

Lecture 3

Examples and Problems

Mechanics & thermodynamics

Equipartition

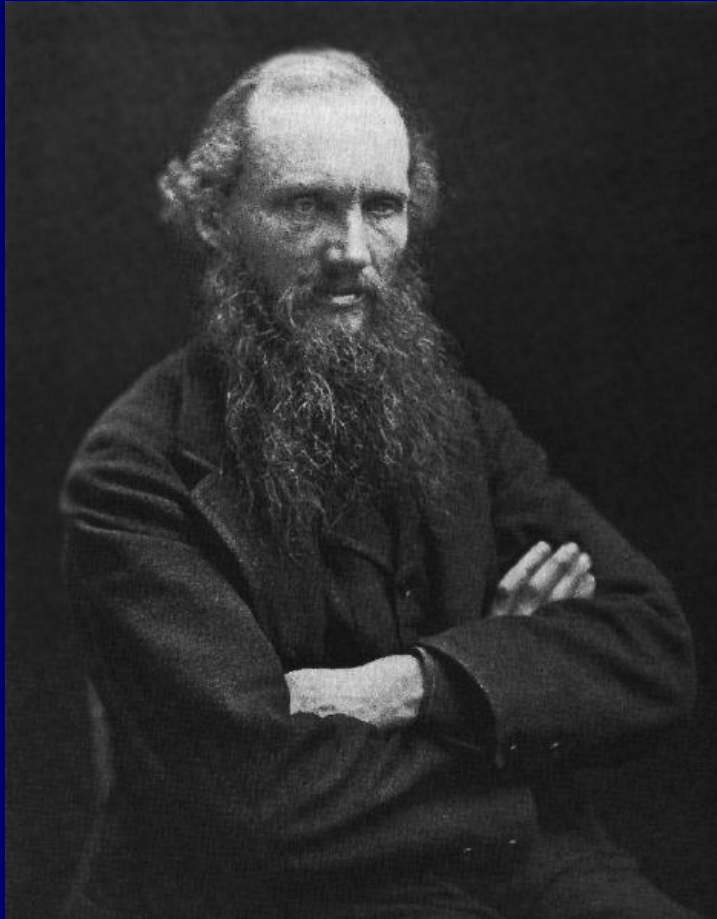
First Law of Thermodynamics

Ideal gases

Isothermal and adiabatic processes

William Thomson (1824 – 1907)

a.k.a. “Lord Kelvin”



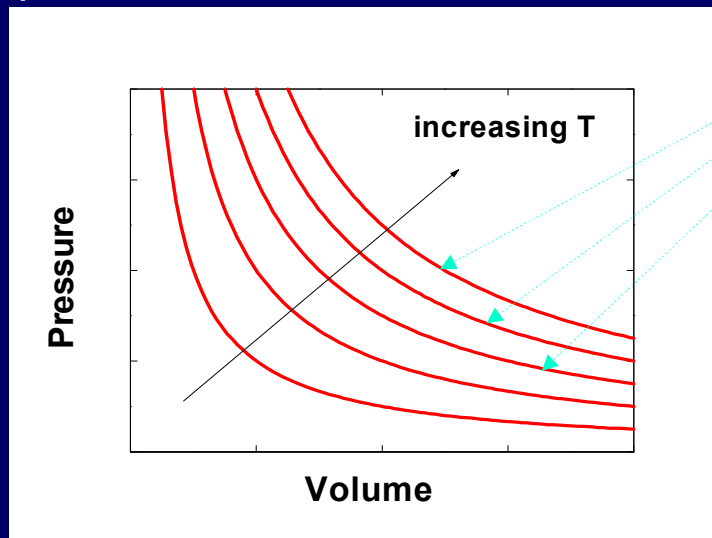
- First wrote down Second Law of Thermodynamics (1852)
- Became Professor at University of Glasgow at age 22!
- (not age 1.1×10^{21})

-

Ideal Gas p-V, p-T Diagrams

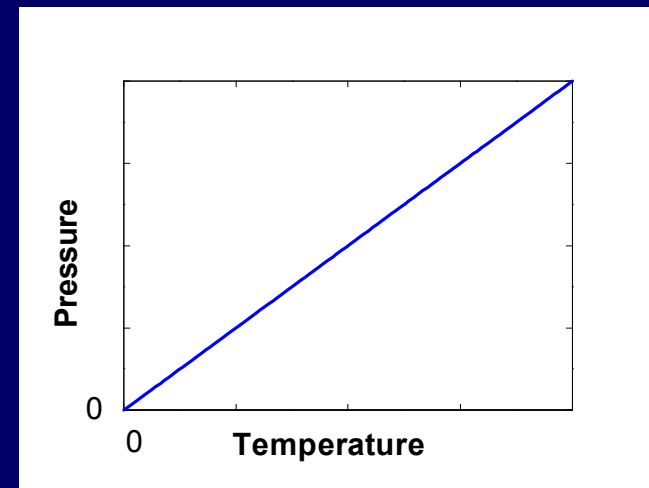
$$p = \frac{NkT}{V}$$

p vs V at various constant T's



For an ideal gas at constant T, p is inversely proportional to the volume.

p vs T at constant V



Pressure → zero as
T → absolute zero, because
the thermal kinetic energy of
the molecules vanishes.

