

# Thermodynamics: An Engineering Approach

## 8th Edition

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## CHAPTER 4

# ENERGY ANALYSIS OF CLOSED SYSTEMS

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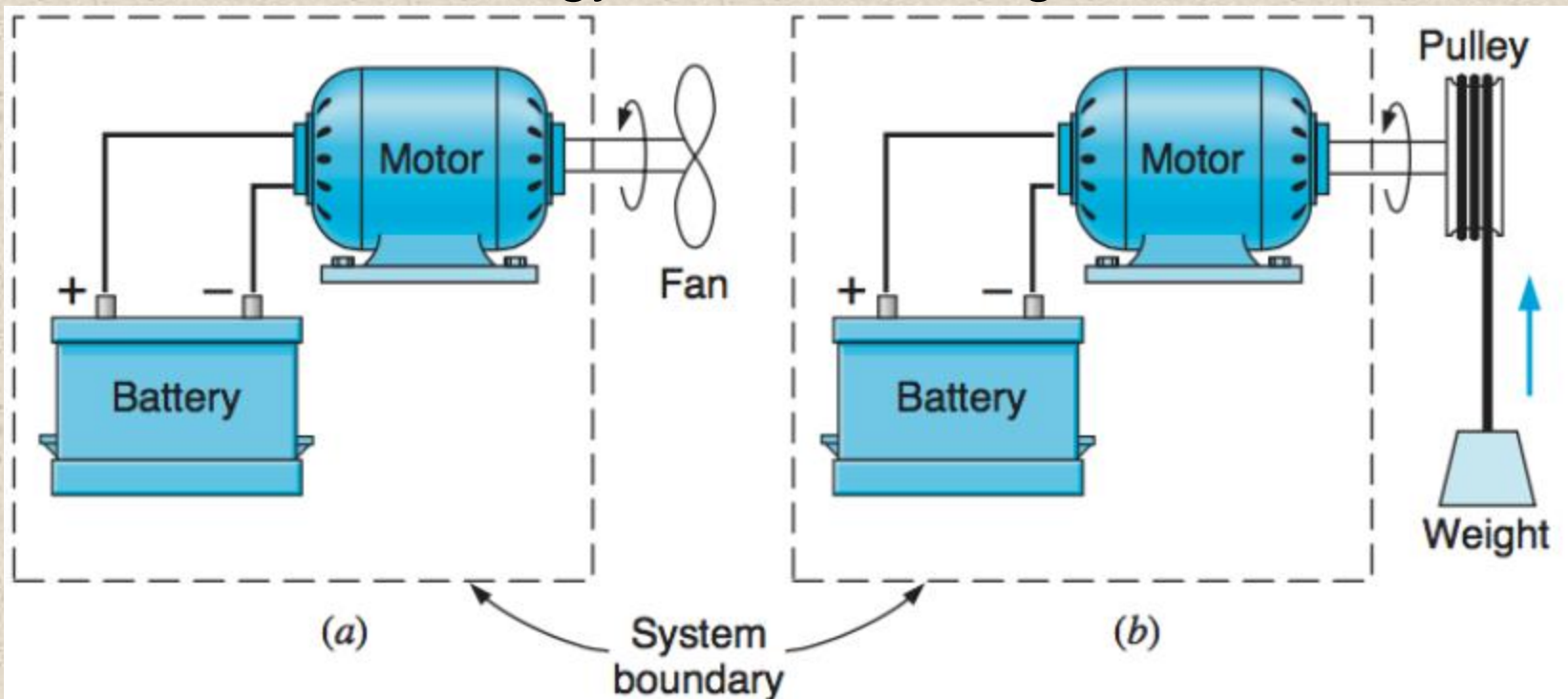
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# Objectives

- Examine the moving boundary work or  $P dV$  work commonly encountered in reciprocating devices (e.g. engines)
- Identify the first law of thermodynamics as the conservation of energy principle for closed (fixed mass) systems
- Develop the general energy balance applied to closed systems
- Define the specific heat at constant volume and the specific heat at constant pressure
- Relate the specific heats to the calculation of the changes in internal energy and enthalpy of ideal gases
- Describe incompressible substances and determine the changes in their internal energy and enthalpy
- Solve energy balance problems for closed (fixed mass) systems that involve heat and work interactions for general pure substances, ideal gases, and incompressible substances

# WORK

- Work is usually defined as a force  $F$  acting through a displacement  $x$ , where the displacement is in the direction of the force:
$$W = \int_1^2 F dx$$
- *Work is done by a system if the sole effect on the surroundings (everything external to the system) could be the raising of a weight*
- Work is a form of energy in transit, recognized at the boundary



# MOVING BOUNDARY WORK

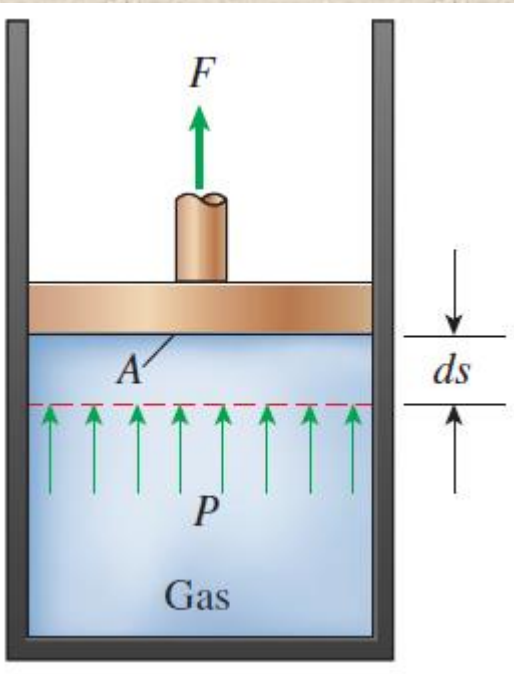
**Moving boundary work ( $P dV$  work):** The expansion and compression work in a piston-cylinder device

$$\delta W_b = F ds = PA ds = P dV$$

$$W_b = \int_1^2 P dV \quad (\text{kJ})$$

$W_b$  is positive  $\rightarrow$  for expansion

$W_b$  is negative  $\rightarrow$  for compression

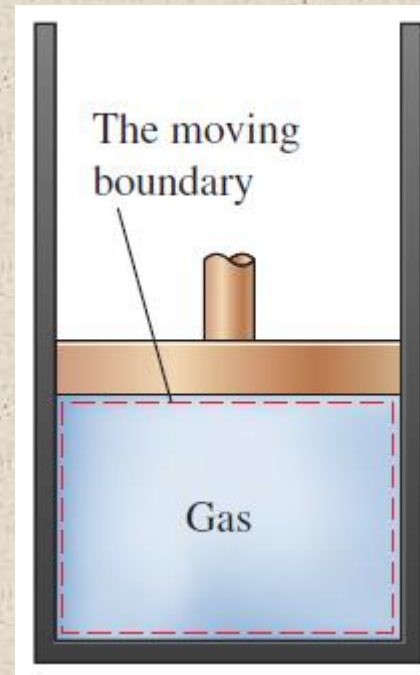


**FIGURE 4–1**

The work associated with a moving boundary is called *boundary work*.

**FIGURE 4–2**

A gas does a differential amount of work  $\delta W_b$  as it forces the piston to move by a differential amount  $ds$ .





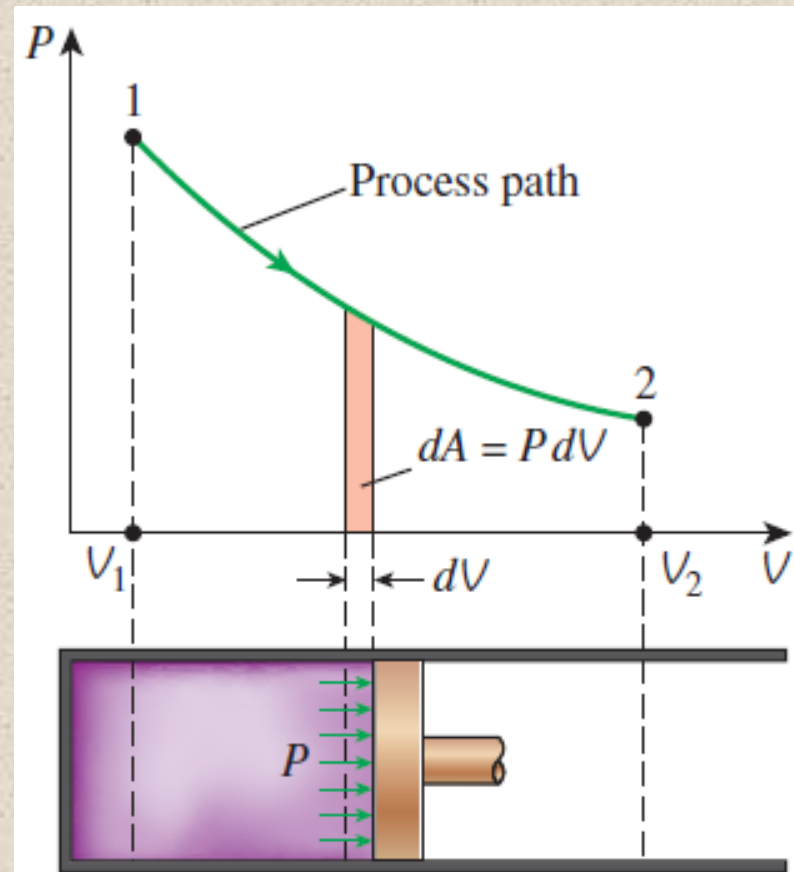
- **Quasi-equilibrium process:**  
A process during which the system remains nearly in equilibrium at all times (uniform pressure, temperature), process curve can be then plotted

$$\text{Area} = A = \int_1^2 dA = \int_1^2 P dV$$

under the curve

- *The area under the process curve on a  $P$ - $V$  diagram is equal, in magnitude, to the work done during a quasi-equilibrium expansion or compression process of a closed system*

