

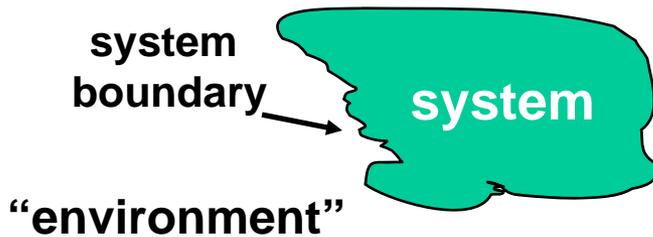
Lecture 2 The First Law of Thermodynamics (Ch.1)

Outline:

- 1. Internal Energy, Work, Heating**
- 2. Energy Conservation – the First Law**
- 3. Quasi-static processes**
- 4. Enthalpy**
- 5. Heat Capacity**

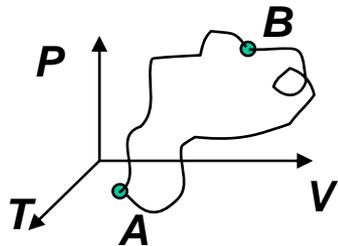
Internal Energy

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).

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

U depends on the kinetic energy of particles in a system and an average inter-particle distance ($\sim V^{1/3}$) – 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 $P = \text{const}$?

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

- 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:

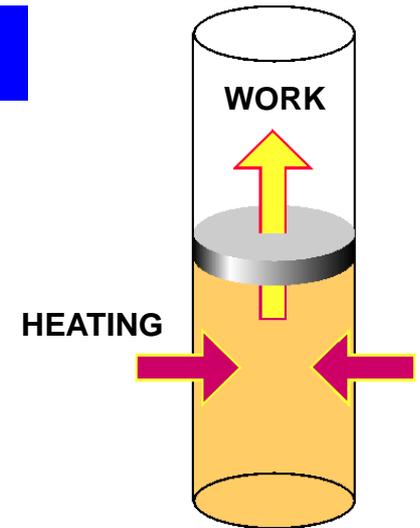
- Q - energy flow between a system and its environment due to ΔT across a boundary and a finite thermal conductivity of the boundary

– **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.

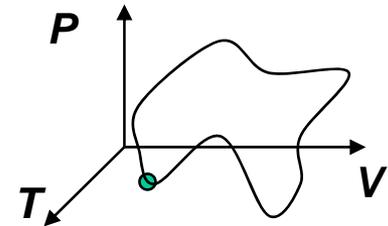
$$\Delta U = Q + W$$

conservation of energy.

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

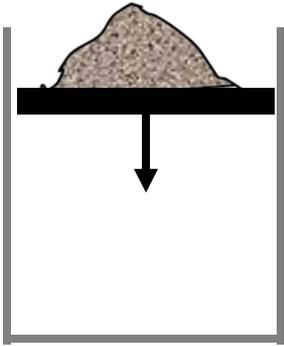
For a cyclic process ($U_i = U_f$) $\Rightarrow Q = -W$.

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



An equivalent formulation:

Perpetual motion machines of the first type do not exist.



Quasi-Static Processes

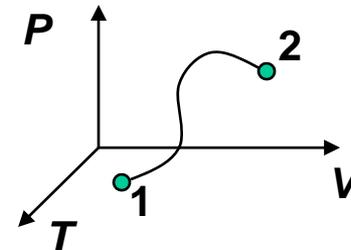
Quasi-static (quasi-equilibrium) processes – sufficiently slow processes, *any* intermediate state can be considered as an equilibrium state (the macroparameters are well-defined for all intermediate states).

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**.

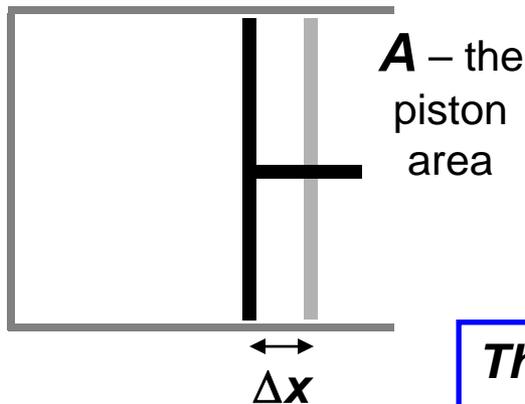
Examples of quasi-equilibrium processes:

- isochoric: $V = \text{const}$
- isobaric: $P = \text{const}$
- isothermal: $T = \text{const}$
- 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.



