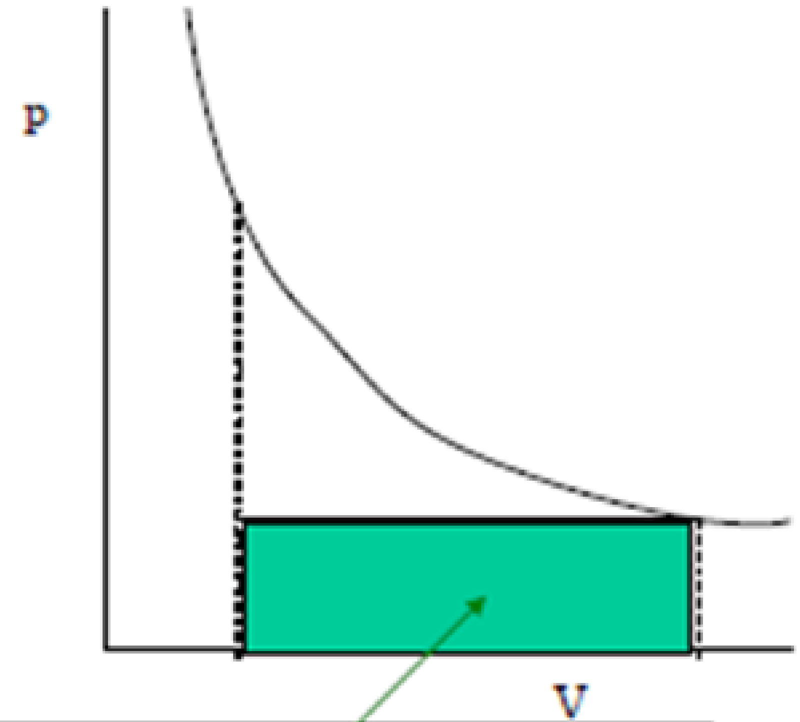
The First Law of Thermodynamics

Rita Prasetyowati
FMIPA UNY
2011

Reversible work is maximum work that can be done by gas: if p_{ex} were any larger, gas would be compressed!



path #	1	2	3
process	$p_{ex} = 0$ vacuum	$p_{ex} = 2$ atm	$p_{ex} \sim p$ reversible
work (J)	0	–607.9	–1124

expressions for pV work

General: $dw = -p_{ex}\,dV$

If p_{ex} is constant: $w = -p_{ex}\,\Delta V$

If the path is reversible, $w = -\int p\,dV$

Ideal gas expanding reversibly at constant temperature

$$w_{rev} = -nRT\ln(V_2/V_1)$$

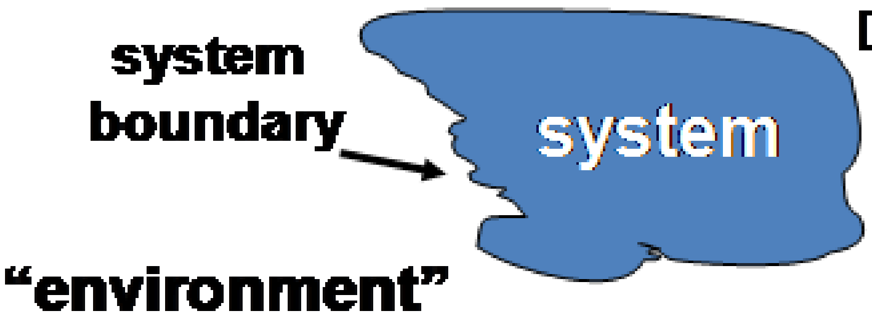
For an ideal gas, if $dT = 0$, then $p_1V_1 = p_2V_2$.

thus $V_2/V_1 = p_1/p_2$

so $w_{rev} = -nRT\ln(p_1/p_2) = +nRT\ln(p_2/p_1)$

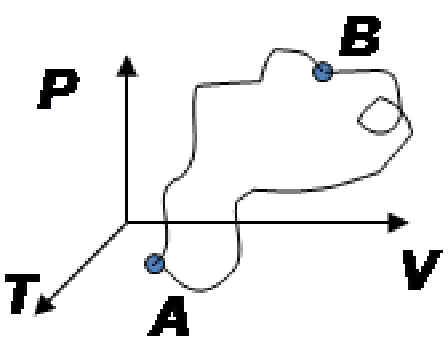
Internal Energy

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?

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



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)

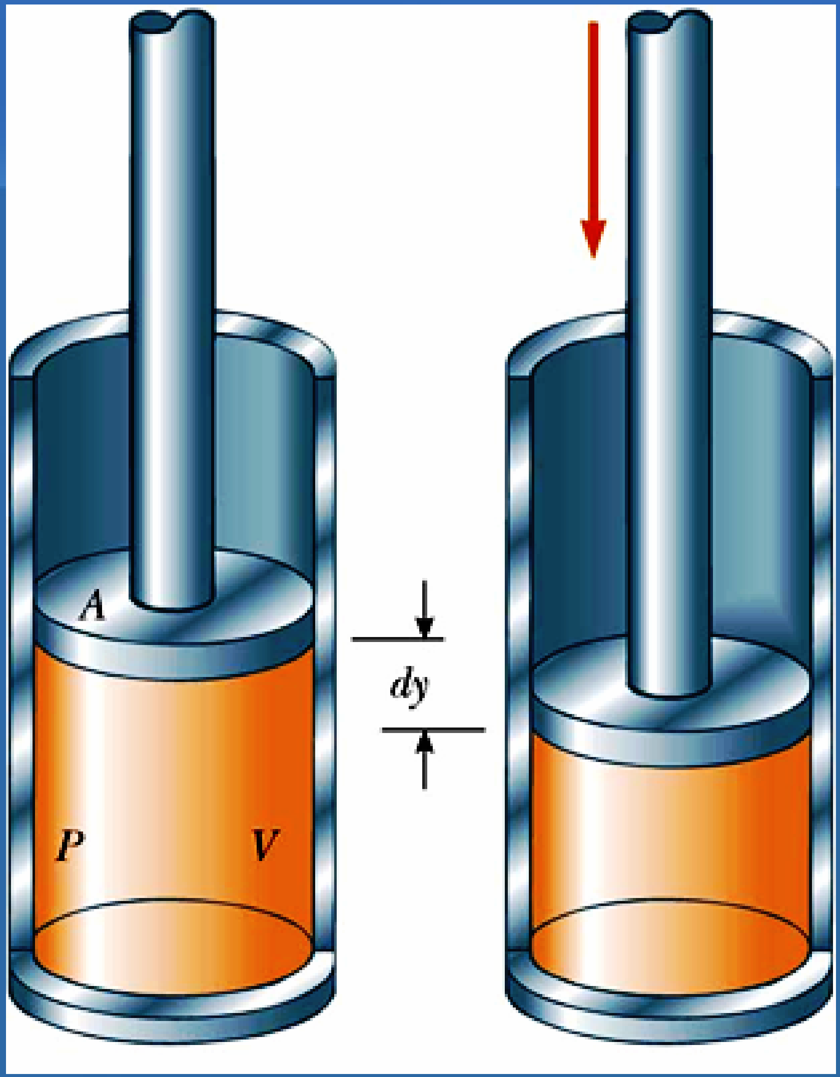
How does the internal energy of air in this (not-air-tight) room change with *T* if the external *P = const*?

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

- 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 Heat

- ***Work*** can be done on a **deformable system**, such as a gas
- A force is applied to ***slowly compress*** the gas in a cylinder with a moveable piston
  - The ***compression is slow*** enough for all the system **to remain** essentially ***in thermal equilibrium***
  - This is said to occur **quasi-statically**



Work, 2

- The piston is pushed downward by a force ***F*** through a displacement of ***dr*** :

$$dW = \mathbf{F} \cdot d\mathbf{r} = -F\hat{\mathbf{j}} \cdot dy\hat{\mathbf{j}} = -Fdy = -PAdy$$

- ***Ady*** is the change in volume of the gas, ***dV***
- Therefore, the work done ***ON*** the gas is

$$dW = -P\,dV$$

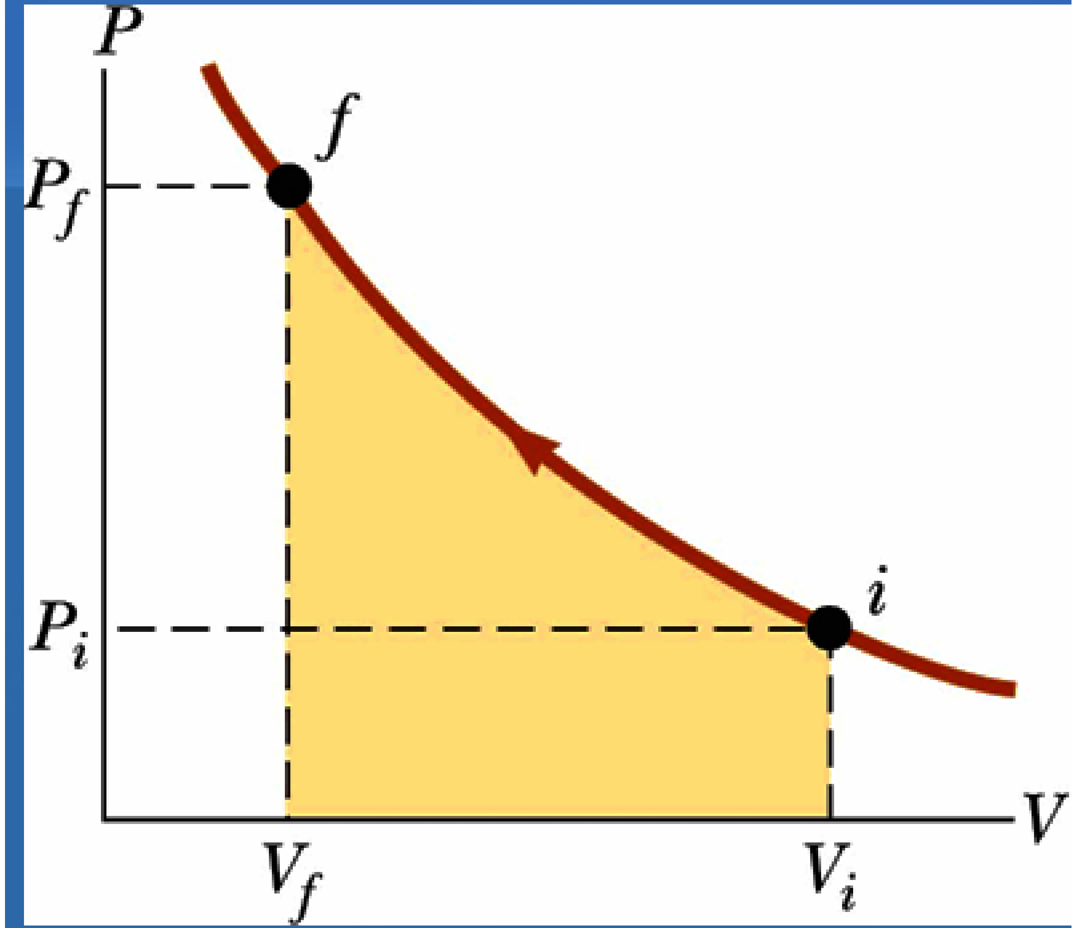
Work, 3

- Interpreting ***dW = −P dV***
  - If the gas is ***compressed***, ***dV*** is ***negative*** and the ***work*** done on the gas is ***positive***
  - If the gas ***expands***, ***dV*** is ***positive*** and the ***work*** done on the gas is ***negative***
  - If the ***volume remains constant***, the ***work done is zero***
- The total work done is:

