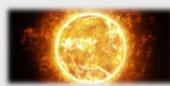




## Chapter 19

### The First Law of Thermodynamics



楊本立副教授

### Thermodynamics – Historical Background

- 3 Thermodynamics and mechanics were considered to be separate branches. Until about 1850, experiments by **James Joule** and others showed a connection between them.
- 3 A connection was found between the transfer of energy by **heat in thermal processes** and the transfer of energy by **work in mechanical processes**.
- 3 The concept of energy was generalized to include **internal energy**.
- 3 The **Law of Conservation of Energy** emerged as a universal law of nature.

## Outline

1. Internal energy
2. State variables, transfer variables
3. The first law of thermodynamics
4. Work in thermodynamics process
5. Various thermodynamics processes
6. Energy transfer mechanisms in thermal processes

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## 1. Internal energy

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## Internal Energy

- 3 Internal energy is all the energy of a system that is associated with its microscopic components (atoms and molecules) – viewed from a reference frame at rest with respect to the center of mass of the system.
- The bulk kinetic energy of the system due to its motion through space is NOT included in internal energy.

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In general,

- 3 Internal energy = thermal energy (kinetic energy relative to C.M.) + bond energy (potential energy).
- 3 Thermal energy is associated with random motion of molecules and, therefore, related to temperature.
- Random translational motion
- Rotational motion
- Vibrational motion
- 3 Bond energy is the intermolecular potential energy, related to latent heat or the energy required for phase transition.

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$$E_{\text{int}} = \underbrace{\text{thermal energy}}_{\substack{\text{Kinetic energy} \\ \rightarrow \text{Temperature}}} + \underbrace{\text{Bond energy}}_{\substack{\text{Potential energy} \\ \rightarrow \text{Phase transition, latent heat}}}$$

$$\Delta E_{\text{int}} = \left( \frac{1}{2} nR\Delta T \right) \times f \pm nL$$

$$= \underbrace{Q}_{=nc\Delta T + nL} + \underbrace{W}_{=-\int PdV}$$

$$c = \frac{Q}{n\Delta T} = \frac{\Delta E_{\text{int}} - W}{n\Delta T} = c_V, c_P, \dots$$

$$c_P - c_V = R$$

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⌚ For **ideal gases**, the internal energy is only the thermal energy and it depends only on **TEMPERATURE**.

$$E_{\text{int}} = \bar{K} = \left( \frac{1}{2} nRT \right) \times f$$

$$\Delta E_{\text{int}} = \left( \frac{1}{2} nR\Delta T \right) \times f$$

$$= (Q + \underbrace{W}_{=0})_{\text{isochoric}} = nc_V\Delta T$$

$$= (Q + \underbrace{W}_{=P\Delta V})_{\text{isobaric}} = n(c_P - R)\Delta T$$

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⌚ Is the internal energy of a solid likely to be independent of its volume, as is the case for an ideal gas? No!

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## 2. State variables, Transfer variables

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## State Variables

- 3 State variables describe the state of a system.
- 3 In the macroscopic approach to thermodynamics, variables are used to describe the state of the system, e.g.,
  - Pressure ( $P$ ), temperature ( $T$ ), volume ( $V$ ), internal energy ( $E_{\text{int}}$ ), particle number ( $N$ ).
- 3 The macroscopic state of an isolated system can be specified only if the system is in thermal equilibrium internally.

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## Transfer Variables

- 3 Transfer variables are zero unless a process occurs in which energy is transferred across the boundary of a system.
- 3 Transfer variables are not associated with any given state of the system, only with changes in the state.
  - Heat ( $Q$ ) and work ( $W$ ) are transfer variables.

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### 3. The first law of thermodynamics

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## The First Law of Thermodynamics

3 The First Law of Thermodynamics is an extension of the Law of Conservation of Energy.

3 The First Law of Thermodynamics states that

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

➤  **$E_{\text{int}}$**  is a state variable.

➤  $Q$  and  $W$  each are dependent on the path, BUT  
 $Q + W$  is independent of the path.

