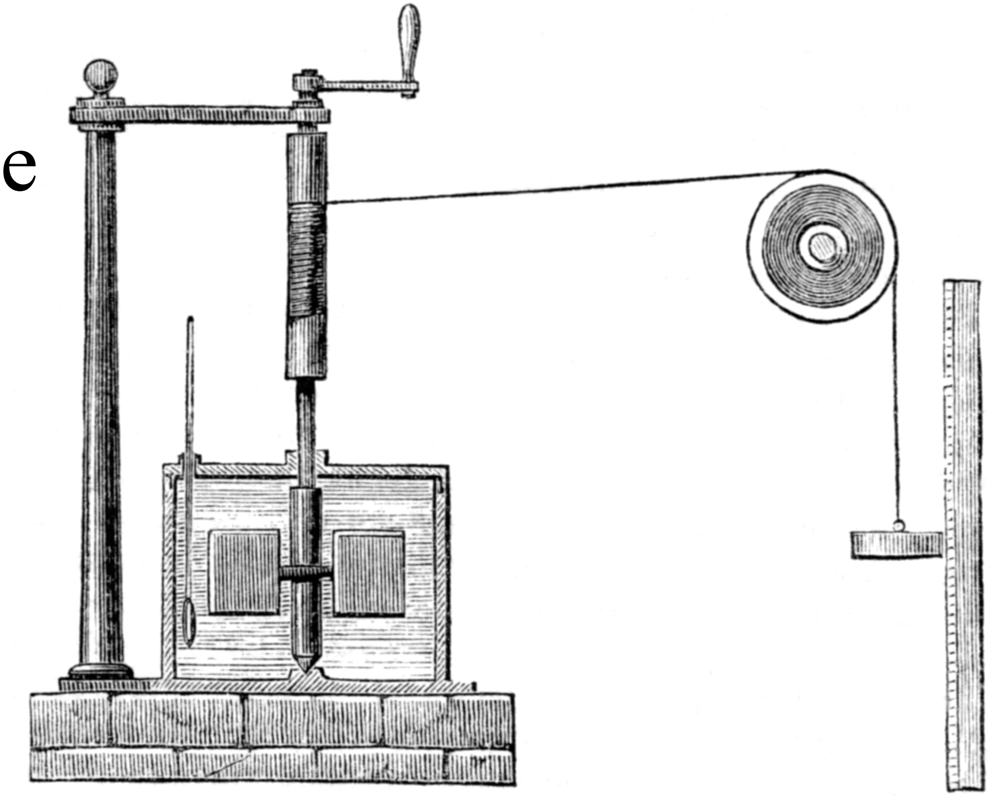
The change in internal energy of a system during any thermodynamic process depends only on the initial and final states, not on the path leading from one to the other.

i.e. U is an *intrinsic property* of the system.

YF §19.4

Equivalence of heat and work

The equivalence of heat and work was demonstrated by Joule in the 1840s. His apparatus converted the potential energy of falling weights into work done on the water by a rotating paddle.



U for an ideal gas

Recall that the internal energy is

$$U = \sum KE + \sum PE$$

Random chaotic motion

interaction between atoms & molecules

We showed that for an ideal gas

$$KE = Nf\left(\frac{1}{2}kT\right)$$

where f is the number of degrees of freedom.

U for an ideal gas

For an ideal gas, there are no forces between molecules, so $PE = 0$.

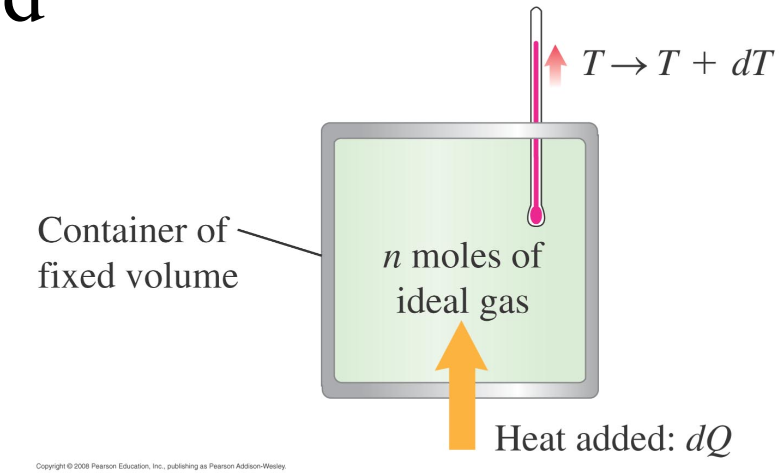
Hence for an ideal gas,

$$U = \frac{f}{2} N k T$$

so the internal energy for an ideal gas depends only on its temperature.

Heat capacity of an ideal gas

Consider adding heat to a fixed volume of an ideal gas. Since the volume is fixed, $W = 0$, so $\Delta U = Q$.