Last time: The First Law of Thermodynamics

Energy is conserved !!!

$$\Delta U = Q + W_{\text{on}}$$

↑
change in
total internal energy

↑
heat added
to system

↑
work done
on the system

alternatively:

$$\Delta U = Q - W_{\text{by}}$$

Note: For the rest of the course, unless explicitly stated, we will ignore KE_{CM} , and only consider internal energy that does not contribute to the motion of the system as a whole.

Heat Capacity

Look at $Q = \Delta U + W_{\text{by}}$

If we add heat to a system, there are two general destinations for the energy:

- It will “heat up” the system (*i.e.*, raise T).
- It can make the system do work on the surroundings.

Heat capacity is defined to be the heat required to raise the temperature of a system by 1K ($=1^\circ\text{C}$). Its SI units are J/K.

$$C \equiv \frac{Q}{\Delta T} \text{ (for small } \Delta T\text{)}$$

The heat capacity will depend on whether energy goes into work, instead of only increasing U . Therefore, we distinguish between:

- Heat capacity at constant volume (C_V), for which $W = 0$.
- Heat capacity at constant pressure (C_p), for which $W > 0$ (most systems expand when heated).

Constant-Volume Heat Capacity of an α -ideal Gas

Add heat to an ideal gas at constant volume:

$$W = 0 \text{ so } \Delta U = Q = C_V \Delta T$$

$$U = \alpha NkT = \alpha nRT$$

$$\Rightarrow C_V = \Delta U / \Delta T = \alpha Nk = \alpha nR$$

available modes
per atom (or molecule)



	Monatomic gas	$\rightarrow C_V = (3/2)Nk = (3/2)nR$
	Diatomic gas	$\rightarrow C_V = (5/2)Nk = (5/2)nR$
	Non-linear gas	$\rightarrow C_V = (6/2)Nk = (6/2)nR$
	High-T, non-metallic solid	$\rightarrow C_V = (6/2)Nk = (6/2)nR$

For an α -ideal gas, C_V is independent of T . This results from the fact that the number of available modes is constant.

We will see later in the course that:

- this fails at low temperature, because there are fewer available modes.
- this fails at high temperature, because there are more available modes.

$C_V \sim \alpha \rightarrow$ Substances with more internal degrees of freedom require more energy to produce the same temperature increase:

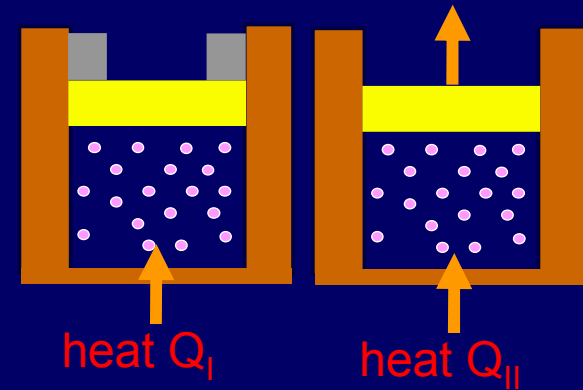
Why? Because some of the energy has to go into “heating up” those other degrees of freedom!

The energy is “partitioned equally” \rightarrow
“equipartition”

ACT 1

Consider the two systems shown to the right. In Case I, the gas is heated at constant volume; in Case II, the gas is heated at constant pressure.

Compare Q_I , the amount of heat needed to raise the temperature 1°C in system I to Q_{II} , the amount of heat needed to raise the temperature 1°C in system II.

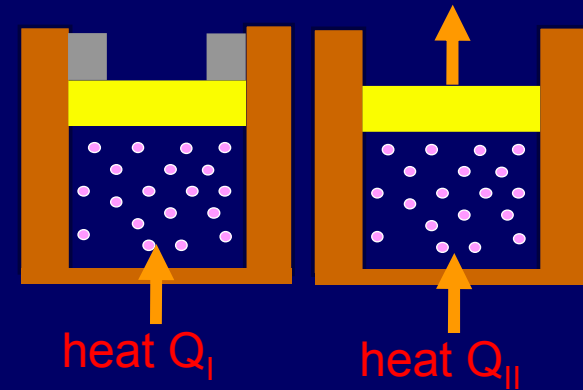


- A) $Q_I < Q_{II}$ B) $Q_I = Q_{II}$ C) $Q_I > Q_{II}$

ACT 1: Solution

Consider the two systems shown to the right. In Case I, the gas is heated at constant volume; in Case II, the gas is heated at constant pressure.