$$W_b = \int_1^2 P dV \quad (\text{kJ})$$

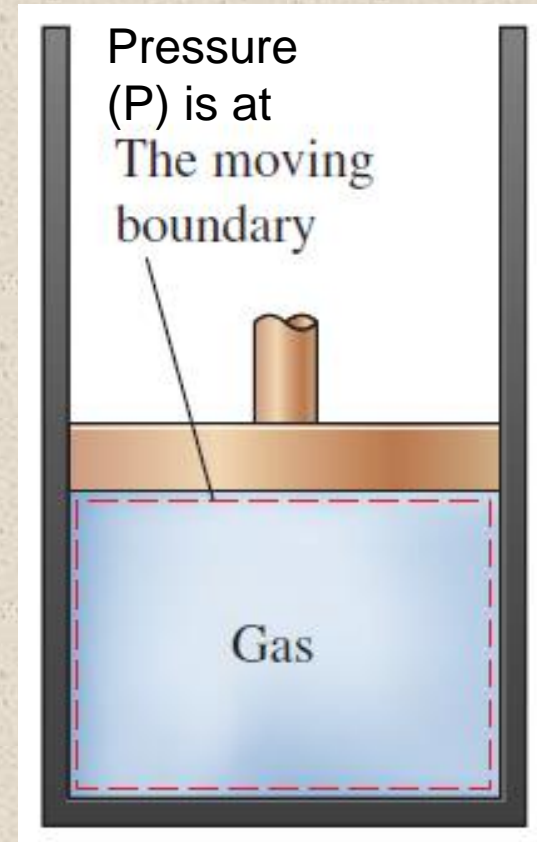


**FIGURE 4–3**

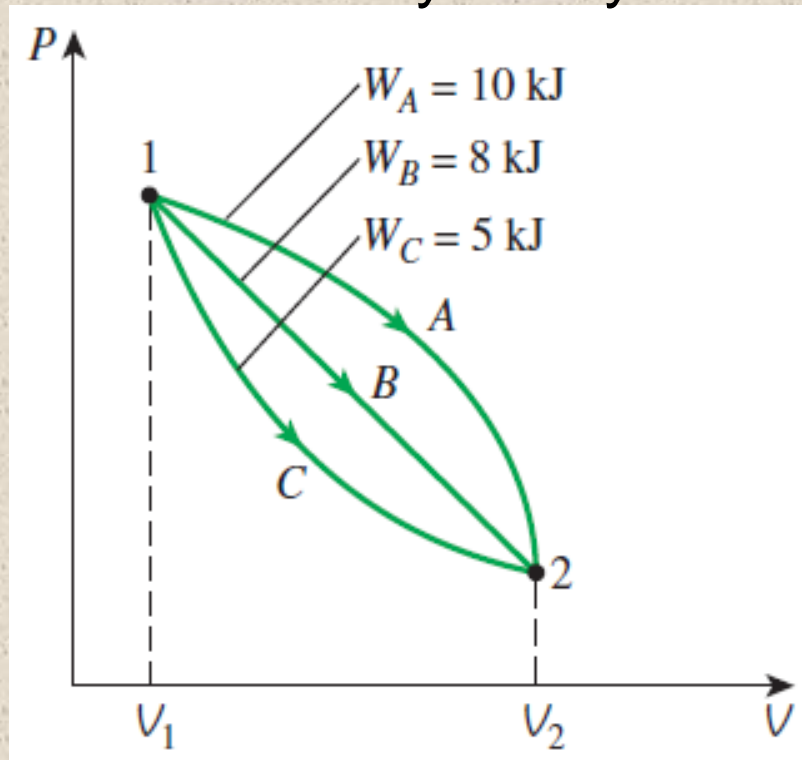
The area under the process curve on a  $P$ - $V$  diagram represents the boundary work.

$$W_b = \int_1^2 P dV \quad (\text{kJ})$$

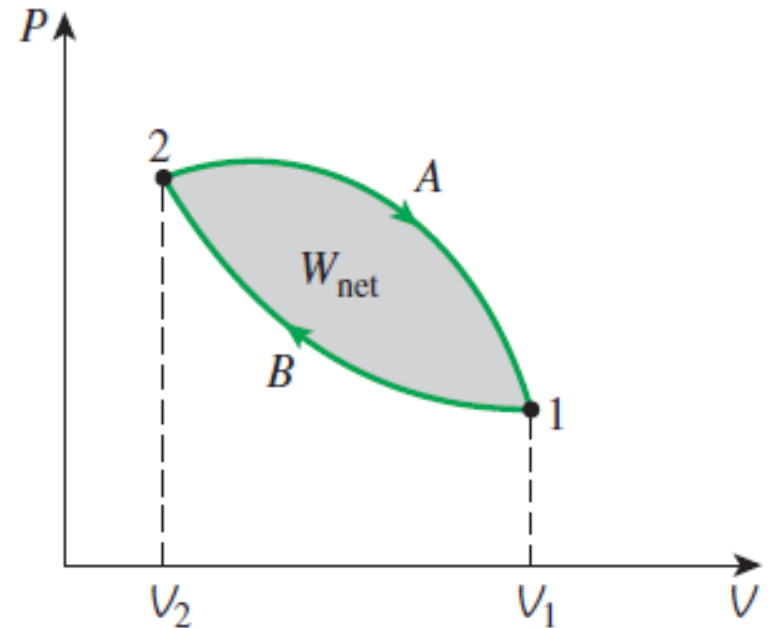
- Strictly speaking, *the pressure  $P$  is the pressure at the inner surface of the piston*
- It becomes equal to *the pressure of the gas in the cylinder only if the process is quasi equilibrium* and thus the entire gas in the cylinder is at the same pressure at any given time
- The equation (for  $W_b$ ) can also be used for nonquasi-equilibrium processes provided that the pressure at the inner face of the piston is used for  $P$
- We cannot speak of the pressure of a system during a nonquasi-equilibrium process since properties are defined for equilibrium states only



Positive sign suggests that the work is done by the system



- The boundary work done during a process depends on the path followed between the end states



**FIGURE 4-5**

The net work done during a cycle is the difference between the work done by the system and the work done on the system.

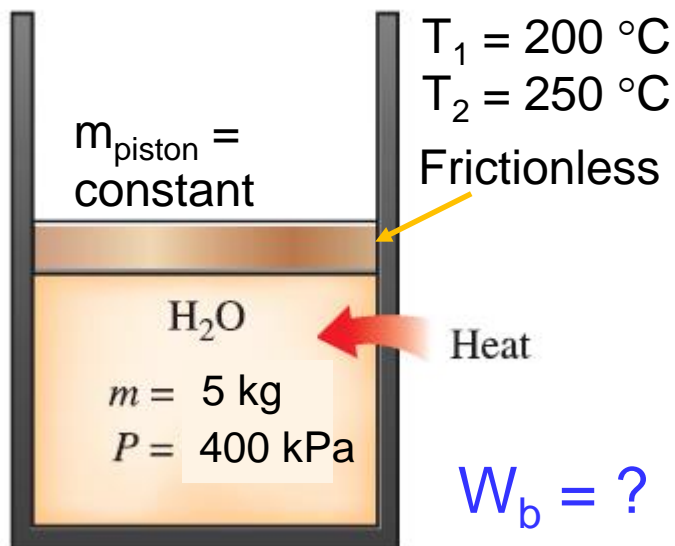
## Boundary Work for a Constant-Pressure Process

A frictionless piston-cylinder device contains 5 kg of steam at 400 kPa and 200 °C. Heat is now transferred to the steam until the temperature reaches 250 °C. If the piston is not attached to a shaft and its mass is constant, determine the work done by the steam during this process

**Assumption** The expansion process is quasi-equilibrium.

**Analysis** Even though it is not explicitly stated, the pressure of the steam within the cylinder remains constant during this process since both the atmospheric pressure and the weight of the piston remain constant. Therefore, this is a constant-pressure process,

System: Water vapor inside the piston/cylinder



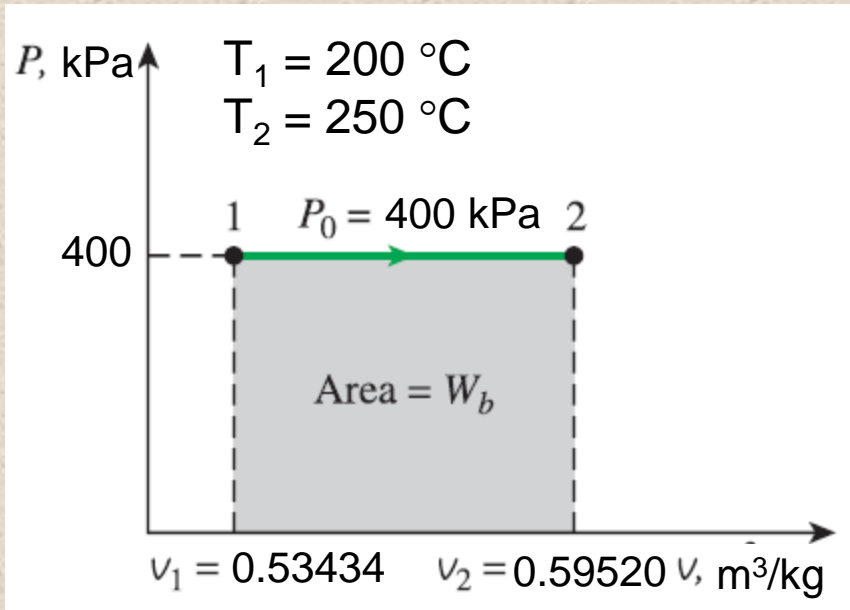
$$W_b = \int_1^2 P dV = P_0 \int_1^2 dV = P_0(V_2 - V_1)$$

$$V = mv.$$

$$W_b = mP_0(v_2 - v_1)$$



# Boundary Work for a Constant-Pressure Process



$$W_b = mP_0(v_2 - v_1)$$

Water is in superheated vapor state (check this!!)

$$\left. \begin{array}{l} v_1 = 0.53434 \text{ m}^3/\text{kg} \\ v_2 = 0.59520 \text{ m}^3/\text{kg} \end{array} \right\} \text{Table A-6}$$

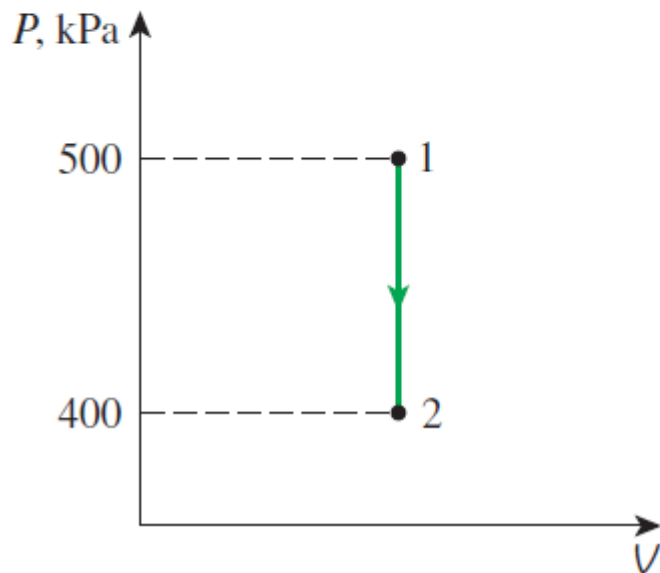
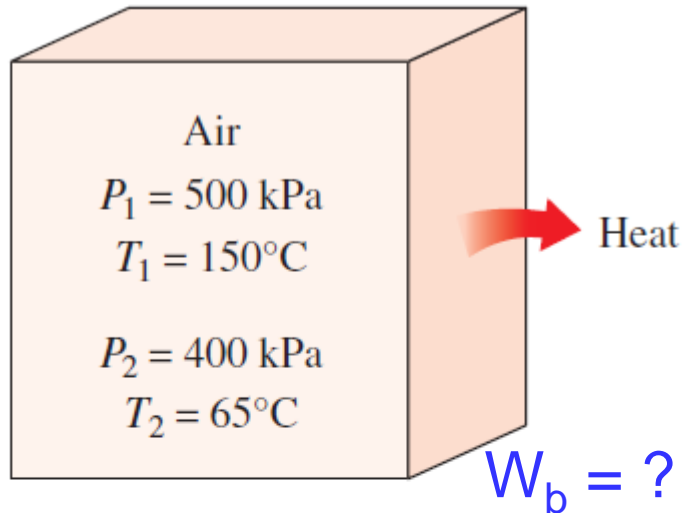
$$W_b = 122 \text{ kJ}$$

Work is done by the system as sign of  $W_b$  is positive (expansion)

# Boundary Work for a Constant-Volume Process

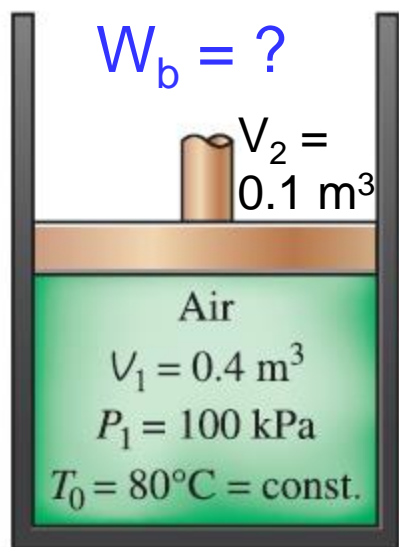
A rigid tank contains air at 500 kPa and 150 °C. As a result of heat transfer to the surroundings, the temperature and pressure inside the tank drop to 65 °C and 400 kPa, respectively. Determine the boundary work done during this process.