$$W = -\int_{V_i}^{V_f} P\, dV$$

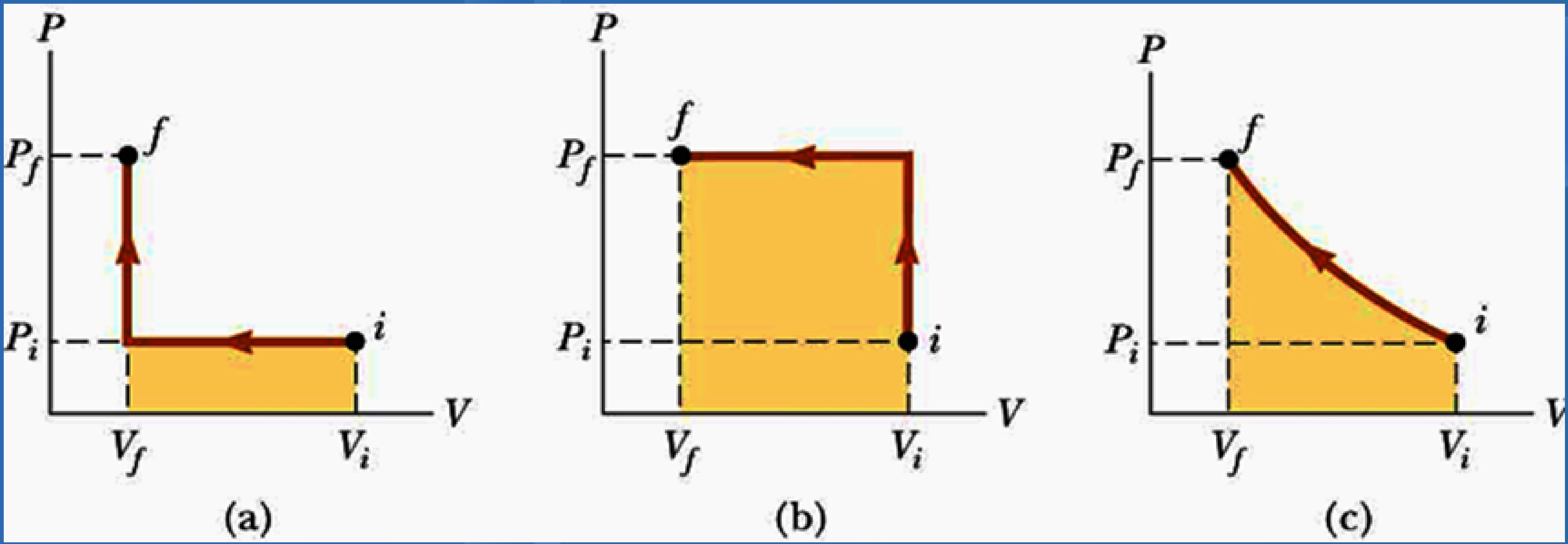
PV Diagrams

- Used when the ***pressure*** and ***volume*** are known at each step of the process
- The state of the gas at each step can be plotted on a graph called a ***PV* diagram**
  - This allows us to visualize the process through which the gas is progressing
- The curve is called the ***path***



- ***The work*** done on a gas in a quasi-static process that takes the gas from an **initial state** to a **final state** is the ***negative of the area*** under the curve on the ***PV*** **diagram**, evaluated between the initial and final states
  - This is true whether or not the pressure stays constant
  - The work done ***does*** depend on the path taken

Work Done By Various Paths



- Each of these processes has the ***same initial*** and ***final states***, but ***different areas***
- **The work done differs in each process**
- **The work done depends on the path**

- Work
- Internal energy

1

- The first law of thermodynamics
- Heat flow
- Quasi –static processes

2

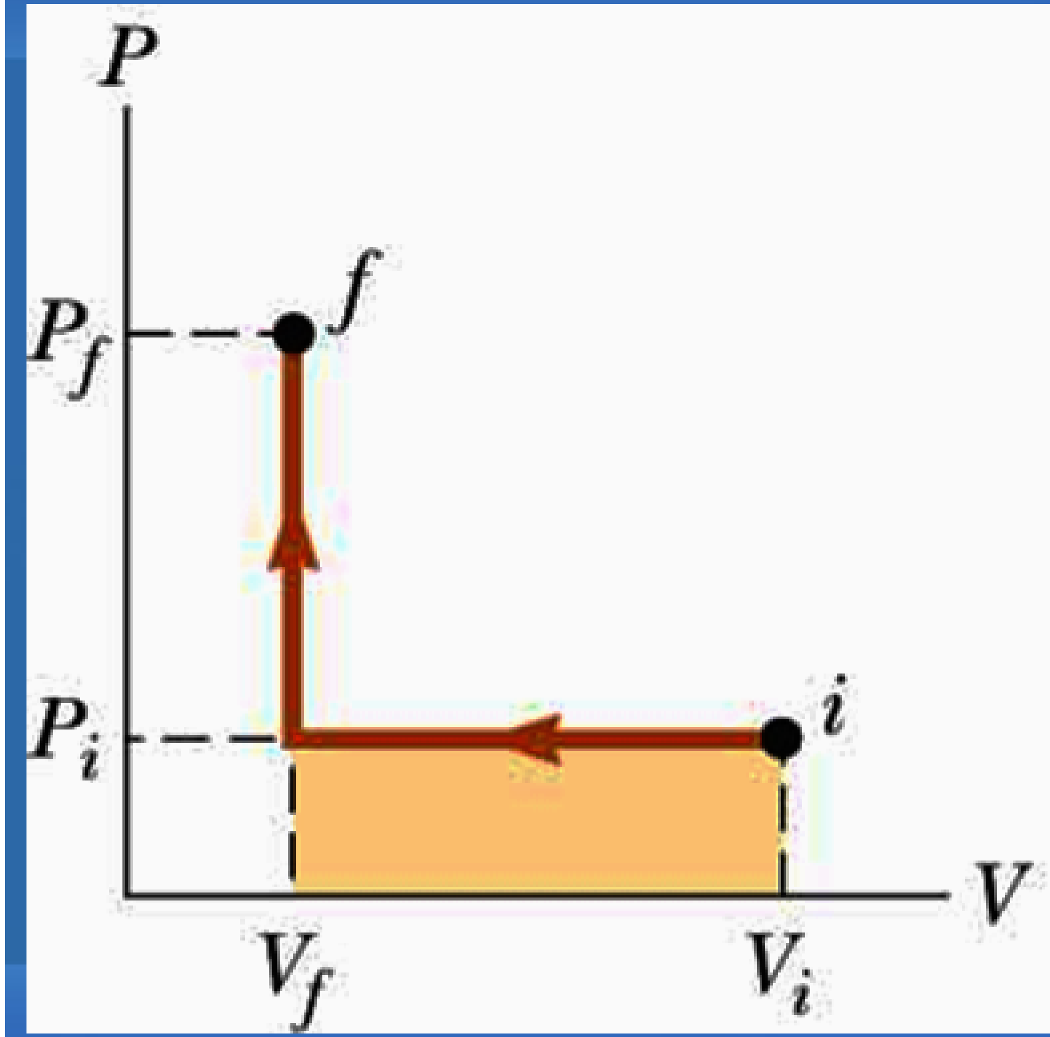
- Enthalpy
- Heat Capacity

3

Work From a *PV* Diagram 1

- The ***volume*** of the gas is first ***reduced*** from V_i to V_f at ***constant pressure*** P_i
- Next, the pressure ***increases*** from P_i to P_f by heating at ***constant volume*** V_f

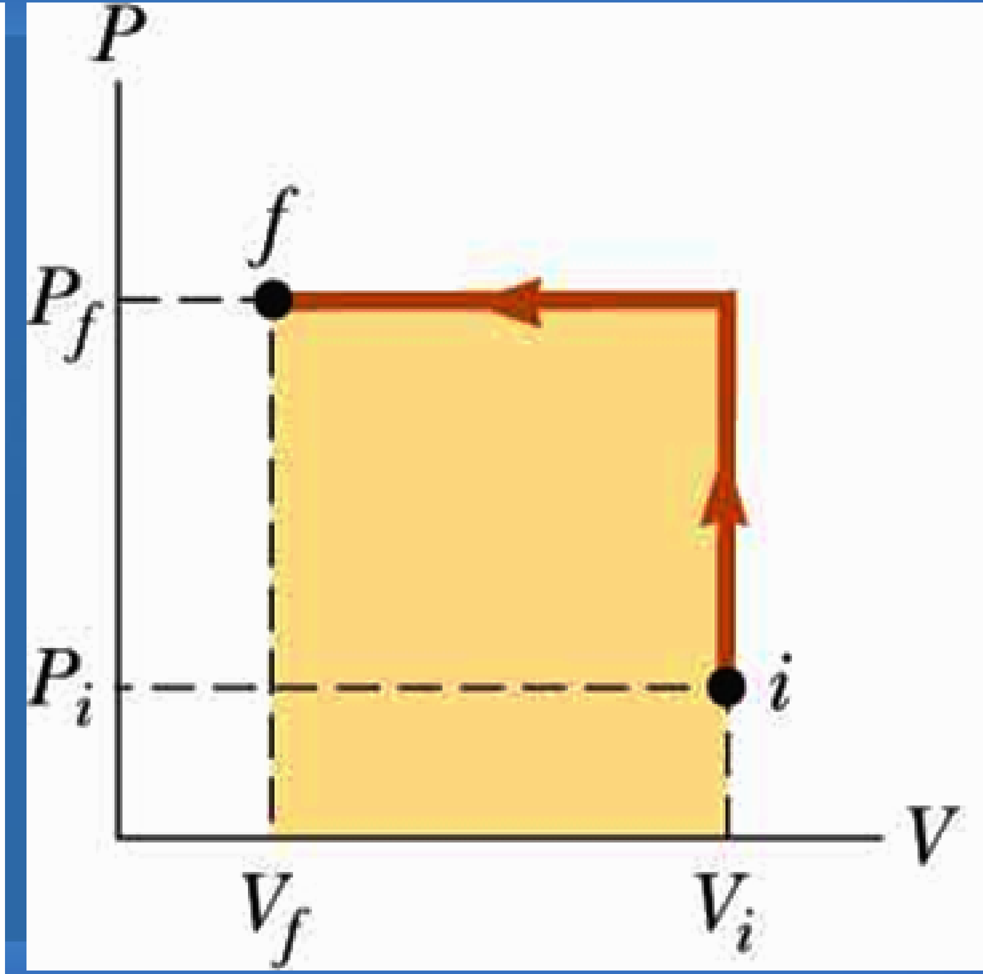
$$W = -P_i(V_f - V_i)$$



Work From a *PV* Diagram, 2

- The ***pressure*** of the gas is ***increased*** from P_i to P_f at a ***constant volume***
- The ***volume*** is ***decreased*** from V_i to V_f