Compare Q_I , the amount of heat needed to raise the temperature 1°C in system I to Q_{II} , the amount of heat needed to raise the temperature 1°C in system II.



A) $Q_I < Q_{II}$

B) $Q_I = Q_{II}$

C) $Q_I > Q_{II}$

Apply the First Law: $Q = \Delta U + W_{by}$

In Case I, $W_{by} = 0$, because the volume does not change.

In Case II, $W_{by} > 0$, because the gas is expanding.

Both cases have the same ΔU , because the temperature rise is the same.

→ more heat is required in Case II

→ $C_p > C_v$

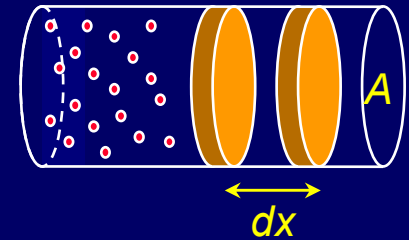
Work Done by a Gas

When a gas expands, it does work on its environment.

Consider a cylinder filled with gas.

For a small displacement dx , the work done by the gas is

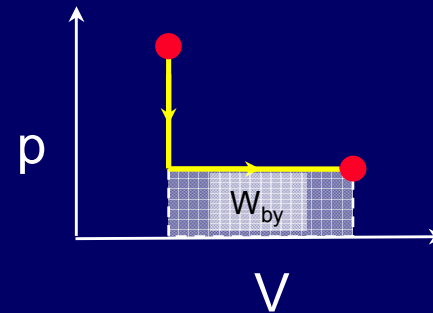
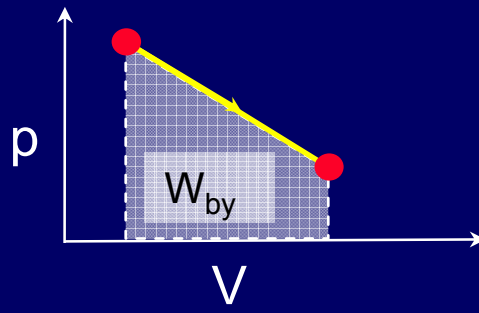
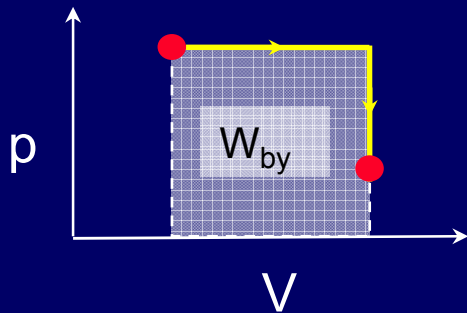
$$dW_{by} = F dx = pA dx = p (A dx) = p dV$$



This is just the area under the p-V curve:

$$W_{by} = \int_{V_i}^{V_f} p dV$$

Examples:



The paths differ because T varies differently along the paths. (Heat is added at different times.)

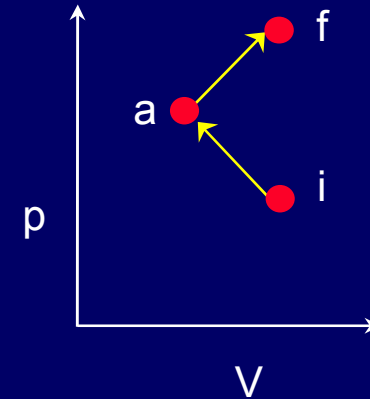
The amount of work performed while going from one state to another is not unique! It depends on the path taken, i.e., at what stages heat is added or removed.

That's why W is called a process variable.

Act 2: Work along different paths

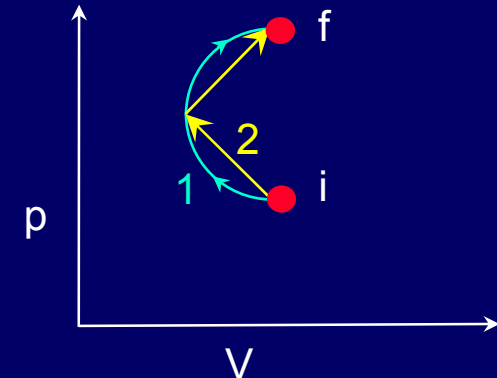
1) Consider the two paths, ia, and af connecting points i and f on the pV diagram. Compare the work done by the system in going from i to a (W_{ia}) to that done by the system in going from a to f (W_{af}):

- A) $W_{ia} > W_{af}$ B) $W_{ia} = W_{af}$ C) $W_{ia} < W_{af}$



2) Consider the two paths, 1 and 2, connecting points i and f on the pV diagram. Compare the work W_2 , done by the system along path 2, with the work W_1 , along path 1.