System: Air in the tank



$$W_b = \int_1^2 P dV$$

The boundary work during a constant volume process is always zero (since  $dV = 0$ ), this is evident from the P-V diagram of the process (the area under the process curve is zero)



## Boundary Work for an Isothermal Compression Process for an Ideal Gas

A piston-cylinder device initially contains  $0.4 \text{ m}^3$  of air at  $100 \text{ kPa}$  and  $80^\circ\text{C}$ . The air is now compressed to  $0.1 \text{ m}^3$  in such a way that the temperature inside the cylinder remains constant. Determine the work done during this process.

System: Air inside the piston/cylinder

**Assumptions** 1 The compression process is quasi-equilibrium. 2 At specified conditions, air can be considered to be an ideal gas since it is at a high temperature and low pressure relative to its critical-point values.

**Analysis** For an ideal gas at constant temperature  $T_0$ ,

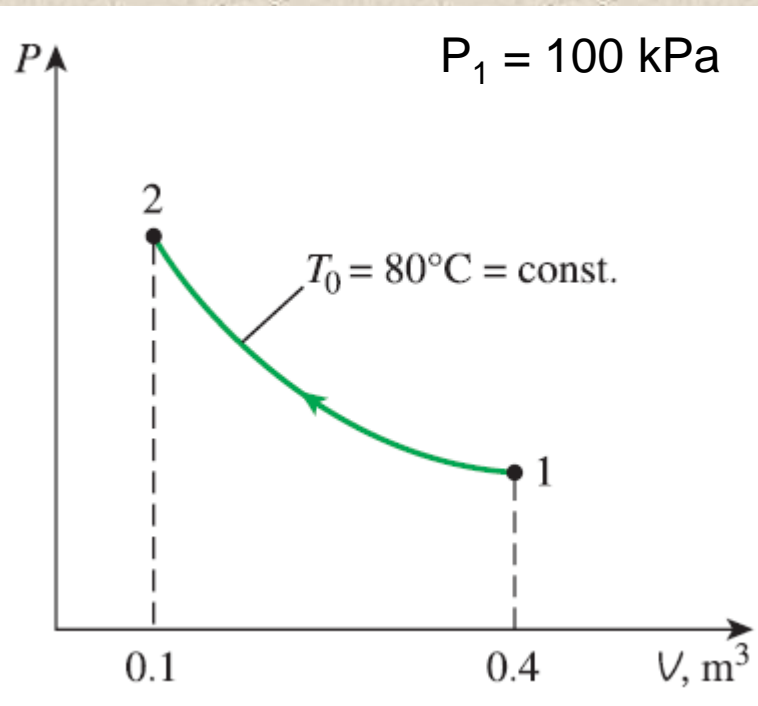
$$PV = mRT_0 = C \quad \text{or} \quad P = \frac{C}{V} \quad \text{Ideal gas equation of state}$$

$C$  is a constant

$$W_b = \int_1^2 P dV = \int_1^2 \frac{C}{V} dV = C \int_1^2 \frac{dV}{V} = C \ln \frac{V_2}{V_1} = P_1 V_1 \ln \frac{V_2}{V_1}$$

$P_1 V_1$  can be replaced by  $P_2 V_2$  or  $mRT_0$ , also  $V_2/V_1$  can be replaced by  $P_1/P_2$  for this case (**ideal gas assumption**)

# Boundary Work for an Isothermal Compression Process for an Ideal Gas



$$W_b = P_1 V_1 \ln \frac{V_2}{V_1}$$

$W_b = -55.5 \text{ kJ}$  (negative sign indicates that this work is done on the system)



# Boundary Work for a Polytropic Process

$$PV^n = C$$

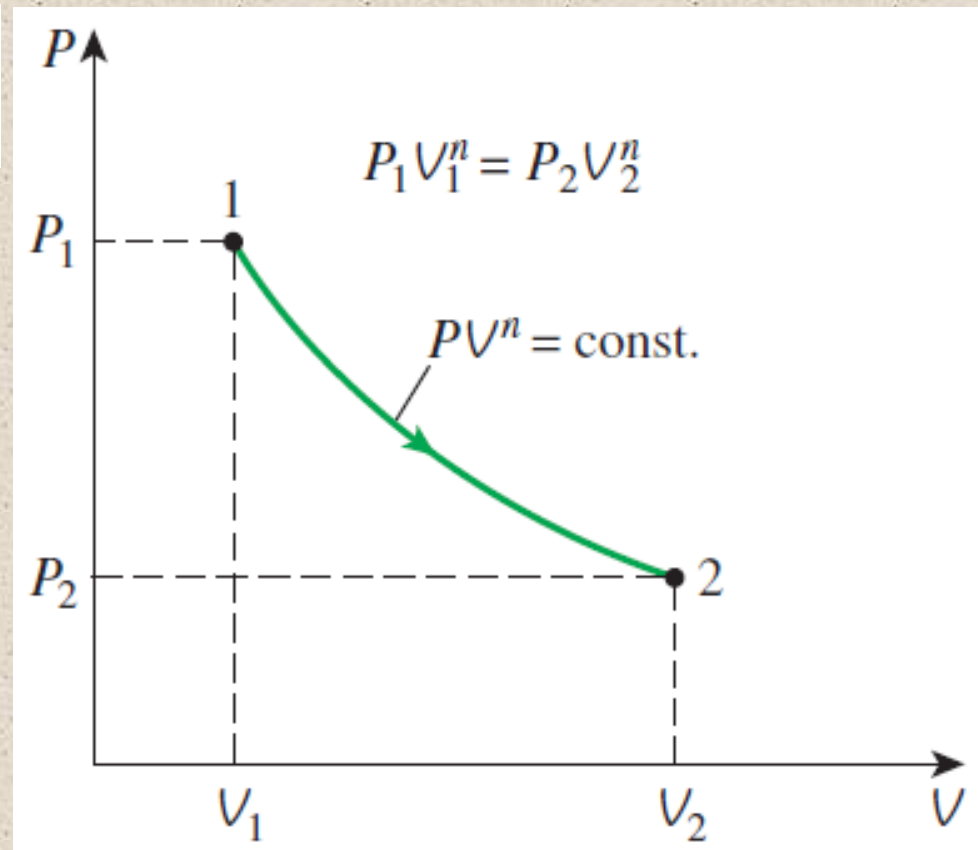
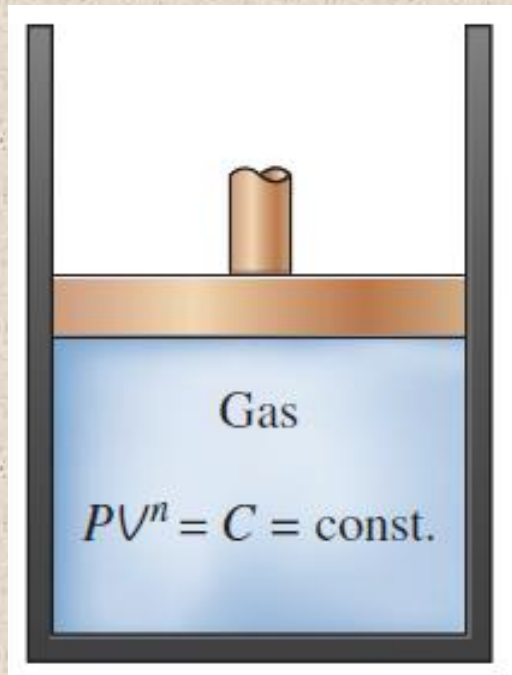
$$P = CV^{-n}$$

$n$  and  $C$  are constants

$$W_b = \int_1^2 P dV = \int_1^2 CV^{-n} dV = C \frac{V_2^{-n+1} - V_1^{-n+1}}{-n + 1} = \frac{P_2 V_2 - P_1 V_1}{1 - n}$$

for ideal gas  
( $PV = mRT$ )

$$W_b = \frac{mR(T_2 - T_1)}{1 - n}$$



System: Gas inside the piston/cylinder

For polytropic process:  $n$

$$PV^n = C$$

$$W_b = \frac{P_2 V_2 - P_1 V_1}{1 - n}$$

Real gas

$$W_b = \frac{mR(T_2 - T_1)}{1 - n}$$

Ideal gas (PV = mRT)

For isobaric process:  $n = 0$

$$P = P_0 = C$$

$$W_b = P_0(V_2 - V_1)$$

Real gas

$$W_b = mR(T_2 - T_1)$$

Ideal gas (PV = mRT)

For ideal gas and isothermal process:  $n = 1$

$$PV = mRT_0 = C$$

Ideal gas (PV = mRT)

$$W_b = P_1 V_1 \ln \frac{V_2}{V_1}$$

Ideal gas (PV = mRT)

