

The changes in the internal energy of water depends only

on the net energy transferred



This is a statement of cons. of energy (note that "heat" is now included in this statement)



1st law of thermodynamics
The change in the internal energy of a system depends only on the net heat transferred to the system and the net work done on the system independent of the particular processes involved



Mathematically

$$\Delta E_{int} = Q + W$$

net change in a system's int. energy

heat transferred to the system

work done ON the system

Side note

E_{int} is a thermodynamic state variable

a quantity whose value does not depend on how a system got into its particular state (e.g. temp. and pressure) (heat and work are not therm. state variables)

Often we care about rates and not the actual value of E_{int} , Q , and W :

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$$\Delta E_{int} = W + Q \quad \Rightarrow \quad \frac{dE_{int}}{dt} = \frac{dQ}{dt} + \frac{dW}{dt}$$

Note

1st law of ther. applies to any system (it's universal) but it's easier if use it for an ideal gas

↓

$$pV = nRT$$

Recall

$$pV = NKT = nN_AKT = nRT$$

$$N = nN_A$$

$$N_AK = R$$

$N \equiv$ # of molecules in the gas

$n \equiv$ # of moles

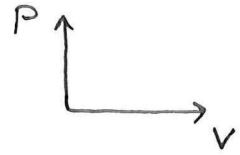
$N_A \equiv$ Avogadro's number (atoms or molecules)

$R \equiv$ Universal gas constant

PV diagram

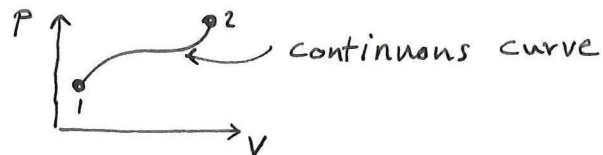
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- The thermodynamic state of a system is completely determined by 2 of p , V , and T .
- Can represent states as points on a PV diagram



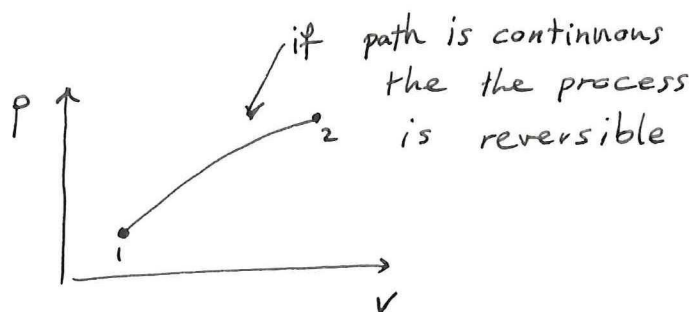
A quasi-static process

- when the system (gas) remains in equilibrium w/ the reservoir it's in (both have the same temp.) while the temp. changes slowly



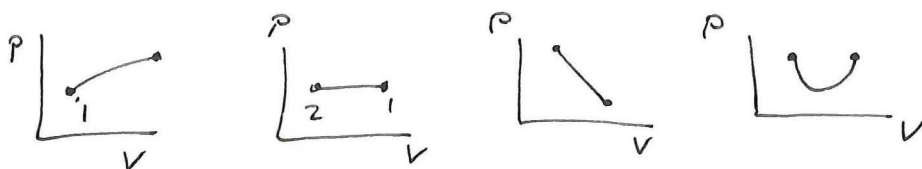
- we could always reverse the path $1 \rightarrow 2$ to get $2 \rightarrow 1$ for a QSP. QSP is a reversible process
- For an irreversible process, sys. is not in equil. and variables like T and p don't have a well defined relationship.

The path matters not the end points.



we can think of all sorts of processes in a PV diagram.

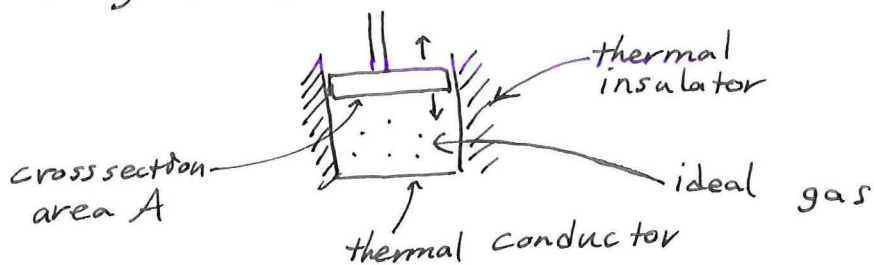
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but we're going to focus on a few special cases
(all involving ideal gas)

before getting there:

