# Thermodynamic systems



**Isolated systems** can exchange neither energy nor matter with the environment.



**Heat**

**Work**
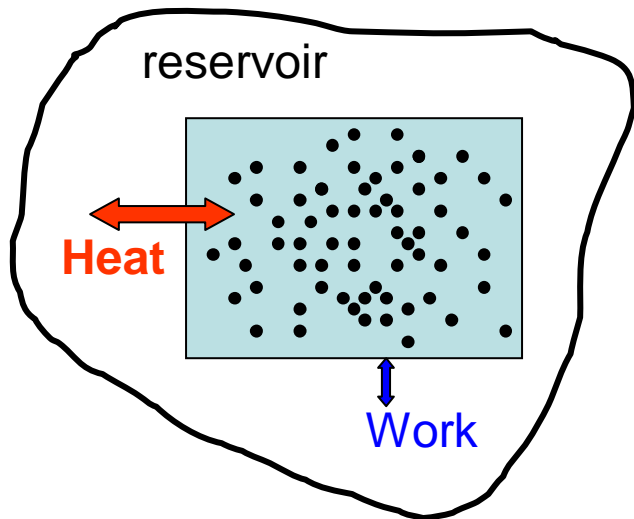
**Closed systems** exchange energy but not matter with the environment.



**Heat**

Work
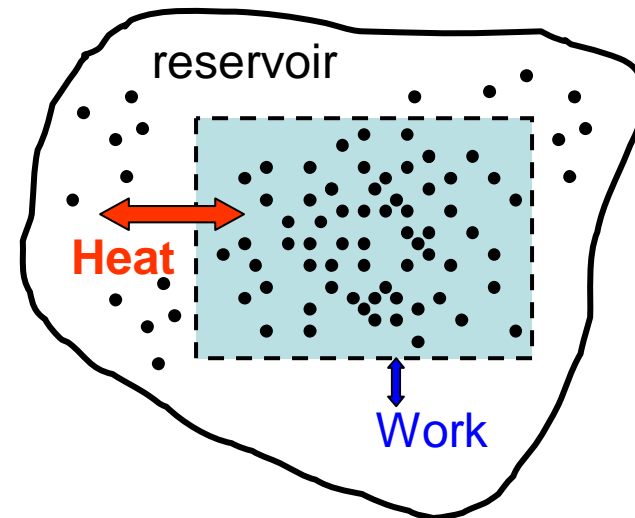
**Open systems** can exchange both matter and energy with the environment.
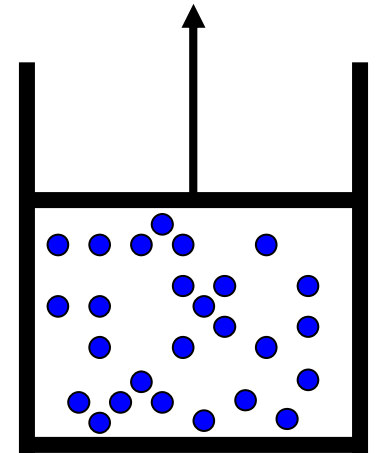
# Quasi-static processes

**Quasi-static processes**: near equilibrium

Initial state, final state, intermediate state: p, V & T well defined

Sufficiently slow processes = any intermediate state can considered as at thermal equilibrium.
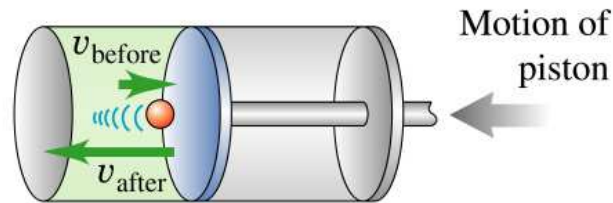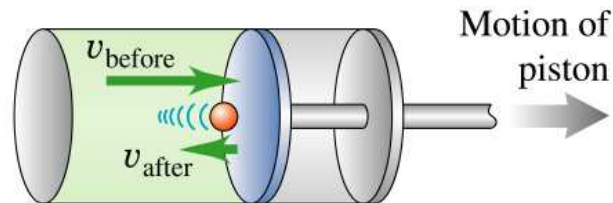Thermal equilibrium means that It makes sense to define a temperature.

**Examples of quasi-static processes:**
- **- isothermal:** **T = constant**
- **- isochoric:** **V = constant**
- **- isobaric:** **P = constant**
- **- adiabatic:** **Q = 0**

# Work in thermodynamics



(b) Piston moves toward molecule during collision: molecule gains kinetic energy, does negative work on piston

(a) Piston moves away from molecule during collision: molecule loses kinetic energy, does positive work on piston

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**Expansion:** work on piston positive, work on gas negative
**Compression:** work on piston negative, work on gas positive

# Work during a volume change



System

$dx$

$pA$

$A$

Force that system
exerts on piston
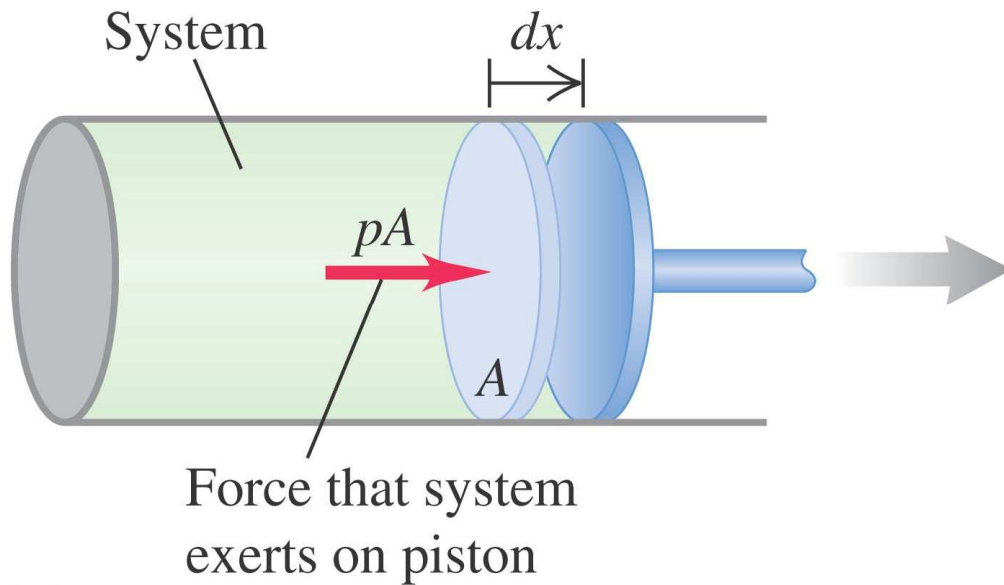
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$$dW = F.dx$$

$$= p.Adx$$

$$= pdV$$

$$\Rightarrow W = \int_{V_1}^{V_2} pdV$$

# Work in $pV$ diagrams



(a) Volume increases ($V_2 > V_1$): work and area are positive

Work = Area $= \int_{V_1}^{V_2} p\, dV > 0$

(b) Volume decreases ($V_2 < V_1$): work and area are negative (shown by cross-hatching)