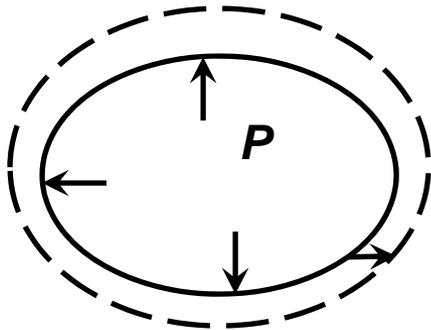
Work



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

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

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

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

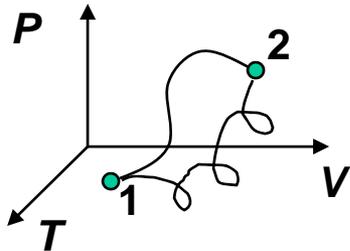
$$dU = Q - PdV$$

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

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

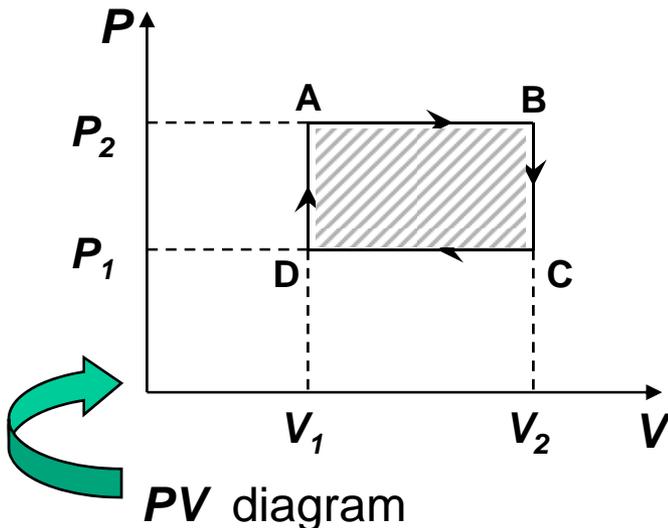
- we can bring the system from state 1 to state 2 along infinite # of paths, and for each path $\mathbf{P(T, V)}$ will be different.



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 \Rightarrow thus, Q is not a state function either.



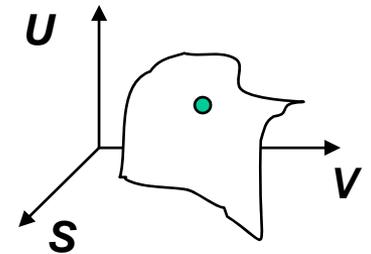
$$\begin{aligned} W_{net} &= W_{AB} + W_{CD} = -P_2(V_2 - V_1) - P_1(V_1 - V_2) \\ &= -(P_2 - P_1)(V_2 - V_1) < 0 \end{aligned}$$

- 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.

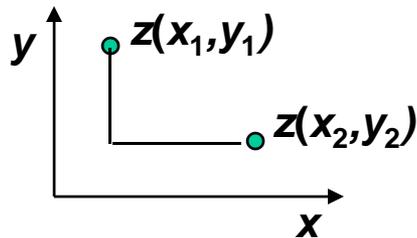
Comment on State Functions

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 (δQ and δW).



$$dU = T dS - P dV \quad - \text{an exact differential}$$



$dz = A_x(x, y)dx + A_y(x, y)dy$ - 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: $\frac{\partial A_x(x, y)}{\partial y} = \frac{\partial A_y(x, y)}{\partial x}$