- A) $W_2 > W_1$ B) $W_2 = W_1$ C) $W_2 < W_1$



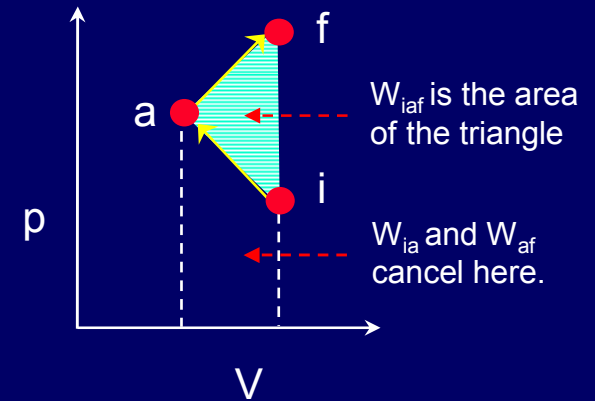
Solution

1) Consider the two paths, ia, and af connecting points i and f on the pV diagram. Compare the work done by the system in going from i to a (W_{ia}) to that done by the system in going from a to f (W_{af}):

A) $W_{ia} > W_{af}$

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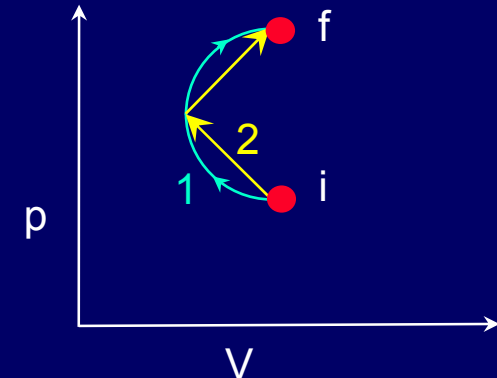
Not only is the area under ia less than the area under af, but W_{ia} is negative, because the volume is decreasing. The net work, $W_{ia} + W_{af}$, is the (positive) area of the triangle.

2) Consider the two paths, 1 and 2, connecting points i and f on the pV diagram. Compare the work W_2 , done by the system along path 2, with the work W_1 , along path 1.

A) $W_2 > W_1$

B) $W_2 = W_1$

C) $W_2 < W_1$



Solution

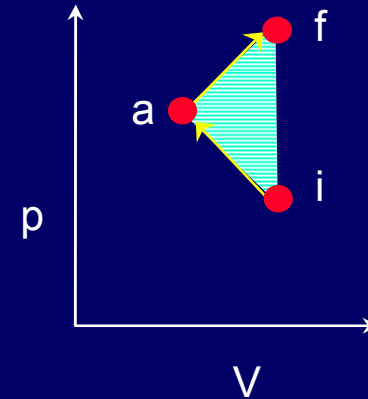
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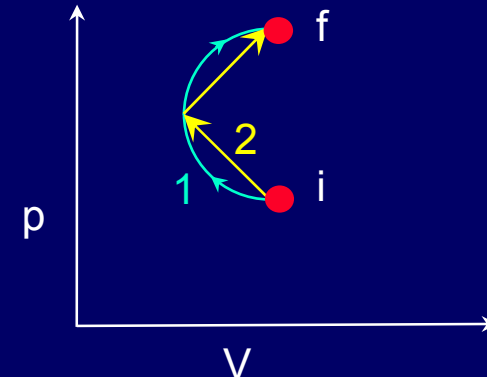
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A) $W_2 > W_1$

B) $W_2 = W_1$

C) $W_2 < W_1$

The area of the semicircle is larger than the area of the triangle.



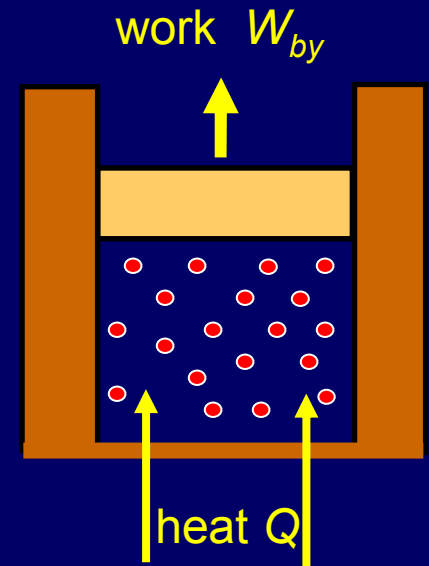
Constant-Pressure Heat Capacity of an Ideal Gas