$$W = -P_f(V_f - V_i)$$

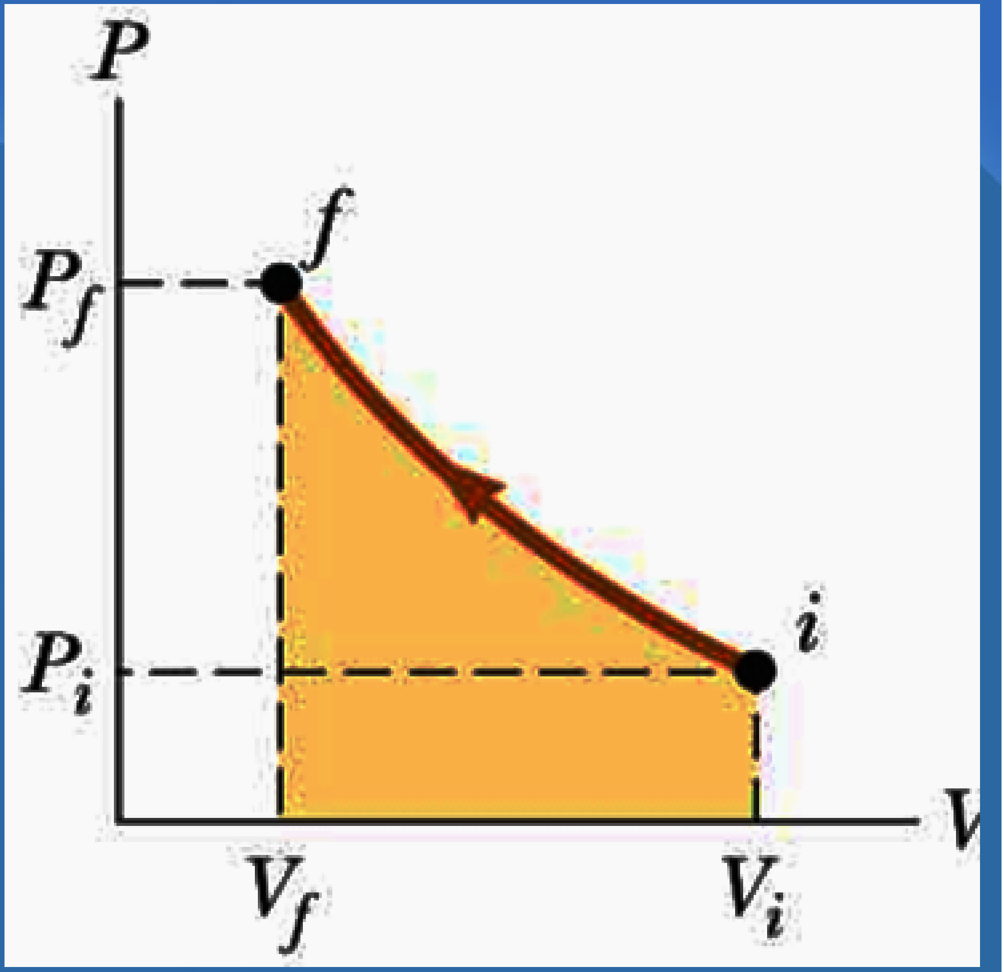


Work From a *PV* Diagram, 3

- The ***pressure*** and the ***volume continually change***
- The work is some intermediate value between

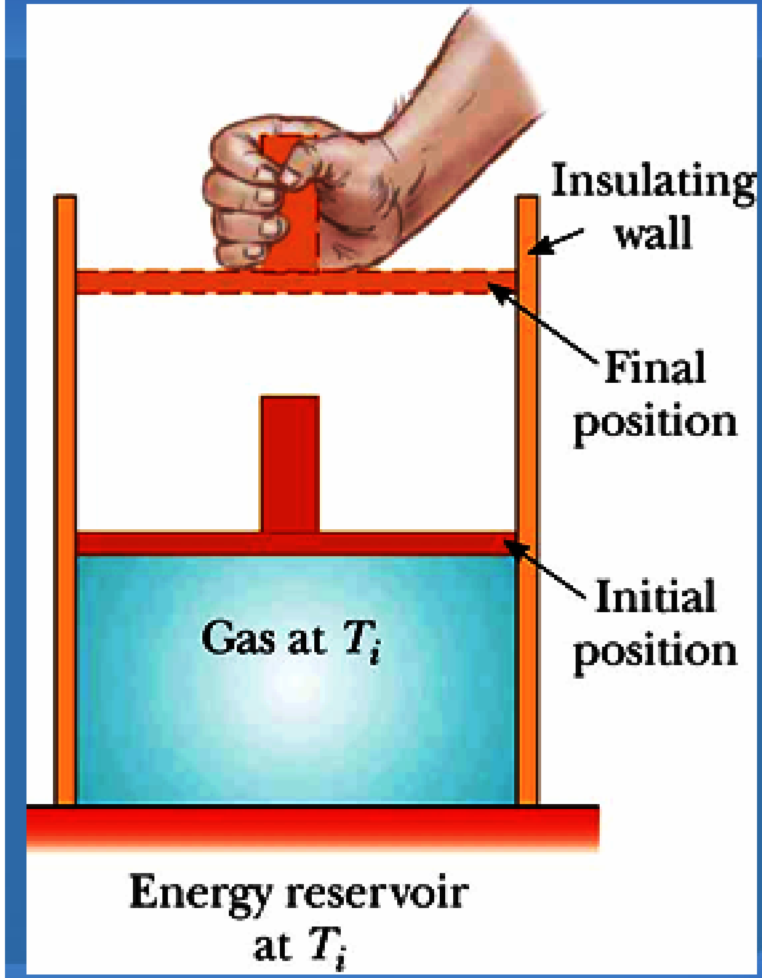
$-P_f(V_f - V_i)$ and $-P_i(V_f - V_i)$

- To evaluate the actual amount of work, the function ***P(V)*** ***must be known***, then apply calculus (***integration***)



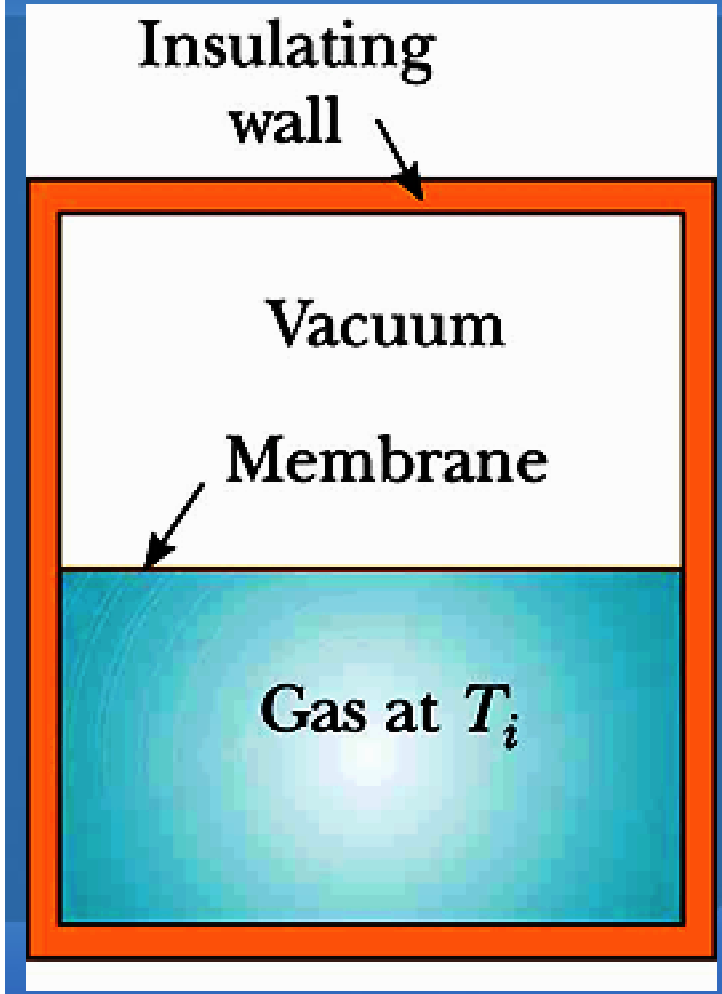
Heat Transfer, Example 1

- ***The energy transfer (Q)*** into or out of a system also **depends on the process**
- The gas at temperature T_i expands slowly while ***absorbing energy*** from a reservoir in order to maintain a ***constant temperature*** (T_i)
- The **energy reservoir** is a source of energy that is considered to be so great that a finite transfer of energy does not change its temperature
- ***The piston is pushed upward, the gas is doing work on the piston***



Heat Transfer, Example 2

- ***Gas expands*** rapidly into an evacuated region after a membrane is broken
- Gas has the ***same initial*** **volume**, **temperature** and **pressure** as the previous example
- The ***final states*** are also **identical**
- ***No energy is transferred*** by heat through the insulating wall
- ***No work is done*** by the gas expanding into the vacuum