Work = Area $= \int_{V_1}^{V_2} p\, dV < 0$

(c) Volume increases ($V_2 > V_1$): work and area are positive

Work = Area $= p(V_2 - V_1) > 0$
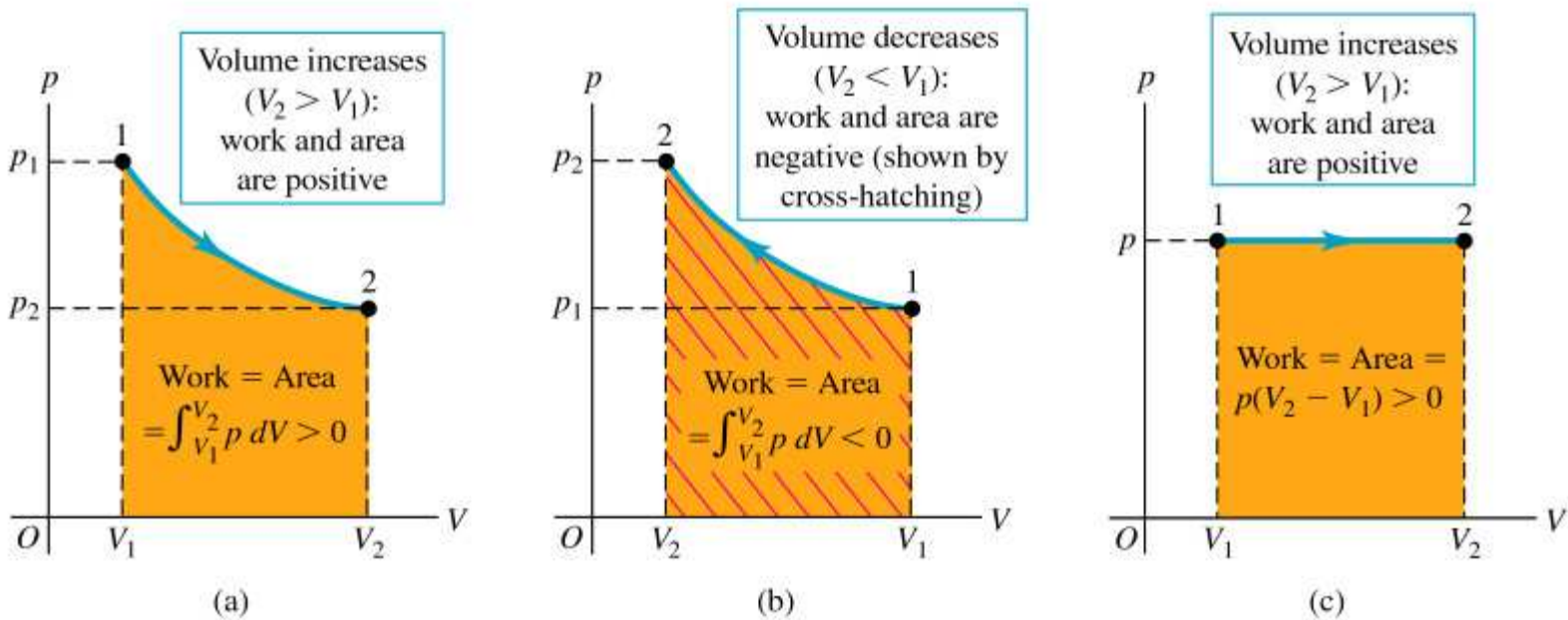
## Work done equals area under curve in $pV$ diagram

Careful with the signs…

# 1ˢᵗ Law of Thermodynamics



Surroundings (environment)
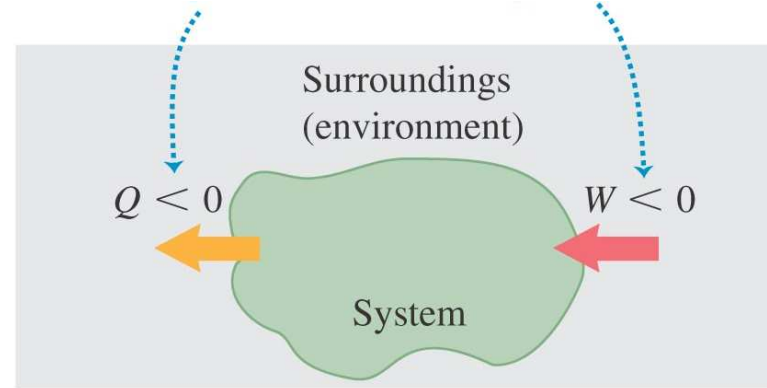
$Q > 0$   System   $W > 0$
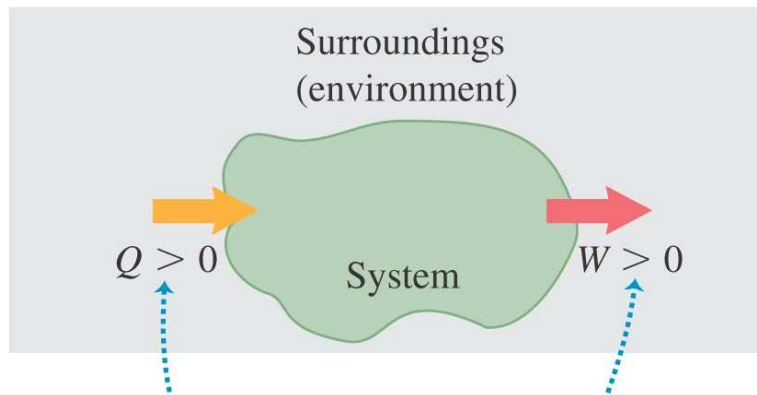
Heat is *positive* when it *enters* the system

