EPFL

Thermodynamics of Earth systems

Lecture 3:
The First Law of Thermodynamics

Material covered in Lecture 3

Conclusion of Part 1: Introduction

- Hydrostatic equation: application to ocean and hypothetical constant density atmosphere; solid earth
- Hypsometric equation (atmosphere)

In-class worksheets

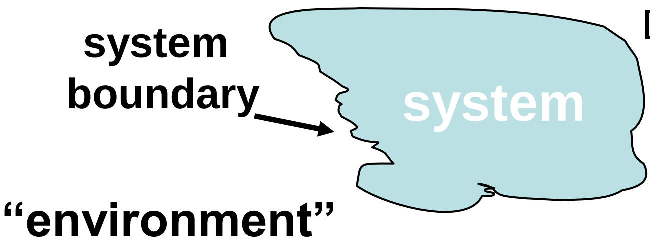
Part 2: Framework

First Law of thermodynamics

- Basic concepts & processes
- Work; expansion work
- Heat: heat capacity, basics of heat transfer mechanisms
- First law: internal energy, enthalpy, specific heats, heat capacity.
- Applications of first law to ideal gases

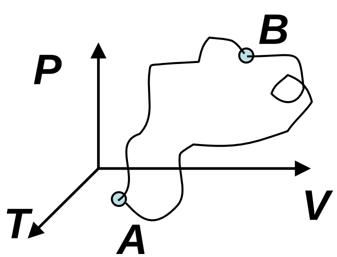
Internal Energy

The ***internal energy*** of a system of particles, ***U***, is the sum of the kinetic energy *in the reference frame in which the center of mass is at rest* and the potential energy arising from the forces of the particles on each other.



Difference between the total energy and the internal energy?

$$U = \textit{kinetic} + \textit{potential}$$



The internal energy is a **state function** – it depends only on the values of macroparameters (the state of a system), not on the method of preparation of this state (the "path" in the macroparameter space is irrelevant).

In equilibrium [f (P,V,T)=0] : $U = U(V, T)$

U depends on the kinetic energy of particles in a system and an average inter-particle distance (~ $V^{-1/3}$) – interactions.

For an ideal gas (no interactions) : $U = U(T)$ - **"pure" kinetic**

Internal Energy of an Ideal Gas

The internal energy of an ideal gas with ***f*** degrees of freedom:

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

f $\Rightarrow$ 3 (monatomic), 5 (diatomic), 6 (polyatomic)

(here we consider only trans.+rotat. degrees of freedom, and neglect the vibrational ones that can be excited at very high temperatures)

How does the internal energy of air in this (not-air-tight) room change with ***T*** if the external ***P = const***?

$$U = \frac{f}{2} N_{in\,room} k_B T = \left[N_{in\,room} = \frac{PV}{k_B T} \right] = \frac{f}{2} PV$$

- does not change at all, an increase of the kinetic energy of individual molecules with ***T*** is compensated by a decrease of their number.

Work and Heating ("Heat")

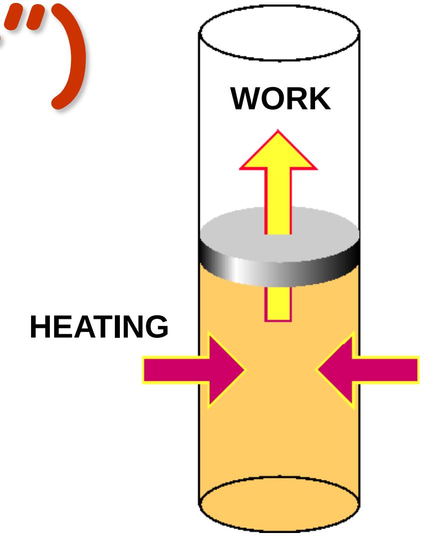
We are often interested in ΔU , not U. ΔU is due to:

- ***Q*** - energy flow between a system and its environment due to ΔT across a boundary and a finite thermal conductivity of the boundary

  – ***heating*** **(*Q* > 0) */cooling*** **(*Q* < 0)**

  (there is no such physical quantity as "heat"; to emphasize this fact, it is better to use the term "heating" rather than "heat")

- ***W*** - any *other* kind of energy transfer across boundary - ***work***



Work and Heating are both defined to describe ***energy transfer*** *across a system boundary.*

Heating/cooling processes:

conduction: the energy transfer by molecular contact – fast-moving molecules transfer energy to slow-moving molecules by collisions;

convection: by macroscopic motion of gas or liquid

radiation: by emission/absorption of electromagnetic radiation.

The First Law

The first law of thermodynamics: the internal energy of a system can be changed by doing work on it or by heating/cooling it.

