State Variables

- State variables describe the state of a system
- In the macroscopic approach to thermodynamics, some of the variables used to describe the state of the system are:
  - Pressure, temperature, volume, internal energy
- The macroscopic state of an isolated system can be specified only if the system is in **thermal equilibrium** internally

Transfer Variables

- Transfer variables are zero unless a process occurs in which energy is transferred across the boundary of a system
- Transfer variables are not associated with any given state of the system, only with **changes in the state**
- **Heat** and **work** are transfer variables
  - Example of heat: we can only assign a value of the heat if energy crosses the system boundary by heat

Work in Thermodynamics

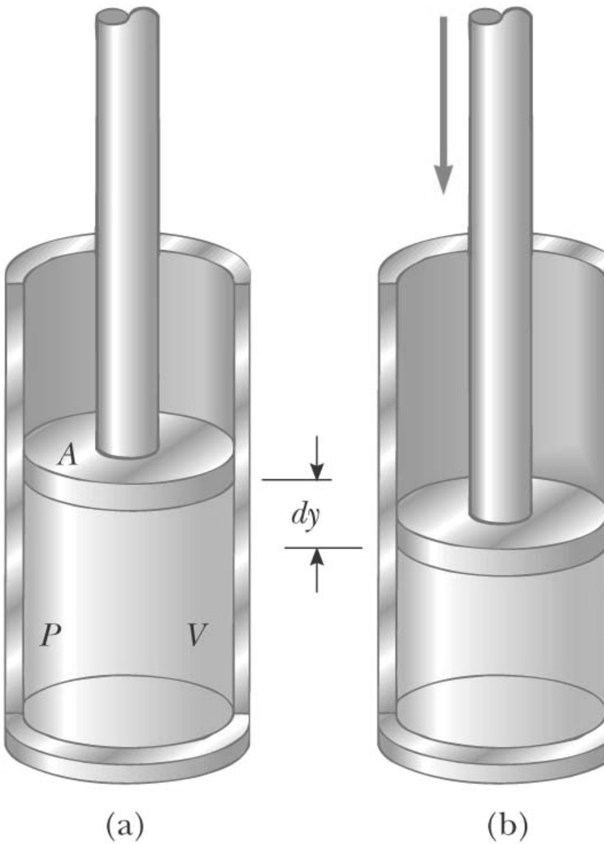
Work can be done on a **deformable** system, such as a gas

Consider a cylinder with a moveable piston

A force is applied to slowly compress the gas

- The compression is **slow** enough for all the system to remain essentially **in thermal equilibrium**
- This is said to occur

quasi-statically



Work

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

$$dW = \mathbf{F} \cdot d\mathbf{r} = \square F\hat{\mathbf{j}} \cdot dy\hat{\mathbf{j}} = \square F dy = \square PA\, dy$$

- *A*·*dy* is the change in volume of the gas, *dV*
- Therefore, the work done on the gas is

