

Chapter 19

- The First Law of Thermodynamics

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Learning Goals

- Calculating work done on a system during a volume change.
- Interpretation of 1st law and internal energy of a system.
- Types of thermodynamics processes (4 of them).
- Internal energy of an ideal gas.
- Molar heat capacities at constant volume or pressure.

Introduction



- We should now have a solid understanding of the basic principles and descriptions of thermal properties.
 - Now let's see how heat and energy relate to work and the 1st law.
- It's also time to investigate thermodynamics processes in systems.
 - In ch. 20, we'll see specific examples of processes involving heating and cooling systems and mechanical devices.



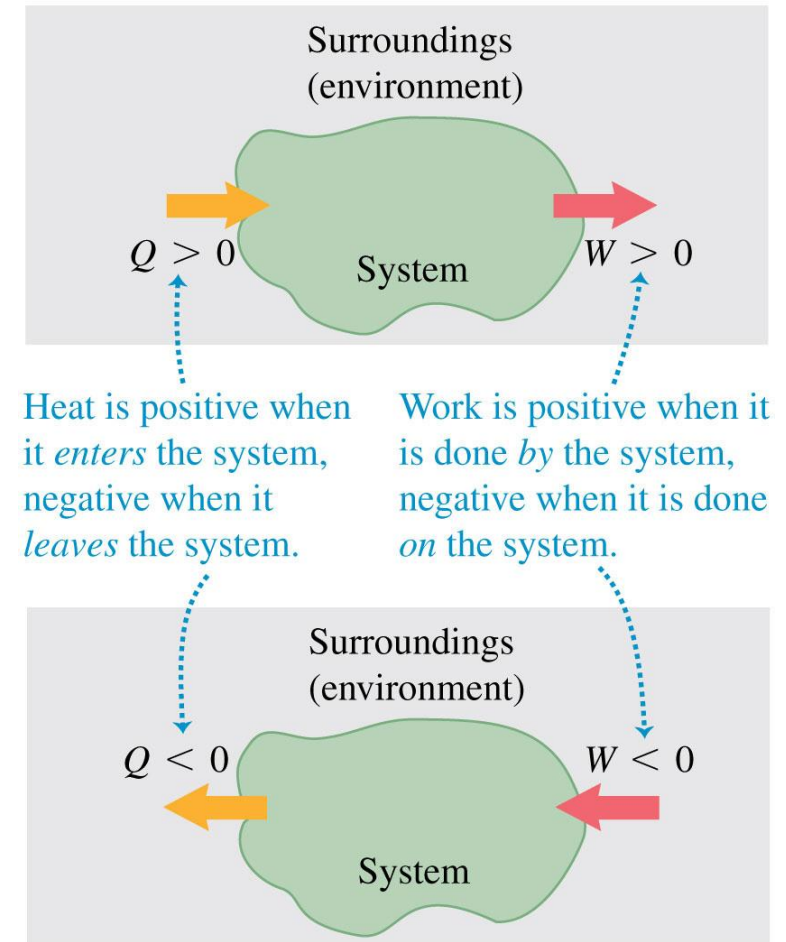
Thermodynamic systems

- A **thermodynamic system** is any collection of objects that may exchange energy with its surroundings.
- Take a pot of popcorn for example.
 - Heat added to system by conduction (bottom).
 - The system does work on its surroundings (lifts lid).
 - The *state* of popcorn changes and this is an example of a **thermodynamic process**.



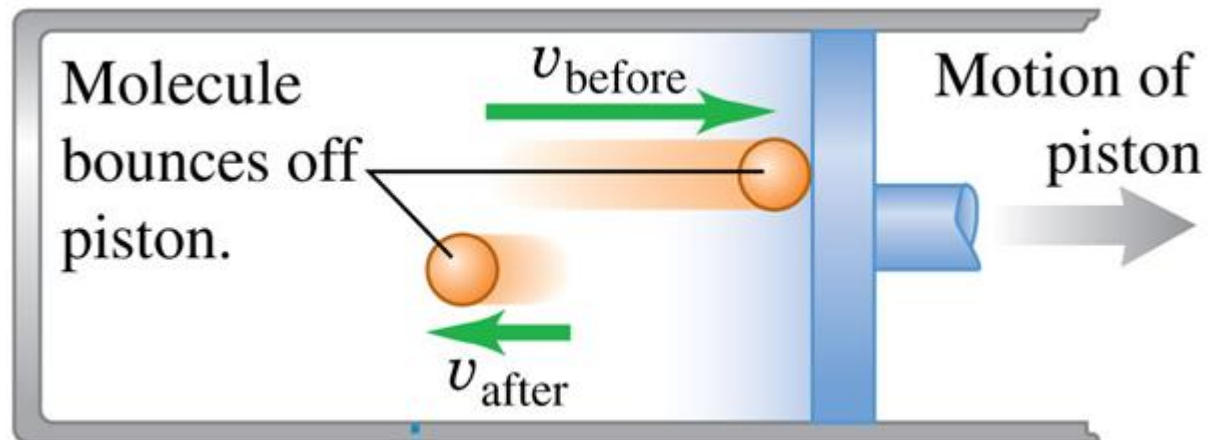
Signs (+, -) of heat and work

- Heat (Q) and work (W) are used to describe the system's energy.
- Q is a positive when heat flows *into* a system.
- W is positive when work is done *by* the system against its surroundings
 - Ie. when energy *leaves* the system.
- Be consistent with these signs!



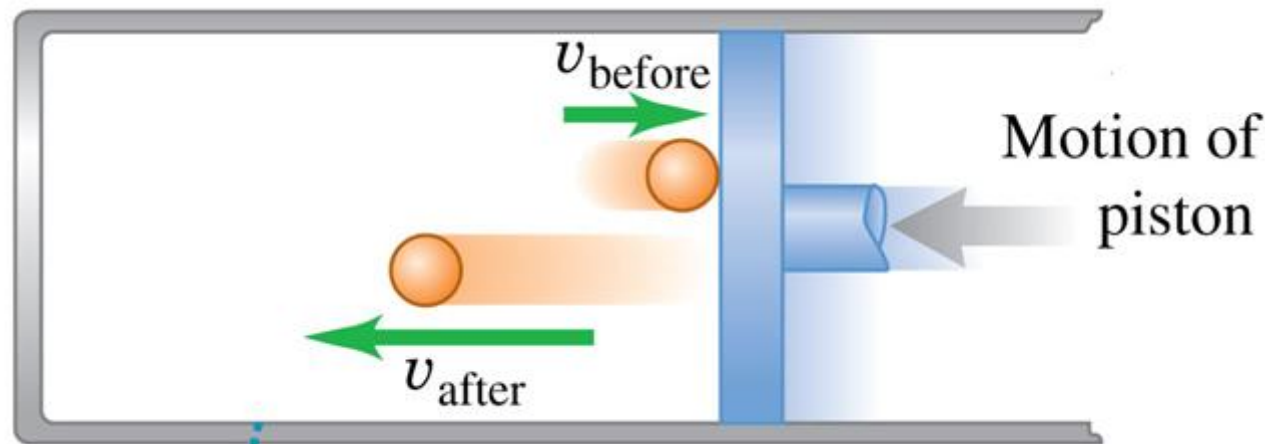
Work done during change in volume (expansion)

- A simple example of a thermodynamic system and process:
 - Gas in a cylinder with a movable piston.
- Consider expansion (as shown). Piston is moving to the right. Molecules that bounce off the piston will lose kinetic energy. The molecules do work *on* the piston. **The *expanding* gas is doing *positive* work** on its surroundings.