Work is *positive* when it is done *by* the system

Heat is *negative* when it *leaves* the system

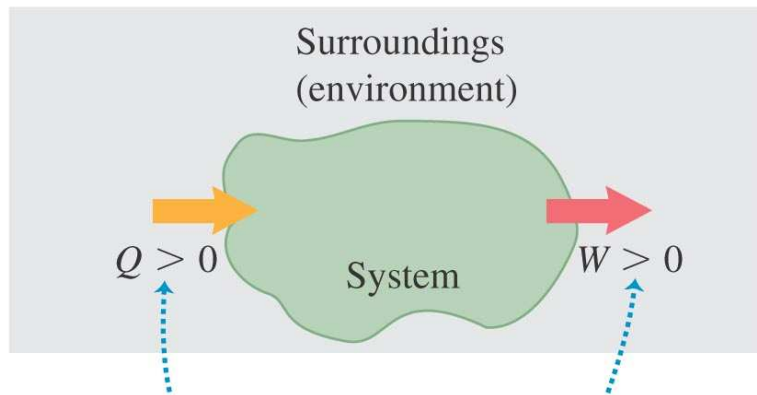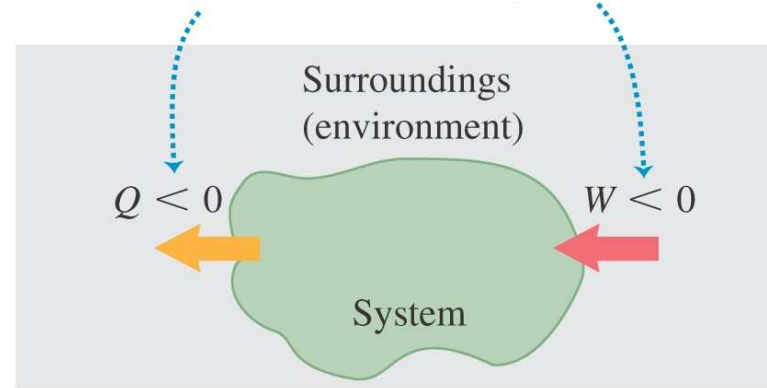Work is *negative* when it is done *on* the system

Surroundings (environment)

$Q < 0$   $W < 0$   System

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$$\Delta U = Q - W$$

Conservation of energy

# 1st Law of Thermodynamics



Heat is *negative* when it *leaves* the system

Work is *negative* when it is done *on* the system

Heat is *positive* when it *enters* the system

Work is *positive* when it is done *by* the system

Surroundings (environment)

$Q > 0$

System

$W > 0$

Surroundings (environment)
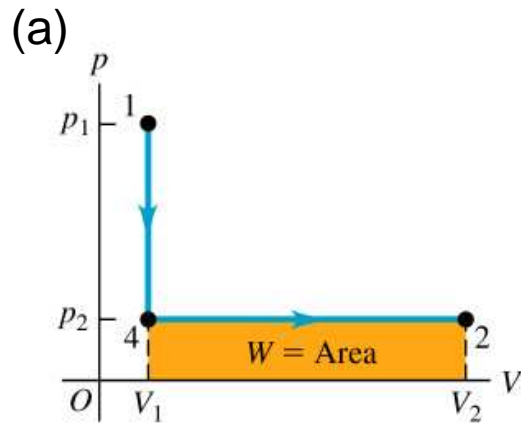
$Q < 0$

System

$W < 0$

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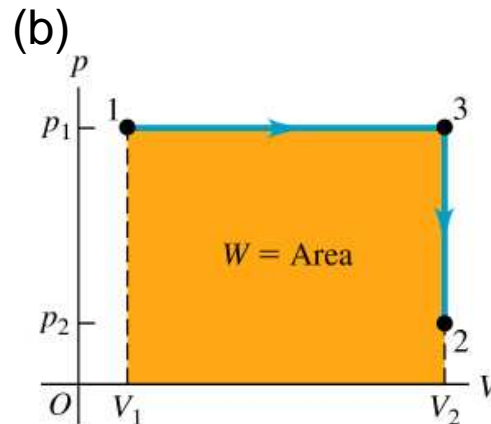
$$dU = dQ - pdV$$

Conservation of energy

# State Functions

(a)



a. isochoric
b. isobaric

$$W = p_2(V_2 - V_1)$$

(b)



W = Area

a. isobaric
b. isochoric

$$W = p_1(V_2 - V_1)$$

(c)



W = Area
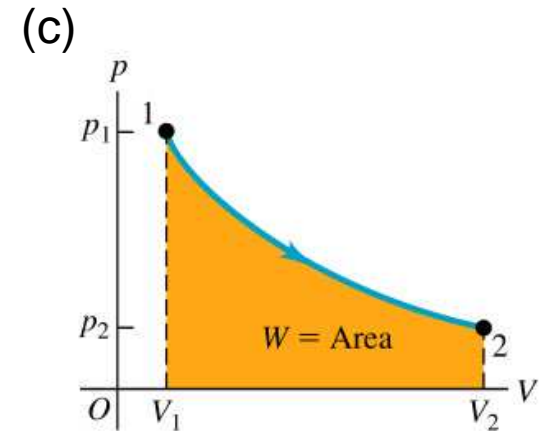
isothermal

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

- The work done by a system depends on the initial and final states and on the path → it is <u>not</u> a state function.

- Amount of heat transferred also depends on the initial, final, <u>and intermediate states</u> → it is <u>not</u> a state function either.

# State Functions

$$\Delta U = Q - W = U_2 - U_1$$

The internal energy $U$ <u>*is*</u> a state function: the energy gain (loss) only depends on the initial and final states, and not on the path.

Even though $Q$ and $W$ depend on the path, $\Delta U$ does not!

# CPS question

This $pV$–diagram shows two ways to take a system from state $a$ (at lower left) to state $c$ (at upper right):

- via state $b$ (at upper left), or
- via state $d$ (at lower right)

For which path is $W > 0$?



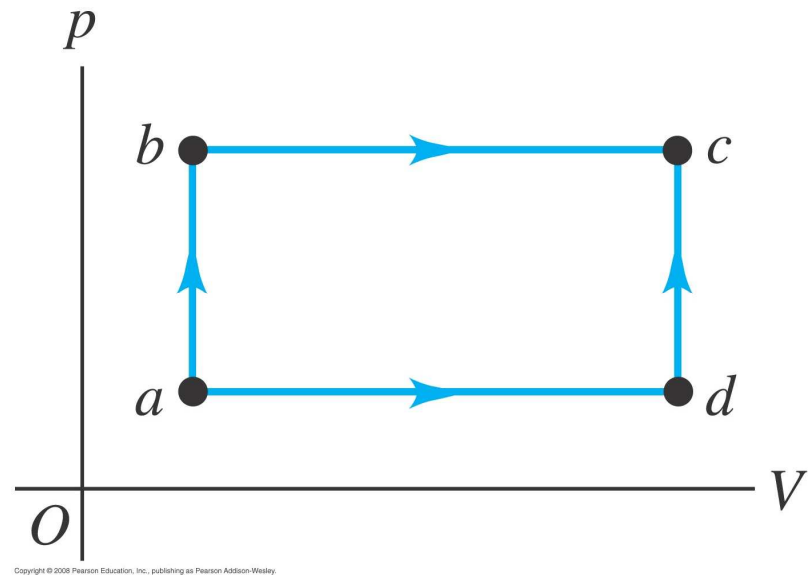Copyright © 2008 Pearson Education, Inc., publishing as Pearson Addison-Wesley.