Add heat to an ideal gas at constant pressure, allowing it to expand. We saw in the Act that more heat is required than in the constant volume case, because some of the energy goes into work:

$$Q = \Delta U + W_{by} = \Delta U + p \Delta V$$

For an ideal gas at constant pressure, $p \Delta V = Nk \Delta T$

$$\begin{aligned} C_P &= \frac{Q}{\Delta T} = \frac{\Delta U}{\Delta T} + \frac{p \Delta V}{\Delta T} \\ &= C_V + Nk = (\alpha + 1) Nk \end{aligned}$$



The ratio of heat capacity at constant pressure to that at constant volume will be useful:

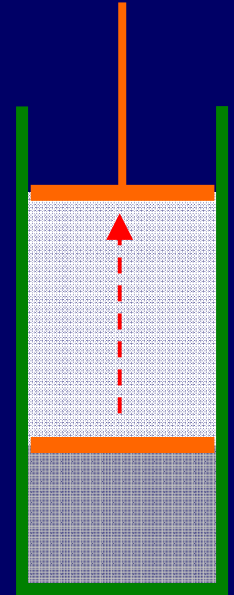
$$\frac{C_p}{C_v} = \frac{(\alpha + 1)}{\alpha} \equiv \gamma$$

definition

Work Done by an Expanding Gas (1)

Suppose that 10 moles of O_2 gas are allowed to expand **isothermally** ($T = 300 \text{ K}$) from an initial volume of 10 liters to a final volume of 30 liters.

How much work does the gas do on the piston?

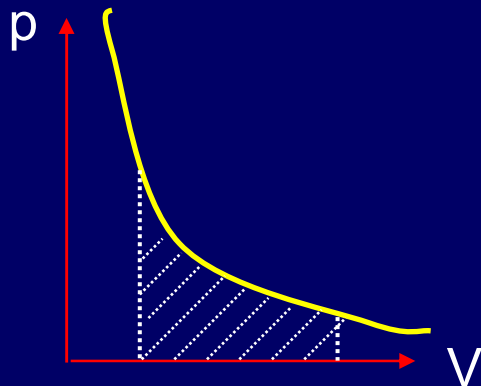


Solution

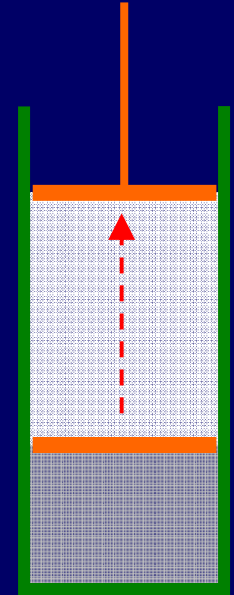
Suppose that 10 moles of O_2 gas are allowed to expand **isothermally** ($T = 300\text{ K}$) from an initial volume of 10 liters to a final volume of 30 liters.

How much work does the gas do on the piston?

$$W_{\text{by}} = \int_{V_i}^{V_f} p dV = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln\left(\frac{V_f}{V_i}\right)$$
$$= 10 \times 8.314 \times 300 \times \ln(3) = 2.7 \times 10^4 \text{ J}$$



$$\text{Note: } p_i = \frac{nRT}{V_i}$$
$$= \frac{10 \times 8.314 \times 300}{0.01}$$
$$= 2.49 \times 10^6 \text{ Pa} = 24.6 \text{ atm}$$



Adiabatic ($Q = 0$) Process of an α -ideal Gas

How are p and V related when $Q = 0$? In this case, $\Delta U = -W_{by}$.

$$\Delta U = -W_{by}$$
$$\alpha Nk \Delta T = -p \Delta V = -\frac{NkT}{V} \Delta V$$

$$\alpha \frac{\Delta T}{T} = -\frac{\Delta V}{V} \rightarrow \alpha \int \frac{dT}{T} = -\int \frac{dV}{V}$$