- ① First: we need a system that allows us to vary P, V, T of an ideal gas



we can change the thermodynamic state of ideal gas inside by:

- mechanically: moving the piston up or down
- thermally: heating the gas from the bottom

- ② Second: need to calculate the work done on the gas which holds for all processes

the force that the gas inside exerts on the piston is

$$F_{\text{gas}} = PA$$

Recall that $W = \vec{F} \cdot \vec{d}$

thus if the piston moves a small distance Δx , then

$$\Delta W_{\text{gas on piston}} = F_{\text{gas}} \Delta x = PA \Delta x = P \underbrace{A \Delta x}_{\substack{\text{change in gas} \\ \text{volume}}}$$

Recall that 1st law was

$$\Delta E_{\text{int}} = Q + \underset{\substack{\uparrow \\ \text{work done on gas}}}{W}$$

by Newton's 3rd law $W_{\text{done on gas}} = -W_{\text{done by gas}}$

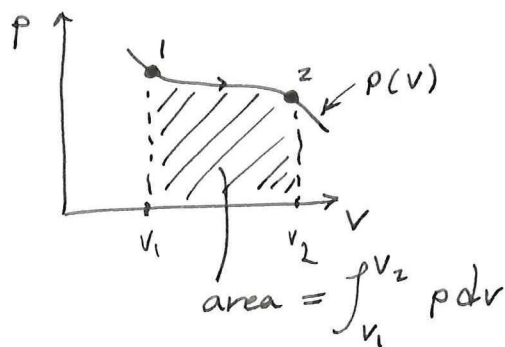
$$\Delta W_{\text{done on gas}} = -F_{\text{gas}} \Delta x = -P \Delta V \quad \leftarrow \quad \Delta W_{\text{done on gas}} = -P \Delta V$$

but since P can change as V changes,



$$W = \int dw = - \int_{V_1}^{V_2} p dv$$

work done on gas as vol. changes from V_1 to V_2



$\left\{ \begin{array}{l} W > 0 \text{ if } V_2 < V_1 \text{ (gas is compressed)} \\ W < 0 \text{ if } V_2 > V_1 \text{ (gas expands)} \end{array} \right.$

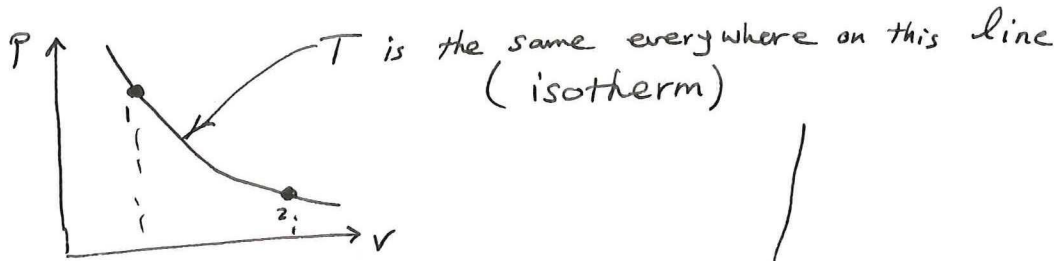
done on gas

special processes in PV diagram

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continuous processes transitions between thermodynamic states

1. Isothermal processes \Leftrightarrow constant temp.



$$W_{\text{on gas}} = - \int_{V_1}^{V_2} P(V) dV \stackrel{PV = nRT}{=} - \int_{V_1}^{V_2} \frac{nRT}{V} dV = - \frac{nRT}{\cancel{nRT}} \int_{V_1}^{V_2} \frac{1}{V} dV =$$

$$= -nRT \ln V \Big|_{V_1}^{V_2} = -nRT (\ln V_2 - \ln V_1) = -nRT \ln \frac{V_2}{V_1}$$