Work done during change in volume (compression)

- This time, the piston is moving to the left so volume decreases. A molecule colliding with the piston has an increase of kinetic energy.
- Positive work is done *on* the molecule thus the molecule (and system) does *negative* work on the piston.
- **A *compressing* gas does *negative* work** on its surroundings.



Work done during change in volume (formula)

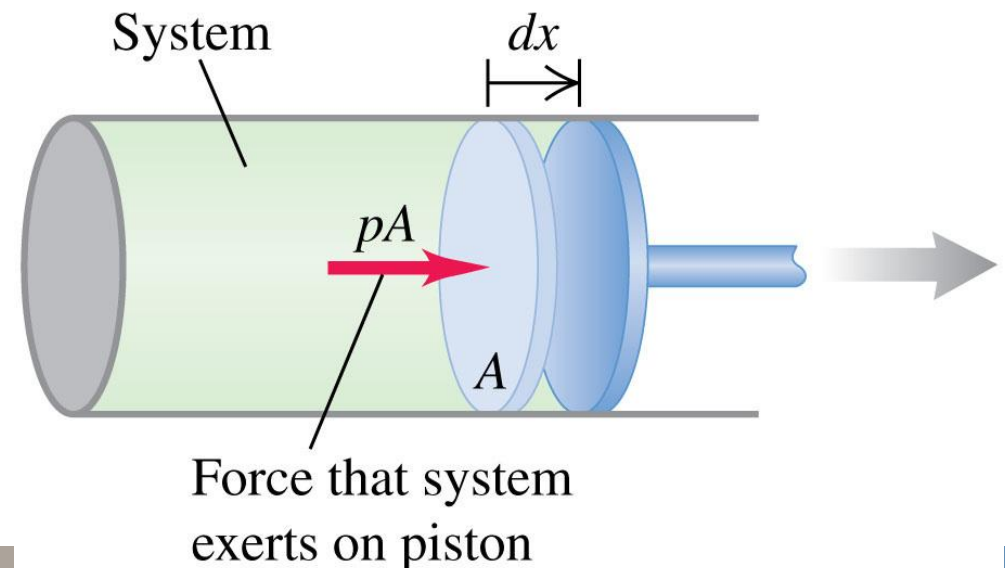
- The tiny amount of work done (dW) is the force of the gas (pA) moving the piston a tiny distance (dx):

$$dW = F dx = pA dx \rightarrow dW = p dV$$

- Therefore in terms of volume change from V_1 to V_2 , we have:

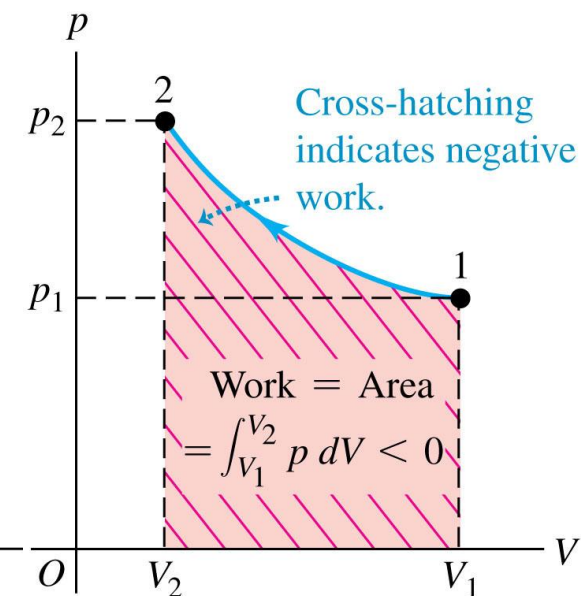
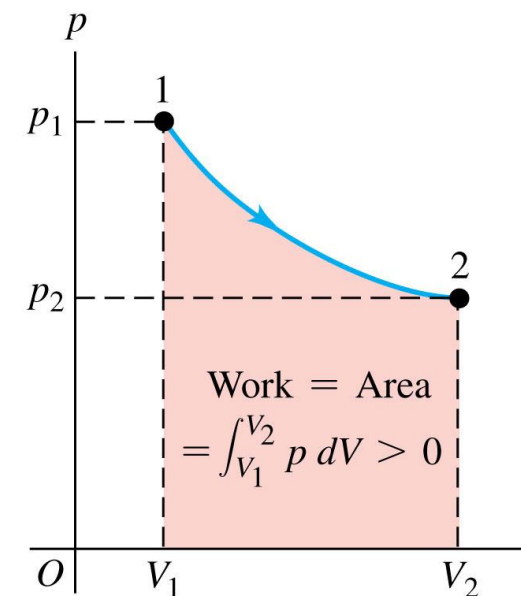
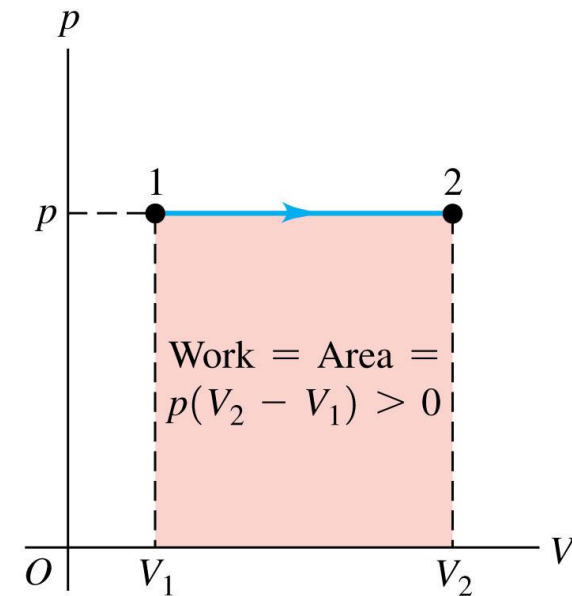
General form:
$$W = \int_{V_1}^{V_2} p dV$$

For uniform P ,
$$W = p(V_2 - V_1)$$



Work done on a pV -diagram

- In order to evaluate the work integral $\int p dV$ we need to know the pressure variation with volume.
- This can be represented using a pV -diagram where the total work done by the system is the area under the curve (between V_1 and V_2).
Top: p uniform. Bottom-left: p non uniform.
- *Bottom-right: negative work (reverse the direction of the arrow) can also be calculated. (use cross-hatch).*



Ex. 19.1 – Isothermal exp. of ideal gas

- If an ideal gas undergoes isothermal (const. T) expansion, how much work is done by the gas when its volume changes from V_1 to V_2 ?