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## 4. Work in thermodynamics process

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## Work in Thermodynamic Process

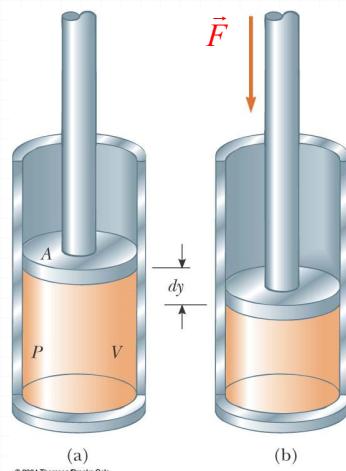
- 3 The piston is pushed downward by a force  $F$  through a displacement of  $dr$ ,

$$dW = \vec{F} \cdot d\vec{r} = -|\vec{F}| \hat{j} \cdot dy \hat{j}$$

$$= -PAdy = -PdV$$

- 3 The total work done on the system is:

$$W_{\text{on system}} = - \int_{V_i}^{V_f} PdV$$

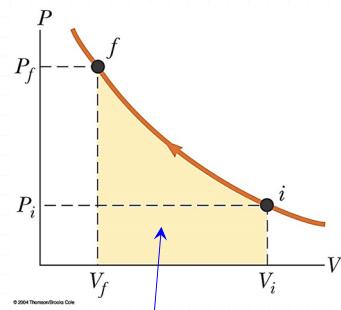


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## P–V Diagrams

- 3 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

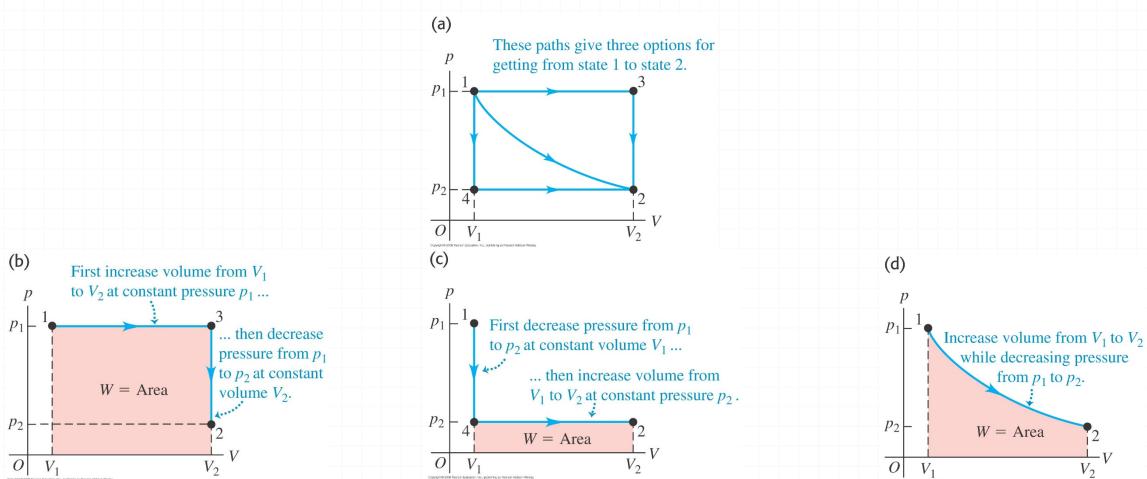


$$W = - \underbrace{\int_{V_i}^{V_f} P dV}_{\text{area}}$$

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## Work Done By Various Paths



Work depends not only on the initial and final states, but also on the path.

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## 5. Various thermodynamics processes

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### (1) Isolated Systems

3 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  $\Delta E_{\text{int}} = 0$

The internal energy of an isolated system remains constant.