A. path $abc$ only

B. path $adc$ only

C. both path $abc$ and path $adc$
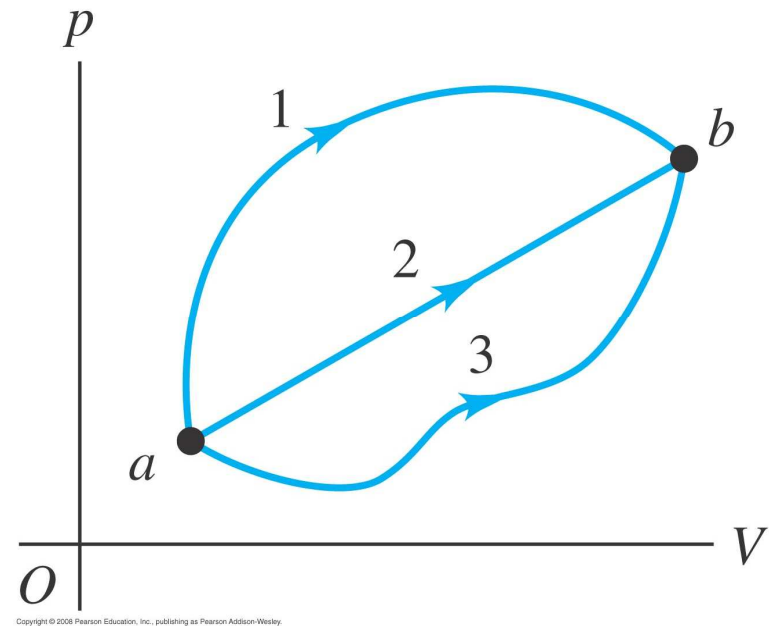
D. neither path $abc$ nor path $adc$

E. The answer depends on what the system is made of.

# CPS question

A system can be taken from state *a* to state *b* along any of the three paths shown in the *pV*–diagram.

If state *b* has greater internal energy than state *a*, along which path is the absolute value |*Q*| of the heat transfer the greatest?

A. path 1          B. path 2          C. path 3

D. |*Q*| is the same for all three paths.

E. not enough information given to decide

# Thermodynamic Processes:

•Adiabatic: no heat transfer (by insulation or by very fast process)

$$Q=0 \rightarrow U_2 - U_1 = -W$$

•Isochoric: constant volume process (no work done)
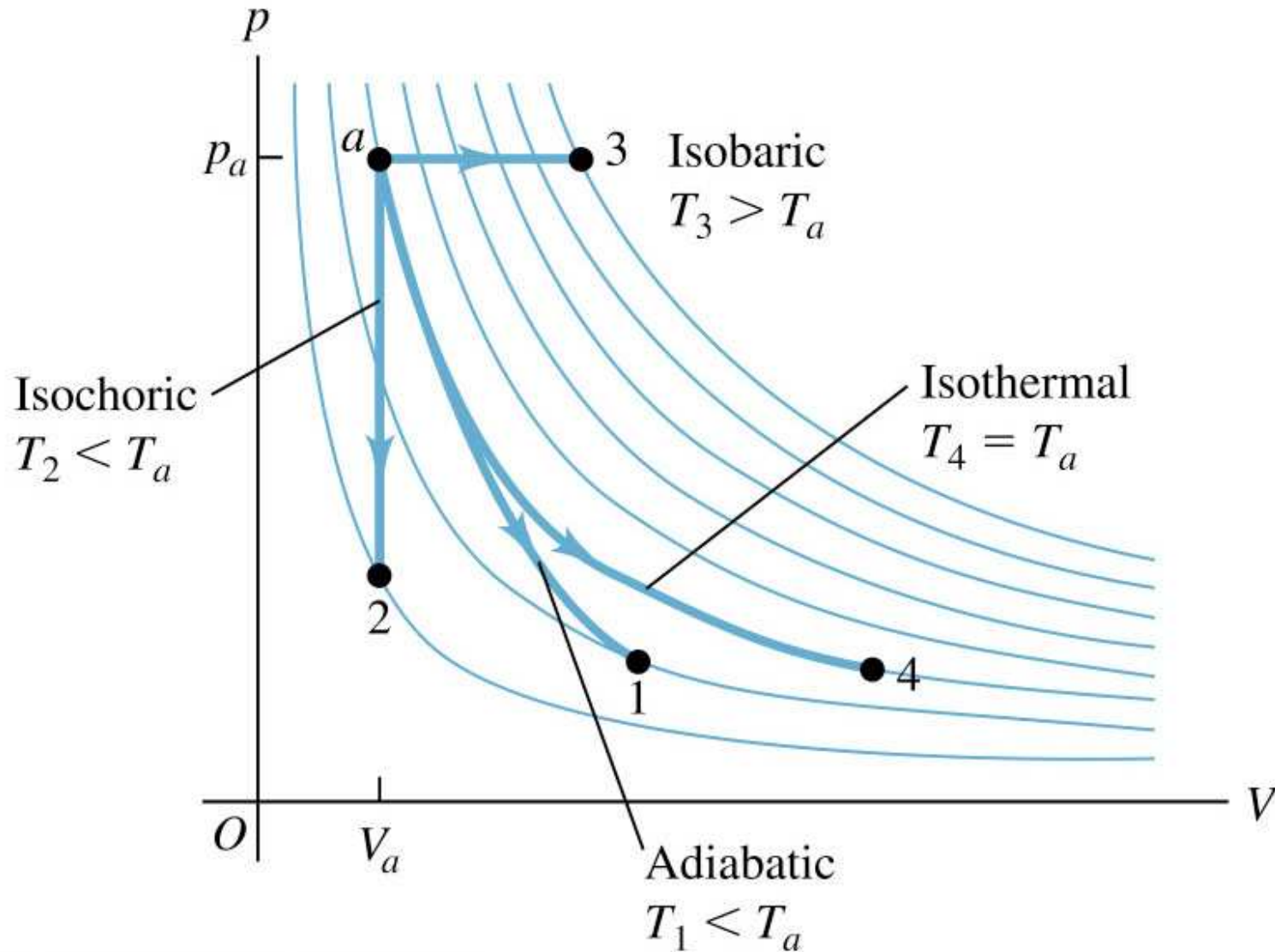
$$W=0 \rightarrow U_2 - U_1 = Q$$