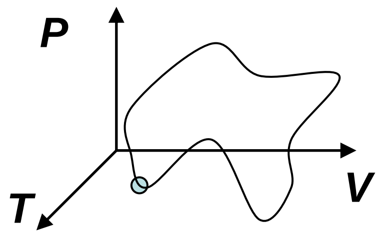
$$\Delta U = Q + W$$

conservation of energy.

Sign convention: we consider ***Q*** and ***W*** to be ***positive*** if energy flows ***into*** the system.

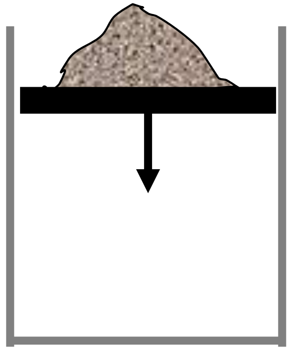
For a cyclic process $(U_i = U_f) \Rightarrow Q = -W$.

If, in addition, $Q = 0$ then $W = 0$



An equivalent formulation:

Perpetual motion machines of the first type do not exist.



Quasi-Static Processes

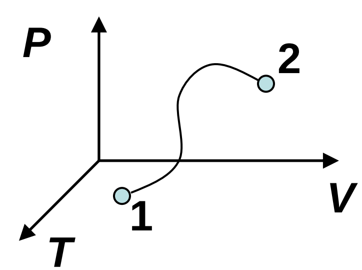
Quasi-static (quasi-equilibrium) processes – sufficiently slow processes, *any* intermediate state can be considered as an equilibrium state (the macroparamers are well-defined for all intermediate states).

Advantage: the state of a system that participates in a quasi-equilibrium process can be described with the ***same (small) number of macro parameters*** as for a system in equilibrium (e.g., for an ideal gas in quasi-equilibrium processes, this could be ***T*** and ***P***). By contrast, for ***non-equilibrium processes*** (e.g. turbulent flow of gas), we need a ***huge number of macro parameters***.

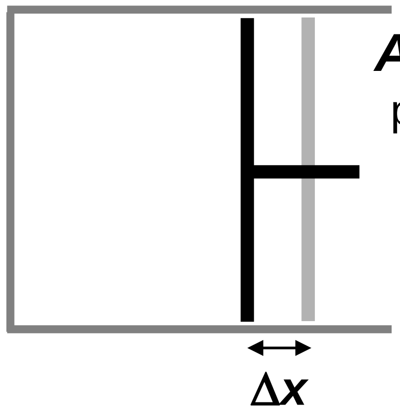
***Examples of quasi-equilibrium processes*:**

- isochoric: V **= const**
- isobaric: P **= const**
- isothermal: T **= const**
- adiabatic: Q **= 0**

For quasi-equilibrium processes, ***P***, ***V***, ***T*** are ***well-defined*** – the "path" between two states is a *continuous lines* in the ***P*, *V*, *T*** space.



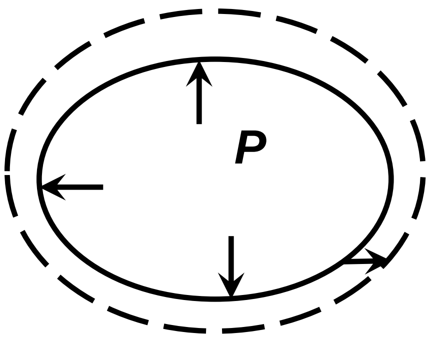
Work



The work done by an external force on a gas enclosed within a cylinder fitted with a piston:

$$\boldsymbol{W = \underbrace{(PA)}_{\text{force}}\, dx = P\,(Adx) = -\,PdV}$$

The sign: if the volume is *decreased*, ***W*** is ***positive*** (by compressing gas, we increase its internal energy); if the volume is *increased*, ***W*** is ***negative*** (the gas decreases its internal energy by doing some work on the environment).



W = - PdV - applies to any shape of system boundary

$$W_{1-2} = -\int_{V_1}^{V_2} P(T,V)\,dV$$

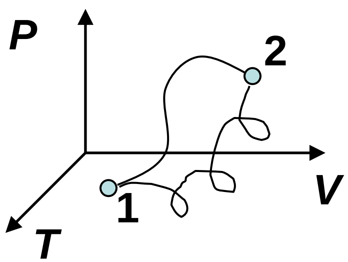
$$\boldsymbol{dU = Q - PdV}$$

The work is not necessarily associated with the volume changes – e.g., in the Joule's experiments on determining the "mechanical equivalent of heat", the system (water) was heated by stirring.