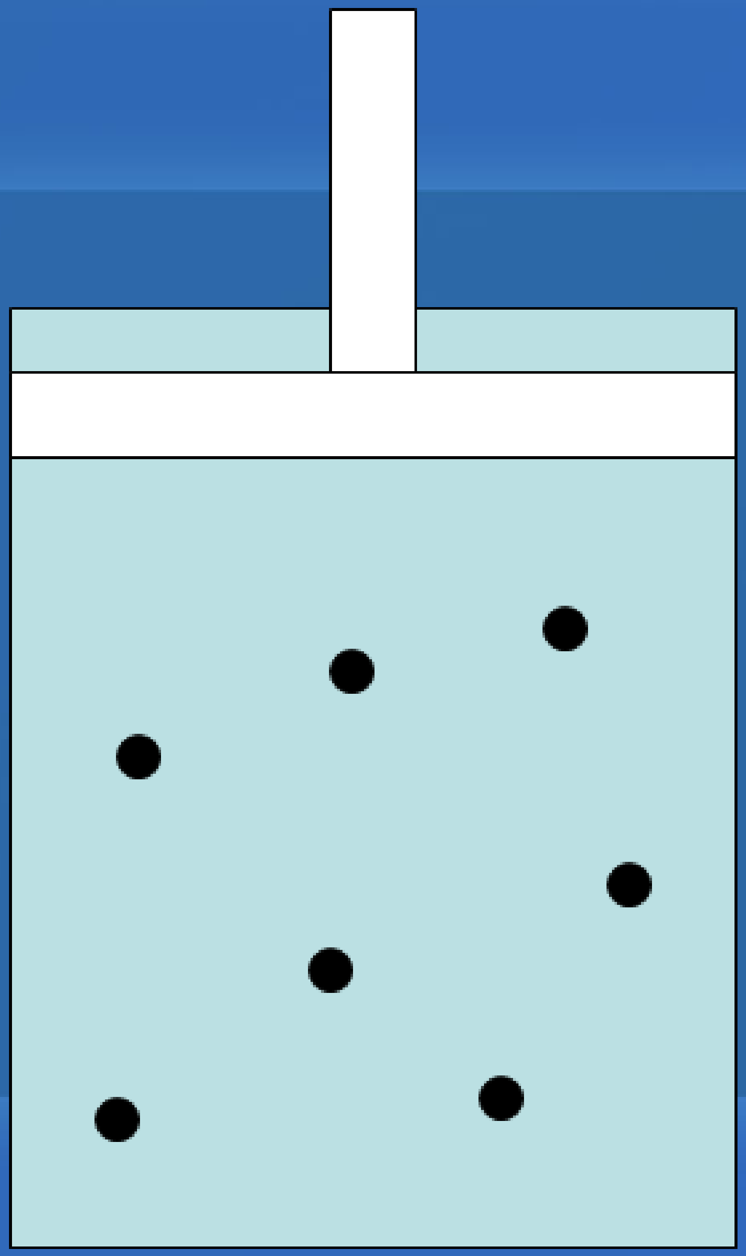


Heat Transfer, summary

- *Energy transfers by heat, like the work done, depend on the initial, final, and intermediate states of the system*
- *Both work and heat depend on the path taken*
- *Neither can be determined solely by the end points of a thermodynamic process*

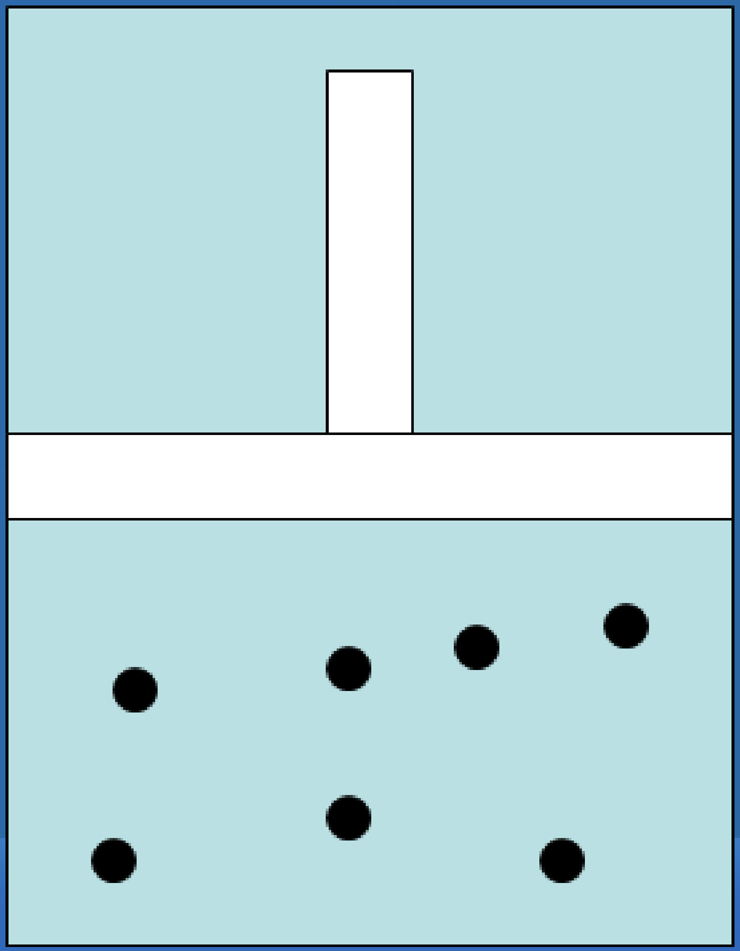
1st Law of Thermodynamics

- Consider an example system of a piston and cylinder with an enclosed dilute gas characterized by P,V,T & n.



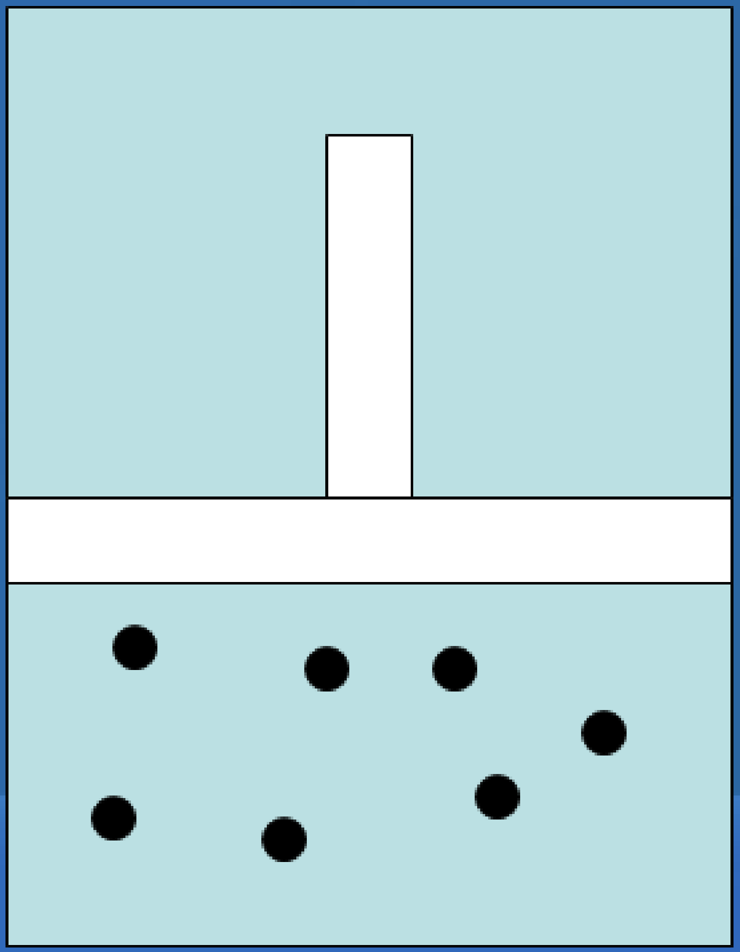
1st Law of Thermodynamics

- What happens to the gas if the piston is moved inwards?



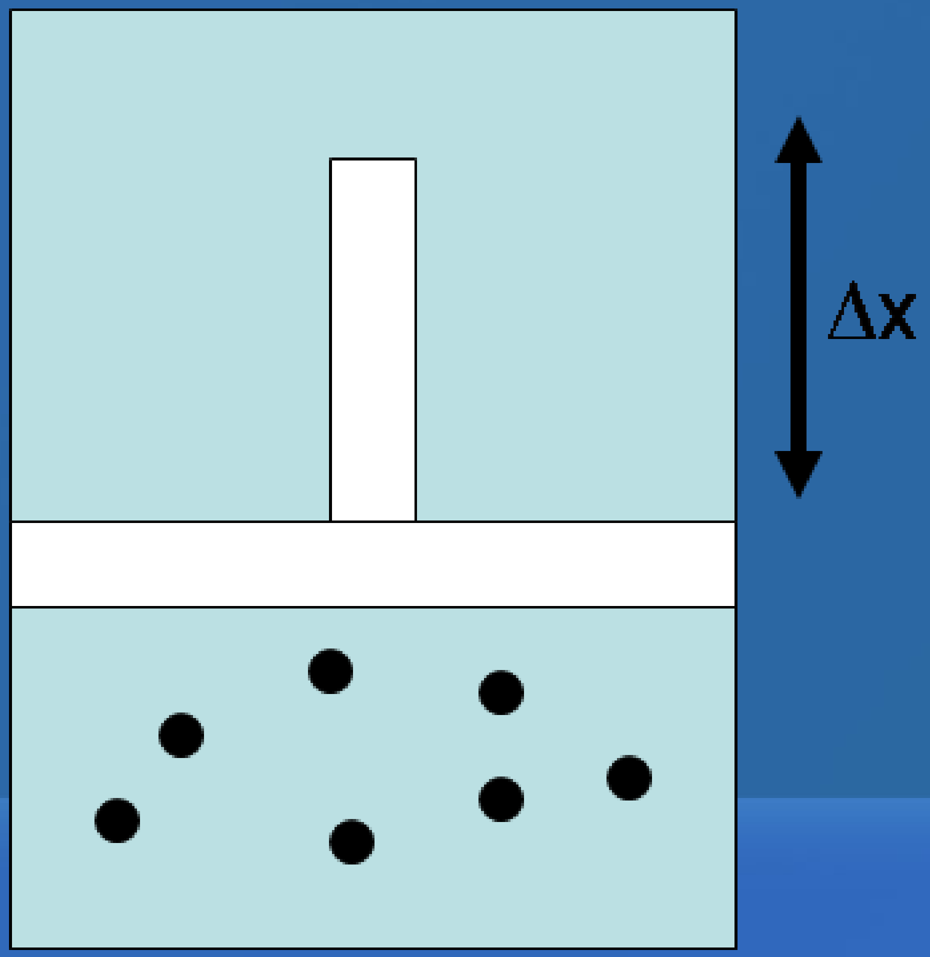
1st Law of Thermodynamics

- If the container is insulated the temperature will rise, the atoms move faster and the pressure rises.
- Is there more internal energy in the gas?