dW* = *P dV

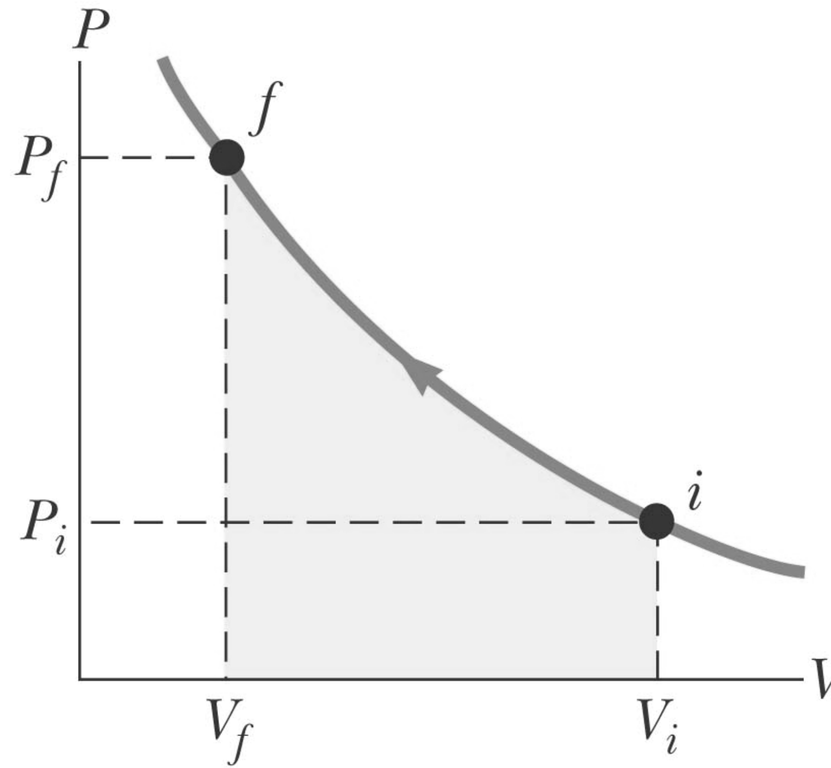
Work

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

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

PV Diagrams

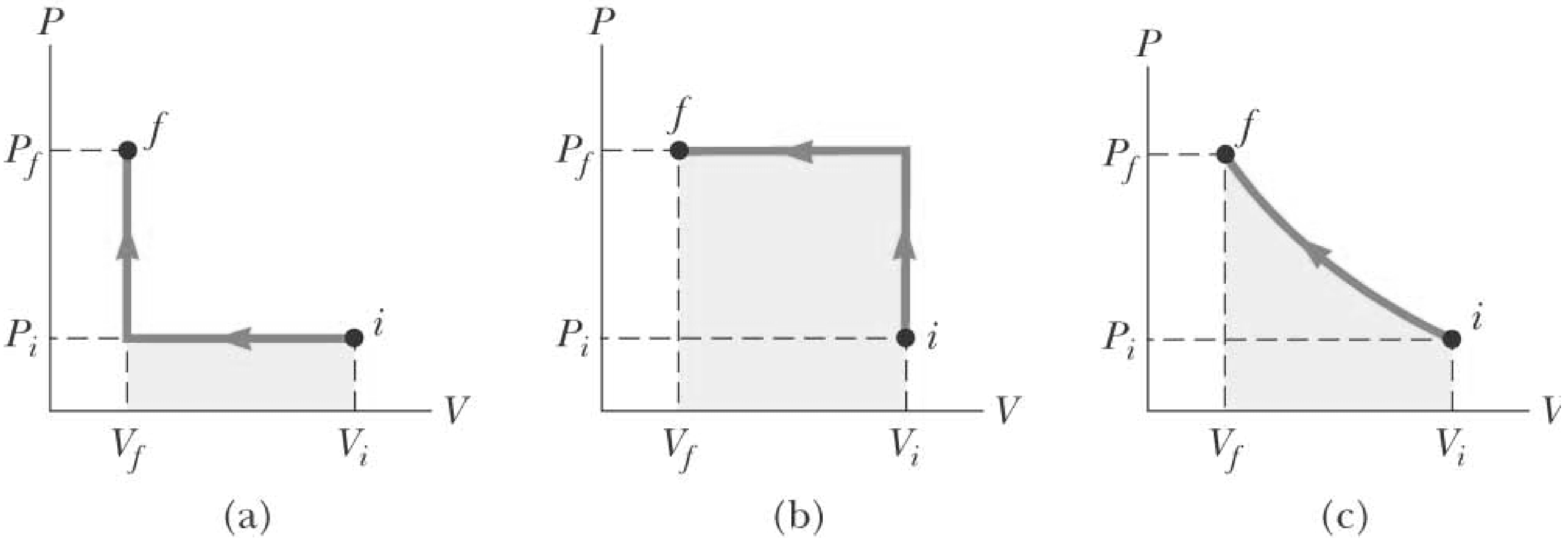
- Used when the pressure and volume are known at each step of the process
- The state of the gas at each step can be plotted on a graph called a ***PV* diagram**
  - This allows us to visualize the process through which the gas is progressing
- The curve is called the *path*