•Isobaric: constant pressure process

$$p=const. \rightarrow W = p (V_2 - V_1)$$

•Isothermal: constant temperature process (heat may flow but very slowly so that thermal equilibrium is not disturbed)
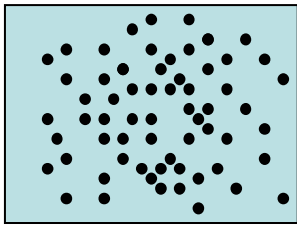
$\Delta U=0, Q =-W$ only for ideal gas. Generally $\Delta U, Q, W$ not zero
any energy entering as heat must leave as work

# Thermodynamic processes

# First Law for Several Types of Processes

**Isolated systems:**
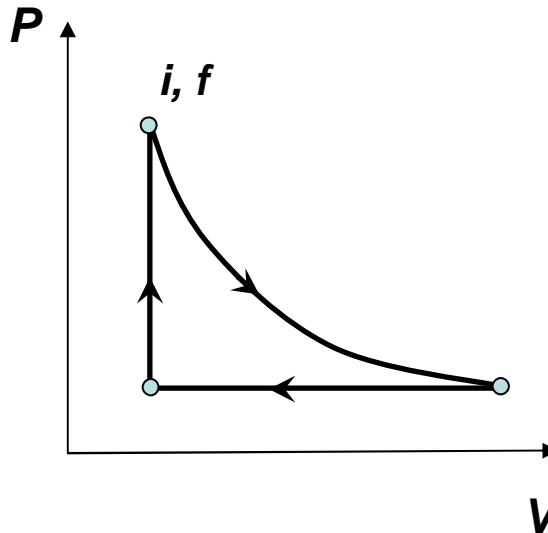


$$Q = W = 0$$

$$\rightarrow \Delta U = 0$$

$$\rightarrow U_i = U_f$$

The internal energy
of an isolated systems
remains constant
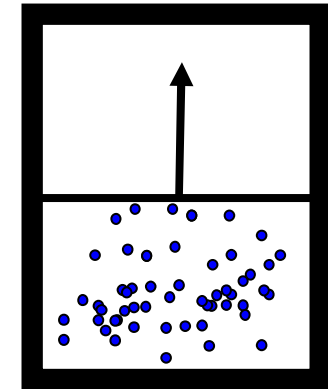
**Cyclic processes**



initial state = final state

$$\Delta U = 0$$

$$\rightarrow Q = W$$

Energy exchange between
"heat" and "work"

**Adiabatic processes**



$$Q = 0$$

$$\rightarrow \Delta U = -W$$

Expansion: *U* decreases
Compression: *U* increases

# More about cyclic processes
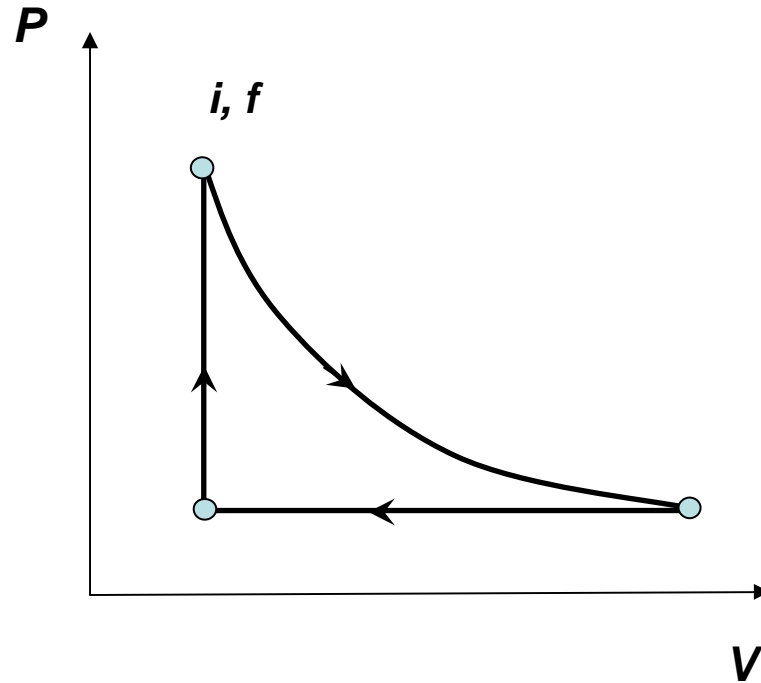


Work equals the area *enclosed* by the curves (careful with the sign!!!)

# CPS question

An ideal gas is taken around the cycle shown in this $pV$–diagram, from $a$ to $b$ to $c$ and back to $a$. Process $b \rightarrow c$ is isothermal.

For this complete cycle,

A. $Q > 0$, $W > 0$, and $\Delta U = 0$.

B. $Q > 0$, $W > 0$, and $\Delta U > 0$.

C. $Q = 0$, $W > 0$, and $\Delta U < 0$.

D. $Q = 0$, $W < 0$, and $\Delta U > 0$.

E. $Q > 0$, $W = 0$, and $\Delta U > 0$.
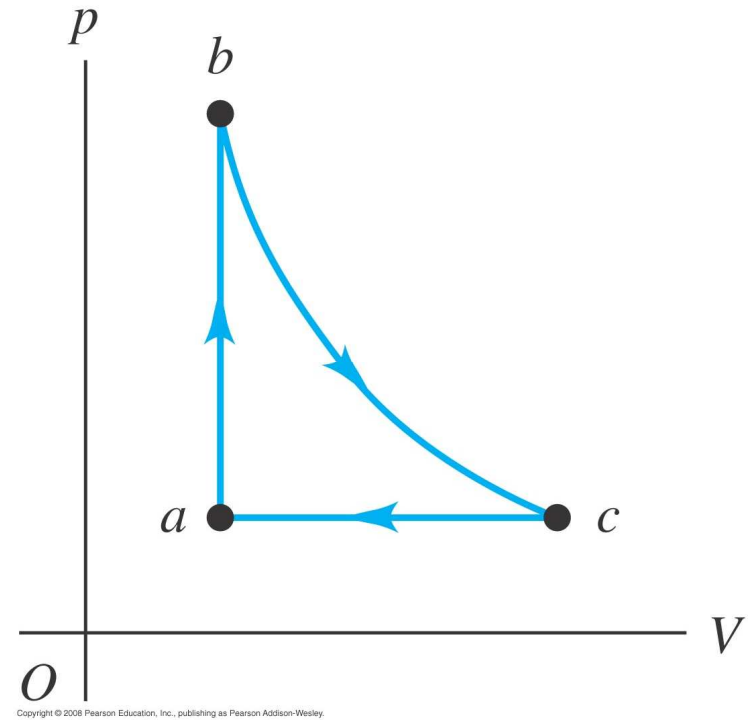
# Important formulas

$\Delta U = Q - W$ (1st law)