1st Law of Thermodynamics

- External agent did work in pushing the piston inward.
- W = Fd
- $=(PA)\Delta x$
- $W = P\Delta V$



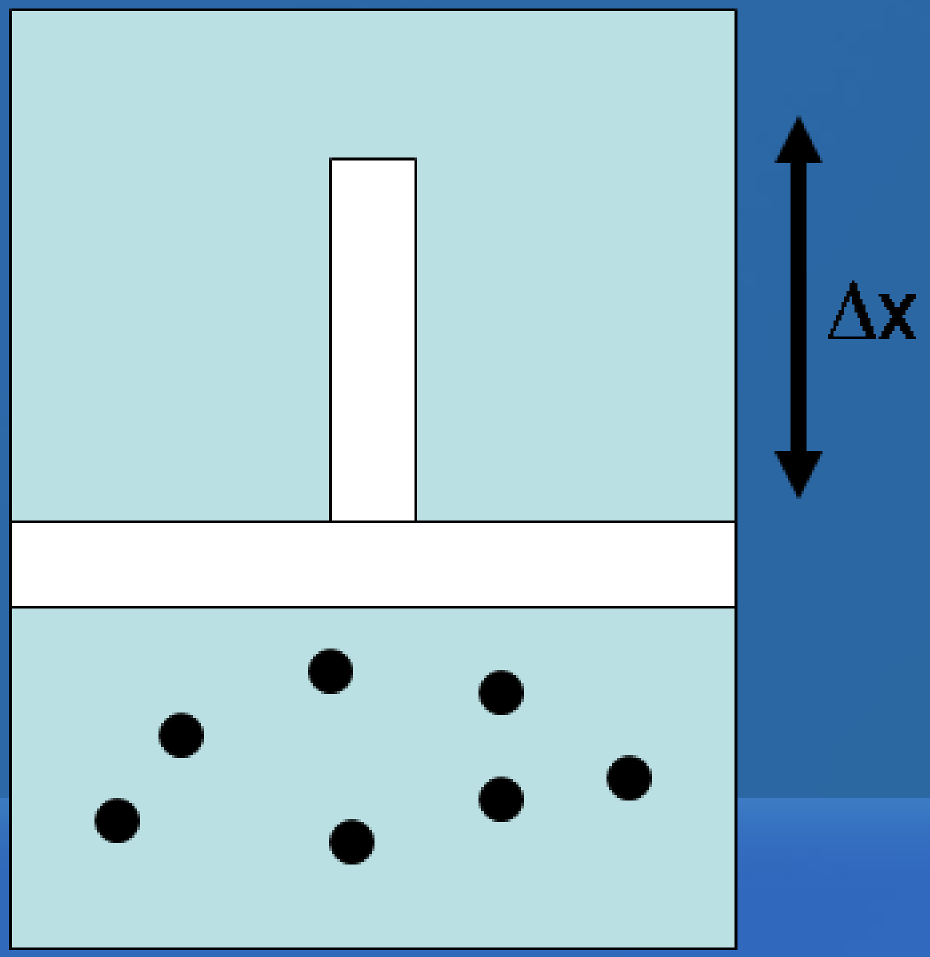
Work and Internal energy

- What is the meaning of work?
  What are the unit of work?
  Explain work in a volume change!
  Explain work depends on path!
- What is the meaning of internal energy?
  What are the unit of internal energy?
  Explain internal energy of an ideal gas!

1st Law of Thermodynamics

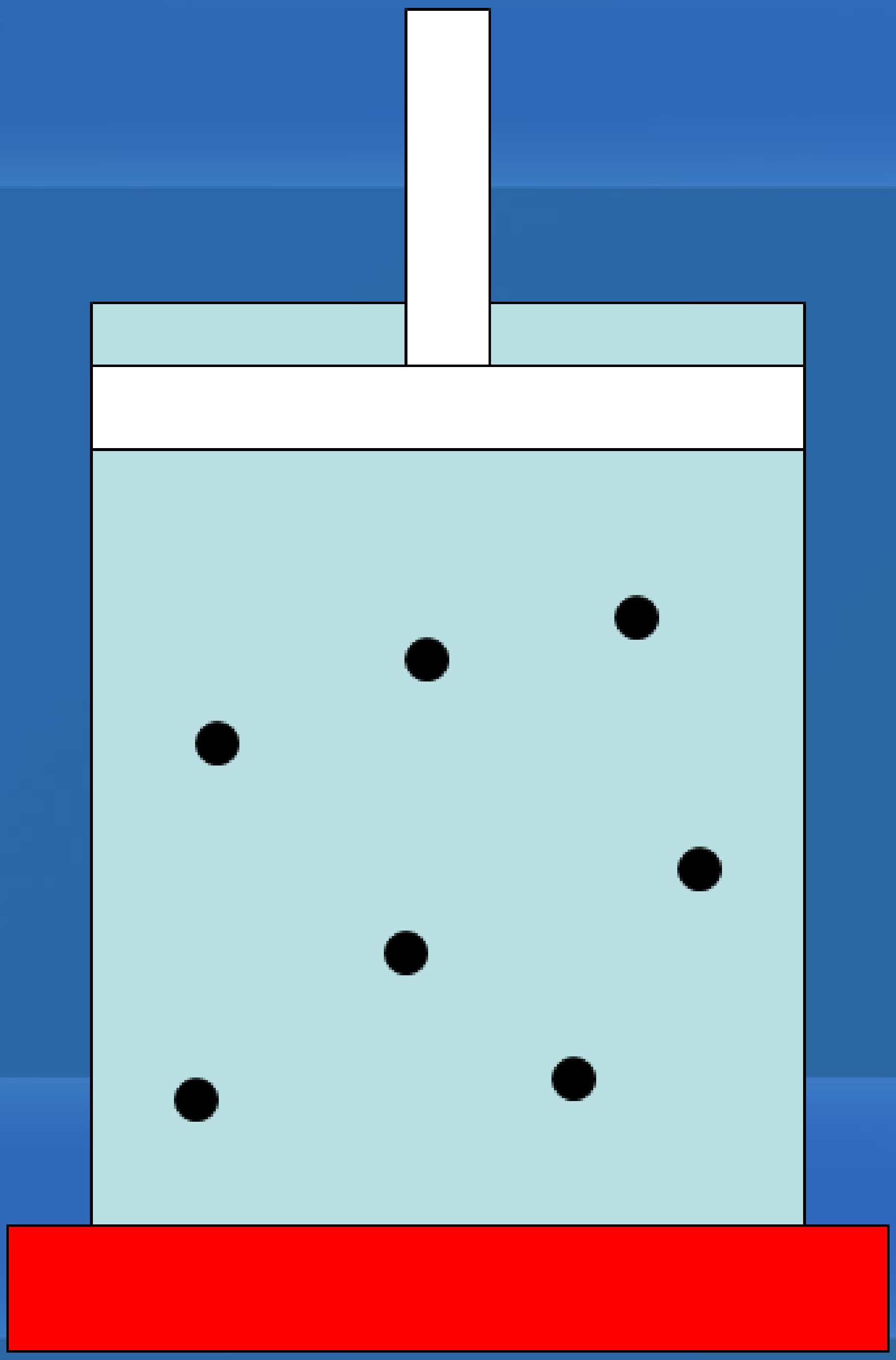
- Work done on the gas equals the change in the gases internal energy,

$$W = \Delta U$$



1^{st} Law of Thermodynamics

- Let's change the situation:
- Keep the piston fixed at its original location.
- Place the cylinder on a hot plate.
- What happens to gas?



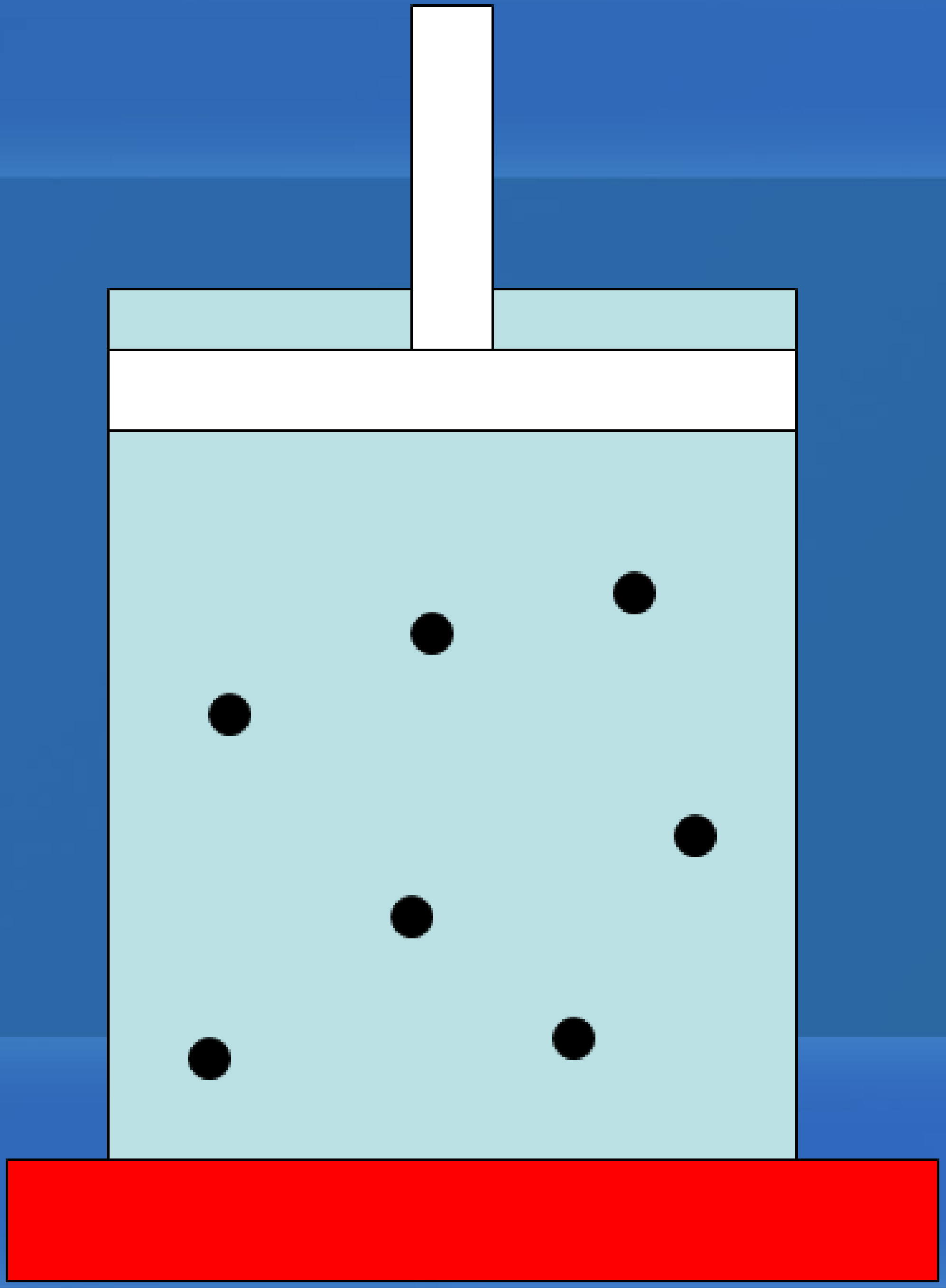
Heat flows into the gas.

Atoms move faster, internal energy increases.