Important

int. energy of a gas depends only on

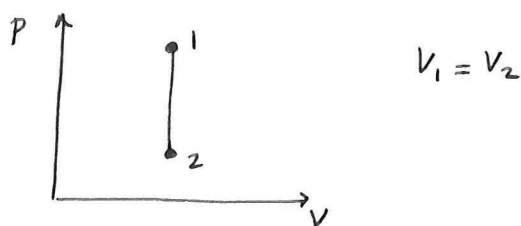
→ kinetic energy of its molecules which depends only on → temperature

$$\Rightarrow \Delta E_{\text{int}} = 0 \Rightarrow \text{1st law: } 0 = Q + W$$

$$Q = -W = nRT \ln \left(\frac{V_2}{V_1} \right)$$

2. Constant Volume process + specific heat C_v

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no piston movement \rightarrow no work done on or by gas

$$\Rightarrow \text{1st law: } \Delta E_{\text{int}} = Q + \cancel{W}$$

Can represent Q as a temperature change ΔT :

$$Q = n C_v \Delta T$$

of moles \rightarrow n
molar specific heat at cons. vol. \rightarrow C_v

(similar to specific heat in ch. 16 but is per mole instead of per unit mass)

Recall ch. 16.2

$$Q = C \Delta T$$

heat capacity (J/K) \rightarrow C
 $C = cm$

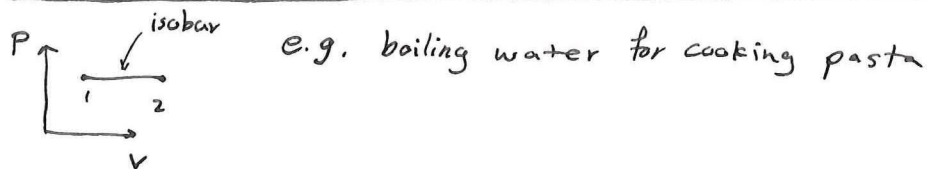
$$\begin{cases} \Delta E_{\text{int}} = Q \\ Q = n C_v \Delta T \end{cases} \Rightarrow \Delta E_{\text{int}} = n C_v \Delta T$$

Important

for ideal gas, int. energy is only a function of ~~the~~ temp.
and hence $\frac{\Delta E_{\text{int}}}{\Delta T} = n C_v$ has the same value ~~no~~ no matter what process

* specific heat measures the heat needed to cause a given temp. change

3. Isobaric Processes + Specific Heat C_p



Since P is constant W is easy to find

$$W = - \int_{V_1}^{V_2} P dV = -P(V_2 - V_1) = -P \Delta V$$

$$Q = \Delta E_{int} - W = \Delta E_{int} + P \Delta V$$

$$\Delta E_{int} = n C_v \Delta T$$

$$Q = n C_v \Delta T + P \Delta V$$

Define

$$Q = n C_p \Delta T \quad (\text{for isobaric processes})$$

↑
molar specific heat at constant pressure

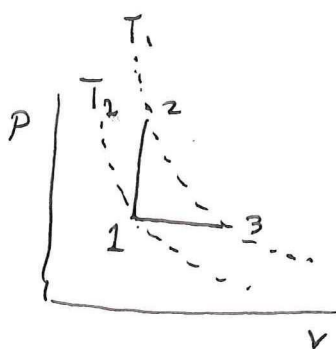
$$\rightarrow \cancel{Q} \quad n C_p \Delta T = n C_v \Delta T + P \Delta V \quad \leftarrow \text{only for isobaric processes}$$

↑
this is a useful equation for calculating ΔT if we know C_p and C_v .

However, we only need one of them.

for ideal gas $PV = nRT$ can write $P \Delta V = nR \Delta T$

$$n C_p \Delta T = n C_v \Delta T + n R \Delta T \quad \Rightarrow \quad \boxed{C_p = C_v + R}$$



← This tells us that a constant P process requires more heat for a given temp change than a constant volume process.

4. Adiabatic processes

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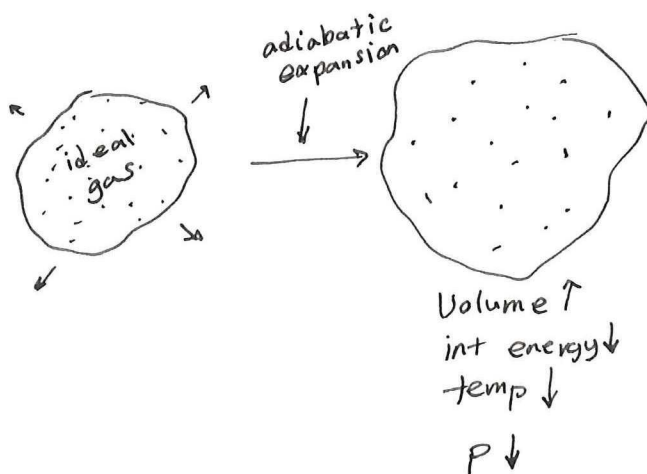
For this process, no heat flows between a system and the environment it's in.