$$W = \int_{V_1}^{V_2} p \, dV$$ (work during a volume change)

$pV = nRT$ (Ideal gas law)

$C_V = f/2 \, nR$ (Equipartition theorem)

# Ideal gas: isochoric process
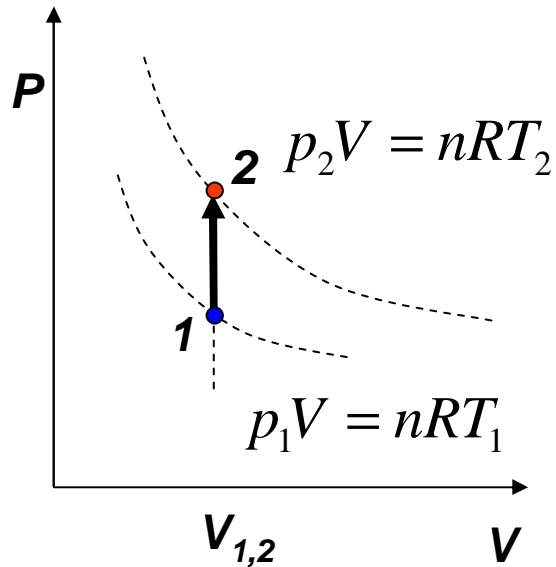


Isochoric process: V = constant

$$\rightarrow W = \int_{V_1}^{V_2} p\,dV = 0$$

$$Q = C_V(T_2 - T_1)$$
$$= C_V \Delta T$$

($C_V$: heat capacity at constant volume)

$$\Delta U = Q - W$$
$$\rightarrow \Delta U = Q = C_V \Delta T$$

During an isochoric process, heat enters (leaves) the system and increases (decreases) the internal energy.

# Ideal gas: isobaric process



$$pV_2 = nRT_2$$

**2**

**1**

$$pV_1 = Nk_BT_1$$

$V_1$   $V_2$   **V**

reservoir
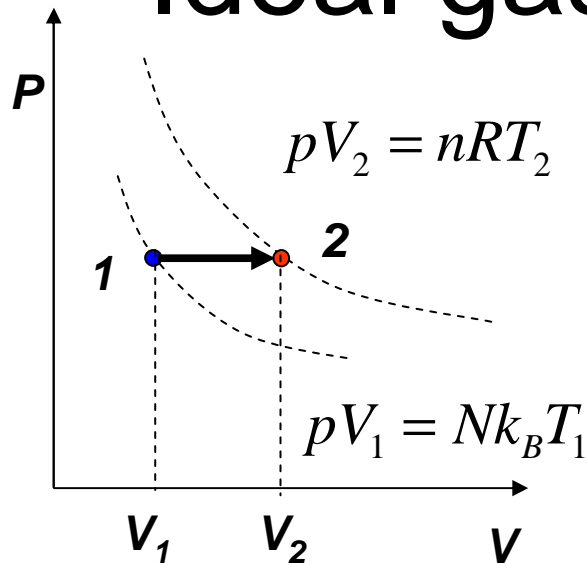
**Heat**

Work

Isobaric process: p = constant

$$\rightarrow W = \int_{V_1}^{V_2} pdV = p(V_2 - V_1) = p\Delta V$$
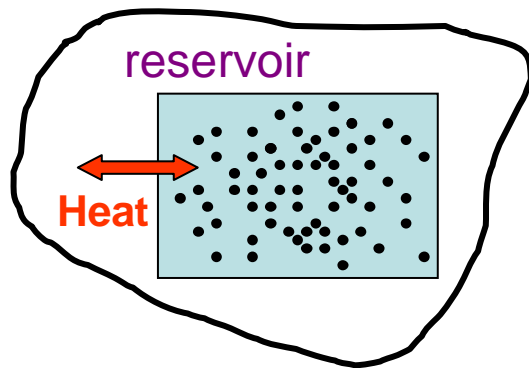
$$Q = C_p(T_2 - T_1)$$

$$= C_p\Delta T$$

($C_{P:}$ heat capacity at constant pressure)

$$\rightarrow \Delta U = Q - W$$

$$= C_P\Delta T - p\Delta V$$

During an isobaric expansion process, heat enters the system. Part of the heat is used by the system to do work on the environment; the rest of the heat is used to increase the internal energy.

# Ideal gas: isothermal process



$pV = nRT$
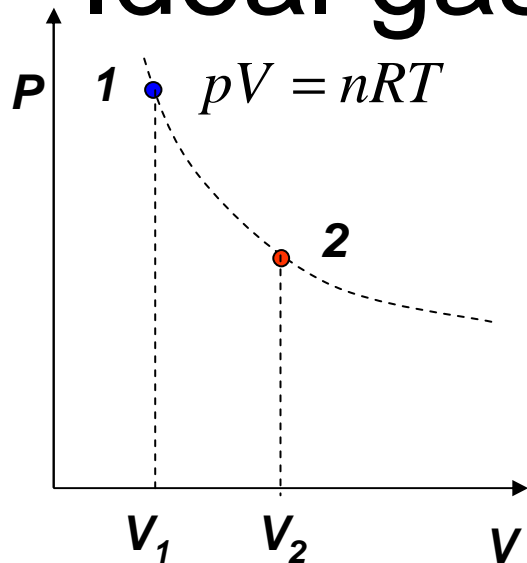
Isothermal process: T = constant