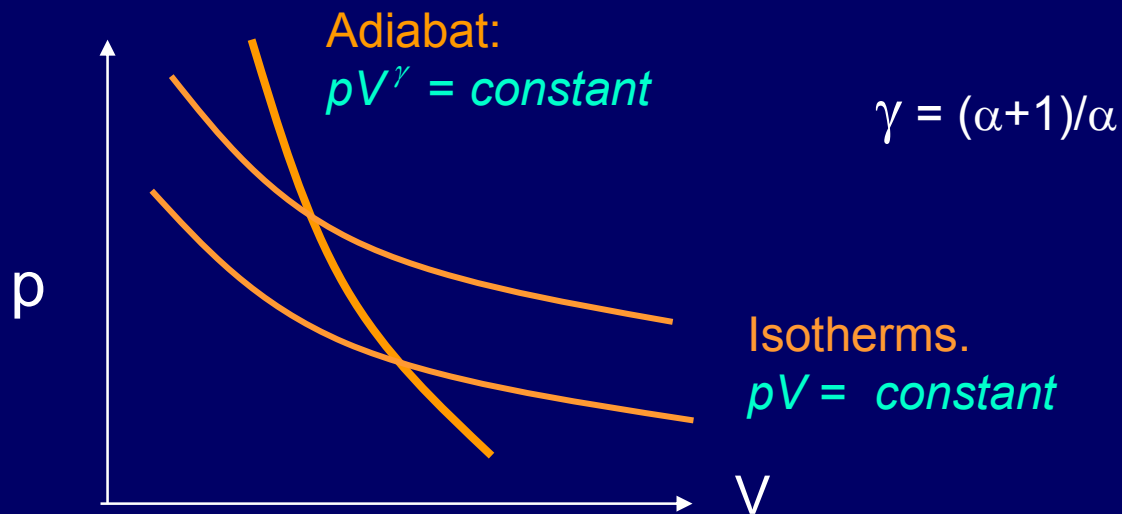
$$\alpha \ln(T) = -\ln(V) + \text{constant}$$
$$\ln(T^\alpha) + \ln(V) = \ln(T^\alpha V) = \text{constant}$$
$$T^\alpha V = \text{constant}$$

Using $pV = NkT$, we can also write this in the form:

$$pV^\gamma = \text{constant}$$

Note that pV is not constant. The temperature is changing.

Compare Adiabats and Isotherms

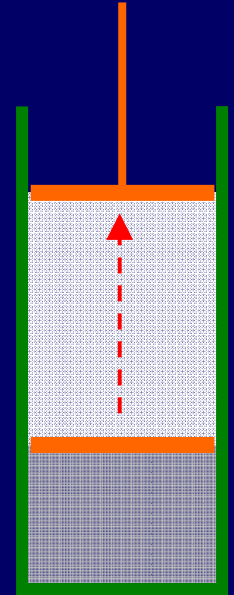


- The adiabat is steeper, because $\gamma > 1$. The temperature drops if the gas expands during an adiabatic process, because U is decreasing.
- Adiabatic and isothermal (quasi-static) processes are reversible, because there is no heat flow from hot to cold.
- This is always true, not just for ideal gases.
- “Quasi-static” means slow enough that the system is always near thermal equilibrium. We’ll discuss this more later.

Work Done by an Expanding Gas (2)

Suppose, instead, that the gas expands **adiabatically** from 10 to 30 liters.

How much work does the gas do?



Solution

Suppose, instead, that the gas expands **adiabatically** from 10 to 30 liters.

How much work does the gas do?

We still have: $W_{\text{by}} = \int_{V_i}^{V_f} p dV$

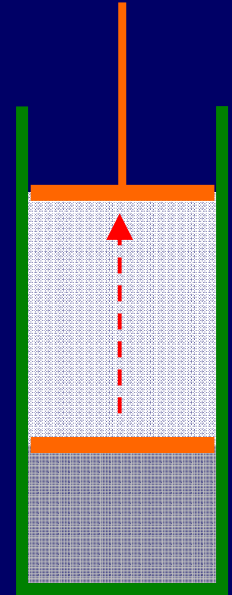
But now: $p = \frac{\text{constant}}{V^\gamma}$

So, $W_{\text{by}} = \text{constant} \int_{V_i}^{V_f} V^{-\gamma} dV = \frac{\text{constant}}{1-\gamma} V^{1-\gamma} \Big|_{V_i}^{V_f}$

But, what's the constant? It's constant, so just use p_i and V_i :

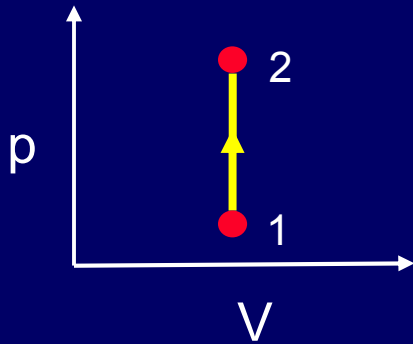
$$\text{constant} = p_i V_i^\gamma = (2.49 \times 10^6)(0.01)^{7/5} = 3946 \text{ SI units}$$

Therefore, $W_{\text{by}} = 2.2 \times 10^4 \text{ J}$. It's smaller than the isothermal result. (why?)