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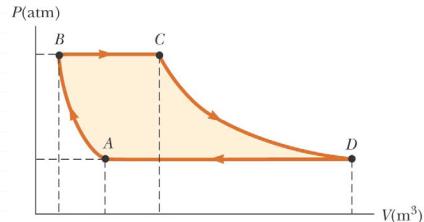
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## (2) Cyclic Processes

- 3 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.

$$\Delta E_{\text{int}} = 0, Q = -W$$



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## (3) Adiabatic Process

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

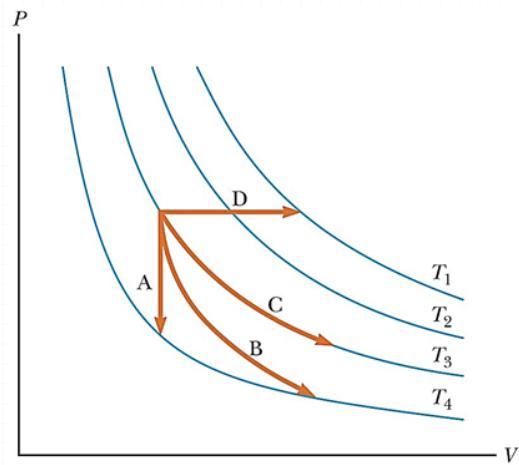
$$\nabla Q = 0, \Delta E_{\text{int}} = W$$

- 3 This can be achieved by:
1. Thermally insulating the walls of the system.
  2. Having the process proceed so quickly that no heat can be exchanged.

☺ If the gas expands adiabatically (but not for freely expansion), the temperature of the gas decreases.

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Path B could be the adiabatic expansion.

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Adiabatic compression.



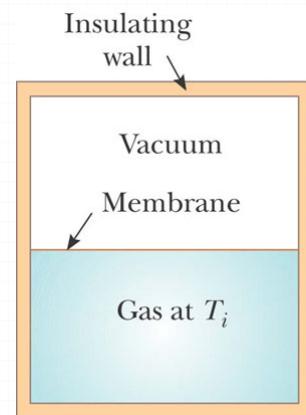
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## (4) Adiabatic Free Expansion

3 Because the gas expands into a vacuum, it does not apply a force on a piston and  $W = 0$ .

- $Q = 0$  and  $W = 0$ ,  $\Delta E_{\text{int}} = 0$  and the initial and final states are the same.
- No change in temperature is expected.

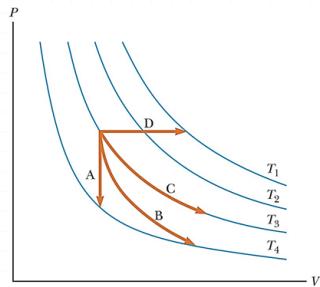


⌚ For nonideal gases, some temperature change occurs during free expansions, even though the internal energy is constant. For such a gas in a free expansion, the temperature usually drops.

$$\therefore \Delta \bar{K} \downarrow = \underbrace{\Delta E_{\text{int}}}_{=0} - \Delta \bar{U} \downarrow$$

## (5) Isobaric Processes

- 3 An isobaric process is one that occurs at a constant pressure (Path D).



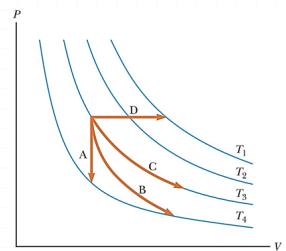
- The values of the heat and the work are generally both nonzero.
- The work done on the gas is  $W = -P(V_f - V_i)$ , where  $P$  is the constant pressure.

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## (6) Isovolumetric (isochoric) Processes

- 3 An isovolumetric process is one in which there is no change in the volume (Path A).



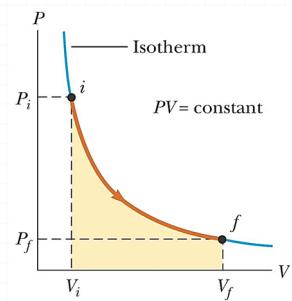
- Since the volume does not change,  $W = 0$ .
- From the first law,  $\Delta E_{\text{int}} = Q$ .