Ideal gas equation: $pV = nRT \rightarrow p = nRT/V$

$$\boxed{W} = \int_{V_1}^{V_2} p \, dV = nRT \int_{V_1}^{V_2} \frac{1}{V} \, dV = \boxed{nRT \ln \frac{V_2}{V_1}}$$

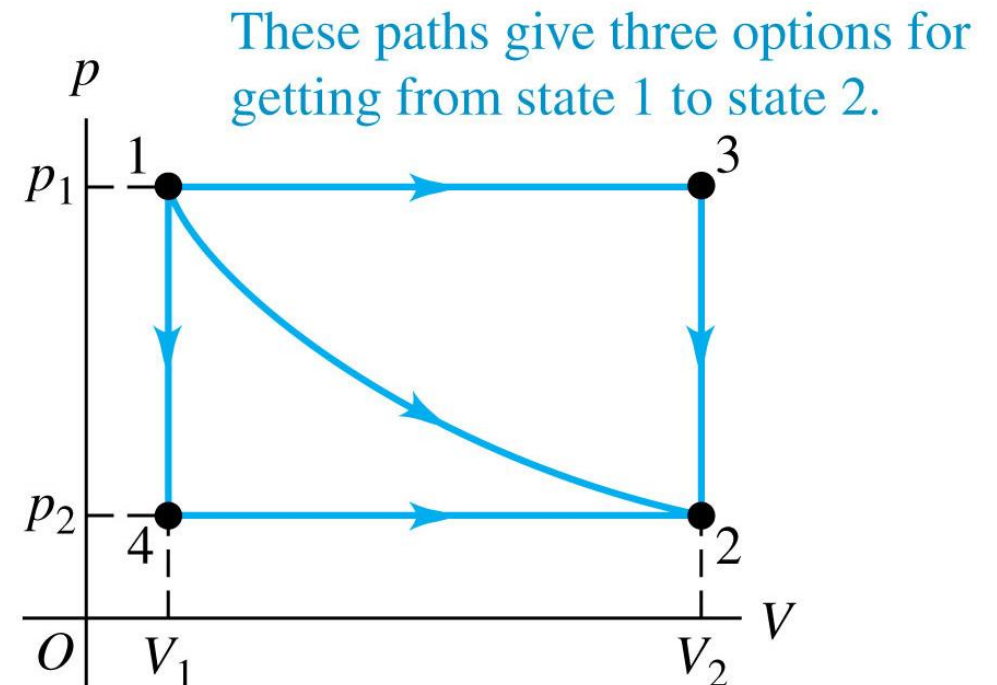
Another way to write it: since T is constant,

$$p_1 V_1 = p_2 V_2 \rightarrow \frac{V_2}{V_1} = \frac{p_1}{p_2}$$

$$\boxed{W = nRT \ln \frac{p_1}{p_2}}$$

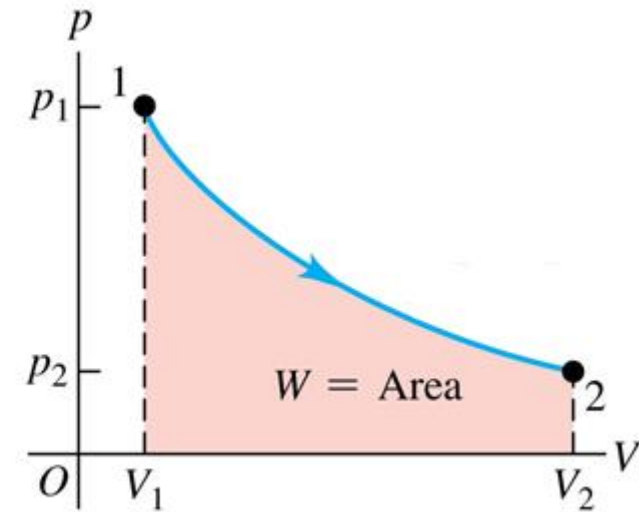
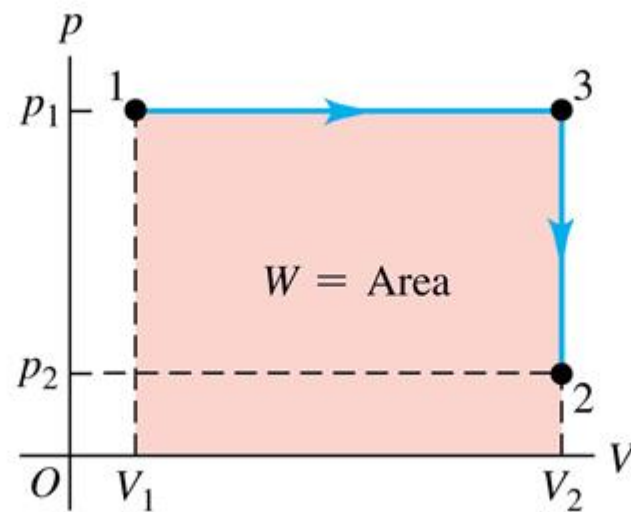
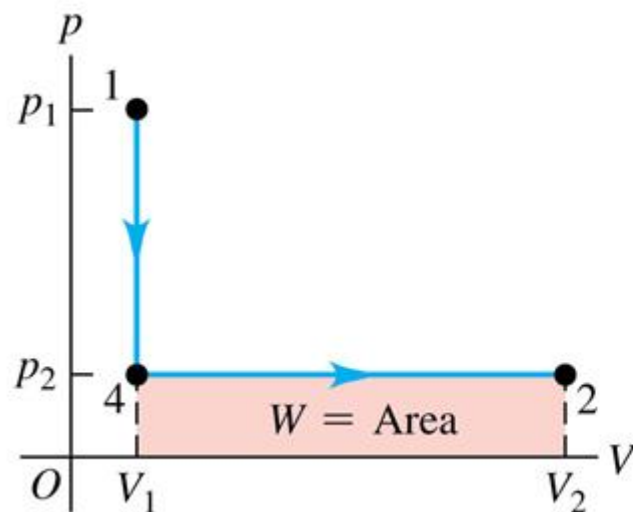
Paths between thermodynamic states

- The amount of work done by a system depends on which **path** is taken to get from initial to final state.
 - Intermediate states must be considered!
- We can also consider a path that brings us back to initial state:
Eg. 1-3-2-4-1.
 - This is a **closed loop** where final state equals initial state but... work is non-zero!