The temperature of the gas changes when we add heat:

$$\Delta U = U_2 - U_1 = \frac{f}{2}NkT_2 - \frac{f}{2}NkT_1 = \frac{f}{2}Nk\Delta T$$

so

$$Q = \frac{f}{2}Nk\Delta T = \frac{f}{2}nR\Delta T$$

YF §18.4

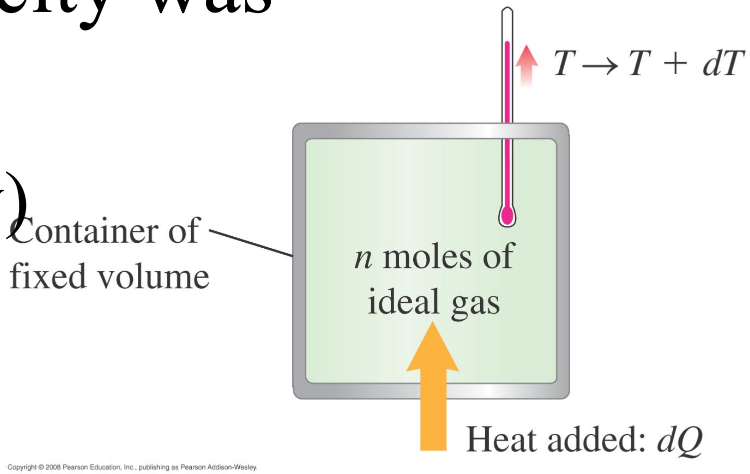
Heat capacity of an ideal gas

But our definition of heat capacity was

$$Q = nC\Delta T$$

(where C is the molar heat capacity)

and so we must have



$$C_V = \frac{f}{2}R$$

So *any* ideal gas has the *same* heat capacity (with the same number of degrees of freedom).

Change in internal energy: $\Delta U = nC_V \Delta T$

YF §18.4

Table 19.1 Molar Heat Capacities of Gases at Low Pressure

Type of Gas	Gas	C_V (J/mol · K)
Monatomic	He	12.47
	Ar	12.47
Diatomic	H_2	20.42
	N_2	20.76
	O_2	20.85
	CO	20.85
Polyatomic	CO_2	28.46
	SO_2	31.39
	H_2S	25.95

U for an ideal gas, again

We calculated *U* for a process at constant volume.

But since the internal energy of an ideal gas only depends on temperature, the change in internal energy during *any* process must be determined only by the temperature change.

For an ideal gas, the internal energy change in any process is give by

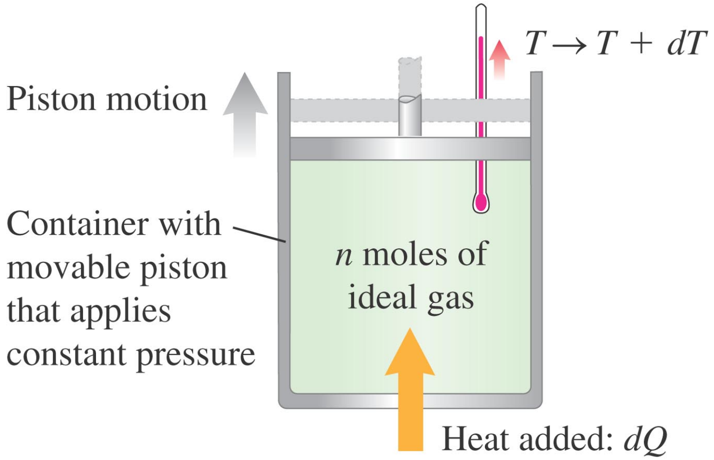
$$\Delta U = nC_V \Delta T$$

whether the volume is constant or not.

YF §19.4

Heat capacity of an ideal gas

Now consider adding heat to an ideal gas at *constant pressure*.



By definition, $Q = nC_p\Delta T$

and $W = p\Delta V = nR\Delta T$

So from $\Delta U = Q - W$

we get $nC_V\Delta T = nC_p\Delta T - nR\Delta T$

or $C_p = C_V + R$

It takes *greater heat input* to raise the temperature of a gas a given amount at constant pressure than constant volume

YF §19.4

Ratio of heat capacities

Look at the ratio of these heat capacities: we have

$$C_V = \frac{f}{2}R$$

and

$$C_p = C_V + R = \frac{f+2}{2}R$$

so

$$\gamma = \frac{C_p}{C_V} > 1$$

For a monatomic gas, $C_V = \frac{3}{2}R$

so $C_p = \frac{3}{2}R + R = \frac{5}{2}R$

and

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$

YF §19.4

Problem

An ideal gas is enclosed in a cylinder which has a movable piston. The gas is heated, resulting in an increase in temperature of the gas, and work is done by the gas on the piston so that the pressure remains constant.

a) Is the work done by the gas positive, negative or zero? Explain

b) From a microscopic view, how is the internal energy of the gas molecules affected?

c) Is the heat less than, greater than or equal to the work? Explain.

Next lecture

The first law of thermodynamics, continued

Read: YF §18.1