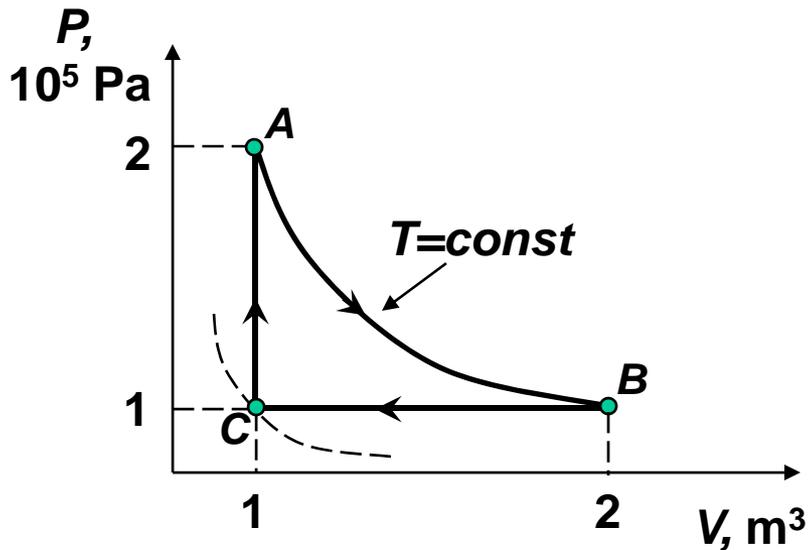
If this condition holds:

$$A_x(x, y) = \frac{\partial z(x, y)}{\partial x} \quad A_y(x, y) = \frac{\partial z(x, y)}{\partial y} \quad dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

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 ΔU for each step.

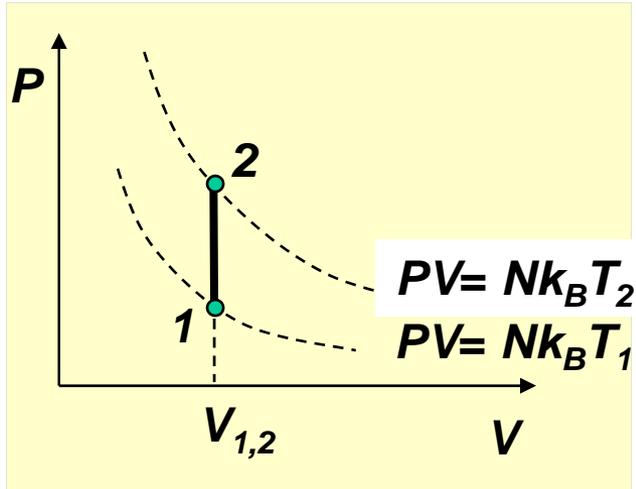


Step	Q	W	ΔU
A \rightarrow B	+	--	0
B \rightarrow C	--	+	--
C \rightarrow A	+	0	+

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

$$PV = N k_B T$$

Quasistatic Processes in an Ideal Gas



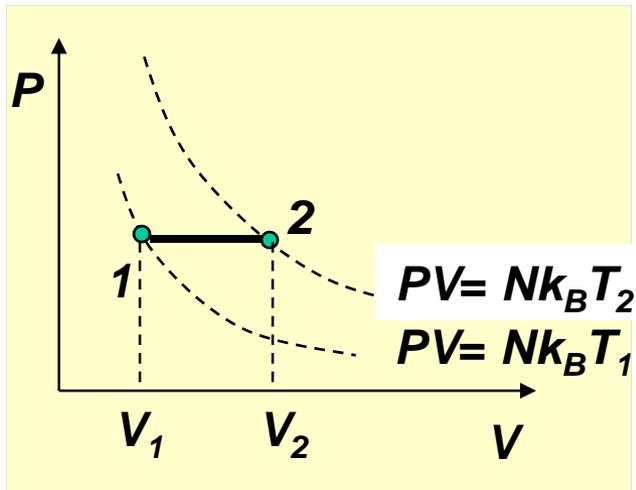
● isochoric ($V = \text{const}$)

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

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

(see the last slide)

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



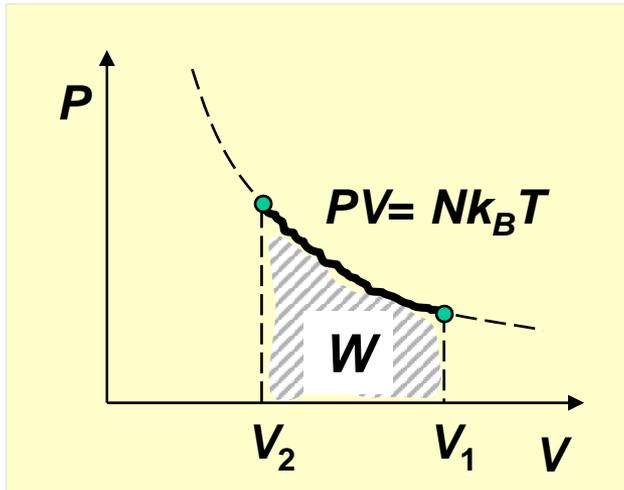
● isobaric ($P = \text{const}$)