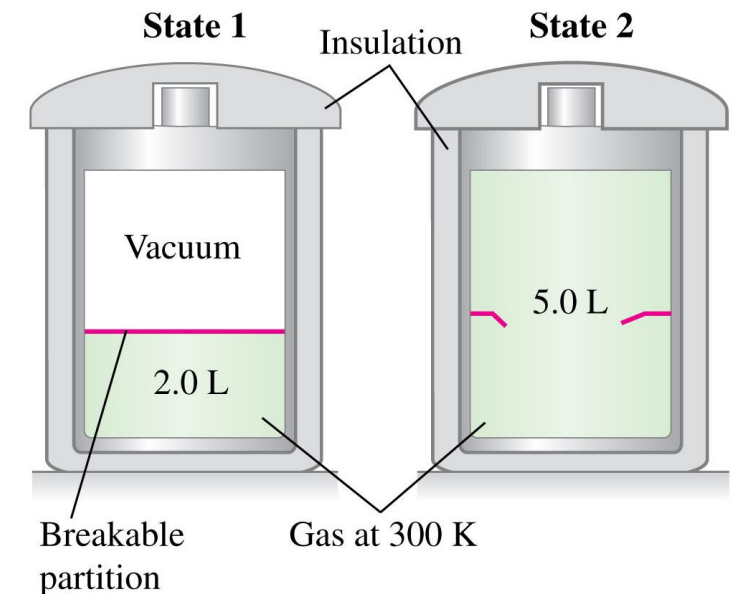
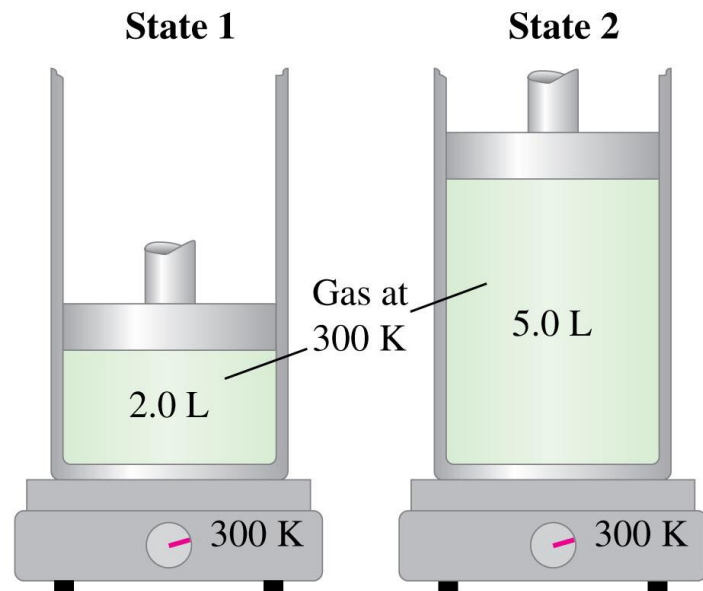
Work done in a thermodynamic process

- Compare the three possible paths from 1 to 2 in the figures.
- A process that changes a system from state 1 to 2 has definite values of p , V , and T at both states but not definite values of W .



Heat added in a thermodynamic process

- The heat added to a thermodynamic system during a change of state also depends on the path.
- Example for expanding an ideal gas from 2 to 5 L (shown below).
 - 1) heat is added. 2) no heat added (*free expansion*)



Internal energy

- All objects and systems possess internal energy.
 - Eg. glass of water. Molecules have kinetic and potential energy. Internal is roughly sum of $E_K + E_P$.
 - Change in E_K and E_P due to surroundings does not affect internal energy.
- Use U to represent internal energy of a system (not potential energy) and $\Delta U = U_2 - U_1$ is the change in energy during a change of state of the system from 1 to 2.
- What affects U ? Heat Q and work W .



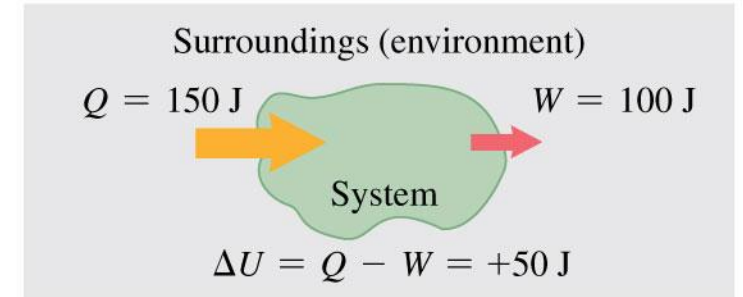
1st law of thermodynamics

- The change in internal energy of a system is:

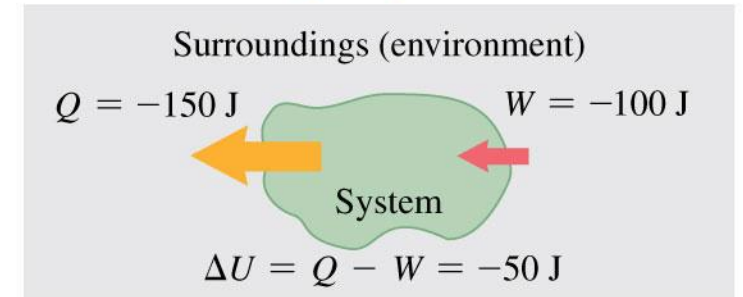
$$\Delta U = Q - W$$

- Internal energy of the system during a process can increase, decrease, or remain the same.
- It's enough to simply consider the work and heat occurring in the system and it's not necessary to think about summing up energies like potential and kinetic.

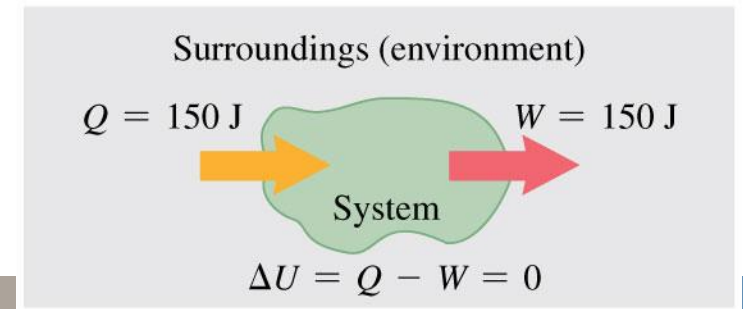
(a) More heat is added to system than system does work: Internal energy of system increases.



(b) More heat flows out of system than work is done: Internal energy of system decreases.



(c) Heat added to system equals work done by system: Internal energy of system unchanged.



1st law of thermodynamics

- There is relevant argument about why ΔU is not path dependent while Q and W are.
- From 1st law, $\Delta U = Q - W$ where both Q and W are measurable. But this does not define U , only ΔU .
- Experiment shows that change in internal energy is independent of path and that internal energy depends only on its thermodynamic state.
 - Eg. cup of coffee.