Q = heat in Joules

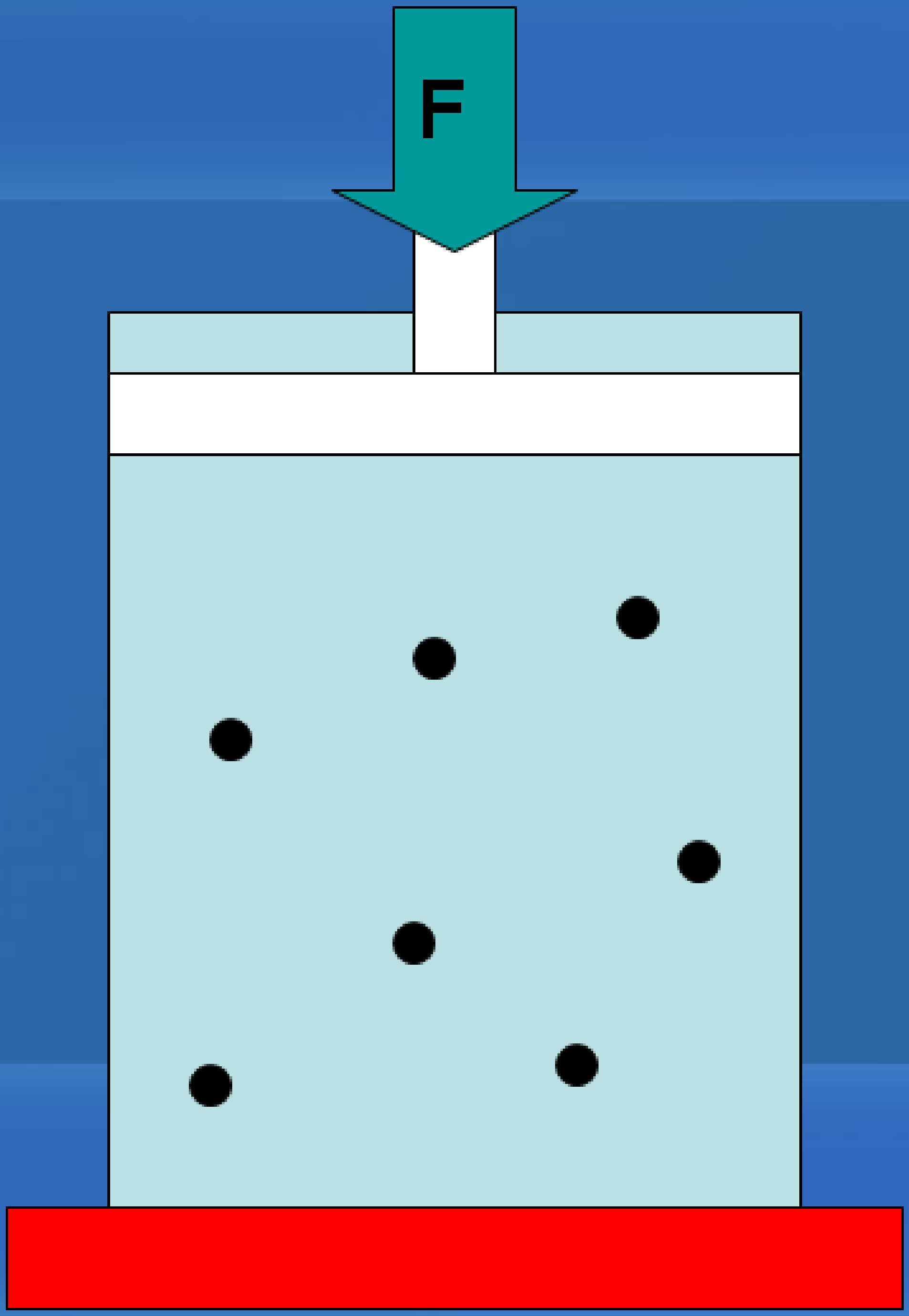
ΔU = change in internal energy in Joules.

$$Q = \Delta U$$



1st Law of Thermodynamics

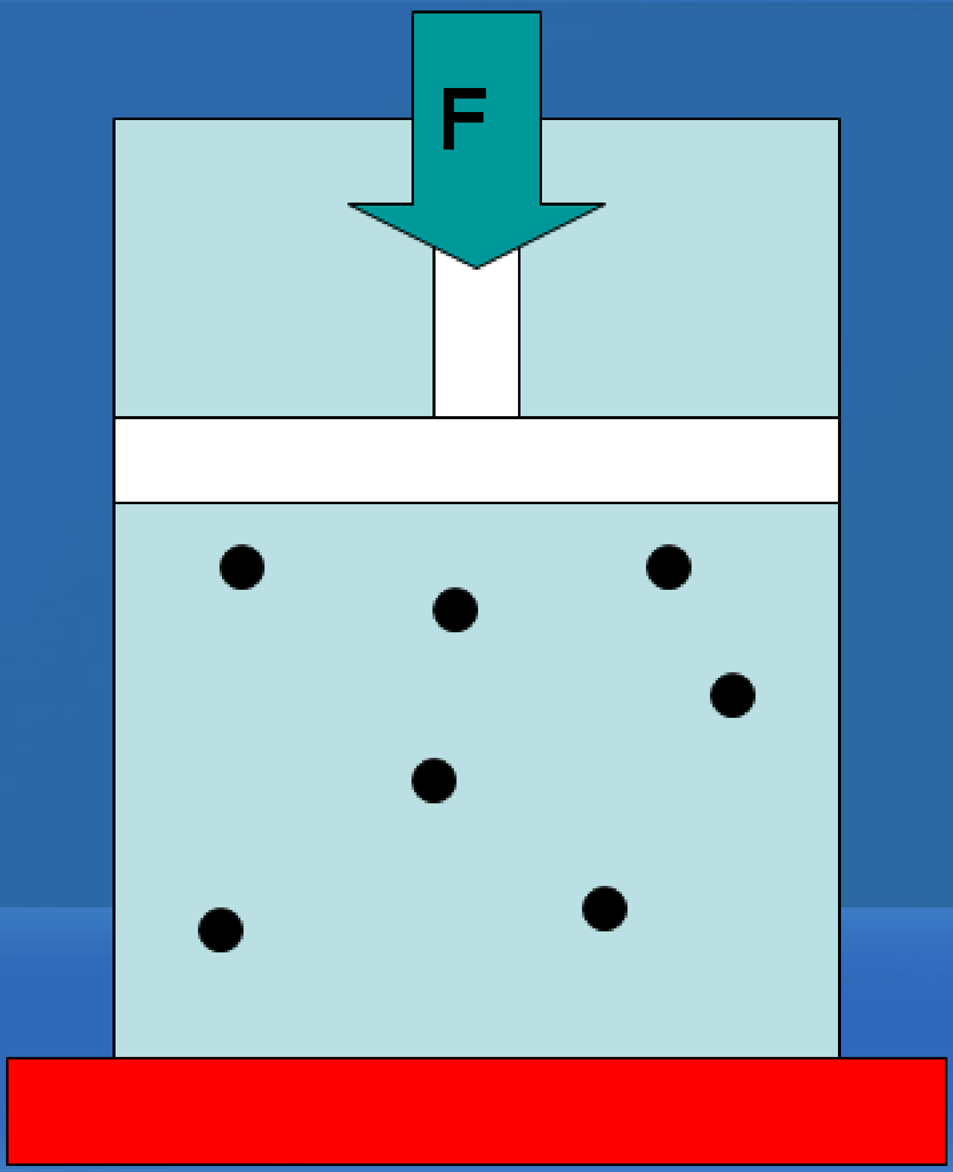
- What if we added heat and pushed the piston in at the same time?



1st Law of TD

- Work is done on the gas, heat is added to the gas and the internal energy of the gas increases!

$$Q = W + \Delta U$$



1st Law of TD

Some conventions:

For the gases perspective:

- heat added is positive, heat removed is negative.
- Work done by the gas is positive, work done on the gas is negative.
- Temperature increase means internal energy change is positive.

Isolated Systems

- ***An isolated system*** is one that **does not interact with its surroundings**
  - **No energy transfer by heat takes place**
  - **The work done on the system is zero**
  - $Q = W = 0$, so $\Delta U = 0$
- ***The internal energy of an isolated system remains constant***

Cyclic Processes

- ***A cyclic process*** is one that **starts and ends in the same state**
  - **This process would not be isolated**
  - On a ***PV*** **diagram**, a ***cyclic process*** appears **as a closed curve**
- The **internal energy must be zero** since it is a state variable

$$\Delta U = 0 \Rightarrow Q = -W \quad \text{(cyclic process)}$$

  - In a ***cyclic process***, the **net work done** on the system per cycle **equals the area enclosed** by the path representing the process on a ***PV*** **diagram**

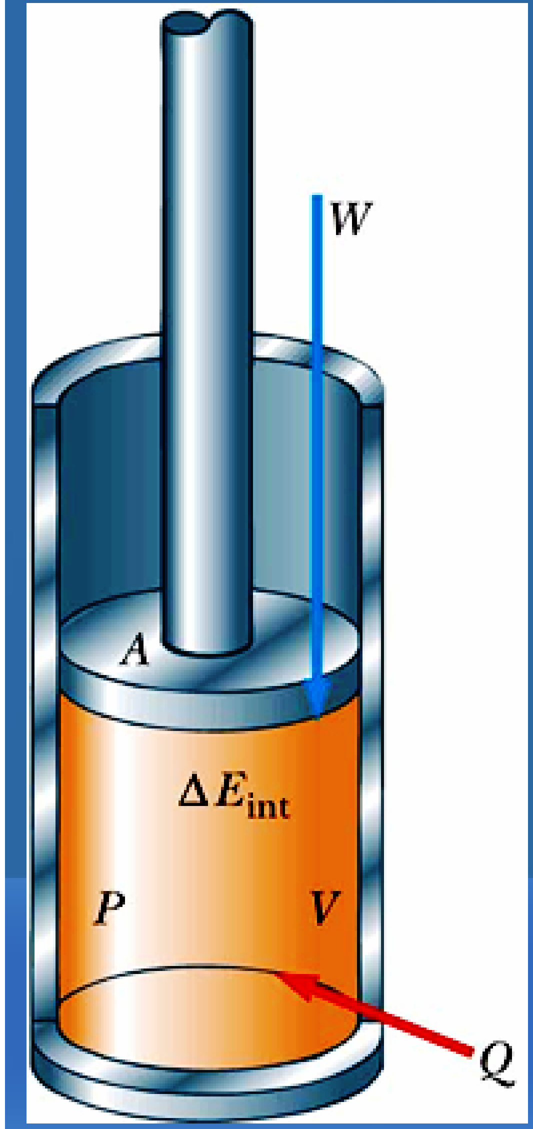
Some Applications of the 1st Law of Thermodynamics

- ***An adiabatic process*** is one during which **no energy enters or leaves the system by heat**

$$Q = 0 \Rightarrow Q = W + \Delta U$$

$$\Rightarrow \Delta U = - W$$

- This is achieved by:
  - ***Thermally insulating the walls of the system***
  - ***Having the process proceed so quickly that no heat can be exchanged***



Adiabatic Process

- *If the gas is compressed adiabatically, W is negatif so ΔU is positive and the temperature of the gas increases*
- *If the gas expands adiabatically, the temperature of the gas decreases*

Work

Work is the energy transfer associated with a force acting through a distance.