For isochoric process:  $n = \infty$

$$V = V_0 = C$$

$$W_b = 0$$

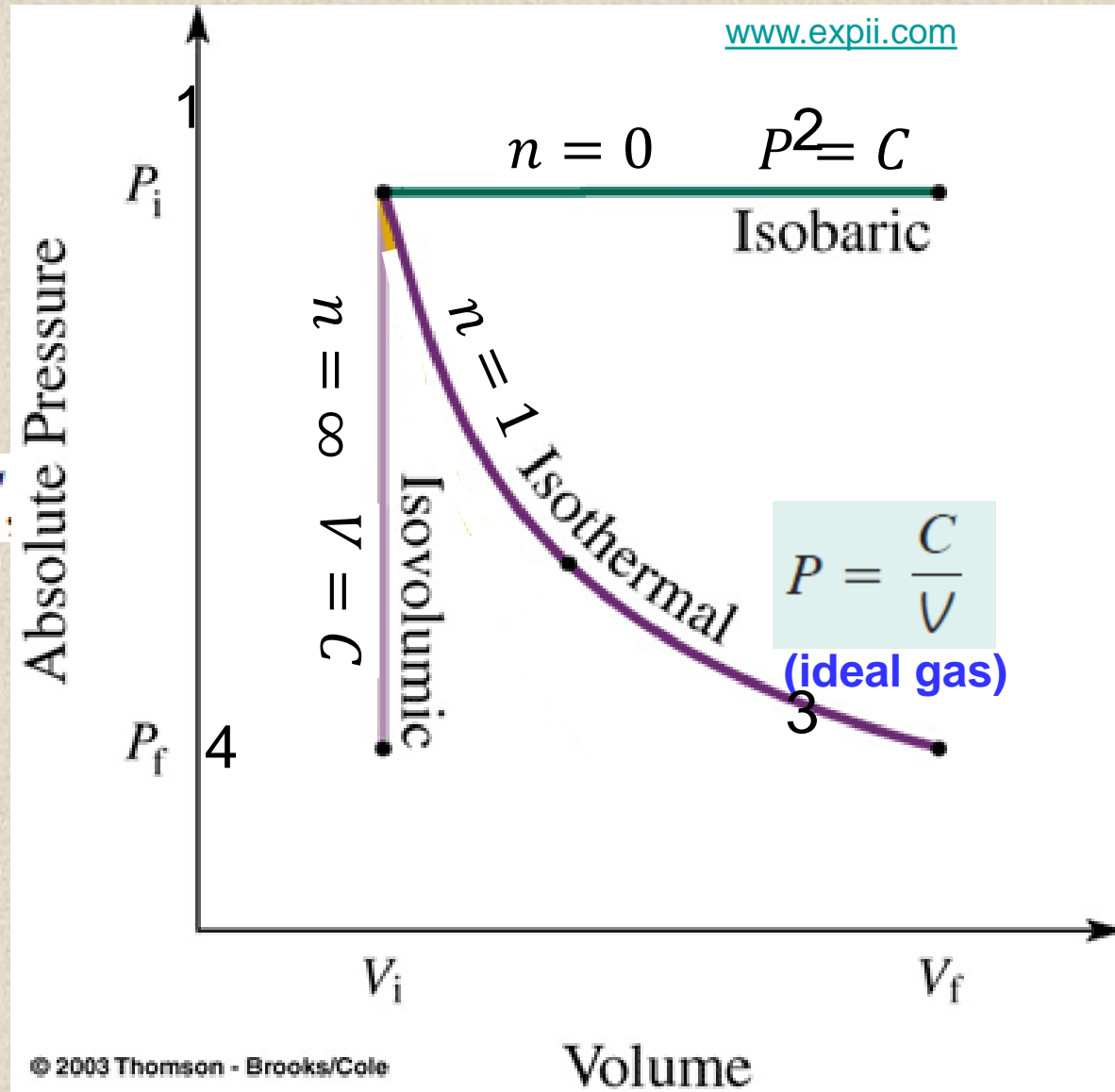
Real gas

$$W_b = 0$$

Ideal gas (PV = mRT)

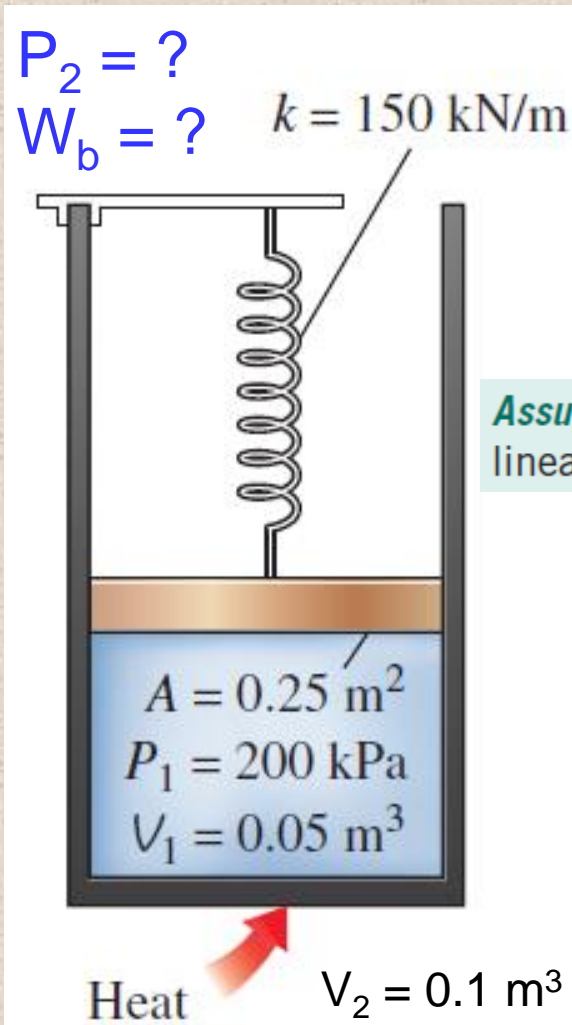
During actual expansion and compression processes of gases, pressure and volume are often related by  $PV^n = C$ , where  $n$  and  $C$  are constants. A process of this kind is called a **polytropic process**

$$PV^n = C$$



# Expansion of a Gas against a Spring

A piston–cylinder device contains  $0.05 \text{ m}^3$  of a gas initially at  $200 \text{ kPa}$ . At this state, a linear spring that has a spring constant of  $150 \text{ kN/m}$  is touching the piston but exerting no force on it. Now heat is transferred to the gas, causing the piston to rise and to compress the spring until the volume inside the cylinder doubles. If the cross-sectional area of the piston is  $0.25 \text{ m}^2$ , determine (a) the final pressure inside the cylinder, (b) the total work done by the gas.



**Assumptions** 1 The expansion process is quasi-equilibrium. 2 The spring is linear in the range of interest.

$$W_b = \int_1^2 P dV$$

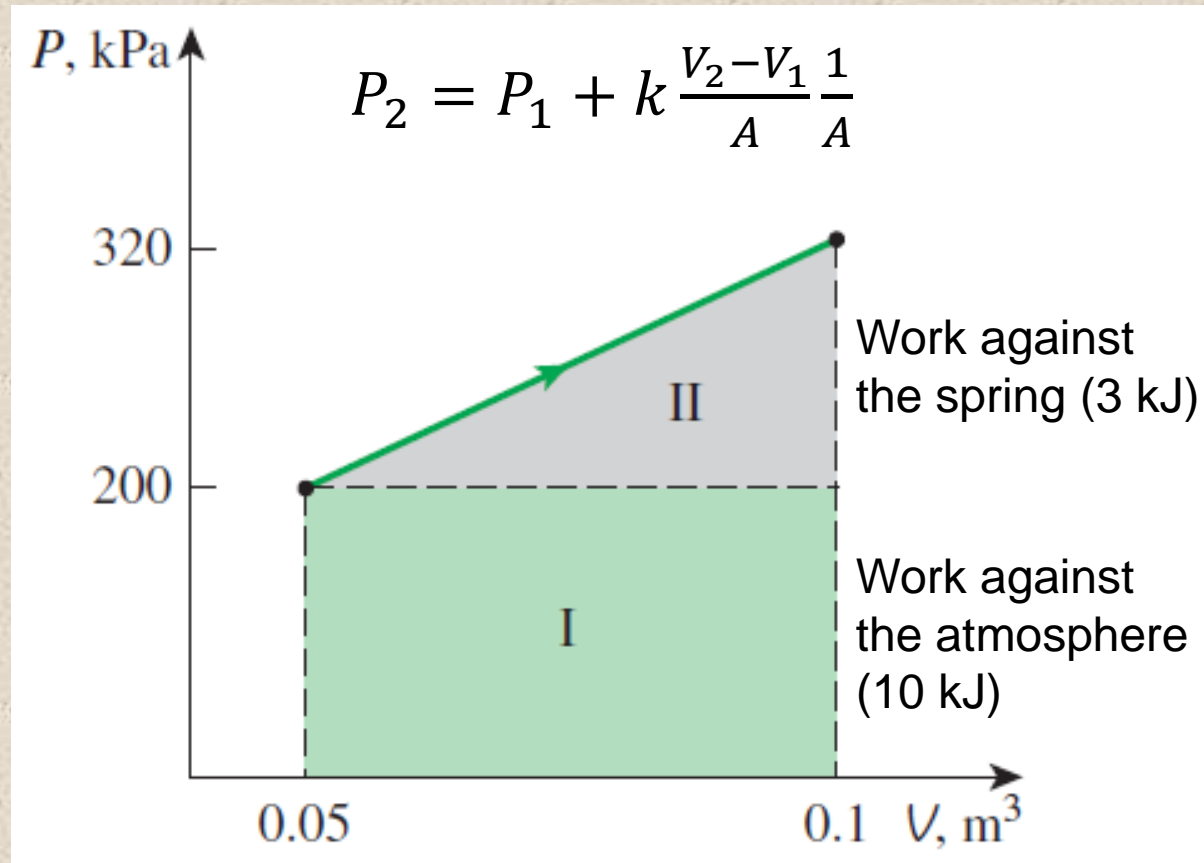
$$P = P_1 + (P_2 - P_1) \frac{V - V_1}{V_2 - V_1}$$

$$W_b = \frac{(P_1 + P_2)}{2} (V_2 - V_1)$$

System: Gas inside the piston/cylinder



# Expansion of a Gas against a Spring



or simply the area under the PV curve:  $W_b = \frac{(P_1 + P_2)}{2} (V_2 - V_1)$

$$W_b = \frac{(200 + 320)}{2} (0.1 - 0.05) = 13 \text{ kJ}$$

# ENERGY BALANCE FOR CLOSED SYSTEMS

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{\Delta E_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}} \quad (\text{kJ})$$

Energy balance for any system undergoing any process

$$\underbrace{\dot{E}_{\text{in}} - \dot{E}_{\text{out}}}_{\text{Rate of net energy transfer by heat, work, and mass}} = \underbrace{dE_{\text{system}}/dt}_{\text{Rate of change in internal, kinetic, potential, etc., energies}} \quad (\text{kW})$$

Energy balance in the rate form

The total quantities are related to the quantities per unit time (for constant rates):

$$Q = \dot{Q} \Delta t, \quad W = \dot{W} \Delta t, \quad \text{and} \quad \Delta E = (dE/dt) \Delta t \quad (\text{kJ})$$

$$e_{\text{in}} - e_{\text{out}} = \Delta e_{\text{system}} \quad (\text{kJ/kg})$$

Energy balance per unit mass basis

$$\delta E_{\text{in}} - \delta E_{\text{out}} = dE_{\text{system}} \quad \text{or} \quad \delta e_{\text{in}} - \delta e_{\text{out}} = de_{\text{system}}$$

Energy balance in differential form

## Energy balance when sign convention is used:

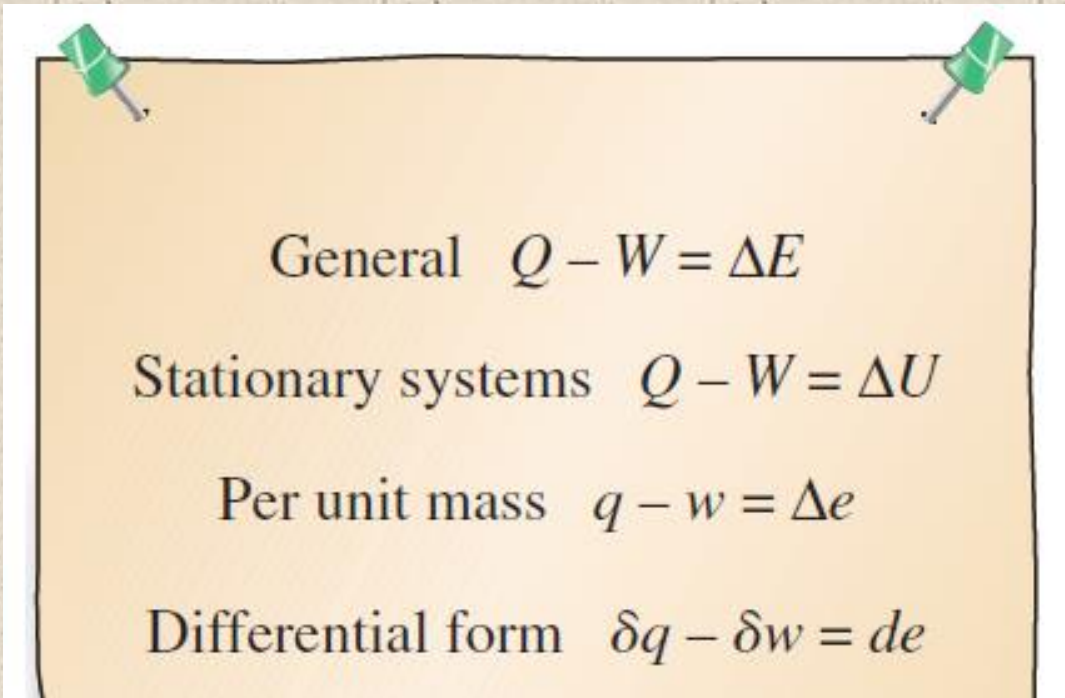
(i.e., heat input and work output are positive; heat output and work input are negative).