Cyclic process and isolated system

- There are two special cases to the first law (worth mentioning). The **first** is a *cyclic process* where the final state is the same as initial state. If $\Delta U = 0$ then:

$$U_2 = U_1 \quad \text{and} \quad Q = W$$

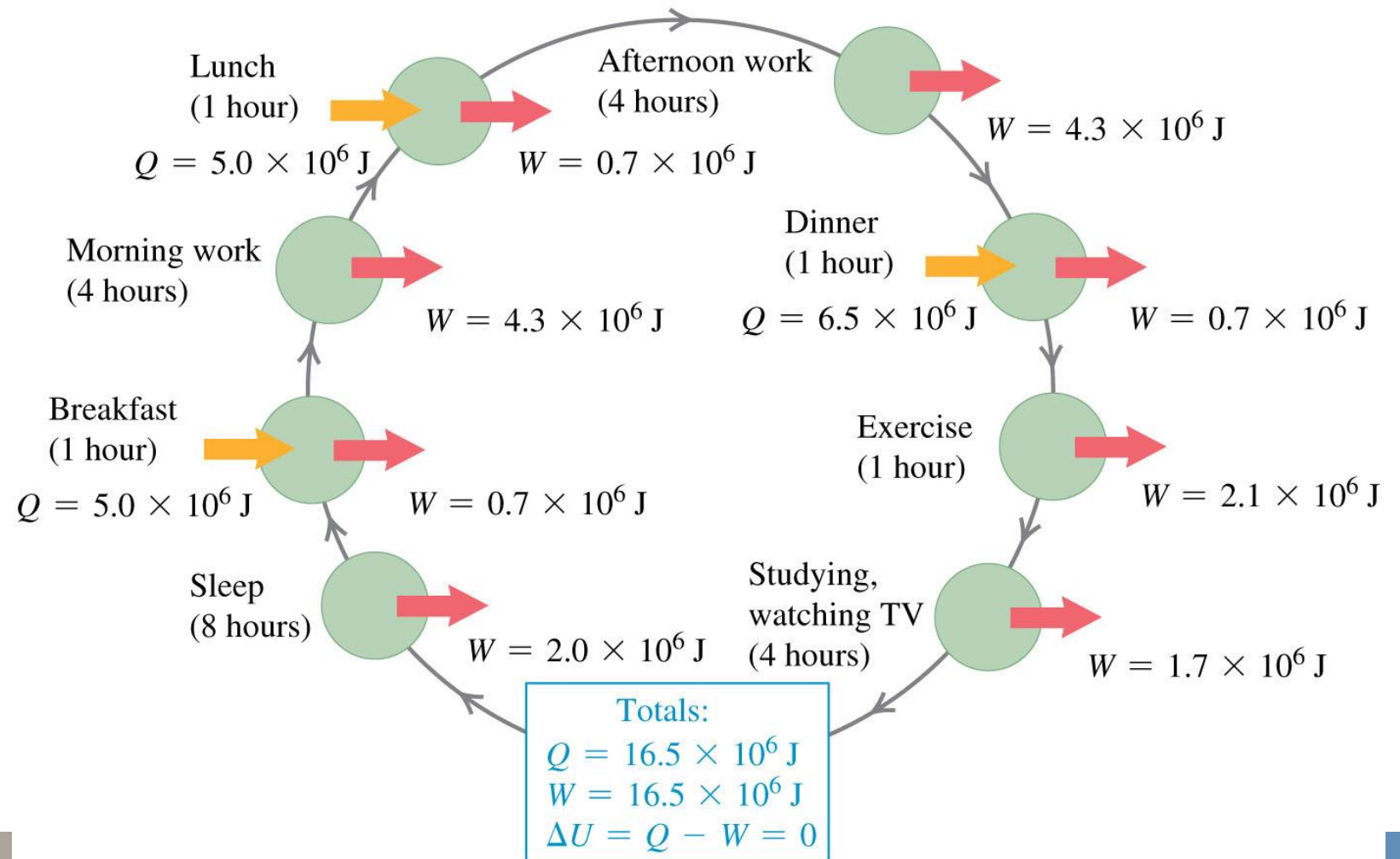
- The **second** special case is an isolated system which does no work on its surroundings and has no heat flow either.

$$W = Q = 0 \rightarrow \Delta U = 0 \text{ (ie. } U_1 = U_2\text{)}$$

In other words, *internal energy of an isolated system is constant.*

A cyclic thermodynamic process

- Your daily schedule:



Tips for solving 1st law problems

- 1) Define the thermodynamic system and each process.
 - Sometimes the process has more than one step!
- 2) List the quantities you know and don't know and identify what you're solving for.
- 3) Apply the correct equations. Step by step by step!
 - Note, you can only apply $\Delta U = Q - W$ once to each process. You can also use $pV = nRT$ or $W = \int p dV$ and don't forget about your $Q = mc \Delta T$ or $Q = \pm mL_f$.
- 4) Make sure you are consistent with sign convention and units!

Ex. 19.2 – Working off your dessert

- You propose to climb several flights of stairs to work off the energy you took in by eating a 900 Calorie hot fudge sundae. How high must you climb? Assume your mass is 60.0 kg.
- Solution: We want $\Delta U = 0$ so that heat energy coming into our body from the sundae is cancelled out by work done by our body to climb stairs.

Heat: $Q = (900 \text{ kcal})(4186 \text{ J/kcal}) = 3.77 \times 10^6 \text{ J}$

Work: $W = mgh = Q$

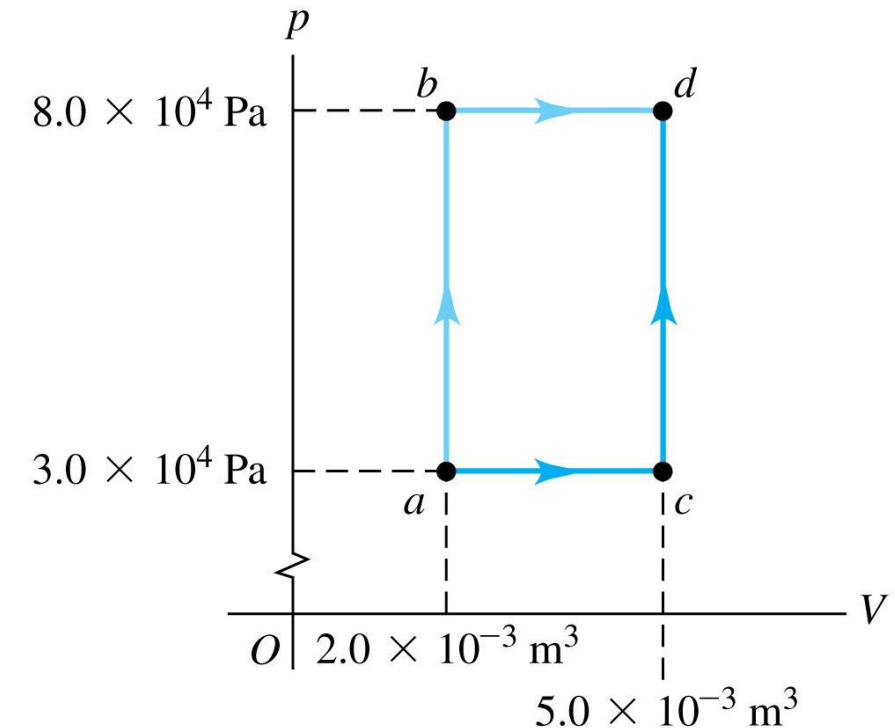
$$\boxed{h} = \frac{Q}{mg} = \frac{3.77 \times 10^6 \text{ J}}{(60 \text{ kg})(9.8 \text{ m/s}^2)} \approx \boxed{6400 \text{ m}} \text{ !!!!!!!}$$

Ex. 19.4 – Comparing thermodynamic processes

- The pV -diagram below shows a series of thermodynamic processes. In process ab , 150 J of heat is added to the system. In process bd , 600 J of heat is added.