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

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

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

Isothermal Process in an Ideal Gas



● isothermal ($T = \text{const}$):

$$dU = 0$$

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

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

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

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

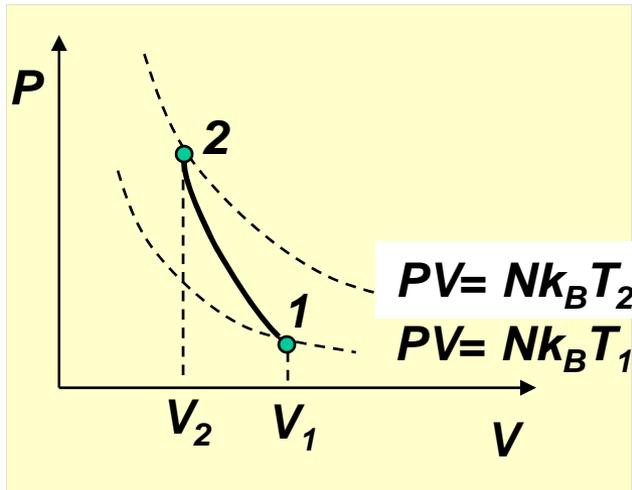
$W_{i \rightarrow f} < 0$ if $V_i < V_f$ (expansion)

Adiabatic Process in an Ideal Gas

● **adiabatic** (*thermally isolated system*)

$$Q_{1 \rightarrow 2} = 0 \quad dU = W_{1 \rightarrow 2}$$

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.



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

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

$$U = \frac{f}{2} Nk_B T \Rightarrow dU = \frac{f}{2} Nk_B dT = -PdV$$

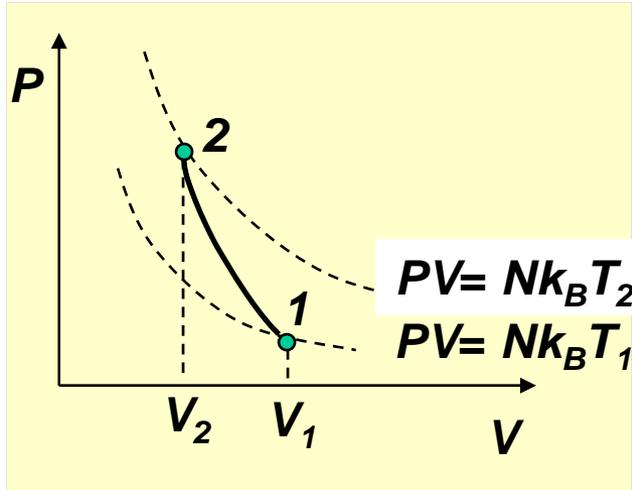
(f – the # of “unfrozen” degrees of freedom)

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

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

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

Adiabatic Process in an Ideal Gas (cont.)



$$PV^\gamma = P_1 V_1^\gamma = \text{const}$$

An adiabat is “steeper” than an isotherm: in an adiabatic process, the work flowing out of the gas comes at the expense of its thermal energy \Rightarrow its temperature will decrease.

$$\begin{aligned} W_{1 \rightarrow 2} &= - \int_{V_1}^{V_2} P(V, T) dV = - \int_{V_1}^{V_2} \frac{P_1 V_1^\gamma}{V^\gamma} dV = - P_1 V_1^\gamma \frac{1}{-\gamma + 1} V^{-\gamma+1} \Big|_{V_1}^{V_2} \\ &= P_1 V_1^\gamma \frac{1}{\gamma - 1} \left(\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right) \end{aligned}$$

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

Prove
$$W_{1 \rightarrow 2} = \frac{f}{2} \Delta(PV) = \frac{f}{2} N k_B \Delta T = \Delta U$$