$$\Rightarrow Q = 0$$

- Two ways:
1. complete insulation of the system
 2. for the process to be so quick that it's over before heat has had time to flow
(e.g. in gasoline engines:

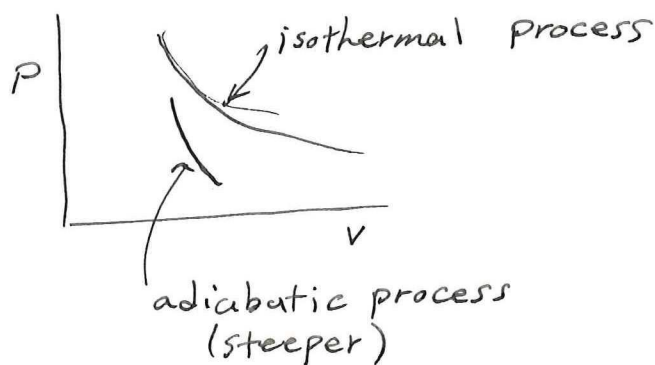
both the compression of gas/air mix and the expansion of the combustion product are almost adiabatic)

1st law $\rightarrow \Delta E_{int} = W$



$$pV = nRT$$

* therefore pressure drop is greater in adiabatic processes than in isothermal ones.



$$\Delta E_{int} = nC_v \Delta T \rightarrow dE_{int} = nC_v dT$$

$$\Delta W = p \Delta V \rightarrow dW = p dV$$

for adiabatic processes where $Q=0$, 1st law

$$dE_{int} = dW \rightarrow nC_v dT = -p dV$$

↑

$$pV = nRT \rightarrow nR dT = d(pV) = dp \cdot V + p dV$$
$$\Rightarrow dT = \frac{p dV + V dp}{nR}$$

$$nC_v \frac{p dV + V dp}{nR} = -p dV \rightarrow C_v (p dV + V dp) = -pR dV$$

$$\rightarrow C_v p dV + C_v V dp + pR dV = 0$$

$$C_v V dp + (C_v p + pR) dV = 0$$

$$C_v V dp + (C_v + R) p dV = 0$$

$$\downarrow C_p = C_v + R$$

$$C_v V dp + (C_v + C_p - C_v) p dV = 0$$

$$C_v V dp + C_p p dV = 0$$

$$\downarrow \times \frac{1}{C_v p V}$$

$$\frac{dp}{p} + \frac{C_p}{C_v} \frac{dV}{V} = 0$$

$$\downarrow \gamma \equiv \frac{C_p}{C_v}$$

$$\int \frac{dp}{p} + \int \gamma \frac{dV}{V} = \text{const.} \Rightarrow \ln(p) + \gamma \ln(V) = \text{constant}$$

$$\Rightarrow ~~pV^\gamma~~$$

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

for adiabatic processes

$$PV^\gamma = C$$

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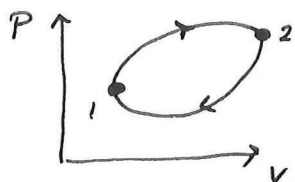
$$PV = nRT \rightarrow P = \frac{nRT}{V}$$

$$\frac{nRT}{V} V^\gamma = C \rightarrow TV^{\gamma-1} = \frac{C}{nR} = C' \Rightarrow TV^{\gamma-1} = \text{constant}$$

$$W = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} C \frac{dV}{V^\gamma} = - C \frac{(V_2^{1-\gamma} - V_1^{1-\gamma})}{1-\gamma}$$