Find:

- the internal energy change in process ab .
- the internal energy change in process abd .
- the total heat added in the process acd .



Ex. 19.5 – Thermodynamics of boiling water

- One gram of water (1 cm^3) becomes 1671 cm^3 of steam when boiled at a constant pressure of 1 atm ($1.013 \times 10^5 \text{ Pa}$).

Compute (a) the work done by the water when it vaporizes and (b) its increase in internal energy.

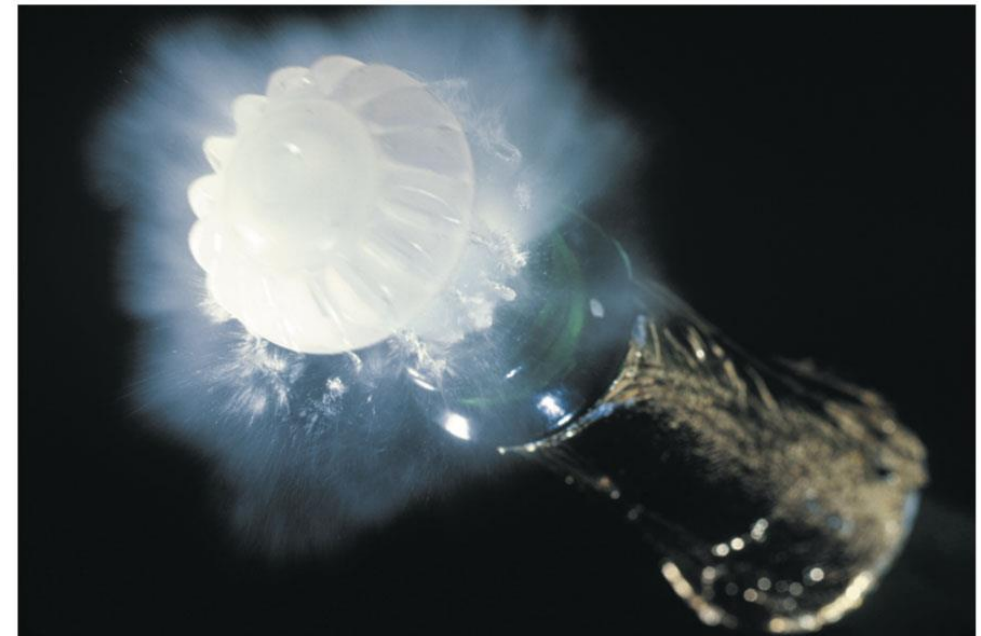
- For water at this pressure, $L_v = 2.256 \times 10^6 \text{ J/kg}$

4 types of thermodynamics processes

- There exist 4 specific types of thermo. processes:
- **Adiabatic:** No heat is transferred in and out of the system.
$$Q = 0 \quad \text{and} \quad \Delta U = -W$$
- **Isochoric:** The volume remains constant.
$$W = 0 \quad \text{and} \quad \Delta U = Q$$
- **Isobaric:** The pressure remains constant.
$$W = p(V_2 - V_1)$$
- **Isothermal:** The temperature remains constant
 - No simple link between ΔU , Q and W .

Adiabatic process (example)

- When the cork is popped on a champagne bottle, the pressurized gas inside the bottle quickly expands and does positive work on the outside air.
- Barely any time for heat exchange with outside air (process is “nearly” adiabatic).
- Internal energy decreases and temperature drops creating water vapor condensation and a mini “cloud”.



Isobaric process (example)

- Most types of cooking involves isobaric process (constant pressure).
- The air pressure inside your microwave or above your pan remains constant while your food is heating up.



4 processes on a pV -diagram

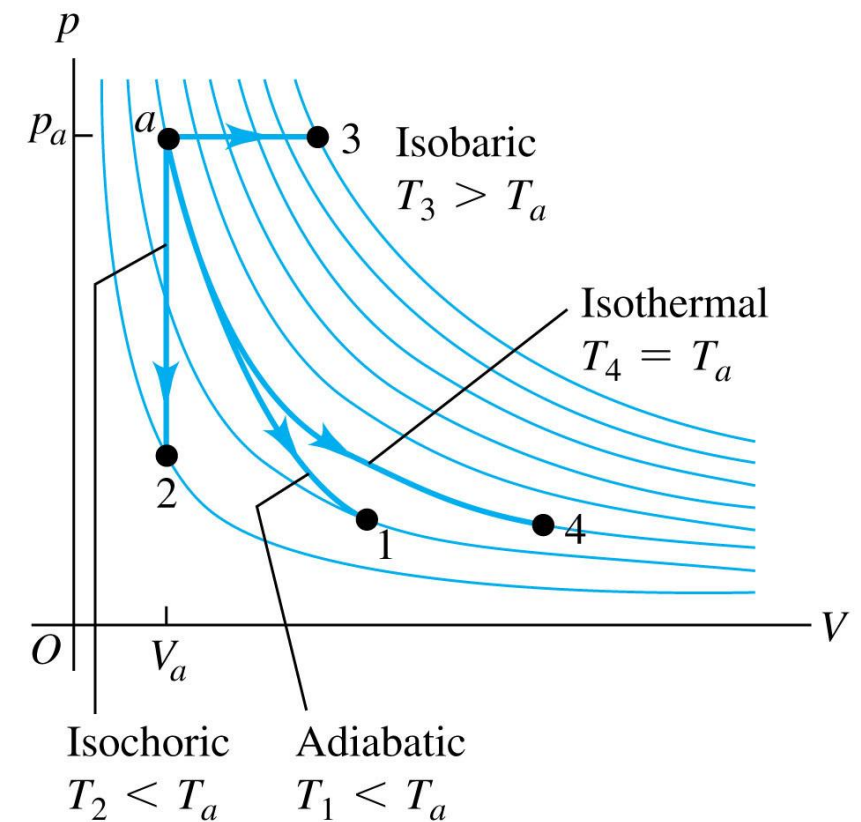
- The pV -diagram below shows the 4 processes for a constant amount of an ideal gas.

The path from a to 1 is called an *adiabat*.

Vertical line (a to 2) is an *isochor*.