$$Q_{\text{net,in}} - W_{\text{net,out}} = \Delta E_{\text{system}} \quad \text{or} \quad Q - W = \Delta E$$

$$Q = Q_{\text{net,in}} = Q_{\text{in}} - Q_{\text{out}}$$

$$W = W_{\text{net,out}} = W_{\text{out}} - W_{\text{in}}$$

Various forms of the first-law relation for closed systems when sign convention is used



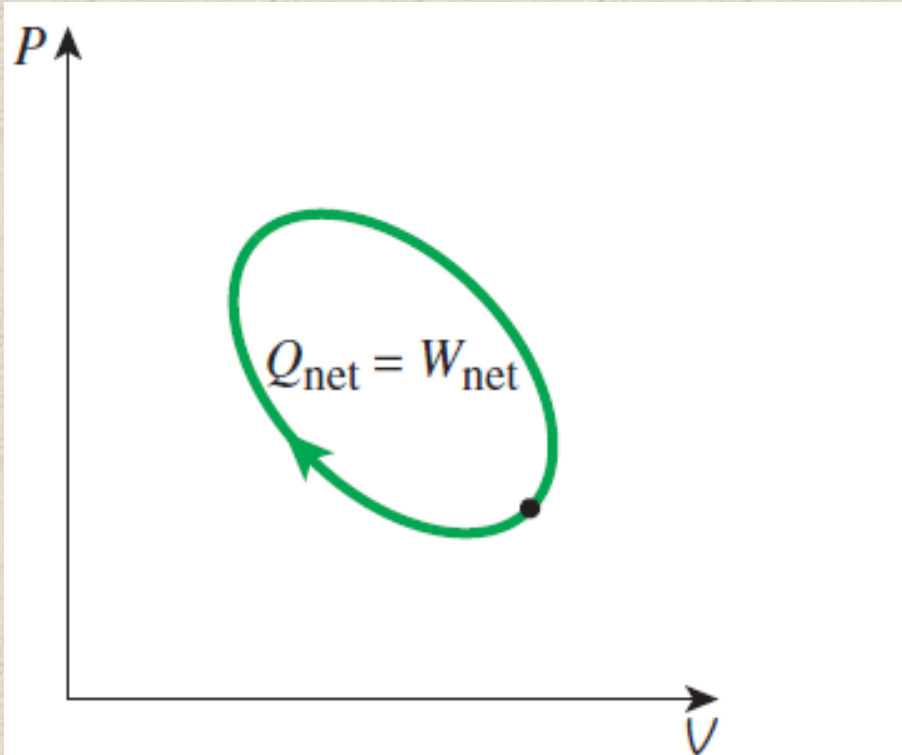
General  $Q - W = \Delta E$

Stationary systems  $Q - W = \Delta U$

Per unit mass  $q - w = \Delta e$

Differential form  $\delta q - \delta w = de$

# Energy balance for a cycle



**FIGURE 4-11**

For a cycle  $\Delta E = 0$ , thus  $Q = W$ .

$$W_{\text{net,out}} = Q_{\text{net,in}}$$

$$\dot{W}_{\text{net,out}} = \dot{Q}_{\text{net,in}}$$

The first law cannot be proven mathematically, but no process in nature is known to have violated the first law, and this should be taken as sufficient proof



# Energy balance for a constant-pressure expansion or compression process

General analysis for a closed system undergoing a quasi-equilibrium **constant-pressure process**

$Q$  is *to* the system and  $W$  is *by* the system

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{\Delta E_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}}$$

$$Q - W = \Delta U + \cancel{\Delta KE}^0 + \cancel{\Delta PE}^0$$

$$Q - W_{\text{other}} - W_b = U_2 - U_1$$

$$Q - W_{\text{other}} - P_0(V_2 - V_1) = U_2 - U_1$$

$$Q - W_{\text{other}} = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$H = U + PV$$

$$Q - W_{\text{other}} = H_2 - H_1$$

Separating out the boundary work ( $W_b$ ):

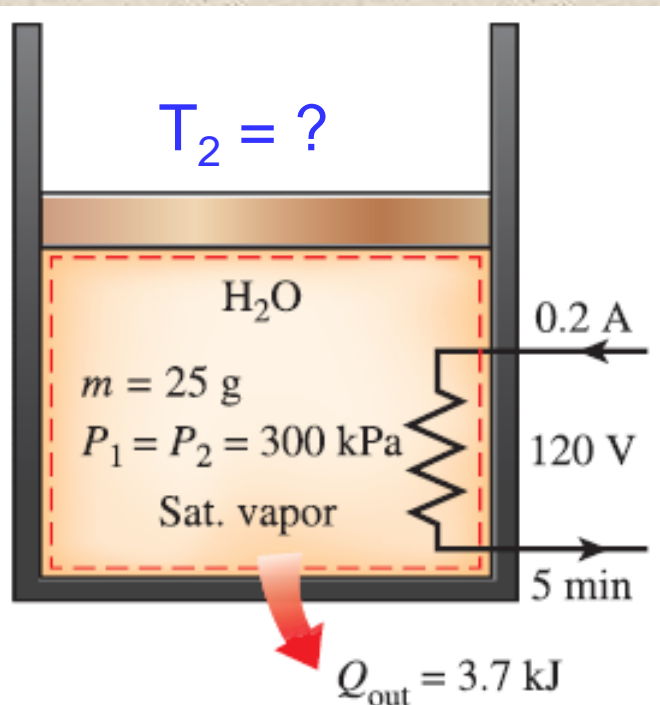
$$W = W_b + W_{\text{other}}$$

↑                      ↑  
boundary              e.g.  
work                      electric,  
                                 shaft work

## An example of **constant-pressure** quasi-equilibrium process

A piston–cylinder device contains 25 g of saturated water vapor that is maintained at a constant pressure of 300 kPa. A resistance heater within the cylinder is turned on and passes a current of 0.2 A for 5 min from a 120-V source. At the same time, a heat loss of 3.7 kJ occurs. (b) Determine the final temperature of the steam.

**Assumptions** 1 The tank is stationary and thus the kinetic and potential energy changes are zero,  $\Delta KE = \Delta PE = 0$ . Therefore,  $\Delta E = \Delta U$  and internal energy is the only form of energy of the system that may change during this process. 2 Electrical wires constitute a very small part of the system, and thus the energy change of the wires can be neglected.



$$E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$$

Constant pressure quasi-equilibrium process, boundary work is automatically taken care of by the enthalpy terms

$$W_{e,\text{in}} - Q_{\text{out}} - W_b = \Delta U$$

$$W_{e,\text{in}} - Q_{\text{out}} = \Delta H = m(h_2 - h_1)$$

System: Water vapor inside the piston/cylinder

## An example of **constant-pressure** quasi-equilibrium process

$$W_{e,in} - Q_{out} = \Delta H = m(h_2 - h_1)$$

$$W_{e,in} = VI\Delta t = 7.2 \text{ kJ}$$

$$Q_{out} = 3.7 \text{ kJ}$$

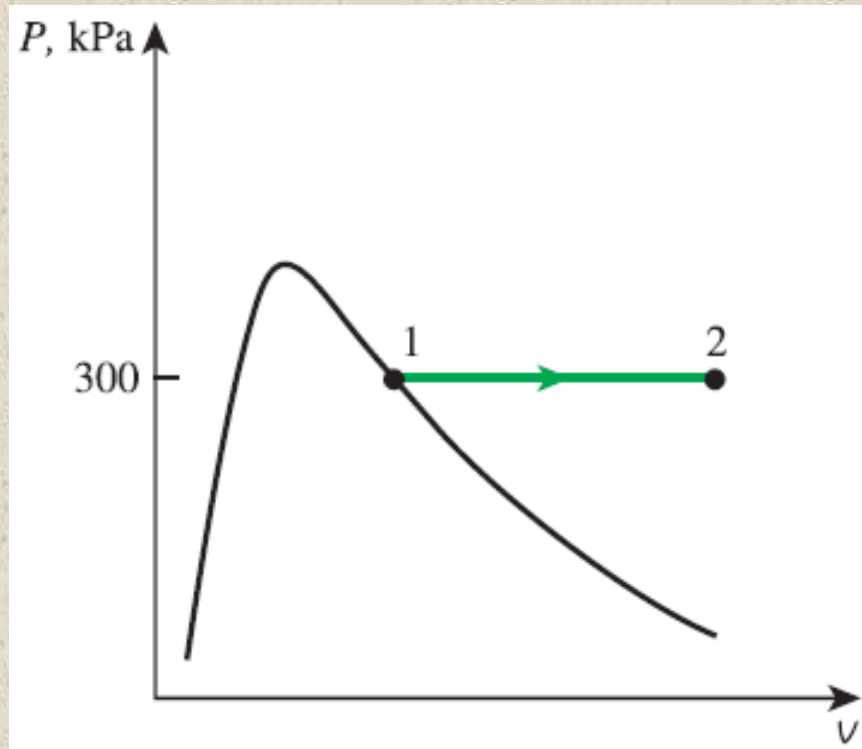
$$\Delta H = 3.5 \text{ kJ}$$

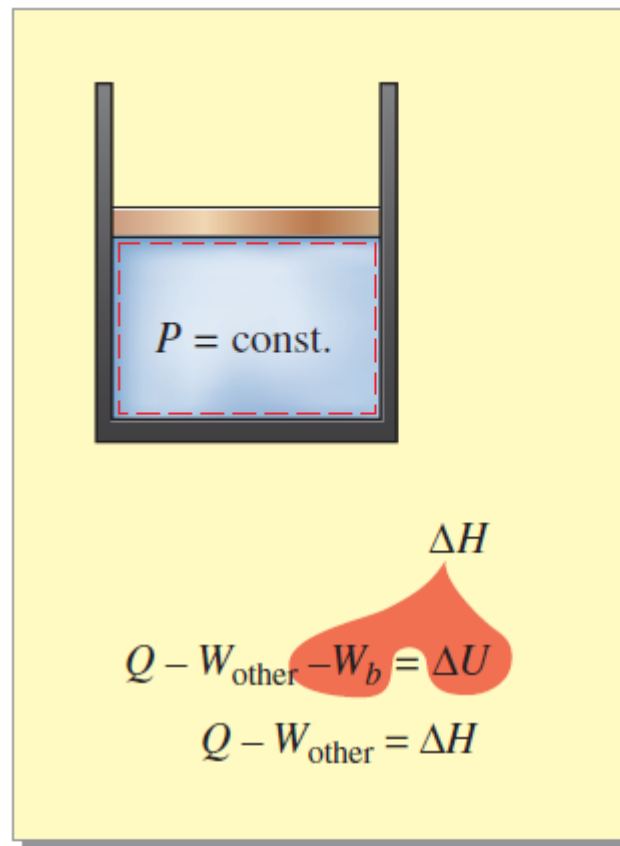
$$m = 25 \text{ g}$$

$$h_2 - h_1 = 140 \text{ kJ/kg}$$

$$h_1 = h_{g@300 \text{ kPa}} = 2724.9 \text{ (Table A5)}$$

$$\left. \begin{array}{l} h_2 = 2864.9 \text{ kJ/kg} \\ P_2 = 300 \text{ kPa} \end{array} \right\} \begin{array}{l} T_2 = 200 \text{ }^\circ\text{C} \\ \text{(Table A6)} \end{array}$$