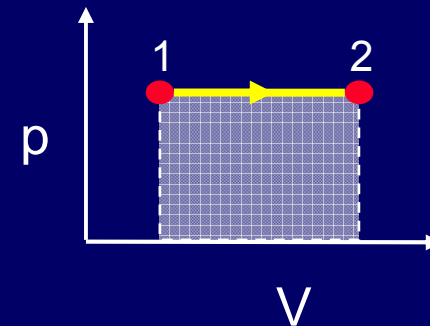


Four Thermodynamic Processes of Particular Interest to Us

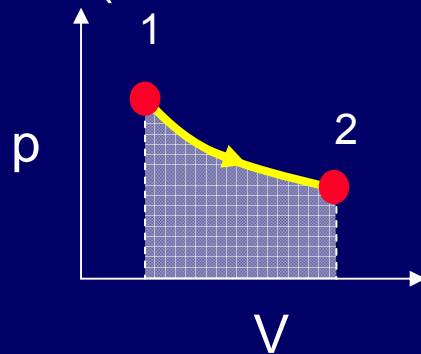
- Isochoric (constant volume)



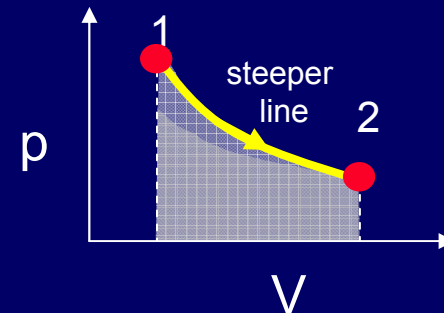
- Isobaric (constant pressure)



- Isothermal (constant temperature)



- Adiabatic ($Q = 0$)



These processes will illustrate most of the physics we're interested in.

Remember the FLT

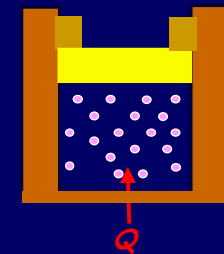
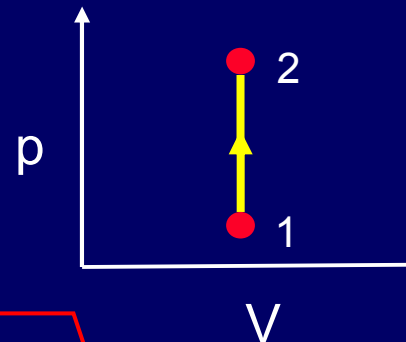
$$\Delta U = Q - W_{\text{by}}$$

Isochoric and Isobaric

Isochoric (constant volume)

$$W_{by} = \int p dV = 0$$

$$Q = \Delta U = C_V \Delta T^* \\ = \alpha Nk \Delta T^* = \alpha V \Delta p^*$$



Temperature changes

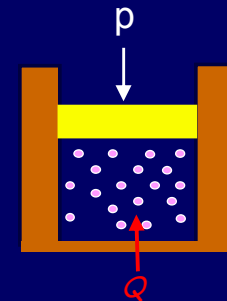
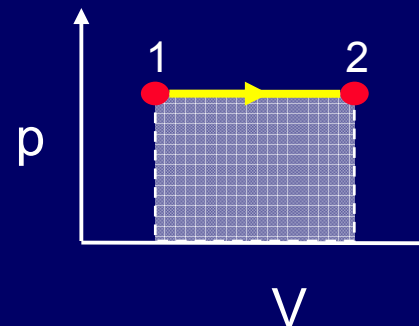
Isobaric (constant pressure)

$$W_{by} = \int p dV = p \Delta V$$

$$\Delta U = \alpha Nk \Delta T^* = \alpha p \Delta V^*$$

$$Q = C_p \Delta T$$

$$= \Delta U + W_{by} = (\alpha + 1) p \Delta V^*$$



Temperature and volume change

Make sure
you understand
these equations!
Don't just memorize!

Beware!!! Many of these equations (marked with *) rely on the ideal gas law.

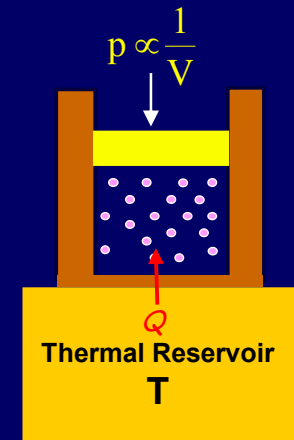
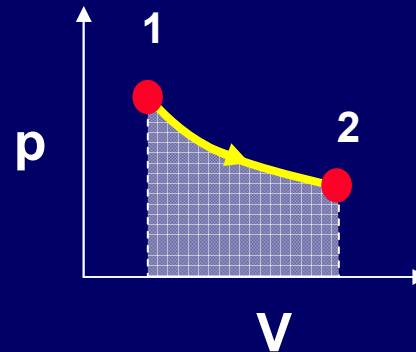
Isothermal and Adiabatic