Summary of quasi-static processes of ideal gas

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

Quasi-Static process	ΔU	Q	W	Ideal gas law
● isobaric ($\Delta P=0$)	$\Delta U = \frac{f}{2} Nk_B \Delta T = \frac{f}{2} P \Delta V$	$\frac{f+2}{2} P \Delta V$	$-P \Delta V$	$\frac{V_i}{T_i} = \frac{V_f}{T_f}$
● isochoric ($\Delta V=0$)	$\Delta U = \frac{f}{2} Nk_B \Delta T = \frac{f}{2} (\Delta P) V$	$\frac{f}{2} (\Delta P) V$	0	$\frac{P_i}{T_i} = \frac{P_f}{T_f}$
● isothermal ($\Delta T=0$)	0	$-W$	$-Nk_B T \ln \frac{V_f}{V_i}$	$P_i V_i = P_f V_f$
● adiabatic ($Q=0$)	$\Delta U = \frac{f}{2} Nk_B \Delta T = \frac{f}{2} \Delta(PV)$	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°C ($= 295$ 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

$$\left. \begin{array}{l} P_1 V_1 = N k_B T_1 \\ P_2 V_2 = N k_B T_2 \\ P_1 V_1^\gamma = P_2 V_2^\gamma \end{array} \right\} P_2 = \frac{P_1 V_1^\gamma}{V_2^\gamma} \quad \frac{P_1 V_1^\gamma}{V_2^{\gamma-1}} = N k_B T_2 = \frac{P_1 V_1}{T_1} T_2 \Rightarrow \left(\frac{V_1}{V_2} \right)^{\gamma-1} = \frac{T_2}{T_1}$$

For adiabatic processes: $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} = \text{const}$

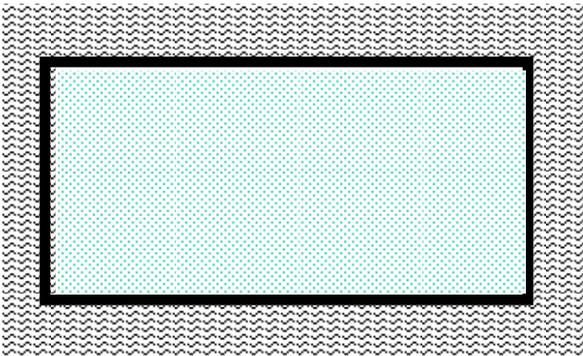
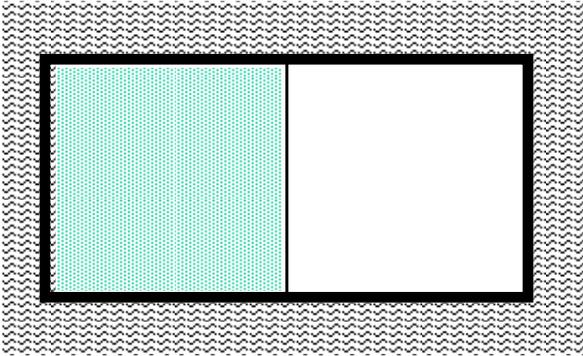
also $P^{\gamma-1} / T^\gamma = \text{const}$

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

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

Non-equilibrium Adiabatic Processes

Free expansion



1. $TV^{\gamma-1} = \text{const}$ V – increases
 $\Rightarrow T$ – decreases (cooling)
2. On the other hand, $\Delta U = Q + W = 0$
 $U \sim T \Rightarrow T$ – 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.

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

The Enthalpy

Isobaric processes ($P = \text{const}$):

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

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

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.

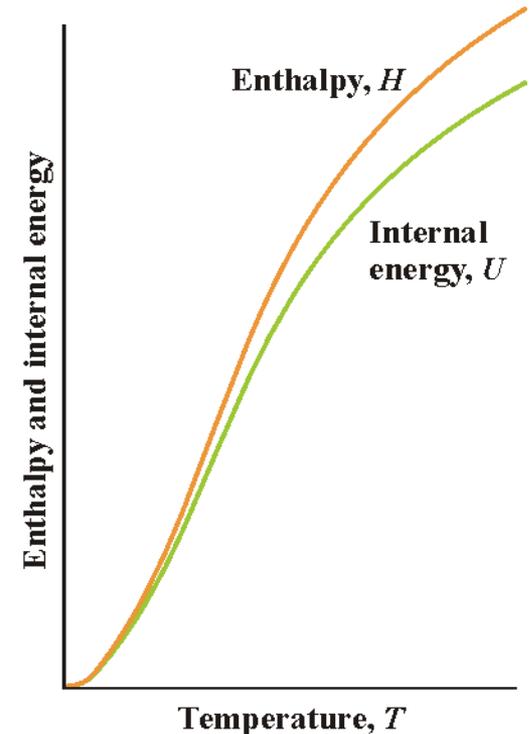
isochoric:

$$\boxed{Q = \Delta U}$$

isobaric:

$$\boxed{Q = \Delta H}$$

} 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.