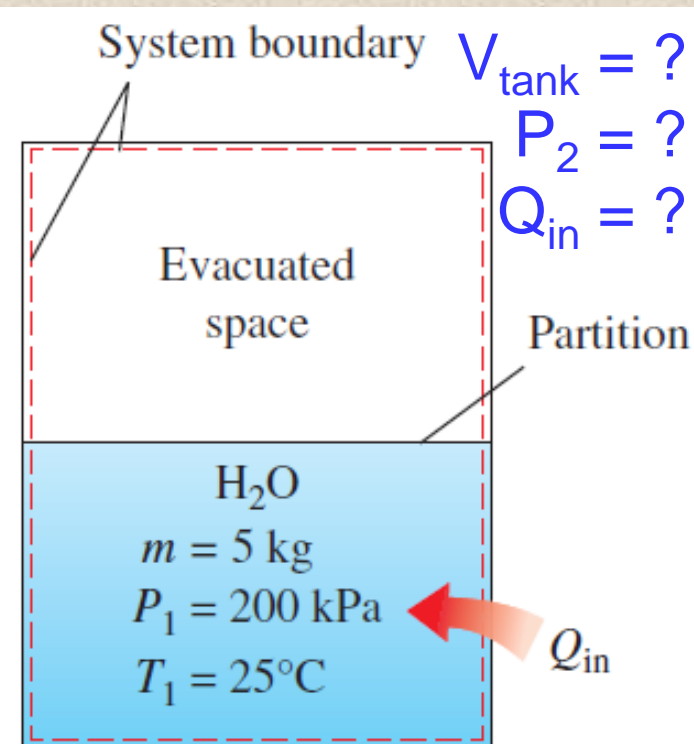
### FIGURE 4-14

For a closed system undergoing a quasi-equilibrium,  $P = \text{constant}$  process,  $\Delta U + W_b = \Delta H$ . Note that this relation is NOT valid for closed systems processes during which pressure DOES NOT remain constant.



# Unrestrained Expansion of Water

A rigid tank is divided into two equal parts by a partition. Initially, one side of the tank contains 5 kg of water at 200 kPa and 25 °C, and the other side is evacuated. The partition is then removed, and the water expands into the entire tank. The water is allowed to exchange heat with its surroundings until the temperature in the tank returns to the initial value of 25 °C. Determine (a) the volume of the tank, (b) the final pressure, and (c) the heat transfer for this process.



System: Contents of the rigid tank

**Assumptions** 1 The system is stationary and thus the kinetic and potential energy changes are zero,  $\Delta KE = \Delta PE = 0$  and  $\Delta E = \Delta U$ . 2 The direction of heat transfer is to the system (heat gain,  $Q_{\text{in}}$ ). A negative result for  $Q_{\text{in}}$  indicates the assumed direction is wrong and thus it is a heat loss. 3 The volume of the rigid tank is constant, and thus there is no energy transfer as boundary work. 4 There is no electrical, shaft, or any other kind of work involved.

# Unrestrained Expansion of Water

since:  $P_1 > P_{sat@25^\circ C}$  (3.17 kPa)

→ *compressed liquid*

$$v_{1-water} \cong v_{f@25^\circ C} = 0.001 \text{ m}^3/\text{kg}$$

Table A-4

$$V_{1-water} = m v_{1-water} = 0.005 \text{ m}^3$$

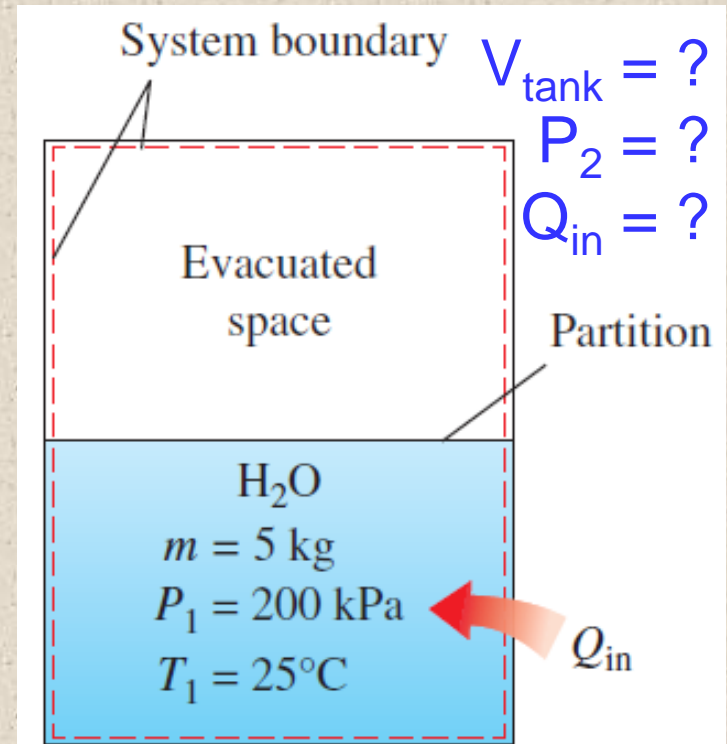
$$V_{tank} = 2V_{1-water} = 0.01 \text{ m}^3$$

$$v_2 = \frac{V_{tank}}{m} = 0.002 \text{ m}^3/\text{kg}$$

$$\text{at } 25^\circ C: v_f = 0.001 \text{ m}^3/\text{kg}, v_g = 43.340 \text{ m}^3/\text{kg} \quad \text{Table A-4}$$

since:  $v_f < v_2 < v_g$ , therefore water is sat. liq – vap mixture

$$P_2 = P_{sat@25^\circ C} = 3.17 \text{ kPa}$$



System: Contents of the rigid tank

# Unrestrained Expansion of Water

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer} \\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,} \\ \text{potential, etc., energies}}}$$

$$Q_{\text{in}} = \Delta U = m(u_2 - u_1)$$

$$W = 0$$

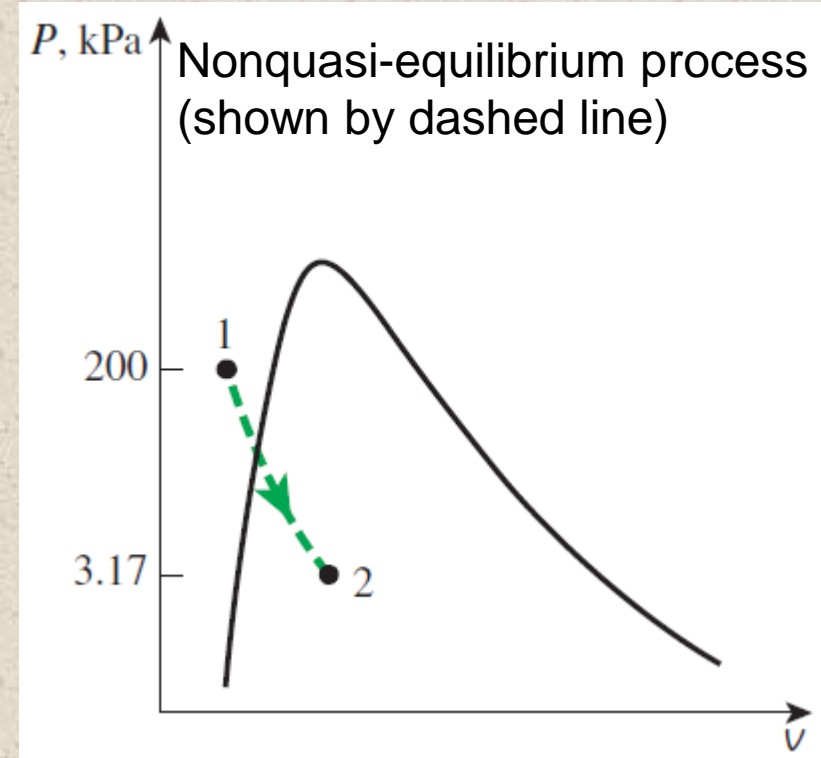
$$u_1 \cong u_{f@25^\circ\text{C}} = 104.83 \text{ kJ/kg} \quad \text{Table A-4}$$

$$x_2 = \frac{v_2 - v_f}{v_{fg}} = 2.3 \times 10^{-5}$$

$$u_2 = u_f + x_2 u_{fg} = 104.88 \text{ kJ/kg}$$

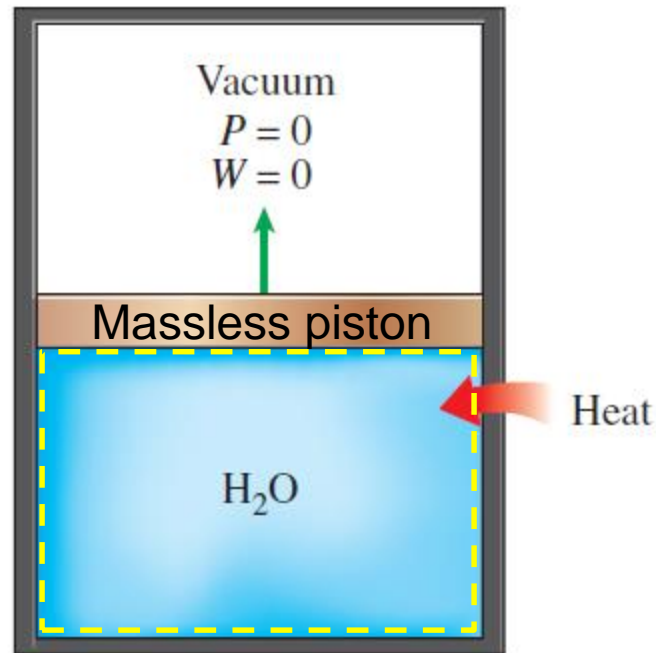
$$Q_{\text{in}} = 0.25 \text{ kJ}$$

The positive sign indicates that the assumed direction is correct, and heat is transferred **to** the water



Notice that even though the water is expanding during this process, the system chosen involves fixed boundaries only (the dashed lines) and therefore the moving boundary work is zero  $W_b = 0$

Since the system does not involve any other work:  $W = 0$



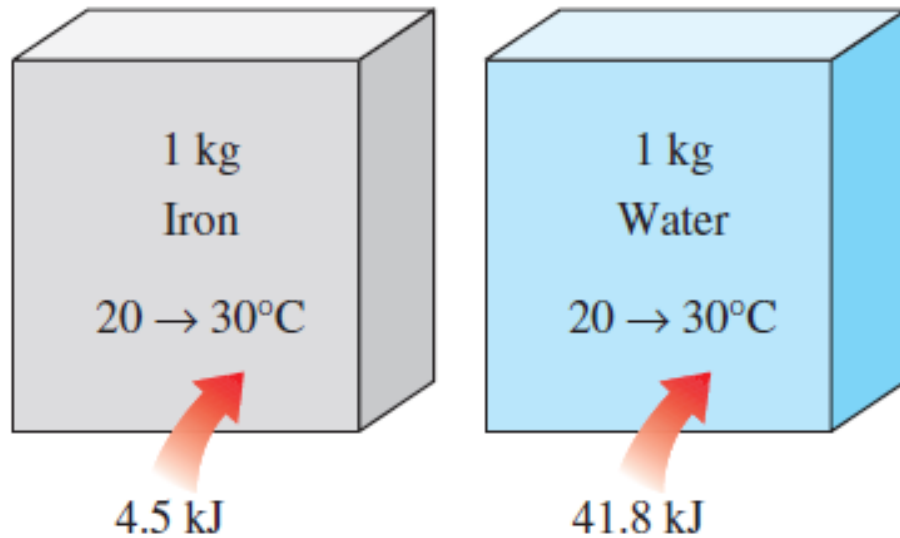
**FIGURE 4–16**

Expansion against a vacuum involves no work and thus no energy transfer.