Isothermal (constant temperature)

$$\Delta U = 0^*$$

$$Q = W_{by}^*$$

$$W_{by} = \int p dV = NkT \int \frac{dV}{V} = NkT \ln\left(\frac{V_2}{V_1}\right)^*$$

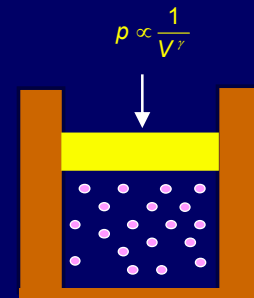
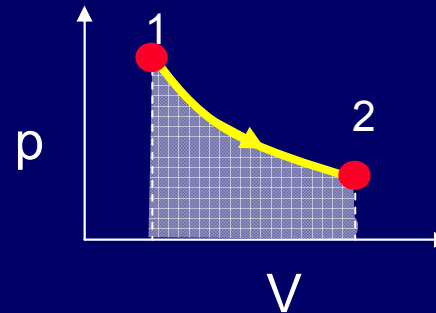


Volume and pressure change

Adiabatic (isolated: no heat flow)

$$Q = 0$$

$$\Delta U = -W_{by} = \alpha Nk\Delta T^* = \alpha (p_2 V_2 - p_1 V_1)^*$$



Volume, pressure and temperature change

Beware!!! Many of these equations (marked with *) rely on the ideal gas law.

Example: Isothermal Compression

Suppose we have 3 moles of an ideal polyatomic gas initially with a volume of 2 m^3 , and a temperature of 273 K . This gas is compressed isothermally to $1/2$ its initial volume. How much heat must be added to the system during this compression?

Solution

Suppose we have 3 moles of an ideal polyatomic gas initially with a volume of 2 m³, and a temperature of 273 K. This gas is compressed isothermally to 1/2 its initial volume. How much heat must be added to the system during this compression?

$$\Delta U = 0$$

$$Q = -W_{on}$$

$$= + \int_{V_i}^{V_f} p dV = nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$= nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$= -nRT \ln 2$$

$$= -4.7 \text{ kJ}$$

Isothermal process - ideal gas.

FLT

Definition of work then use ideal gas law

Integral of dV/V

Note that the heat added is negative - heat actually must be removed from the system during the compression to keep the temperature constant.

Example: Escape Velocity

How much kinetic energy must a nitrogen molecule have in order to escape from the Earth's gravity, starting at the surface? Ignore collisions with other air molecules. How about a helium atom? At what temperatures will the average molecule of each kind have enough energy to escape?

Solution

How much kinetic energy must a nitrogen molecule have in order to escape from the Earth's gravity, starting at the surface? Ignore collisions with other air molecules. How about a helium atom? At what temperatures will the average molecule of each kind have enough energy to escape?

$$\begin{aligned} KE &= GM_E m / r_E = g m r_E \\ &= 2.9 \times 10^{-18} \text{ J} \end{aligned}$$

To escape, a molecule must overcome the negative potential energy. Simplify using $GM_E m / r_E^2 = g = 9.8 \text{ m/s}^2$. Use $r_E = 6.4 \times 10^6 \text{ m}$ (4000 mi), and $m_{N_2} = 4.7 \times 10^{-26} \text{ kg}$.

$$\begin{aligned} T_{N_2} &= 2\langle KE \rangle / 3k \\ &= 1.4 \times 10^5 \text{ K} \end{aligned}$$

Equipartition tells us that $\langle KE \rangle = 3kT/2$.
That's hot!

$$T_{He} = 2 \times 10^4 \text{ K}.$$

The mass of a helium atom is smaller by a factor of 4/28. KE and T needed for escape are reduced by the same factor.

T is still too low to let much He escape, but it does get high enough to get ionized by the Sun's UV, and then other processes sweep it away.

Next Week

- ● Heat capacity of solids & liquids
-
- ● Thermal conductivity
- ● Irreversibility

A Quick Probability Problem

We'll spend a lot of time calculating probabilities. Here's a quick introduction.

This lecture room is approximately a cube 15 m on a side. Calculate the probability that all the air molecules will be found in the left half of the room.

The number of gas molecules in the room is: $N = pV / kT \sim 10^{29}$. Each molecule is equally likely to be found in either half, so the probability that they are all in the same half is $(1/2)^{10^{29}} \sim 10^{-3 \times 10^{28}}$.

It is hard to conceive how small this number is. All the molecules will be in the left half of the room once every $10^{+3 \times 10^{28}}$ years (*i.e.*, never). You can divide this time by any conceivable number you want (a billion, a trillion, a google) without affecting this result significantly.