$$\Delta T = 0 \Rightarrow \Delta U = 0$$

$$W = \int_{V_1}^{V_2} p\,dV = \int_{V_1}^{V_2} \frac{nRT}{V}\,dV$$
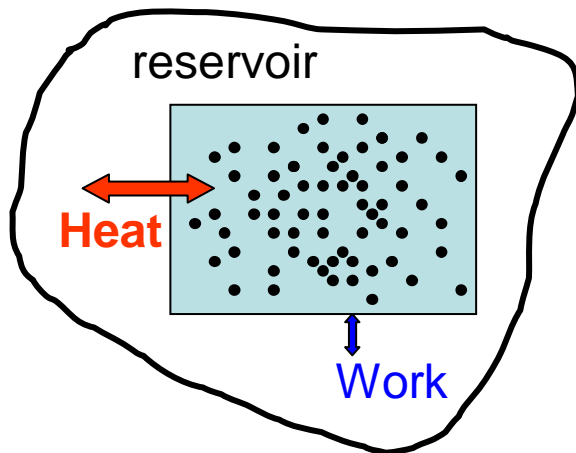
$$= nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= nRT \ln \frac{V_2}{V_1}$$

$$\rightarrow Q = W = nRT \ln \frac{V_2}{V_1}$$

Expansion:
heat enters the system
all of the heat is used by the system
to do work on the environment.

Compression:
the work done on the system increases
its internal energy,
all of the energy leaves the system at
the same time as the heat is removed.

# Heat capacities of an Ideal gas

Consider an isobaric process p=constant

$$Q_p = C_p \Delta T$$

From the 1st Law of Thermodynamics:

but

$$\left. \begin{array}{l} dQ_p = C_p dT = dU + pdV \\ \\ dU = C_V dT \end{array} \right\} \Rightarrow C_p dT = C_V dT + pdV$$

From the Ideal gas law:

$$pV = nRT \Rightarrow pdV + Vdp = pdV = \boxed{nRdT}$$

$$\Rightarrow C_p dT = C_V dT + nRdT \Rightarrow \boxed{C_p = C_V + nR}$$

# Heat capacities of an Ideal gas

f = #degrees
of freedom

$$C_p = C_V + nR$$

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

$$\Rightarrow C_p = \frac{f+2}{2}nR$$

$$\Rightarrow \frac{C_p}{C_V} = \frac{f+2}{2}nR / \frac{f}{2}nR = \frac{f+2}{f}$$

For a monoatomic gas f=3

$$\Rightarrow C_p = \frac{5}{2}nR ; \frac{C_p}{C_V} = 5/3 = 1.67$$

# Molar heat capacities of various gases at (25 C)

| Gas | Cp | Cv | Cv/R | Cp-Cv | (Cp-Cv)/R |
|-----|------|-------|------|-------|-----------|
| *Monoatomic* | | | | | |
| He | 20.79 | 12.52 | 1.51 | 8.27 | 0.99 |
| Ne | 20.79 | 12.68 | 1.52 | 8.11 | 0.98 |
| Ar | 20.79 | 12.45 | 1.50 | 8.34 | 1.00 |
| Kr | 20.79 | 12.45 | 1.50 | 8.34 | 1.00 |
| Xe | 20.79 | 12.52 | 1.51 | 8.27 | 0.99 |
| *Diatomic* | | | | | |
| N2 | 29.12 | 20.80 | 2.50 | 8.32 | 1.00 |
| H2 | 28.82 | 20.44 | 2.46 | 8.38 | 1.01 |
| O2 | 29.37 | 20.98 | 2.52 | 8.39 | 1.01 |
| CO | 29.04 | 20.74 | 2.49 | 8.40 | 1.00 |
| *Polyatomic* | | | | | |
| CO2 | 36.62 | 28.17 | 3.39 | 8.45 | 1.02 |
| N2O | 36.90 | 28.39 | 3.41 | 8.51 | 1.02 |
| H2S | 36.12 | 27.36 | 3.29 | 8.76 | 1.05 |

# Ideal gas: adiabatic process

$P$

**2**

$p = p(V,T)$

**1**

$V_2$   $V_1$

$V$
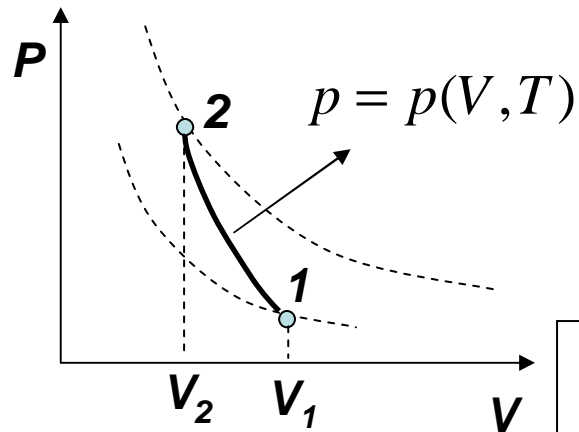
Adiabatic process: $Q = 0$

$$W = \int_{V_1}^{V_2} p\,dV = \int_{V_1}^{V_2} p(V,T)\,dV$$

$$pV = Nk_BT$$
$$\rightarrow d(pV) = d(nRT)$$
$$\rightarrow pdV + Vdp = nRdT$$

$$dU = -dW = -pdV$$
$$\rightarrow C_V dT = -pdV$$
$$\rightarrow n\frac{f}{2}RdT = -pdV$$

$$pdV + Vdp = -\frac{2}{f}pdV$$

**$f$ is the # of degrees of freedom**

# Ideal gas: adiabatic process (contd)
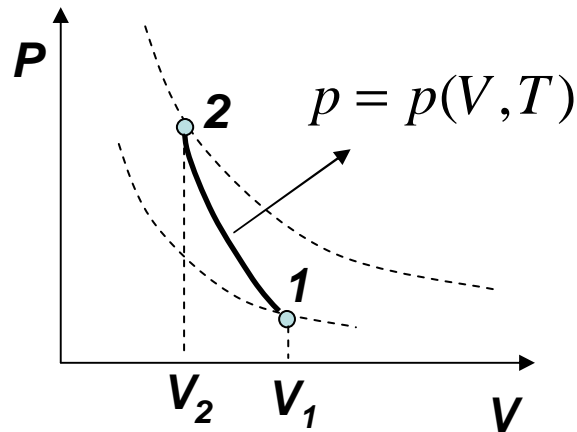


$$pdV + Vdp = -\frac{2}{f}pdV$$

$$\rightarrow Vdp + (1+\frac{2}{f})pdV = 0$$

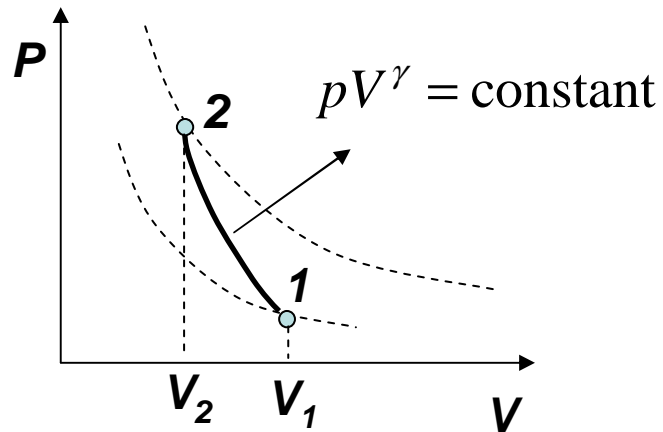let $\quad \gamma = (1+\frac{2}{f})$, and dividing by $pV$