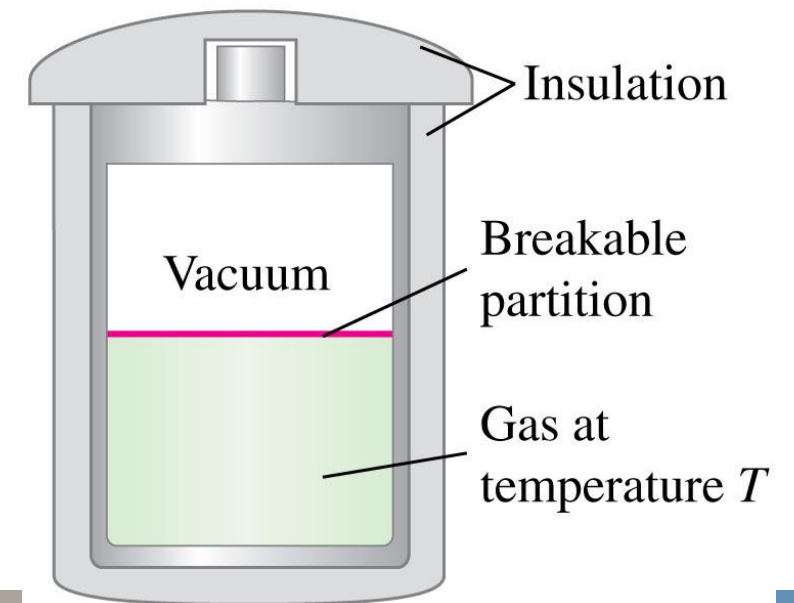
Horizontal line (a to 3) is an *isobar*.

Curve with constant temp. (a to 4) is an *isotherm*.



Internal energy of an ideal gas

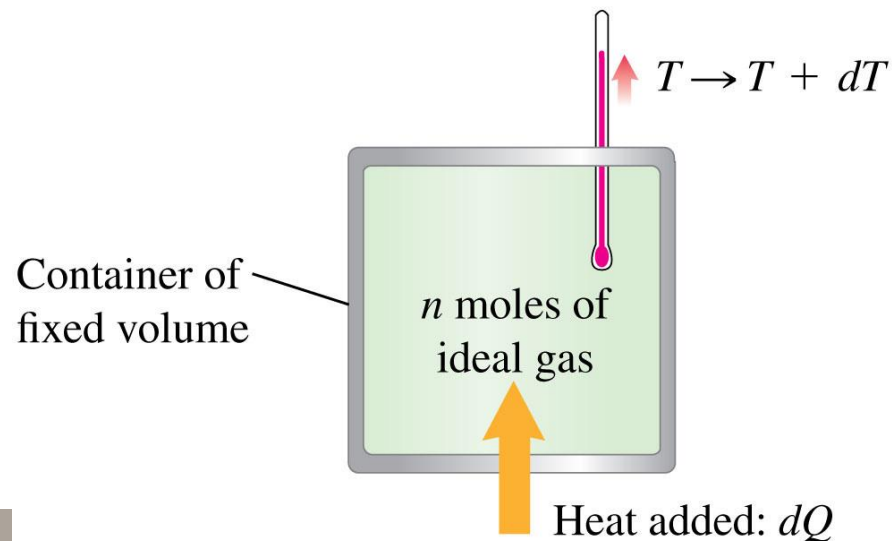
- Consider the *free expansion* situation from Section 19.3. One region has **ideal gas**, other region under vacuum.
- If the partition is broken, the gas expands to fill the container. There is **no heat flow** ($Q = 0$) through insulation. There is **no work done** ($W = 0$) by the gas because the walls do not move.
- Since Q and W are zero therefore **internal energy is constant** ($\Delta U = 0$).
- Experiments show T is also constant therefore **U depends only on T** .



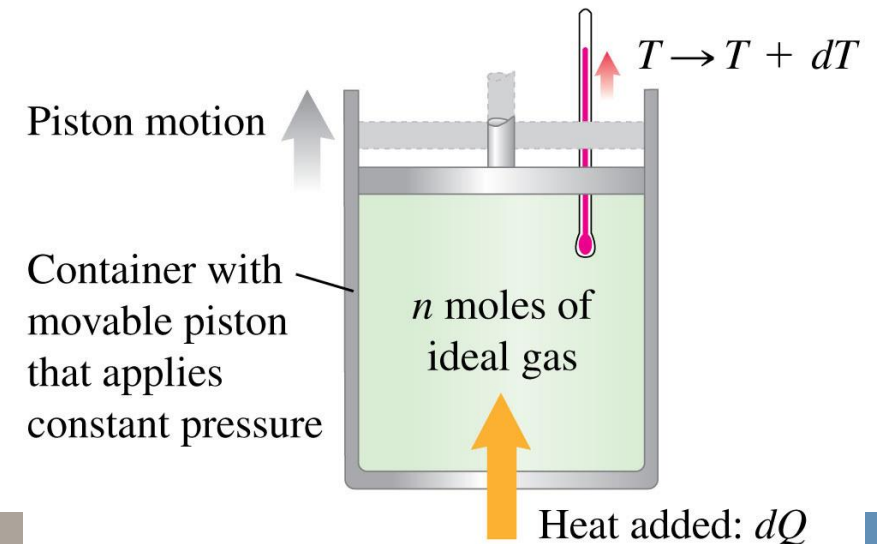
Heat capacities of an ideal gas

- 2 **molar heat capacities** to consider, C_V (constant V) and C_p (constant p) for an ideal gas.
- The figures show ways to measure them. But do they have to be different? (next slide)

Constant volume: $dQ = nC_V dT$



Constant pressure: $dQ = nC_p dT$

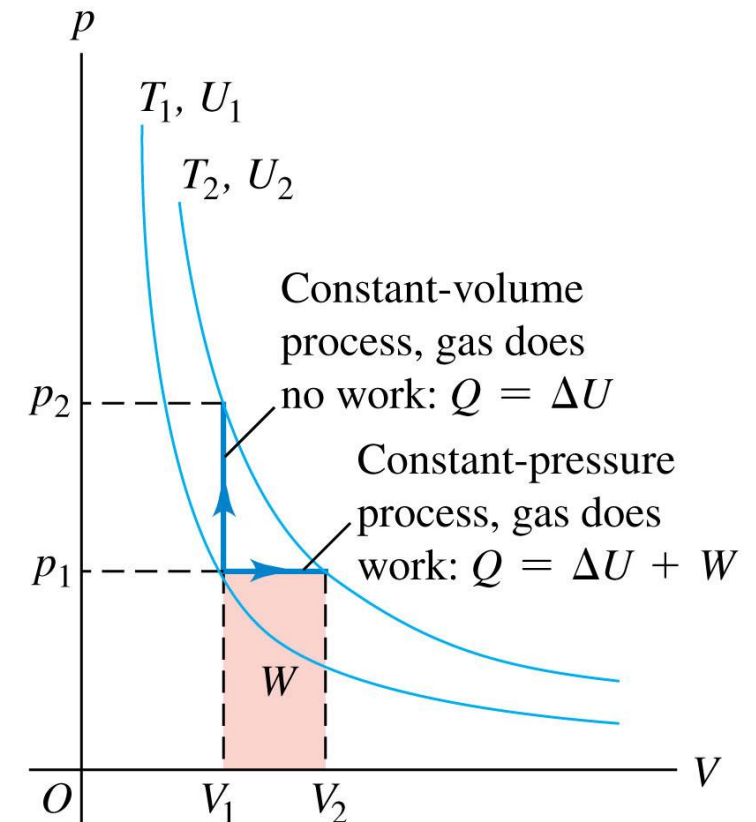


Heat capacities of an ideal gas

- For **constant-volume** (C_V), no work is done ($W = 0$) therefore $\boxed{Q = \Delta U}$.