PV Diagrams

- 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 **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 **depends on the path taken**

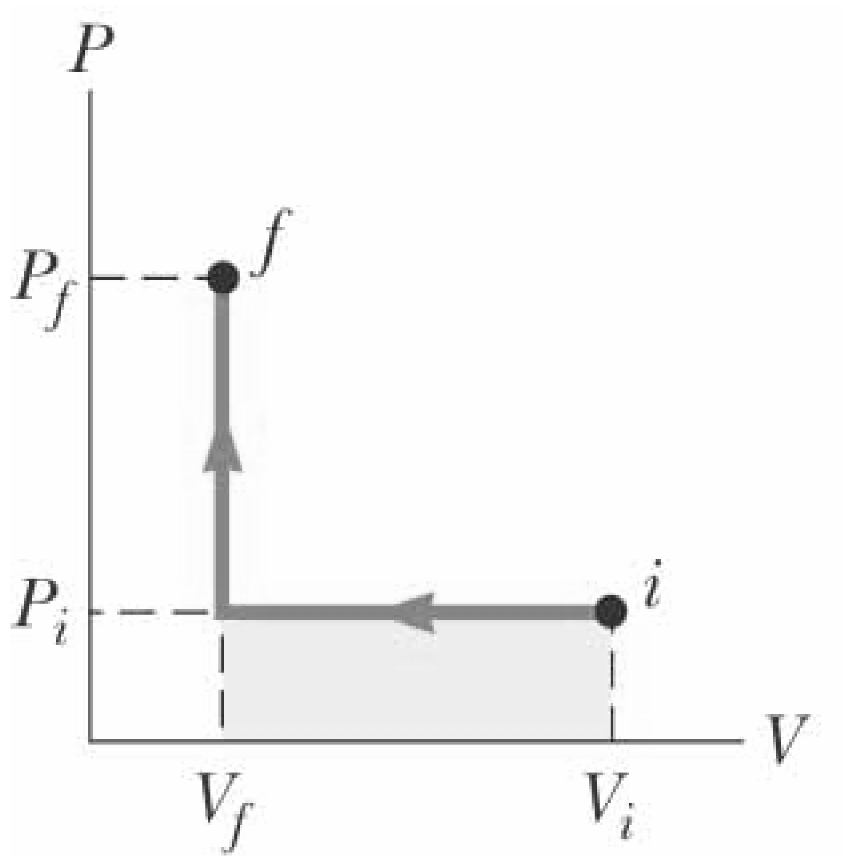
Work Done By Various Paths



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

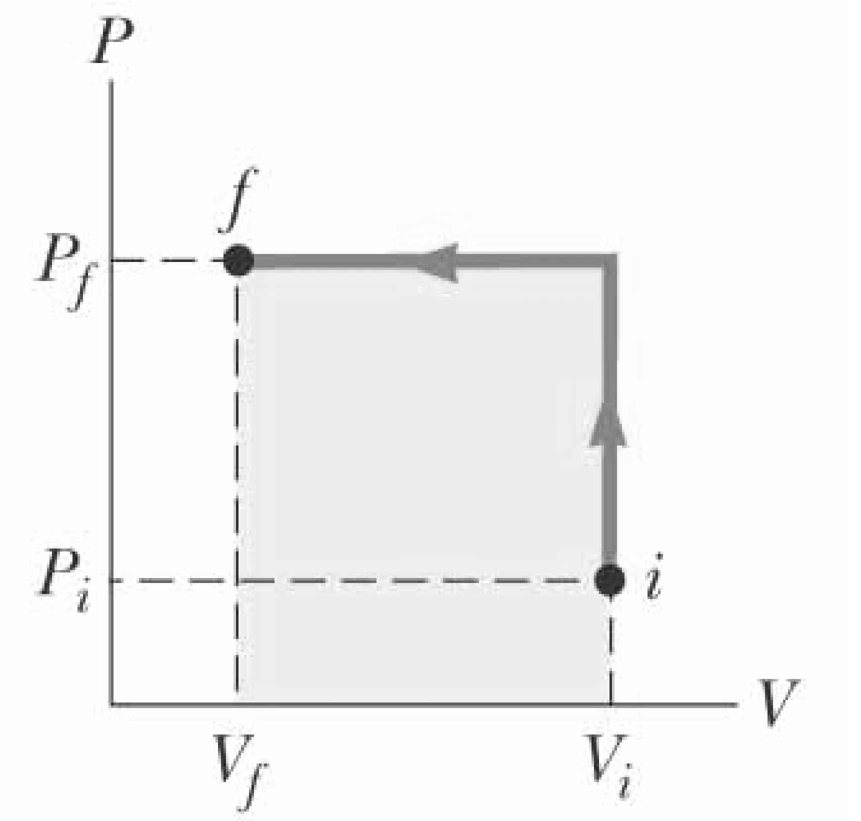
Work From a PV Diagram, Example 1

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



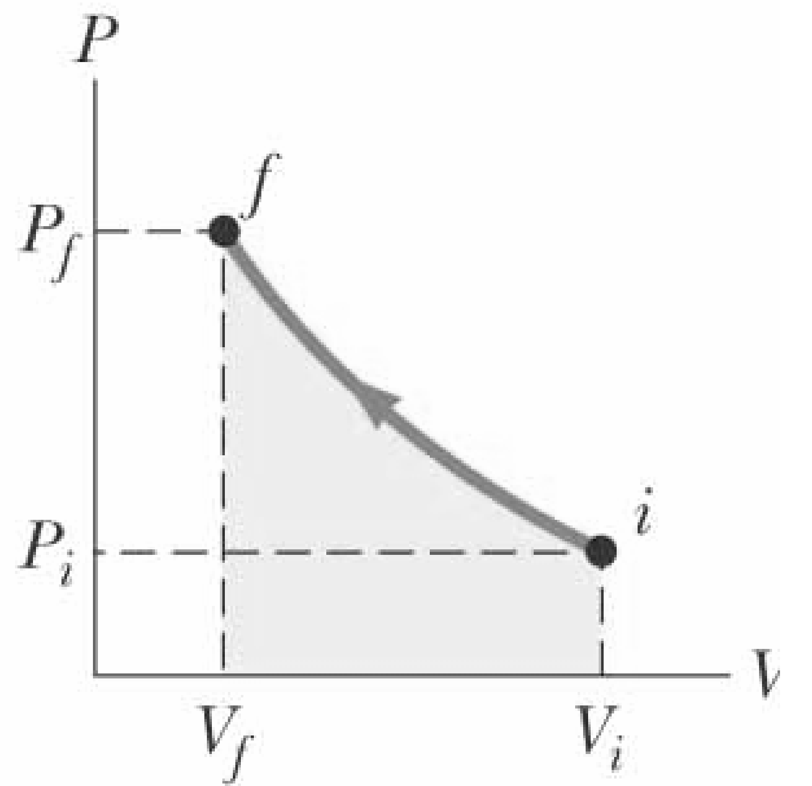
Work From a *PV* Diagram, Example 2

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



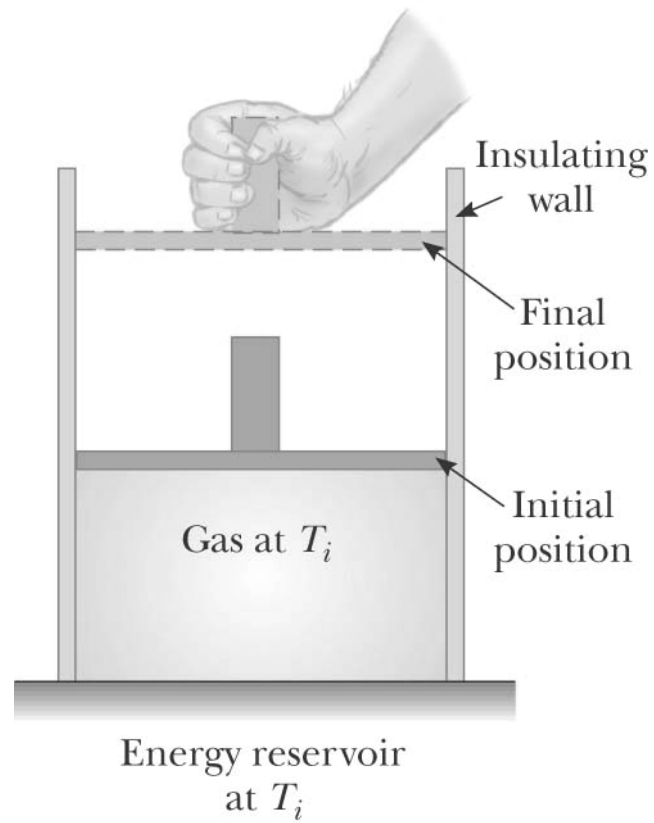
Work From a *PV* Diagram, Example 3

- 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



Heat Transfer, Example 1

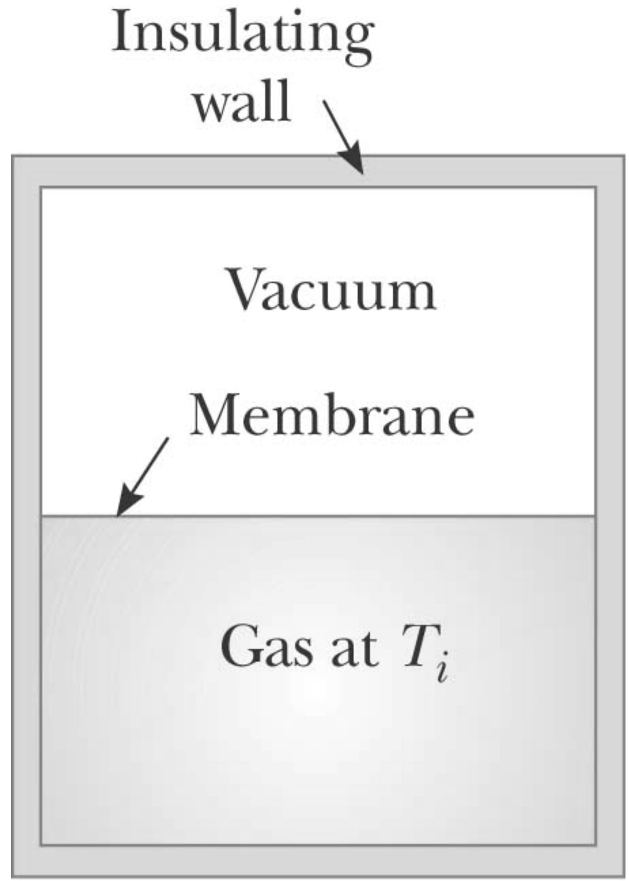
- The energy transfer, *Q*, into or out of a system also **depends on the process**
- The **energy reservoir** is a source of energy that is considered to be so great that a finite transfer of energy does not change its temperature
- The piston is pushed upward, the gas is doing work on the piston



(a)

Heat Transfer, Example 2

- This 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



(b)

Energy Transfer, Summary

- **Energy transfers by heat and 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

The First Law of Thermodynamics

- The First Law of Thermodynamics is a special case of the Law of Conservation of Energy
  - It takes into account changes in internal energy and energy transfers by heat and work
- Although *Q* and *W* each are dependent on the path,

  ***Q* - *W* is independent of the path**
- The First Law of Thermodynamics states that

$$\mathrm{D}\boldsymbol{E}_{\mathbf{int}} = \boldsymbol{Q} - \boldsymbol{W}$$

  - All quantities must have the same units of measure of energy

NOTE: Only CHANGE in internal energy matters

The First Law of Thermodynamics

- One consequence of the first law is that there must exist some quantity known as internal energy which is determined by the state of the system
- For infinitesimal changes in a system

$$\boldsymbol{dE_{\mathrm{int}} = dQ - dW}$$

- The first law is an energy conservation statement specifying that the only type of energy that changes in a system is internal energy