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## (7) Isothermal Process

- 3 An isothermal process is one that occurs at a constant temperature.
- 3 Since there is no change in temperature,  $\Delta E_{\text{int}} = 0$ .
  - Therefore,  $Q = -W$ .
  - $Q \neq 0$  in an isothermal process.  
(Don't confuse it with  $Q = C\Delta T$ .)



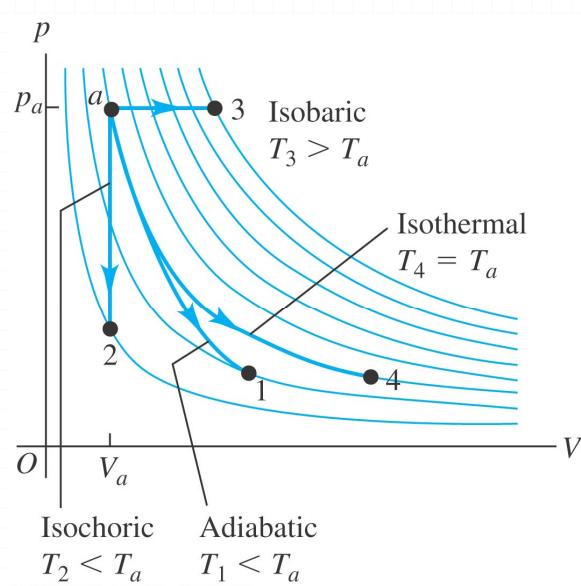
- 3 Because it is an ideal gas and the process is quasi-static,  $PV = nRT$  and

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

$$= -nRT \int_{V_i}^{V_f} \frac{dV}{V} \quad \Rightarrow \quad W = nRT \ln\left(\frac{V_f}{V_i}\right)$$

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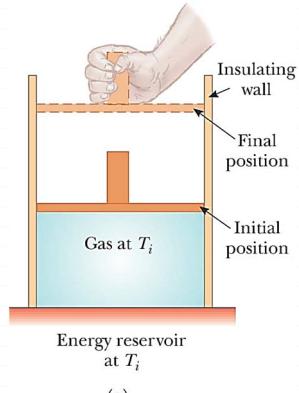
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### Isothermal process



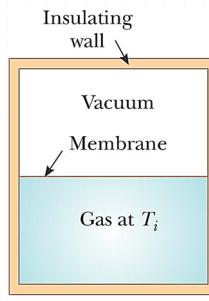
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$$W \neq 0$$

$$Q \neq 0$$

$$\Delta E_{\text{int},a} = 0$$

### Adiabatic free expansion



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$$W = 0$$

$$Q = 0$$

$$\Delta E_{\text{int},b} = 0$$

$E_{\text{int},a} = E_{\text{int},b}$ , although the process is different!

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| Situation  | System                        | $Q$ | $W$ | $\Delta E_{\text{int}}$ |
|--|-------------------------------|-----|-----|-------------------------|
| (a) Rapidly pumping up a bicycle tire                    | Air in the pump               | 0   | +   | +                       |
| (b) Pan of room-temperature water sitting on a hot stove | Water in the pan              | +   | 0   | +                       |
| (c) Air quickly leaking out of a balloon                 | Air originally in the balloon | 0   | -   | -                       |

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### Ex. An Isothermal Expansion

A 1.0-mol sample of an ideal gas is kept at 0.0°C during an expansion from 3.0 L to 10.0 L.

(A) How much work is done on the gas during the expansion?

$$\begin{aligned}W &= nRT \ln\left(\frac{V_f}{V_i}\right) \\&= (1.0 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(273 \text{ K}) \ln\left(\frac{10.0 \text{ L}}{3.0 \text{ L}}\right) \\&= -2.7 \times 10^3 \text{ J}\end{aligned}$$

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

$$\begin{aligned}\Delta E_{\text{int}} &= Q + W \\0 &= Q + W \\Q &= -W = 2.7 \times 10^3 \text{ J}\end{aligned}$$

(C) If the gas is returned to the original volume by means of an isobaric process, how much work is done on the gas?