Try the same problem by choosing the system as shown in the figure

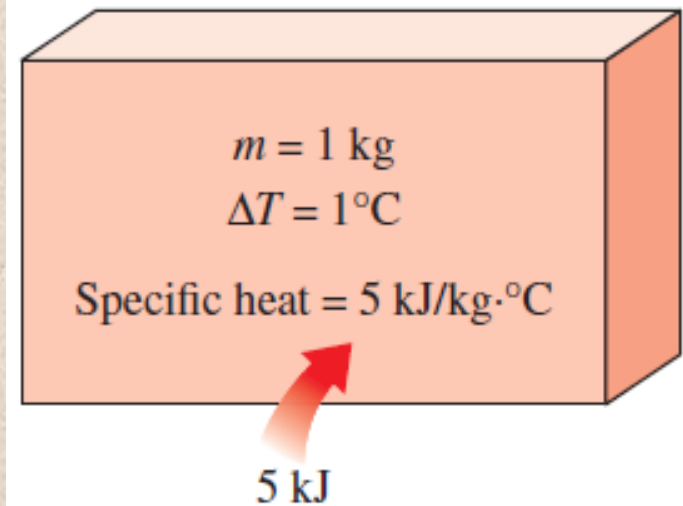


# SPECIFIC HEATS



**FIGURE 4-17**

It takes different amounts of energy to raise the temperature of different substances by the same amount.



**FIGURE 4-18**

Specific heat is the energy required to raise the temperature of a unit mass of a substance by one degree in a specified way.

- **Specific heat** is defined as *the energy required to raise the temperature of the unit mass of a substance by one degree*
- In general, this energy depends on how the process is executed. In thermodynamics we are interested in two kinds of specific heats:  $c_v$ ,  $c_p$
- **Specific heat at constant volume,  $c_v$** : *The energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant*
- **Specific heat at constant pressure,  $c_p$** : *The energy required to raise the temperature of the unit mass of a substance by one degree as the pressure is maintained constant*

# Specific Heat at Constant Volume ( $c_v$ )

- Consider a *stationary closed system* ( $\Delta KE$  and  $\Delta PE$  terms are negligible) undergoing a *constant volume process* (thus no expansion or compression work is involved)

**Conservation of energy principle:**  $e_{in} - e_{out} = \Delta e_{system}$

**For this stationary system  
in differential form:**  $\delta e_{in} - \delta e_{out} = du$

- The left hand side of this equation represents the net amount of energy transferred to the system. From the definition of  $c_v$  this energy must be equal to  $c_v dT$ , where  $dT$  is the differential change in temperature

$$c_v dT = du \quad \text{Stationary system at constant volume}$$

$$c_v = \left( \frac{\partial u}{\partial T} \right)_v$$

## Specific Heat at Constant Pressure ( $c_p$ )

- Consider a *stationary closed system* ( $\Delta KE$  and  $\Delta PE$  terms are negligible) undergoing a *constant pressure process* (consider that only expansion or compression work is involved)

**Conservation of energy principle:**

$$e_{in} - e_{out} = \Delta e_{system}$$

$$q_{in} - q_{out} + w_{in} - w_{out} = \Delta e_{system}$$

**For this stationary system in differential form:**

$$\delta q_{in} - \delta q_{out} + \delta w_{in-other} - \delta w_{out-other} - \delta w_b = du$$

$$\delta q_{in} - \delta q_{out} + \delta w_{in-other} - \delta w_{out-other} = du + Pdv$$

**For constant pressure process:**

$$\delta q_{in} - \delta q_{out} + \delta w_{in-other} - \delta w_{out-other} = du + d(Pv)$$

$$\delta q_{in} - \delta q_{out} + \delta w_{in-other} - \delta w_{out-other} = d(u + Pv)$$

$$\delta q_{in} - \delta q_{out} + \delta w_{in-other} - \delta w_{out-other} = dh$$

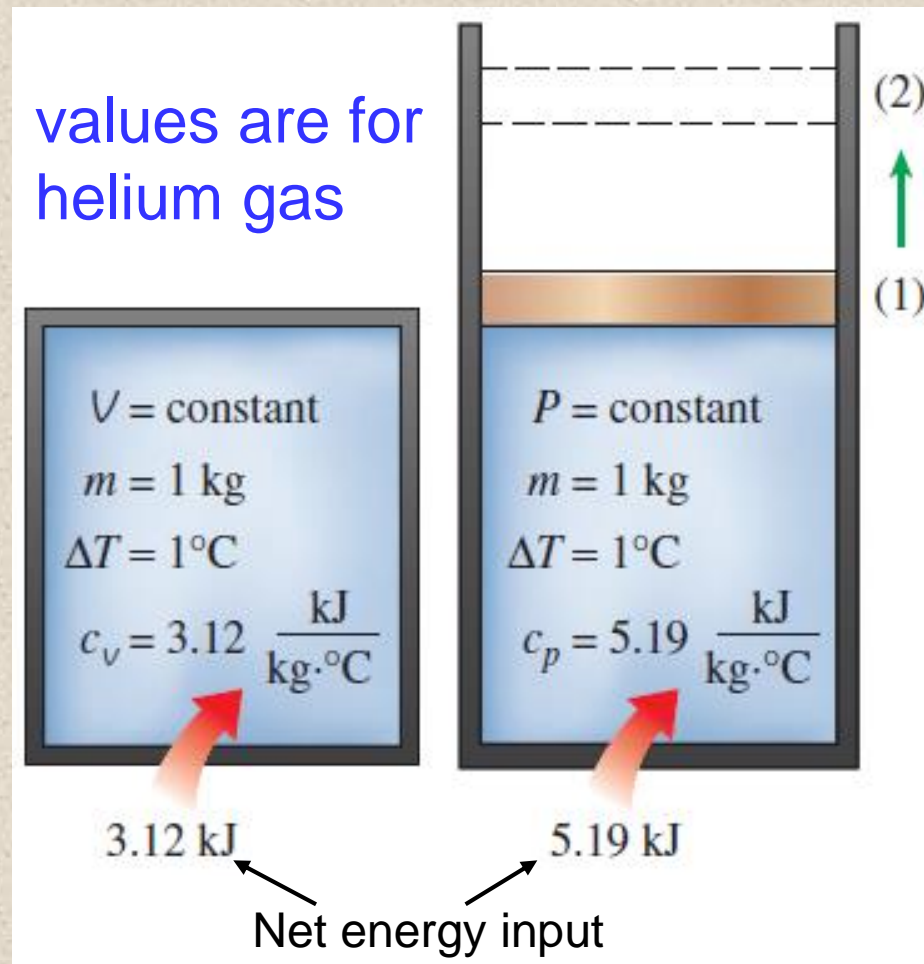
- From the definition of  $c_p$  the net amount of energy transferred to the system (*except the moving boundary work*) must be equal to  $c_p dT$ , where  $dT$  is the differential change in temperature

$$c_p dT = dh \quad \text{Stationary system at constant pressure}$$

$$c_p = \left( \frac{\partial h}{\partial T} \right)_p$$



$c_p$  is always greater than  $c_v$  to accommodate energy needed for the expansion work ( $W_b$ )



- Note that the net energy input (3.12 kJ or 5.9 kJ) could be in the form of heat input, or work done by a stirrer or electric resistance wire etc... (*except the moving boundary work which is subsumed in enthalpy for the constant pressure process and is zero for the constant volume process*)

## Formal definitions of $c_v$ and $c_p$

- $c_v$  is related to the changes in *internal energy* and  $c_p$  to the changes in *enthalpy*
- In fact it would be more proper (and much better!!) to define  $c_v$  as *the change in the internal energy of a substance per unit change in temperature at constant volume*
- Likewise,  $c_p$  can be defined as *the change in enthalpy of a substance per unit change in temperature at constant pressure*

$$c_v = \left( \frac{\partial u}{\partial T} \right)_v$$

= the change in internal energy with temperature at constant volume

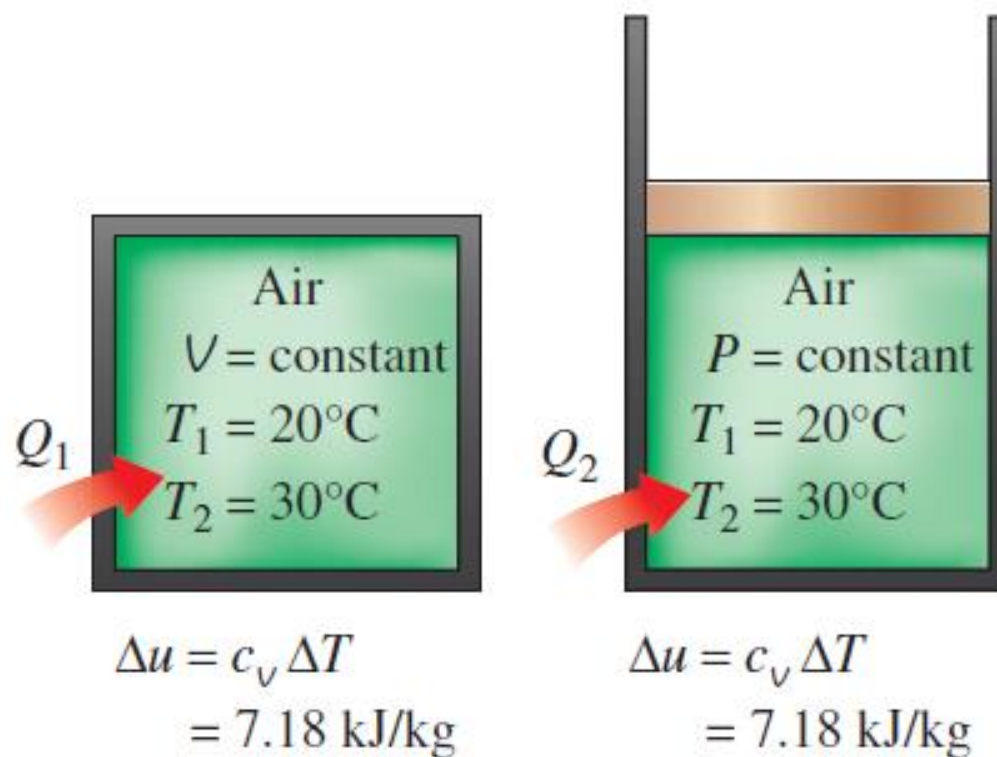
$$c_p = \left( \frac{\partial h}{\partial T} \right)_p$$