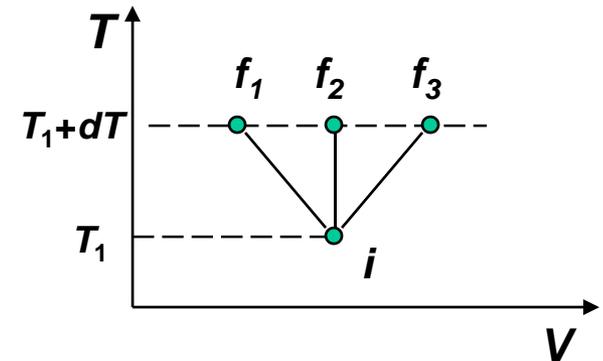
The enthalpy of an ideal gas: $H = U + PV = \frac{f}{2} Nk_B T + Nk_B T = \left(\frac{f}{2} + 1 \right) Nk_B T$
(depends on T only)

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 – $C = \infty$, 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 →

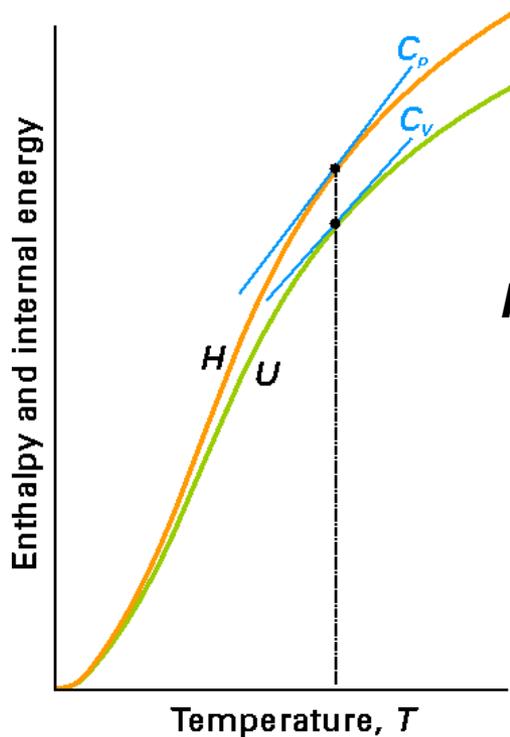
$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

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 $U = \frac{f}{2} Nk_B T$ $H = \left(\frac{f}{2} + 1 \right) Nk_B T$

$$C_V = \frac{f}{2} Nk_B = \frac{f}{2} nR$$

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

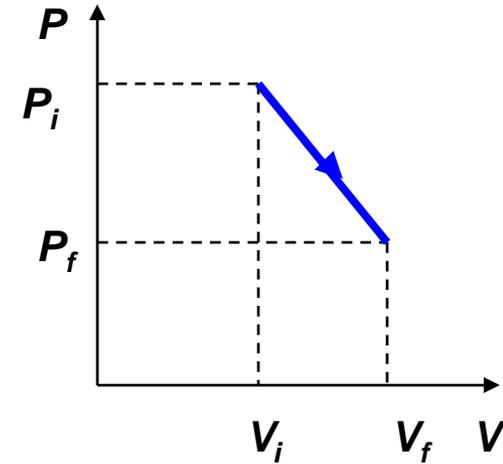
of moles

For one mole of a monatomic ideal gas:

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

Another Problem

During the ascent of a meteorological helium-gas filled balloon, its volume increases from $V_i = 1 \text{ m}^3$ to $V_f = 1.8 \text{ m}^3$, and the pressure inside the balloon decreases from 1 bar ($=10^5 \text{ N/m}^2$) 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) $PV = Nk_B T \quad T = \frac{PV}{Nk_B} \quad T_f = T_i \frac{P_f V_f}{P_i V_i} = 300\text{K} \frac{0.5\text{bar} \times 1.8\text{m}^3}{1\text{bar} \times 1\text{m}^3} = 270\text{K}$

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

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

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

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