$$\int \frac{dx}{x^a} = \frac{x^{1-a}}{1-a} + \text{constant}$$

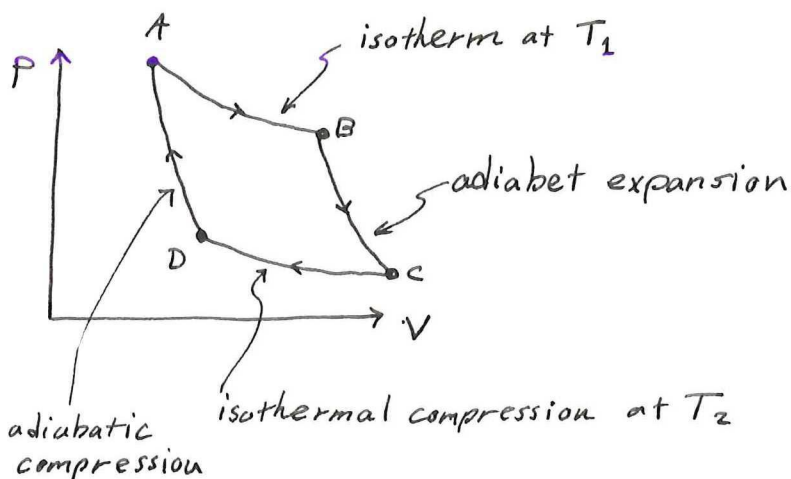
Cyclic Processes



- Requires both expansion and compression
- Internal energy of a system depends only on the thermodynamic state of that system, therefore, for a cyclic process the net change of internal energy is zero:

$$\Delta E_{int} = 0 \implies Q_{net} = -W_{net}$$

Carnot Cycle



this is the PV-diagram of an ideal gas going through what's called a "Carnot Cycle"

Process A → B

- isothermal expansion at constant temperature T_1
- During any isothermal process $\Delta E_{int} = 0$

Therefore, 1st law for process A → B is:

$$\Delta E_{int, A \rightarrow B} = Q_{AB} + W_{AB} \implies Q_{AB} = -W_{AB}$$

Heat transferred to the gas during process A → B

Work done on the gas during process A → B

$$W_{AB} = - \int_{V_A}^{V_B} p dv = -nRT_1 \ln\left(\frac{V_B}{V_A}\right)$$

← this tells us that the work done on the gas is negative

But since $Q_{AB} = -W_{AB}$ then the heat transferred to the gas is positive and it's equal to $nRT_1 \ln\left(\frac{V_B}{V_A}\right)$

Process B → C

- Adiabatic expansion
- During an adiabatic process $Q = 0$, therefore, for here:

$$Q_{BC} = 0$$

which means no heat is exchanged between the gas and its surrounding.

1st law: $\Delta E_{int, B \rightarrow C} = \overset{0}{\cancel{Q}_{BC}} + W_{BC}$

Also we know that for any process $\Delta E_{int} = nC_v \Delta T$
and therefore, $\Delta E_{int, B \rightarrow C} = nC_v \Delta T_{BC} = nC_v (T_2 - T_1)$

$$\Rightarrow \left. \begin{aligned} \Delta E_{int, B \rightarrow C} &= W_{BC} \\ \Delta E_{int, B \rightarrow C} &= nC_v (T_2 - T_1) \end{aligned} \right\} \Rightarrow W_{BC} = nC_v (T_2 - T_1)$$

In class, I mistakenly put a negative sign here.
One of your classmates pointed out my mistake.

Process C → D.

- Isothermal compression $\Delta E_{int} = 0$
C → D
- positive work is done on the gas

1st law: $Q_{CD} = -W_{CD}$

$$W_{CD} = - \int_{V_C}^{V_D} p dv = -nRT_2 \ln\left(\frac{V_D}{V_C}\right) = nRT_2 \ln\left(\frac{V_C}{V_D}\right)$$

$-\ln\left(\frac{a}{b}\right) = \ln\left(\frac{b}{a}\right)$

Work done on gas is positive

$V_C > V_D$

$$Q_{CD} = -W_{CD} = -nRT_2 \ln\left(\frac{V_C}{V_D}\right)$$

this negative sign tells us that $nRT_2 \ln\left(\frac{V_C}{V_D}\right)$ is the amount of heat that is leaving the gas

Process D → A

- Adiabatic compression → $Q_{DA} = 0$

$$\Delta E_{int} = Q_{DA} + W_{DA}$$

D → A

$$\Delta E_{int} = nC_V \Delta T = nC_V (T_1 - T_2)$$

D → A

$$W_{DA} = nC_V (T_1 - T_2)$$

Net heat absorbed by the gas:

$$Q_{net \text{ absorbed}} = Q_{AB} + Q_{CD} = nRT_1 \ln\left(\frac{V_B}{V_A}\right) + \left(-nRT_2 \ln\left(\frac{V_C}{V_D}\right)\right) =$$

$$= nR \left[T_1 \ln\left(\frac{V_B}{V_A}\right) + T_2 \ln\left(\frac{V_D}{V_C}\right) \right]$$