W and Q are not State Functions

$$W_{1-2} = -\int_{V_1}^{V_2} P(T,V)dV$$

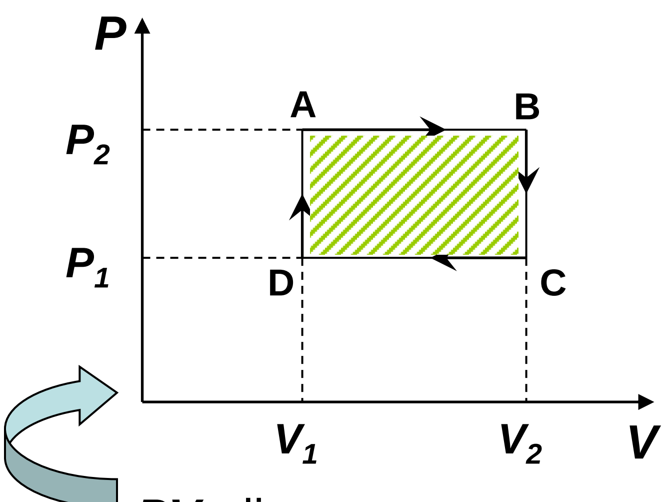
- we can bring the system from state 1 to state 2 along infinite # of paths, and for each path ***P*(*T*,*V*)** will be different.



Since **the work** done on a system depends not only on the ***initial*** and ***final*** states, but also on the ***intermediate*** states, it **is not a state function.**

$$\Delta U = Q + W$$

U is a state function, ***W*** - is not ⇒ thus, ***Q* is not a state function either**.



PV diagram

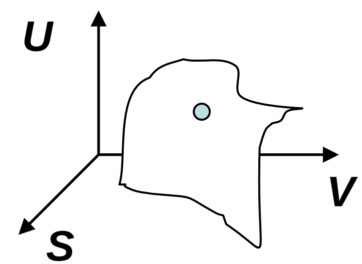
$$W_{net} = W_{AB} + W_{CD} = -P_2\left(V_2 - V_1\right) - P_1\left(V_1 - V_2\right)$$
$$= -\left(P_2 - P_1\right)\left(V_2 - V_1\right) < 0$$

- the work is negative for the "clockwise" cycle; if the cyclic process were carried out in the reverse order (counterclockwise), the net work done on the gas would be positive.

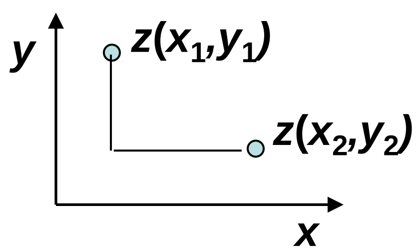
Comment on State Functions

U, ***P, T,*** and ***V*** are the state functions, ***Q*** and ***W*** are not. Specifying an initial and final states of a system does not fix the values of ***Q*** and ***W***, we need to know the whole process (the intermediate states). Analogy: in classical mechanics, if a force is not conservative (e.g., friction), the initial and final positions do not determine the work, the entire path must be specified.

In math terms, ***Q*** and ***W*** are not exact differentials of some functions of macroparameters. To emphasize that ***W*** and ***Q*** are NOT the state functions, we will use sometimes the curled symbols δ (instead of ***d***) for their increments (δ***Q*** and δ***W***).



$$dU = T\,dS - P\,dV$$ - an exact differential



$dz = A_x(x,y)dx + A_y(x,y)dy$ - it is an exact differential if it is the difference between the values of some (state) function **z(x,y)** at these points: $dz = z(x+dx, y+dy) - z(x,y)$

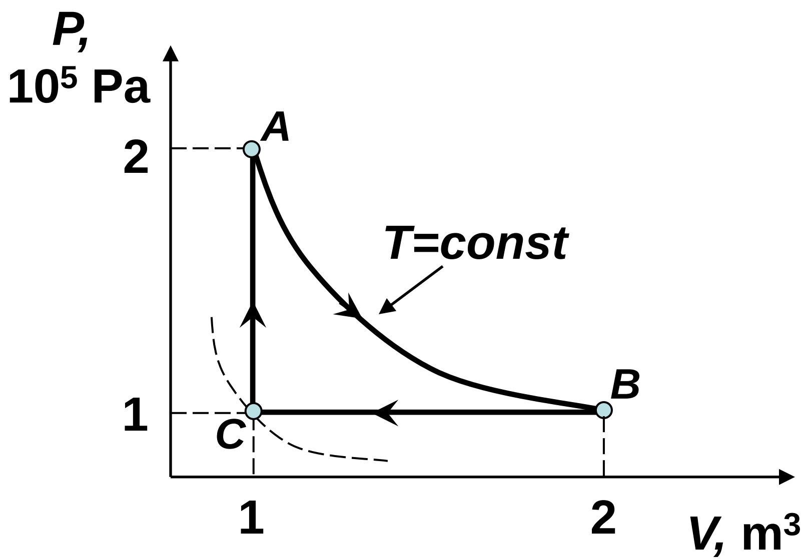
A necessary and sufficient condition for this: $$\frac{\partial A_x(x,y)}{\partial y} = \frac{\partial A_y(x,y)}{\partial x}$$