➔Work is energy in transition

Denoted by W, satuan Joule (J)

Work on a unit-mass basis is denoted by w, satuan J/kg.

Work done per unit time is called power, denoted by P

Work done by a system is positive; and work done on a system is negative

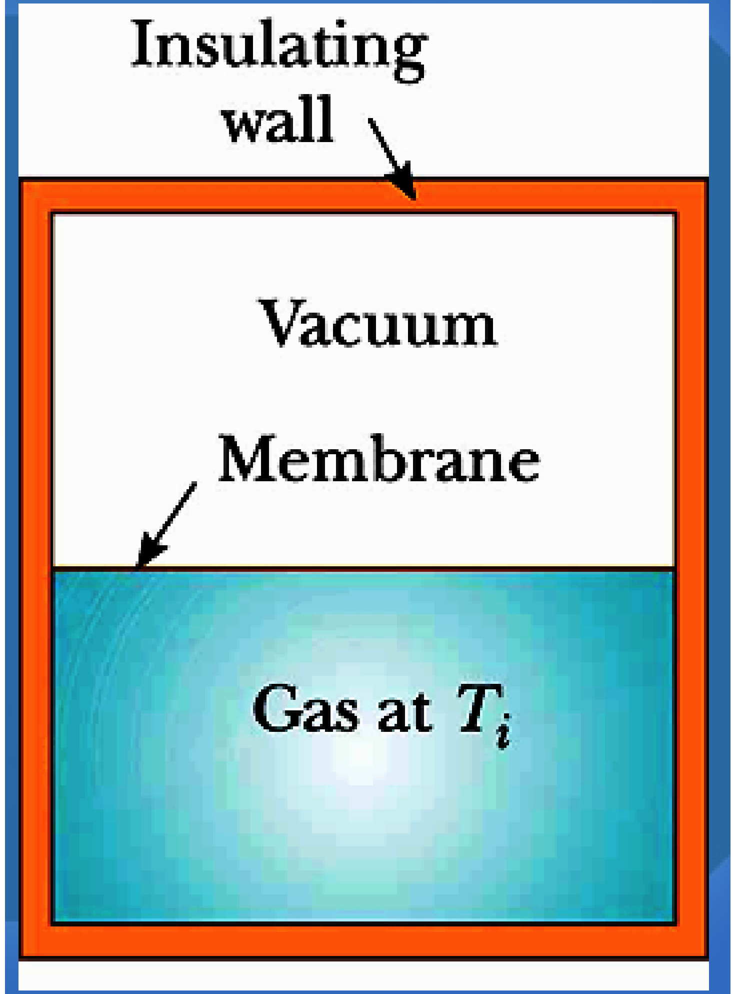
Adiabatic Processes, Examples

- Some important ***examples of adiabatic processes*** related to engineering are:
  - **The expansion of hot gases in an internal combustion engine**
  - **The liquefaction of gases in a cooling system**
  - **The compression stroke in a diesel engine**

Adiabatic Free Expansion

- An example of ***adiabatic free expansion***
  - The process is adiabatic because it takes place in an insulated container
- Because the gas expands into a vacuum, it ***does not apply a force*** on a piston and $W = 0$
- Since $Q = 0$ and $W = 0 \Rightarrow$

  $\Delta U = 0$ and the initial and final states are the same
  - **No change in temperature is expected**



Isobaric Processes

- An ***isobaric process*** is one that occurs at a ***constant pressure***
- The values of the **heat** and the **work** are generally both **nonzero**
- The work done is

$$W = -P\,(V_f - V_i)$$

where P is the **constant pressure**

Isovolumetric Processes

- An ***isovolumetric (isochoric) process*** is one in which there is **no change** in the **volume**
- Since the volume does not change: $W = P\,\Delta V = 0$
- From the first law: $Q = \Delta U + W \Rightarrow \Delta U = Q$
- ***If energy is added by heat to a system kept at constant volume, all of the transferred energy remains in the system as an increase in its internal energy***

Isothermal Process

- An ***isothermal process*** is one that occurs at a **constant temperature**
- Since there is ***no change in temperature***,

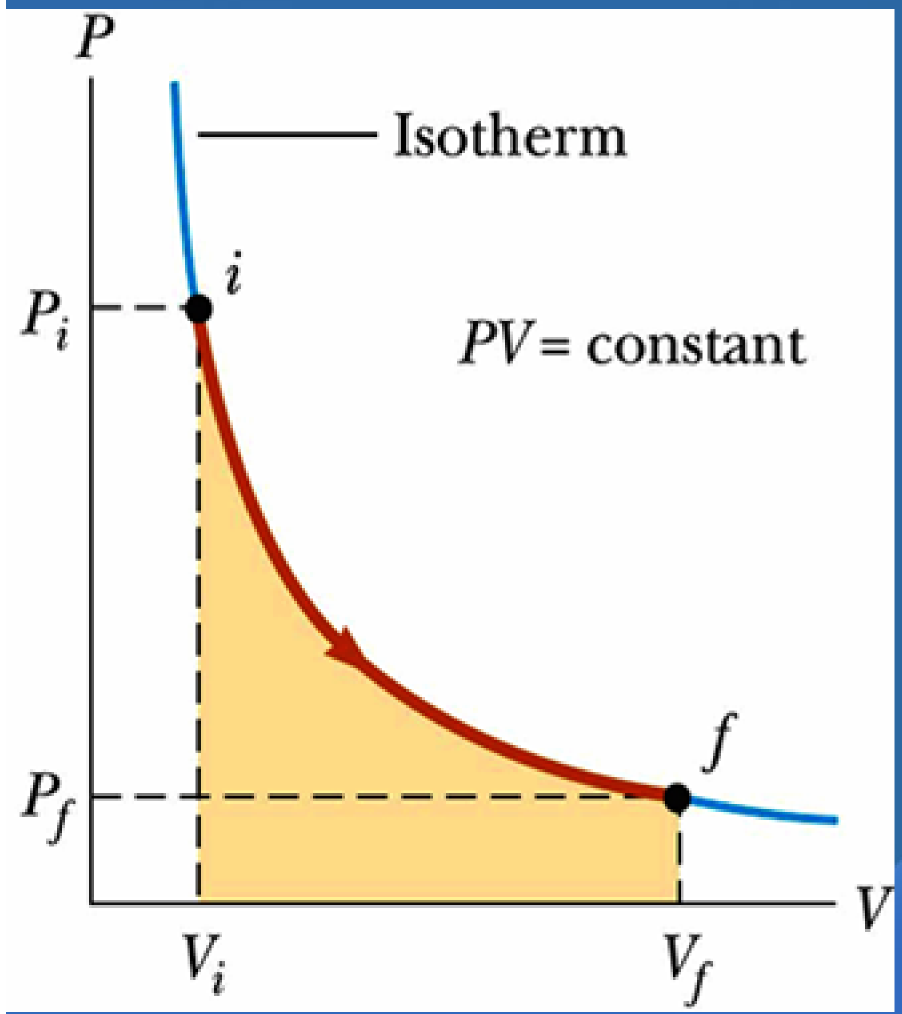
$$\Delta U = 0$$

- Therefore, $Q = W$
- ***Any energy that enters the system by heat must leave the system by work***

Isothermal Process

- At right is a ***PV* diagram** of an ***isothermal expansion***
- The curve is a **hyperbola**
- The curve is called an ***isotherm***
- Diagram indicates

  ***PV* = constant**



Isothermal Expansion, Details

- Because it is an ideal gas and the process is ***quasi-static***, ***PV = nRT*** and

$$W = -\int_{V_i}^{V_f} P\,dV = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV = -nRT\int_{V_i}^{V_f} \frac{dV}{V}$$

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

Isothermal Expansion, final

- Numerically, **the work** equals the **area under** the ***PV* curve**
  - **The shaded area in the diagram**
- **If the gas *expands*, $V_f > V_i$ and the work done on the gas is negative (work done by gas/system)**
- **If the gas is compressed, $V_f < V_i$ and the work done on the gas is positive (work done by surrounding)**

Special Processes, Summary 1

- ***Adiabatic***

  No heat exchanged

  $Q = 0$ and $\Delta U = -W$

- ***Isobaric***

  Constant pressure

  $W = P(V_f - V_i)$ and $Q = \Delta U + W$

Special Processes, Summary 2

- ***Isothermal***

  Constant temperature

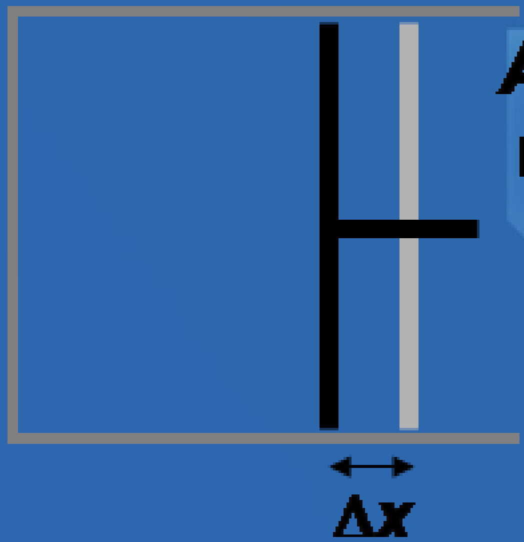
  $\Delta U = 0$ and $Q = W$

- ***Isochoric***

  Constant volume

  $W = 0$ and $Q = \Delta U$

Work in a volume change

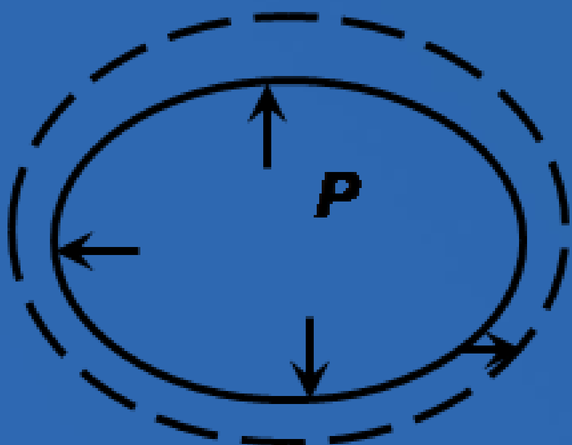


A – the piston area

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).



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

dW* = - *PdV - applies to any shape of system boundary

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.

Example
An Isothermal Expansion

- A **1.0 mol** of an ideal gas is kept at **0°C** during an expansion from **3.0 L** to **10.0 L**.
- **(A).** Find the work done by the gas during the expansion. Using equation

$$W = nRT\ln\left(\frac{V_1}{V_2}\right) = (1mol)(8.31J/mol\cdot K)(273K)\ln\left(\frac{3.0L}{10.0L}\right) = -2.7x10^3\,J$$

- **(B).** How much energy transfer by heat occurs with the surroundings in this process?