$$\begin{aligned}W &= -P(V_f - V_i) = -\frac{nRT_i}{V_i}(V_f - V_i) \\&= -\frac{(1.0 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(273 \text{ K})}{10.0 \times 10^{-3} \text{ m}^3} \times (3.0 \times 10^{-3} \text{ m}^3 - 10.0 \times 10^{-3} \text{ m}^3) \\&= 1.6 \times 10^3 \text{ J}\end{aligned}$$

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### Ex. Boiling Water

Suppose 1.00 g of water vaporizes isobarically at atmospheric pressure ( $1.013 \times 10^5$  Pa). Its volume in the liquid state is  $V_i = V_{\text{liquid}} = 1.00 \text{ cm}^3$ , and its volume in the vapor state is  $V_f = V_{\text{vapor}} = 1671 \text{ cm}^3$ .

Find the work done in the expansion and the change in internal energy of the system. Ignore any mixing of the steam and the surrounding air – imagine that the steam simply pushes the surrounding air out of the way.

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### Ans:

$$\begin{aligned}W &= -P(V_f - V_i) \\&= -(1.013 \times 10^5 \text{ Pa})(1671 \times 10^{-6} \text{ m}^3 - 1.00 \times 10^{-6} \text{ m}^3) \\&= -169 \text{ J}\end{aligned}$$

$$Q = mL_v = (1.00 \times 10^{-3} \text{ kg})(2.26 \times 10^6 \text{ J/kg}) = 2260 \text{ J}$$

$$\Delta E_{\text{int}} = Q + W = 2260 \text{ J} + (-169 \text{ J}) = 2.09 \text{ kJ}$$

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### Ex. Heating a Solid

A 1.0-kg bar of copper is heated at atmospheric pressure. If its temperature increases from 20°C to 50°C,

- (A) what is the work done on the copper bar by the surrounding atmosphere?

$$\begin{aligned}\Delta V &= \beta V_i \Delta T \\ &= [5.1 \times 10^{-5} (\text{°C})^{-1}] (50\text{°C} - 20\text{°C}) V_i = 1.5 \times 10^{-3} V_i \\ &= 1.5 \times 10^{-3} \times \left( \frac{1.0 \text{ kg}}{8.92 \times 10^3 \text{ kg/m}^3} \right) = 1.7 \times 10^{-7} \text{ m}^3\end{aligned}$$

$$\begin{aligned}W &= -P \Delta V = -(1.013 \times 10^5 \text{ N/m}^2)(1.7 \times 10^{-7} \text{ m}^3) \\ &= -1.7 \times 10^{-2} \text{ J}\end{aligned}$$

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- (B) What quantity of energy is transferred to the copper bar by heat?

$$\begin{aligned}Q &= mc\Delta T = (1.0 \text{ kg})(387 \text{ J/kg} \cdot \text{°C})(30 \text{ °C}) \\ &= 1.2 \times 10^4 \text{ J}\end{aligned}$$

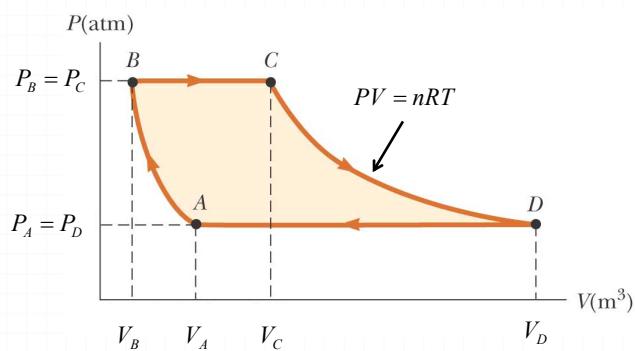
- (C) What is the increase in internal energy of the copper bar?

$$\begin{aligned}\Delta E_{\text{int}} &= Q + W = 1.2 \times 10^4 \text{ J} + (-1.7 \times 10^{-2} \text{ J}) \\ &= 1.2 \times 10^4 \text{ J}\end{aligned}$$