If this condition holds: $$A_x(x,y) = \frac{\partial z(x,y)}{\partial x} \quad A_y(x,y) = \frac{\partial z(x,y)}{\partial y} \quad d\,z = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

e.g., for an ideal gas: $$\delta Q = dU + PdV = Nk_B\left(\frac{f}{2}dT + \frac{T}{V}dV\right)$$ - cross derivatives are not equal

Problem

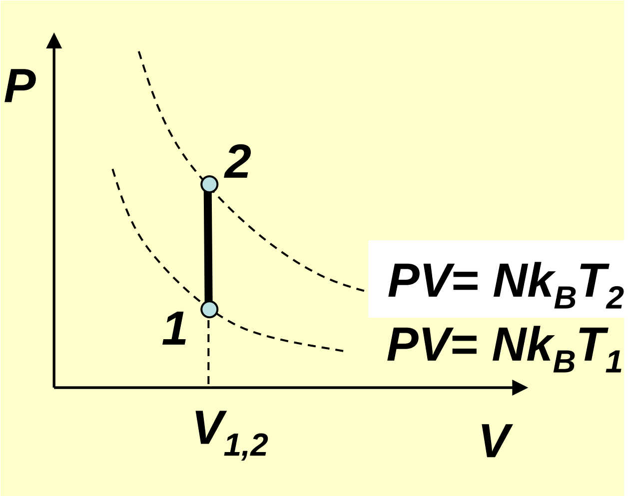
Imagine that an ideal monatomic gas is taken from its initial state ***A*** to state ***B*** by an *isothermal* process, from ***B*** to ***C*** by an *isobaric* process, and from ***C*** back to its initial state ***A*** by an *isochoric* process. Fill in the signs of ***Q***, ***W***, and **Δ*U*** for each step.



Step	*Q*	*W*	Δ*U*
A → B	+	--	0
B → C	--	+	--
C → A	+	0	+

$$U = \frac{f}{2} N k_B T \qquad PV = N k_B T$$

Quasistatic Processes in an Ideal Gas



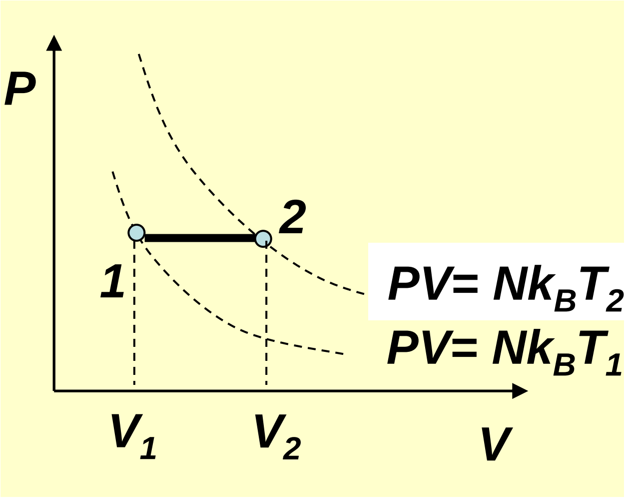
- isochoric (V = const)

$$W_{1\to 2} = 0$$

$$Q_{1\to 2} = \frac{3}{2}Nk_B\left(T_2 - T_1\right) > 0 \quad \left(= C_V \Delta T\right)$$

(see the last slide)

$$dU = Q_{1\to 2}$$



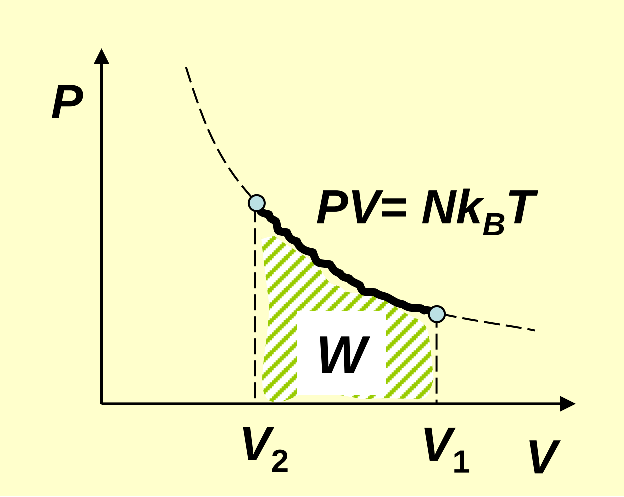
- isobaric (P = const)