- For **constant-pressure** (C_p), the volume *must* increase therefore work is done. $\boxed{Q = \Delta U + W}$

- For any given T increase, ΔU has the same value no matter the process. Therefore heat input for const. p is higher than const. V . $\boxed{C_p > C_V}$



Relating C_p and C_V for an ideal gas

- We can relate the two molar heat capacities by:

$$\boxed{C_p = C_V + R}$$

where R is the ideal gas constant we saw last chapter.

- The derivation follows from the 1st law for a tiny change in heat and work and energy (tiny change in state):

$$dU = dQ - dW$$

and using 1) $dU = nC_V \Delta T$, 2) $dQ = nC_p \Delta T$, and 3) $dW = p dV = nR dT$.

- For most “ideal” gases, (He, Ar, H₂, N₂, O₂, etc...),

$$C_p - C_V = 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

Ratio of heat capacities, γ

- We use the symbol γ to represent the ratio of heat capacities:

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

for monatomic ideal gases, $\gamma = 1.67$

for diatomic ideal gases, $\gamma = 1.40$

- Finally, the **internal energy change for an ideal gas** is: $\Delta U = nC_V \Delta T$
regardless of whether we have constant volume or not.
(This was a big part of the derivation of $C_p - C_V = R$).

Ex. 19.6 – Cooling your room

- A typical dorm or bedroom contains about 2500 moles of air. Find the change in internal energy of this much air when it is cooled from 35°C to 26°C at a constant pressure of 1 atm. Treat the air as an ideal gas (mostly N₂) with $\gamma = 1.4$.

Solution: Find C_V from a table for N₂ or calculate it:

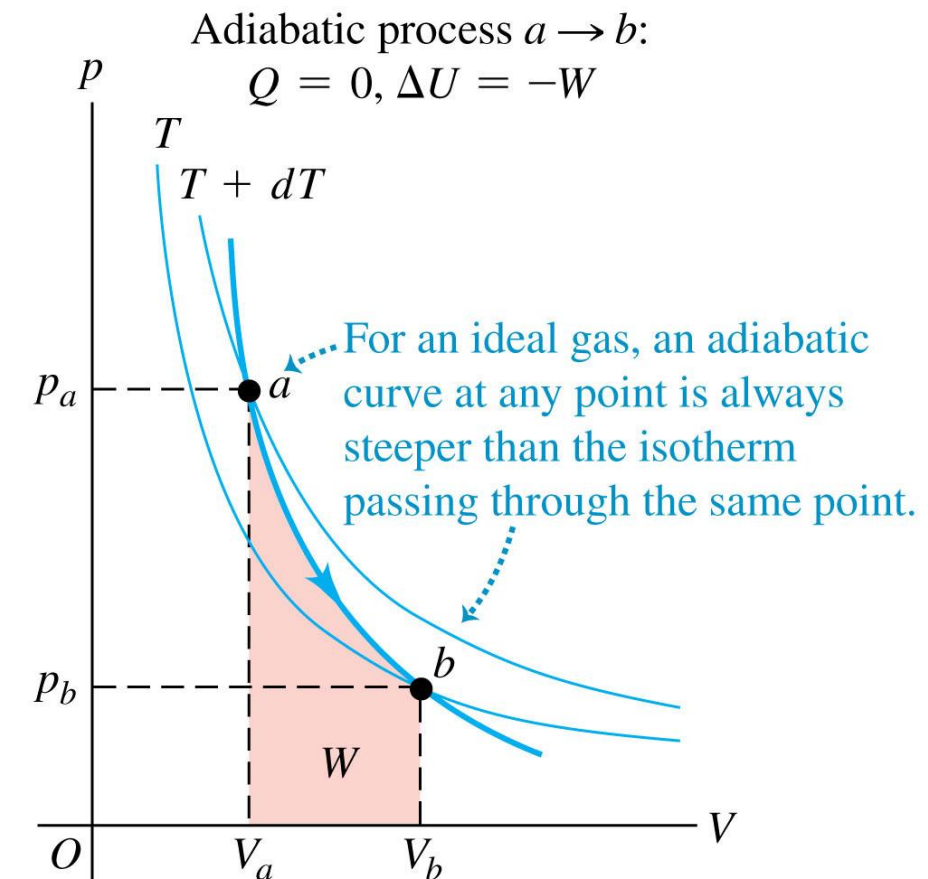
$$\gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V} \quad \rightarrow \quad C_V = \frac{R}{\gamma - 1} = 20.79 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

Now find the internal energy change based on n and ΔT :

$$\begin{aligned} \Delta U &= nC_V \Delta T \\ &= (2500 \text{ mol}) \left(20.79 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (26^\circ\text{C} - 35^\circ\text{C}) \\ &= \boxed{-4.68 \times 10^5 \text{ J}} \end{aligned}$$

Adiabatic processes for an ideal gas

- In an adiabatic process, no heat is transferred in or out of the gas $\rightarrow Q = 0$.
- As the **gas expands**, it does positive work on its environment so its **internal energy decreases (Temperature decreases)**.
- For *adiabatic compression*, temperature increases.
- Note that for an ideal gas, the adiabat is always steeper than the isotherm path.



Adiabatic process for ideal gas: relating V , T , and p

- The relationship between volume and temperature change for an adiabatic process in an ideal gas is:

$$nC_V dT = -p dV$$

- The relationship between volume and temperature:

$$\frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0$$

note that $\gamma - 1 > 0 \rightarrow dT$ and dV have opposite signs.

- There are a variety of other equations which result from the two above if the change in V , T , and p are finite.

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

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

Adiabatic process for ideal gas: work

- Finally, we can calculate the work done by an ideal gas during an adiabatic process which results from $Q = 0$.
- If n and T_1 and T_2 are known then:

$$W = nC_V(T_1 - T_2)$$

- If we apply $pV = nRT$ to above we get two more forms:

$$W = \frac{C_V}{R} (p_1 V_1 - p_2 V_2) \quad \text{and}$$

$$W = \frac{1}{\gamma - 1} (p_1 V_1 - p_2 V_2)$$

Ex. 19.7 – Adiabatic compression in a diesel engine

- The compression ratio of a diesel engine is 15 to 1 (air in a cylinder is compressed to $1/15^{\text{th}}$ of its initial volume).
- (a) If the initial pressure is $1.01 \times 10^5 \text{ Pa}$ and the initial temperature is 27°C (300 K), find the final pressure and the temperature after adiabatic compression.
- (b) How much work does the gas do during the compression if the initial volume of the cylinder is 1 L?

Use $C_V = 20.8 \frac{\text{J}}{\text{mol}\cdot\text{K}}$ and $\gamma = 1.4$ for air.