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

$$\int_{p_1}^{p}\frac{dp}{p} + \gamma\int_{V_1}^{V}\frac{dV}{V} = 0$$

$$\rightarrow \ln\frac{p}{p_1} + \gamma\ln\frac{V}{V_1} = 0$$

$$\rightarrow \ln\frac{pV^{\gamma}}{p_1V_1^{\gamma}} = 0 \rightarrow \boxed{pV^{\gamma} = p_1V_1^{\gamma} = \text{constant}}$$

# Ideal gas: adiabatic process (contd)



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

$$W = -\Delta U = -nC_V \Delta T$$

$$= nC_V(T_1 - T_2)$$

$$= \frac{C_V}{R}(p_1 V_1 - p_2 V_2)$$

$$= \frac{1}{\gamma - 1}(p_1 V_1 - p_2 V_2)$$

Using:

$$pV^{\gamma} = p_1 V_1^{\gamma} = \text{constant}$$

$$\rightarrow W = p_1 V_1^{\gamma} \frac{1}{(\gamma - 1)}\left(\frac{1}{V_1^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}}\right)$$
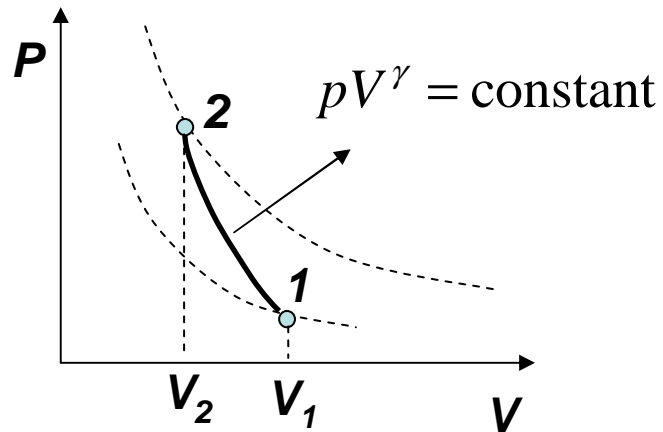
# Ideal gas: adiabatic process (contd)
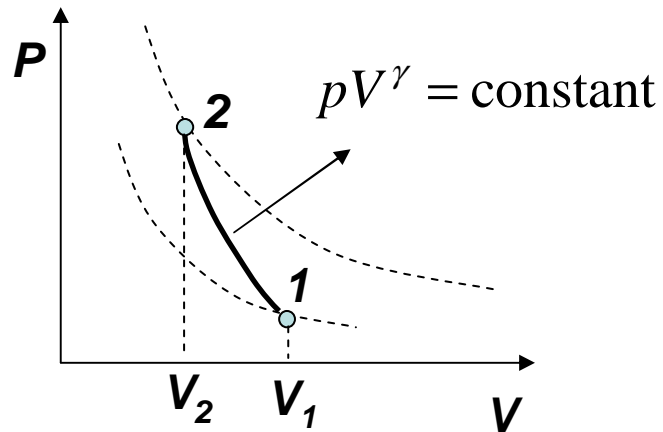


$$pV^{\gamma} = \text{constant}$$

$$pV^{\gamma} = p_1 V_1^{\gamma} = \text{constant}$$

$$\left.\begin{array}{l} p_1 V_1 = nRT_1 \\ p_2 V_2 = nRT_2 \end{array}\right\} \rightarrow \left.\begin{array}{l} \dfrac{p_1}{p_2}\dfrac{V_1}{V_2} = \dfrac{T_1}{T_2} \\ \\ p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \quad \rightarrow \dfrac{p_1}{p_2} = \dfrac{V_2^{\gamma}}{V_1^{\gamma}} \end{array}\right\}$$

$$\rightarrow \frac{V_2^{\gamma-1}}{V_1^{\gamma-1}} = \frac{T_1}{T_2}$$

or $\quad \boxed{T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} = \text{constant}}$

# Ideal gas: adiabatic process (contd)



$$pV^{\gamma} = p_1 V_1^{\gamma} = \text{constant}$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} = \text{constant}$$

$$pV = nRT$$

$$W = \frac{p_1 V_1^{\gamma}}{(\gamma-1)} \left( \frac{1}{V_1^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}} \right)$$

During an adiabatic expansion process, the reduction of the internal energy is used by the system to do work on the environment.

During an adiabatic compression process, the environment does work on the system and increases the internal energy.

# CPS question

When an ideal gas is allowed to expand *isothermally* from volume $V_1$ to a larger volume $V_2$, the gas does an amount of work equal to $W_{12}$.

If the same ideal gas is allowed to expand *adiabatically* from volume $V_1$ to a larger volume $V_2$, the gas does an amount of work that is

A. equal to $W_{12}$.

B. less than $W_{12}$.

C. greater than $W_{12}$.

D. either A., B., or C., depending on the ratio of $V_2$ to $V_1$.

# Summary

| Quasi-static process | Character | $\Delta U$ | $Q$ | $W$ |
|---|---|---|---|---|
| isochoric | V = constant | $\Delta U = Q$ | $Q = C_V \Delta T$ | $W = 0$ |
| isobaric | p = constant | $\Delta U = Q - W$ | $Q = C_P \Delta T$ | $W = p \Delta V$ |
| isothermal | T = constant | $\Delta U = 0$ | $Q = W$ | $W = nRT \ln \dfrac{V_2}{V_1}$ |
| adiabatic | $Q = 0$ | $\Delta U = -W$ | $Q = 0$ | $W = p_1 V_1^{\gamma} \dfrac{1}{(\gamma - 1)} \left( \dfrac{1}{V_2^{\gamma-1}} - \dfrac{1}{V_1^{\gamma-1}} \right)$ |