$$W_{1\to 2} = -\int_1^2 P(V,T)dV = -P\left(V_2 - V_1\right) < 0$$

$$Q_{1\to 2} = \frac{5}{2}Nk_B\left(T_2 - T_1\right) > 0 \quad \left(= C_P \Delta T\right)$$

$$dU = W_{1\to 2} + Q_{1\to 2}$$

Isothermal Process in an Ideal Gas



- isothermal **(** ***T*** **= const**) **:**

$$dU = 0$$

$$W_{1\to 2} = -\int_{V_1}^{V_2} P(V,T)\,dV = -Nk_B T \int_{V_1}^{V_2} \frac{dV}{V} = -Nk_B T \ln \frac{V_2}{V_1}$$

$$Q_{1\to 2} = -W_{1\to 2}$$

$$W_{i-f} = Nk_B T \ln \frac{V_i}{V_f}$$

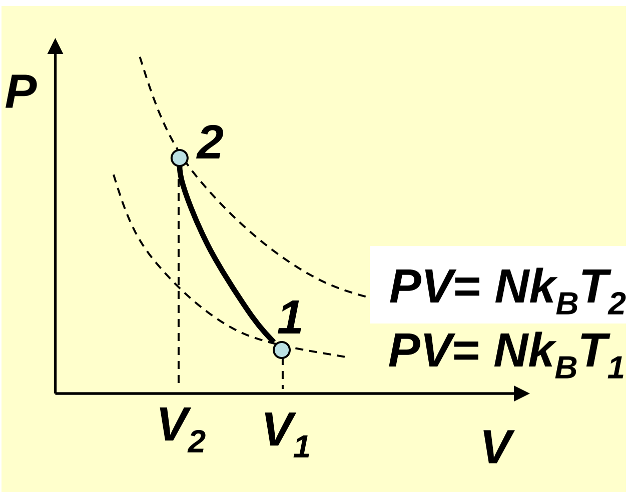
$W_{i\text{-}f} > 0$ if $V_i > V_f$ (compression)

$W_{i\text{-}f} < 0$ if $V_i < V_f$ (expansion)

Adiabatic Process in an Ideal Gas

- **adiabatic** (*thermally isolated* system) $Q_{1\to 2}=0 \quad dU = W_{1\to 2}$

The amount of work needed to change the state of a thermally isolated system depends ***only*** on the *initial* and *final* states and not on the *intermediate* states.



$$W_{1\to 2} = -\int_{V_1}^{V_2} P(V,T)\,dV$$

to calculate $W_{1\text{-}2}$, we need to know ***P (V,T)*** for an adiabatic process

$$U = \frac{f}{2} N k_B T \quad \Rightarrow \quad dU = \frac{f}{2} N k_B dT = -PdV$$

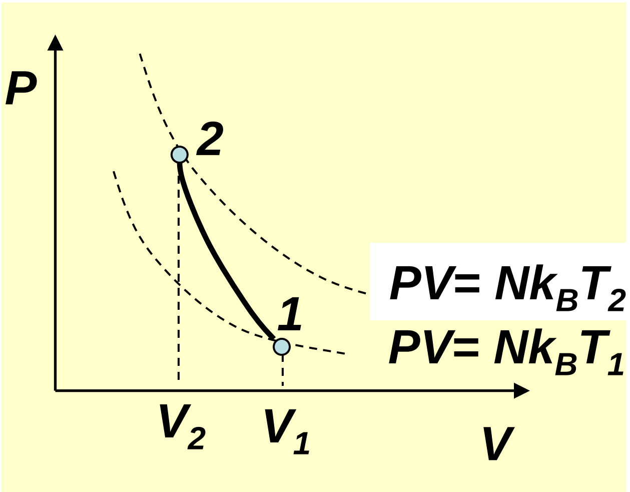
(***f*** – the # of "unfrozen" degrees of freedom)

$$PV = Nk_B T \quad \Rightarrow \quad PdV + VdP = Nk_B dT \qquad PdV + VdP = -\frac{2}{f} PdV \quad \Big| \div PV$$

$$\frac{dV}{V}\left(1+\frac{2}{f}\right) + \frac{dP}{P} = 0 \quad \Big| \int , \qquad \gamma = 1 + \frac{2}{f} \ \text{Adiabatic exponent} \qquad \gamma \int_{V_1}^{V} \frac{dV}{V} + \int_{P_1}^{P} \frac{dP}{P} = 0$$

$$\ln\left(\frac{V}{V_1}\right)^{\gamma} = \ln\left(\frac{P_1}{P}\right) \quad \Rightarrow \quad \boxed{PV^{\gamma} = P_1 V_1^{\gamma} = const}$$