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**Ex.**



A → B, adiabatic

B → C, isobaric,  $Q_{BC}$

C → D, isothermal

D → A, isobaric,  $(-)Q_{DA}$

$$E_{\text{int},B} - E_{\text{int},A} = ?$$

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**Ans:**

$$\Delta E_{\text{int},AB} = E_{\text{int},B} - E_{\text{int},A}$$

$$= (E_{\text{int},B} - E_{\text{int},C}) + (E_{\text{int},C} - E_{\text{int},D}) + (E_{\text{int},D} - E_{\text{int},A})$$

$$= (-)\Delta E_{\text{int},BC} + (-)\Delta E_{\text{int},CD} + (-)\Delta E_{\text{int},DA}$$

$$\Delta E_{\text{int}} = Q + W = (-)[Q_{BC} - P_B(V_C - V_B)] + 0 + (-)[(-)Q_{DA} - P_A(V_A - V_D)]$$

$$= (Q_{DA} - Q_{BC}) + P_B(V_C - V_B) + P_A(V_A - V_D)$$

$$\underbrace{P_C}_{=P_B} V_C = \underbrace{P_D}_{=P_A} V_D = (nRT)$$

$$\Rightarrow \Delta E_{\text{int},AB} = (Q_{DA} - Q_{BC}) + (P_A V_A - P_B V_B)$$

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## 6. Adiabatic process for an ideal gas

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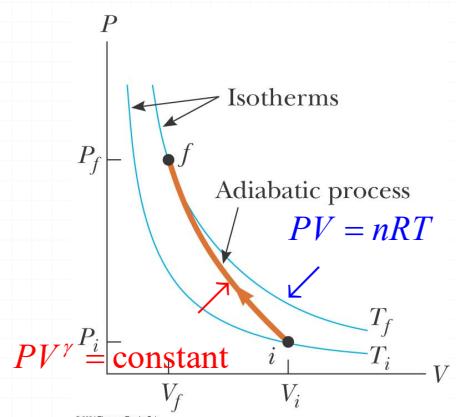
## Adiabatic Processes for an Ideal Gas

3 Assume an ideal gas is in an equilibrium state and so  $PV = nRT$  is valid.

3 The pressure and volume of an ideal gas at any time during an **adiabatic process** are related by

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

➤  $\gamma = C_p / C_V$



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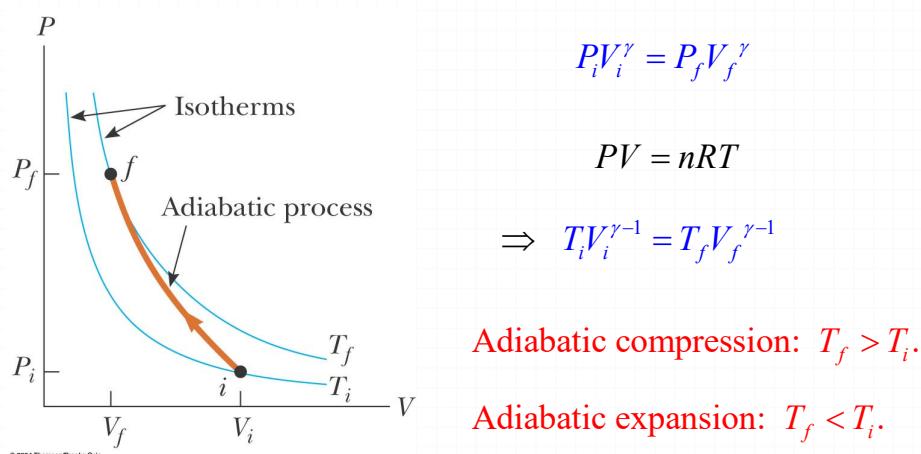
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Adiabatic process:

$$\begin{aligned}
 dE_{\text{int}} &= Q + W \\
 \Rightarrow nc_v dT &= 0 + (-PdV) \\
 PV &= nRT \quad PdV + VdP = nRdT \\
 \Rightarrow PdV + VdP &= -\frac{R}{c_v} PdV \\
 \Rightarrow \frac{dV}{V} + \frac{dP}{P} &= -\left(\frac{c_p - c_v}{c_v}\right) \frac{dV}{V} = (1-\gamma) \frac{dV}{V} \\
 \Rightarrow \frac{dP}{P} + \gamma \frac{dV}{V} &= 0 \\
 \Rightarrow PV^\gamma &= \text{constant}
 \end{aligned}$$