From the first law: $Q = \Delta U + W$

$$\Delta U = 0 \Rightarrow Q = \Delta U + W \Rightarrow Q = W = 2.7x10^3\,J$$

- **(C).** Find the work done on the gas during the compression.

Work done in an ***isobaric process*** is: $W = P\,(V_f - V_i)$

where V_i =10.0L and V_f =3.0L (reverse of part A)

$$W = P\left(V_f - V_i\right) = \left(\frac{nRT_i}{V_i}\right)\left(V_f - V_i\right) \Rightarrow$$

$$W = \frac{(1.0mol)(8.31J/mol\cdot K)(273K)}{10.0x10^{-3}m^3}(3.0-10.0)x10^{-3}m^3 \Rightarrow$$

$$W = -1.6x10^3 J$$

Example
Heating a Solid

- A 1.0 kg bar of copper is heated at atmospheric pressure. If its temperature increases from 20ºC to 50ºC.
- (A). Find the work done on the copper bar by the surrounding atmosphere?

Isobaric Pressure and volumetric thermal expansion:

$$\Delta V = 3\alpha V_i \Delta T = \left(5.1x10^{-5}\left({}^{o}C^{-1}\right)\right)\left(30^{o}C\right)V_i = 1.5x10^{-3}V_i \Rightarrow$$

$$\Delta V = 1.5x10^{-3}\frac{m}{\rho_{Cu}} = 1.5x10^{-3}\frac{1.0kg}{8.92x10^{3}kg/m^{3}} = 1.7x10^{-7}m^{3} \Rightarrow$$

$$W = -P_o \Delta V = -\left(1.013x10^{5}N/m^{2}\right)\left(1.7x10^{-7}m^{3}\right) = -1.7x10^{-2}J$$

Since work is negative, this work is done *by* the copper bar *on* the atmosphere

- **(B).** How much energy is transferred to the copper bar by heat?
  - Using Eqn 20.4

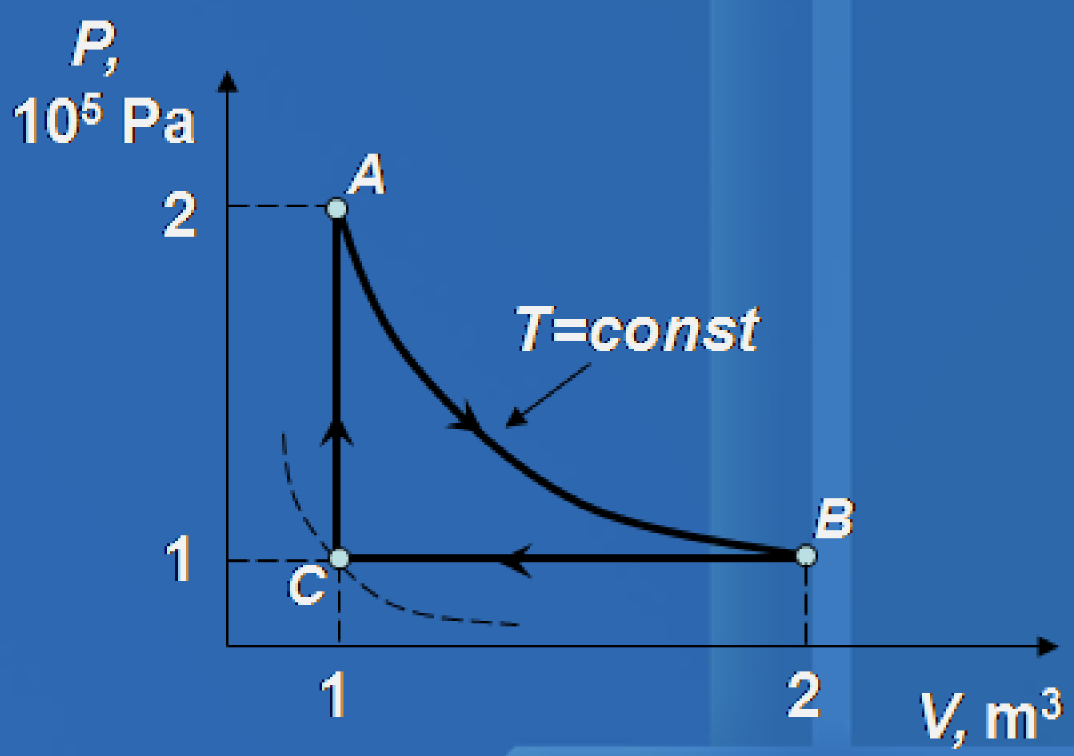
$$Q = mc\Delta T = (1.0kg)(387J/kg\cdot{}^{o}C)(30^{o}C) = 1.2x10^{4}J$$

- **(C).** What is the increase in internal energy of the copper bar

$$\Delta U = Q + W = 1.2x10^{4}J + (-1.7x10^{-2}J) = 1.2x10^{4}J$$

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 → B	+	+	0
B → C	+	+	+
C → A	+	0	+

Work of expansion and compression = "pV work"

$dw = -f\,dx$

f is the external force

pressure = force/area

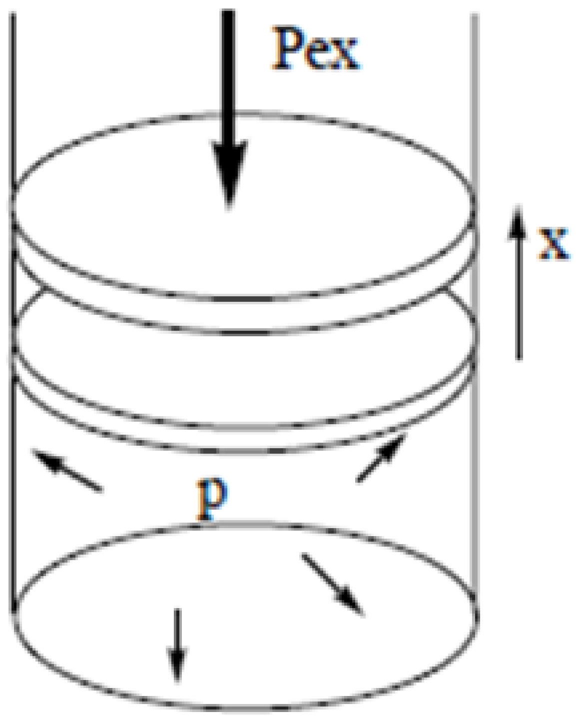
so $f = p_{ex}A$

A is the area of the piston

$V = Ax$, so $dV = A\,dx$

$dw = -(p_{ex}A)\,dx = -p_{ex}\,dV$

so $dw = -p_{ex}\,dV$



Work depends on path. Example 2: isothermal expansion of an ideal gas

constants T = 298.15 and n = 0.327 mole

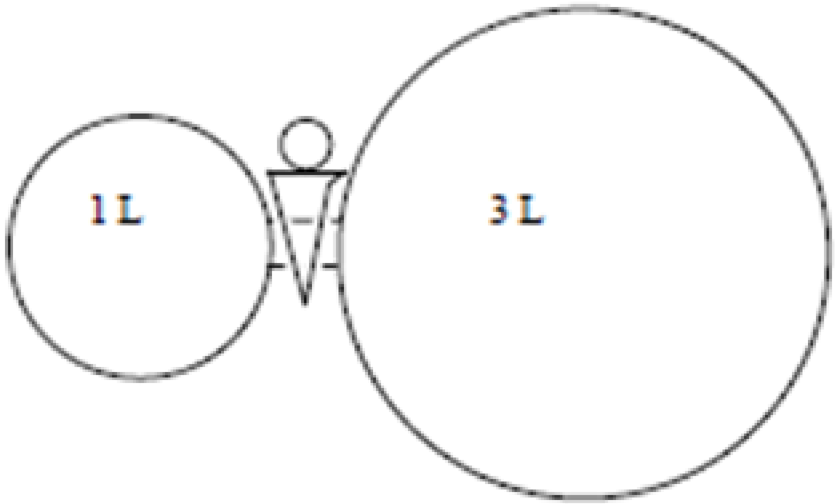
State 1: $p_1 = 8$ atm, $V_1 = 1$ L

State 2: $p_2 = 2$ atm, $V_2 = 4$ L

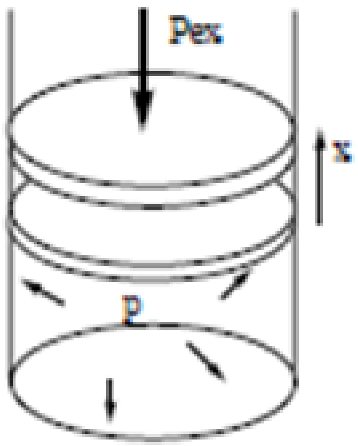
Path 1: expansion into a vacuum:

$dw = -p_{ex}\, dV$

$p_{ex} = 0$ so $w = 0$



isothermal expansion of an ideal gas:
Path 2: constant external pressure



p_{ex} = 2 atm, w = $-p_{ex}\Delta V$

w = –(2 atm)[(4 – 1) L] = –6 L-atm

Work should be reported in joules.

1 L-atm = 101.325 J so

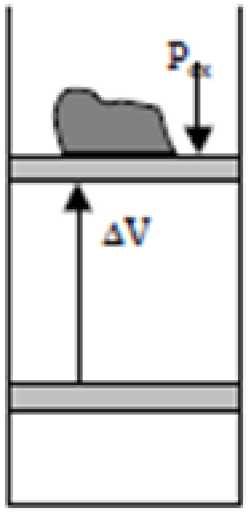
w = (– 6 L-atm)(101.325 J/L-atm) = –607.9 J

w = – 607.9 3 J = work done on the gas

w is negative: expanding system has done work on surroundings, pushing the piston up

{ +607.9 J = work done by the gas }

isothermal expansion of an ideal gas: path 3, **reversible**



$p_{ex} = p - dp$ where dp is infinitesimal

$p_{ex}\, dV = p\, dV - dp\, dV$

dp dV is negligible compared with p dV: omit it

$$w_{rev} = -\int_{V_1}^{V_2} p_{ex}\,dV = -\int_{V_1}^{V_2} p\,dV$$

For an ideal gas,

$$w_{rev} = -\int_{V_1}^{V_2} \left(\frac{nRT}{V}\right) dV = -nRT\int_{V_1}^{V_2} \frac{dV}{V} = -nRT\ln V\Big|_{V_1}^{V_2} = -nRT\ln\frac{V_2}{V_1}$$

$w_{rev} = -$ (0.327 mol)(8.3145 J/mol-K)(298.15 K) ln(4/1)

$= -$ (0.327)(8.3145)(298.15)(1.3863) = $-$1124 J = w