Adiabatic Process in an Ideal Gas (cont.)



$$PV^{\gamma} = P_1V_1^{\gamma} = const$$

An adiabata is "steeper" than an isotherma: in an adiabatic process, the work flowing out of the gas comes at the expense of its thermal energy $\Rightarrow$ its temperature will decrease.

$$W_{1\to 2} = -\int_{V_1}^{V_2} P(V,T)dV = -\int_{V_1}^{V_2} \frac{P_1V_1^{\gamma}}{V^{\gamma}}dV = -P_1V_1^{\gamma}\frac{1}{-\gamma+1}V^{-\gamma+1}\Big|_{V_1}^{V_2}$$

$$= P_1V_1^{\gamma}\frac{1}{\gamma-1}\left(\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right)$$

$\gamma \Rightarrow$ 1+2/3≈1.67 (monatomic), 1+2/5 =1.4 (diatomic), 1+2/6 ≈1.33 (polyatomic)
(again, neglecting the vibrational degrees of freedom)

Prove $\quad W_{1\to 2} = \frac{f}{2}\Delta(PV) = \frac{f}{2}Nk_B\Delta T = \Delta U$

Summary of quasi-static processes of ideal gases

$$\Delta U \equiv U_f - U_i$$

Quasi-Static process	**ΔU**	**Q**	**W**	Ideal gas law
isobaric **(ΔP=0)**	$\Delta U = \frac{f}{2} N k_B \Delta T = \frac{f}{2} P \Delta V$	$\frac{f+2}{2} P \Delta V$	$-P \Delta V$	$\frac{V_i}{T_i} = \frac{V_f}{T_f}$
isochoric **(ΔV=0)**	$\Delta U = \frac{f}{2} N k_B \Delta T = \frac{f}{2} (\Delta P) V$	$\frac{f}{2} (\Delta P) V$	0	$\frac{P_i}{T_i} = \frac{P_f}{T_f}$
isothermal **(ΔT=0)**	0	$-W$	$-N k_B T \ln \frac{V_f}{V_i}$	$P_i V_i = P_f V_f$
adiabatic **(Q=0)**	$\Delta U = \frac{f}{2} N k_B \Delta T = \frac{f}{2} \Delta (PV)$	0	ΔU	$P_i V_i^{\gamma} = P_f V_f^{\gamma}$

Problem

Imagine that we rapidly compress a sample of air whose initial pressure is 10^5 Pa and temperature is 22^0C (= 295 K) to a volume that is a quarter of its original volume (e.g., pumping bike's tire). What is its final temperature?

Rapid compression – approx. ***adiabatic***, no time for the energy exchange with the environment due to thermal conductivity

$$\left.\begin{aligned} P_1V_1 &= Nk_BT_1 \\ P_2V_2 &= Nk_BT_2 \\ P_1V_1^{\gamma} &= P_2V_2^{\gamma} \end{aligned}\right\} \quad P_2 = \frac{P_1V_1^{\gamma}}{V_2^{\gamma}} \qquad \frac{P_1V_1^{\gamma}}{V_2^{\gamma-1}} = Nk_BT_2 = \frac{P_1V_1}{T_1}T_2 \quad \Rightarrow \quad \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{T_2}{T_1}$$

For adiabatic processes: $$\boxed{T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} = const}$$

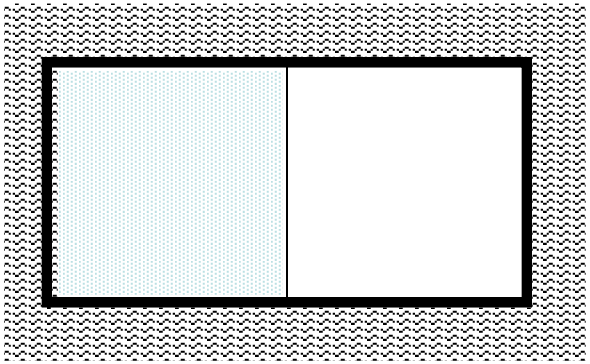
also $\quad P^{\gamma-1}/T^{\gamma} = const$

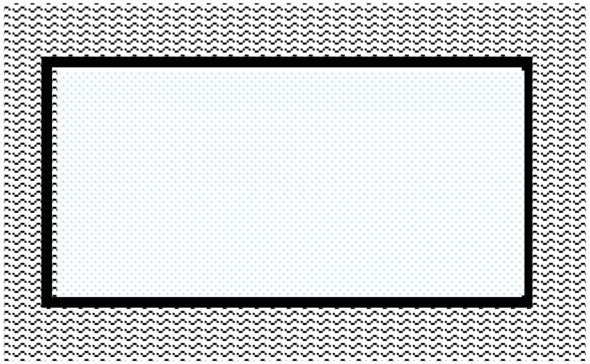
$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 295K\times 4^{0.4} \approx 295K\times 1.74 \approx 514K$$