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$$PV_i^\gamma = PV_f^\gamma$$

$$PV = nRT$$

$$\Rightarrow TV_i^{\gamma-1} = T_fV_f^{\gamma-1}$$

Adiabatic compression:  $T_f > T_i$ .

Adiabatic expansion:  $T_f < T_i$ .

$$W = \Delta E_{\text{int}} = nc_v \Delta T = nc_v(T_f - T_i) = \frac{c_v}{R}(P_fV_f - P_iV_i)$$

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☺ The adiabatic process  $PV^\gamma = \text{const.}$  is valid only for equilibrium states.

In the other hand, the process sometimes has to be fast enough to prevent heat exchange in order to be adiabatic. Nevertheless,  $PV^\gamma = \text{const.}$  is still a good approximation.

**Q:** You have four samples of ideal gas, each of which contains the same number of moles of gas and has the same initial temperature, volume, and pressure. You compress each sample to one-half of its initial volume. Rank the four samples in order from highest to lowest value of the final pressure.

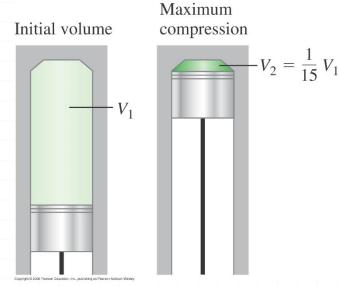
- (i) A monatomic gas compressed isothermally;
- (ii) A monatomic gas compressed adiabatically;
- (iii) A diatomic gas compressed isothermally;
- (iv) A diatomic gas compressed adiabatically.

**Ans:** (ii) > (iv) > (i) = (iii)

### Ex. Adiabatic compression in a diesel engine

The compression ratio of a diesel engine is 15 to 1; this means that air in the cylinders is compressed to 1/15 of its initial volume.

(A) If the initial pressure is  $1.01 \times 10^5$  Pa and the initial temperature is  $27^\circ\text{C}$  (300 K), find the final pressure and the temperature after compression. Air is mostly a mixture of diatomic oxygen and nitrogen; treat it as an ideal gas with  $\gamma = 1.40$ .



(B) How much work does the gas do during the compression if the initial volume of the cylinder is  $1.00 \text{ L} = 1.00 \times 10^{-3} \text{ m}^3$ ? Assume that  $C_V$  for air is  $20.8 \text{ J/mol}\cdot\text{K}$ .

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**Ans:**

$$(A) T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1} = (300 \text{ K})(15)^{0.4} = 886 \text{ K}$$

$$P_2 = P_1 \left( \frac{V_1}{V_2} \right)^{\gamma} = (1.01 \times 10^5 \text{ Pa})(15)^{1.4} = 44.8 \times 10^5 \text{ Pa}$$

(B)

$$n = \frac{P_1 V_1}{R T_1} = \frac{(1.01 \times 10^5 \text{ Pa})(1.00 \times 10^{-3} \text{ m}^3)}{8.314 \text{ J/mol}\cdot\text{K}(300 \text{ K})} = 0.0405 \text{ mol}$$

$$\begin{aligned} W_{\text{by gas}} &= -W_{\text{on gas}} = -\Delta E_{\text{int}} = n C_V (T_1 - T_2) \\ &= (0.0405 \text{ mol})(20.8 \text{ J/mol}\cdot\text{K})(300 \text{ K} - 886 \text{ K}) \\ &= -494 \text{ J} \end{aligned}$$

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