- poor approx. for a bike pump, works better for diesel engines

Non-equilibrium Adiabatic Processes

Free expansion





1. $TV^{\gamma-1} = const$ **V** – increases
   $\Rightarrow$ **T** – decreases (cooling)

2. On the other hand, **Δ*U* = *Q* + *W* = 0**
   U* ~ *T $\Rightarrow$ ***T*** – unchanged
   (agrees with experimental finding)

Contradiction – because approach #1 cannot be justified – violent expansion of gas ***is not*** a quasi-static process. ***T*** must remain the same.

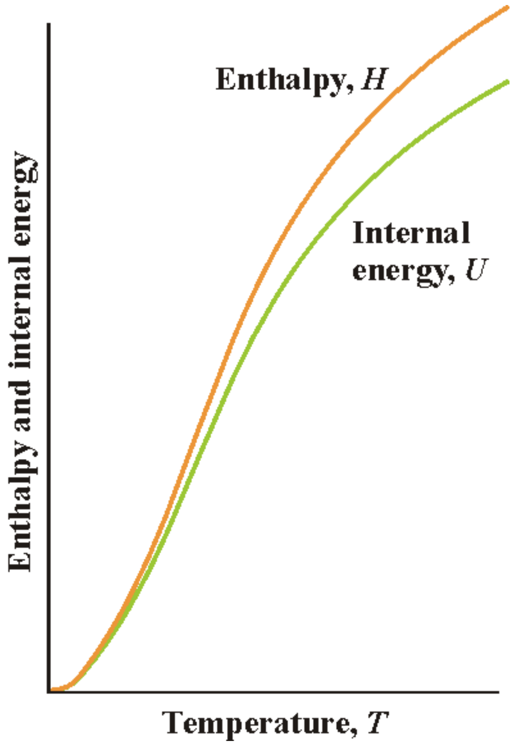
$$TV^{\gamma-1} = const$$ - applies only to ***quasi-equilibrium*** processes !!!

The Enthalpy

Isobaric processes (***P* = const**):

$$dU = Q - P\Delta V = Q - \Delta(PV) \quad \Rightarrow \quad Q = \Delta U + \Delta(PV)$$

$$\Rightarrow \quad \boxed{H \equiv U + PV \quad - \quad \textit{the enthalpy}}$$



The enthalpy is a ***state function***, because ***U***, ***P***, and ***V*** are state functions. In isobaric processes, the energy received by a system by heating equals to the change in enthalpy.

isochoric: $Q = \Delta U$

isobaric: $Q = \Delta H$

in both cases, ***Q*** does not depend on the path from 1 to 2.

Consequence: the energy released (absorbed) in chemical reactions at constant volume (pressure) depends only on the initial and final states of a system.

The enthalpy of an ideal gas: $H = U + PV = \frac{f}{2} N k_B T + N k_B T = \left(\frac{f}{2} + 1\right) N k_B T$

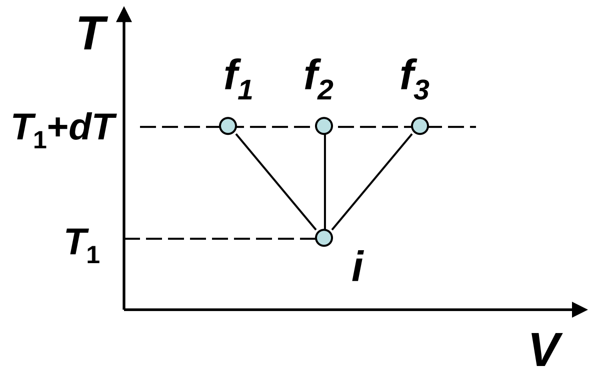
(depends on ***T*** only)

Heat Capacity

The heat capacity of a system - the amount of energy transfer due to heating required to produce a unit temperature rise in that system

$$C \equiv \frac{\delta Q}{\Delta T}$$

C *is NOT a state function* (since ***Q*** is not a state function) – it depends on the path between two states of a system $\Rightarrow$



(isothermic – ***C*** = ∞, adiabatic – ***C*** = 0)

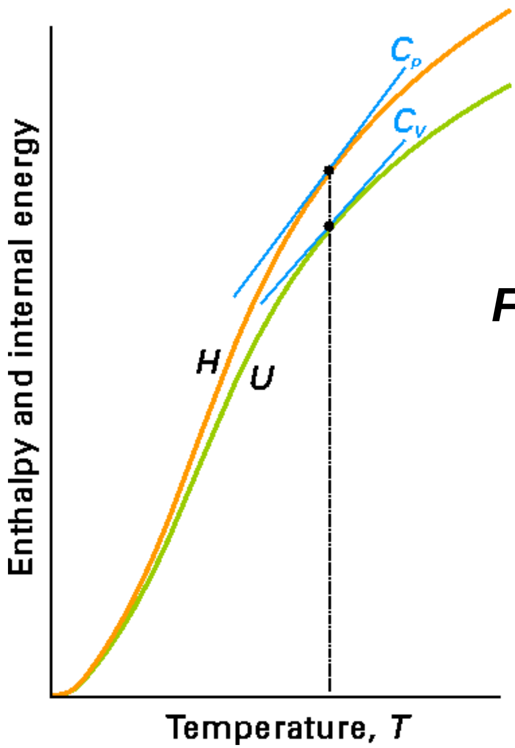
The specific heat capacity $c \equiv \frac{C}{m}$

C_V and C_P

$$C = \frac{\delta Q}{dT} = \frac{dU + PdV}{dT}$$

V = const → $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ the heat capacity at constant volume

P = const → $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ the heat capacity at constant pressure



To find C_P ***and*** C_V, we need $f\,(P,V,T) = 0$ and $U = U\,(V,T)$

For an ideal gas $U = \frac{f}{2} N k_B T$ $\quad H = \left(\frac{f}{2} + 1\right) N k_B T$

$$C_V = \frac{f}{2} N k_B = \frac{f}{2} nR$$

$$C_P = \left(\frac{f}{2} + 1\right) nR$$

# of moles

For one mole of a monatomic ideal gas:

$$C_V = \frac{3}{2} R \qquad C_P = \frac{5}{2} R$$

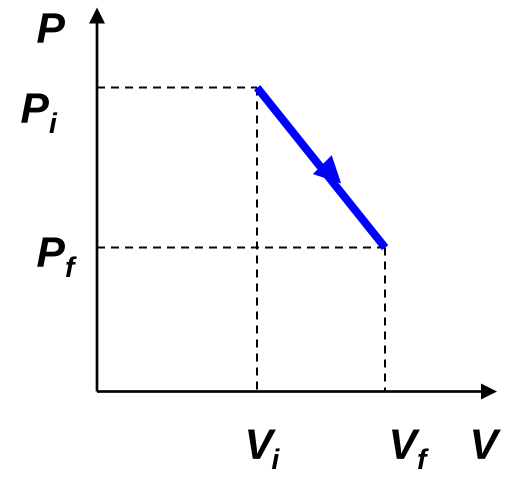
Another Problem

During the ascent of a meteorological helium-gas filled balloon, its volume increases from V_i = 1 m^3 to V_f = 1.8 m^3, and the pressure inside the balloon decreases from 1 bar (=10^5 N/m^2) to 0.5 bar. Assume that the pressure changes linearly with volume between V_i and V_f.

(a) If the initial ***T*** is 300K, what is the final ***T***?

(b) How much work is done ***by*** the gas in the balloon?

(c) How much "heat" does the gas absorb, if any?



$$P(V) = -0.625\,\text{bar/m}^3 \times V + 1.625\,\text{bar}$$

(a) $PV = Nk_B T \qquad T = \dfrac{PV}{Nk_B} \qquad T_f = T_i \dfrac{P_f V_f}{P_i V_i} = 300\text{K}\,\dfrac{0.5\text{bar}\times 1.8\text{m}^3}{1\text{bar}\times 1\text{m}^3} = 270\text{K}$

(b) $\delta W_{ON} = -\int_{V_i}^{V_f} P(V)dV$ - work done **on** a system $\quad \delta W_{BY} = \int_{V_i}^{V_f} P(V)dV$ - work done **by** a system

$$\boxed{\delta W_{ON} = -\delta W_{BY}} \quad \delta W_{BY} = \int_{V_i}^{V_f} P(V)dV = \left(0.5\times 0.8\text{bar}\cdot\text{m}^3 + 0.5\times 0.4\text{bar}\cdot\text{m}^3\right) = 0.6\text{bar}\cdot\text{m}^3 = 6\cdot 10^4\,\text{J}$$

(c) $\Delta U = \delta Q + \delta W_{ON}$

$$\delta Q = \Delta U - \delta W_{ON} = \frac{3}{2}Nk_B\left(T_f - T_i\right) - W_{ON} = \frac{3}{2}P_i V_i\left(\frac{T_f}{T_i} - 1\right) + \delta W_{BY} = 1.5\cdot 10^5\,\text{J}\times(-0.1) + 6\cdot 10^4\,\text{J} = 4.5\cdot 10^4\,\text{J}$$

Worksheet time!

Download Worksheet 3 from the Moodle page and work on it.