= the change in enthalpy with temperature at constant pressure

## $c_v$ and $c_p$

- $c_v$  and  $c_p$  are expressed in terms of other properties; thus, they must be properties themselves
- The specific heats of a substance depend on the state that, in general, is specified by two independent intensive properties. e.g. in general:  $c_v = c_v(T, P)$ ,  $c_p = c_p(T, P)$
- The equations defining  $c_v$  and  $c_p$  are property relations and as such are independent of the type of processes. They are valid for **any** substance undergoing **any** process
- The only relation  $c_v$  has to a constant-volume process is that  $c_v$  happens to be the energy transferred to a system during a constant-volume process per unit mass, per unit degree rise in temperature. This is how the values of  $c_v$  are determined. (likewise for enthalpy)
- A common unit for specific heats is  $\text{kJ/kg}\cdot^\circ\text{C}$  or  $\text{kJ/kg}\cdot\text{K}$





### FIGURE 4–27

The relation  $\Delta u = c_v \Delta T$  is valid for *any* kind of process, constant-volume or not.



$$Q - W = \Delta E$$

$$Q - W_{\text{other}} - W_b = \Delta KE + \Delta PE + \Delta U$$

- Consider no work interaction **except** the moving boundary work ( $W_b$ ); i.e.  $W_{\text{other}} = 0$
- Consider stationary system so that  $\Delta KE = 0$ ,  $\Delta PE = 0$

$$Q = \Delta U + W_b$$

**For constant volume process:** **For constant pressure process:**

$$W_b = 0$$

$$Q = \Delta U$$

$$Q_{12} = U_2 - U_1$$

net heat input =  
change in internal energy

$$W_b = P_0(V_2 - V_1) = P_2V_2 - P_1V_1$$

$$Q = (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$H = U + PV$$

$$Q = \Delta H$$

$$Q_{12} = H_2 - H_1$$

net heat input =  
change in enthalpy

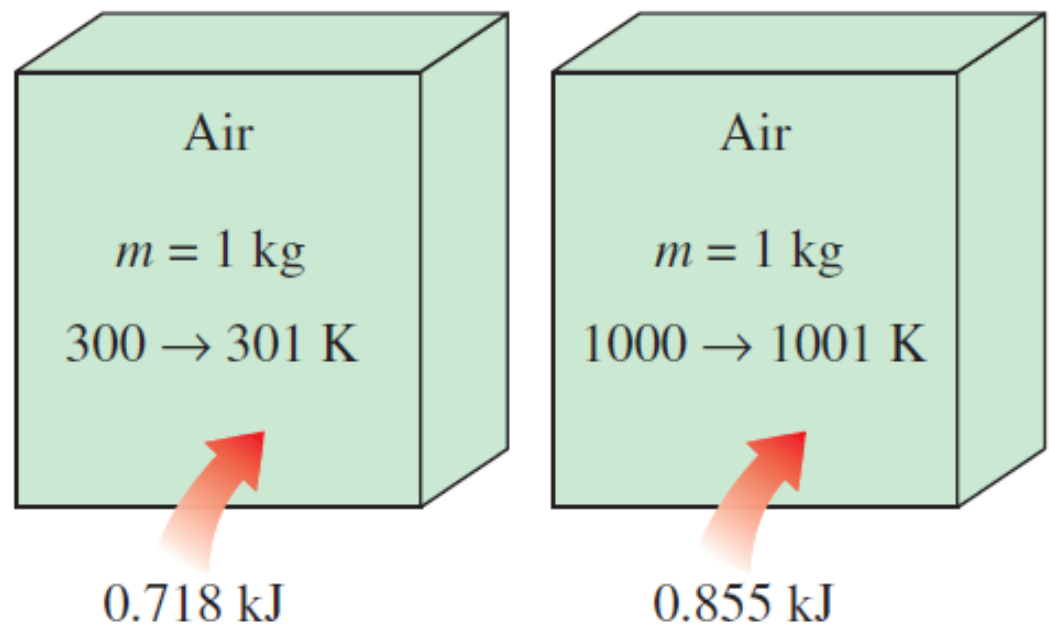
- For a special case of *stationary system* with *no work interaction except moving boundary work*, the net heat input is equal to the change in internal energy (*for constant volume process*) and change in enthalpy (*for constant pressure process*)

For **real gases**:  $u$ ,  $h$ ,  $c_v$ , and  $c_p$  are functions of two independent intensive properties (e.g.  $T$ ,  $P$ ), hence, they can vary with both temperature and pressure:

$$u = u(T, P), \quad h = h(T, P), \quad c_v = c_v(T, P), \quad c_p = c_p(T, P)$$

It can be mathematically shown that for **ideal gases**:  $u$ ,  $h$ ,  $c_v$ , and  $c_p$  vary with temperature only

$$\begin{aligned} u &= u(T) \\ h &= h(T) \\ c_v &= c_v(T) \\ c_p &= c_p(T) \end{aligned}$$



**FIGURE 4–21**

The specific heat of a substance changes with temperature.

# INTERNAL ENERGY, ENTHALPY, AND SPECIFIC HEATS OF IDEAL GASES

$$\left. \begin{array}{l} h = u + P\nu \\ P\nu = RT \text{ (IGL)} \end{array} \right\} h = u + RT$$

**IGL = Ideal Gas Law**

$$u = u(T)$$

$$h = h(T)$$

$$du = c_v(T) dT$$

$$dh = c_p(T) dT$$

$$\Delta u = u_2 - u_1 = \int_1^2 c_v(T) dT$$

$$\Delta h = h_2 - h_1 = \int_1^2 c_p(T) dT$$

Internal energy and  
enthalpy change of  
an ideal gas

- At low pressures, all real gases approach ideal-gas behavior, and therefore their specific heats depend on temperature only
- The specific heats of real gases at low pressures are called *ideal-gas specific heats*, or *zero-pressure specific heats*, and are often denoted  $\bar{c}_{p0}$  and  $\bar{c}_{v0}$ .

Ideal-gas constant-pressure specific heats for some gases (see Table A–2c for  $c_p$  equations)

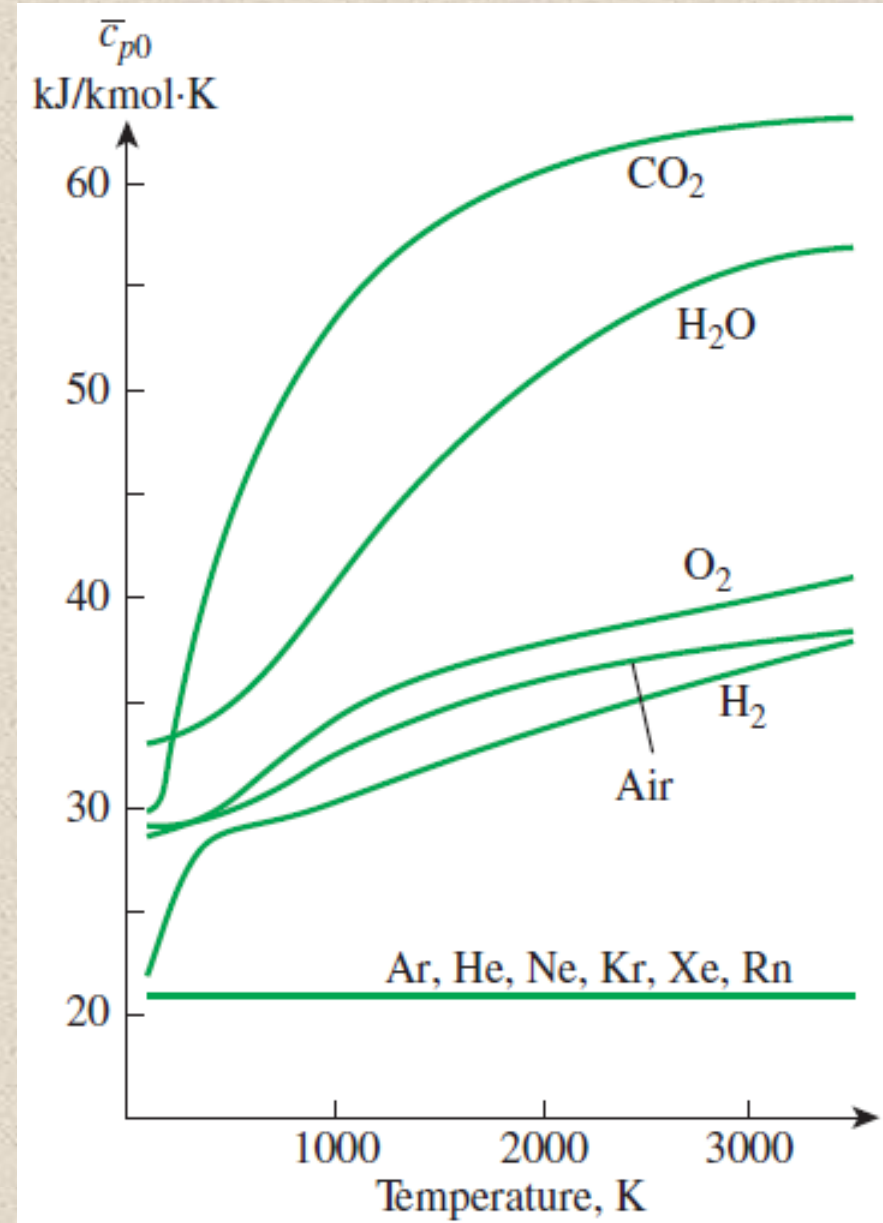




TABLE A-2

Ideal-gas specific heats of various common gases (*Concluded*)

(c) As a function of temperature

$$\bar{c}_p = a + bT + cT^2 + dT^3$$

( $T$  in K,  $c_p$  in kJ/kmol·K)

Substance	Formula	$a$	$b$	$c$	$d$	Temperature range, K	% error	
							Max.	Avg.
Nitrogen	N <sub>2</sub>	28.90	$-0.1571 \times 10^{-2}$	$0.8081 \times 10^{-5}$	$-2.873 \times 10^{-9}$	273–1800	0.59	0.34
Oxygen	O <sub>2</sub>	25.48	$1.520 \times 10^{-2}$	$-0.7155 \times 10^{-5}$	$1.312 \times 10^{-9}$	273–1800	1.19	0.28
Air	—	28.11	$0.1967 \times 10^{-2}$	$0.4802 \times 10^{-5}$	$-1.966 \times 10^{-9}$	273–1800	0.72	0.33
Hydrogen	H <sub>2</sub>	29.11	$-0.1916 \times 10^{-2}$	$0.4003 \times 10^{-5}$	$-0.8704 \times 10^{-9}$	273–1800	1.01	0.26
Carbon monoxide	CO	28.16	$0.1675 \times 10^{-2}$	$0.5372 \times 10^{-5}$	$-2.222 \times 10^{-9}$	273–1800	0.89	0.37
Carbon dioxide	CO <sub>2</sub>	22.26	$5.981 \times 10^{-2}$	$-3.501 \times 10^{-5}$	$7.469 \times 10^{-9}$	273–1800	0.67	0.22

TABLE A-2

Ideal-gas specific heats of various common gases (*Continued*)

(b) At various temperatures

Temperature, K	$c_p$ kJ/kg·K	$c_v$ kJ/kg·K	$k$	$c_p$ kJ/kg·K	$c_v$ kJ/kg·K	$k$	$c_p$ kJ/kg·K	$c_v$ kJ/kg·K	$k$
	<i>Air</i>			<i>Carbon dioxide, CO<sub>2</sub></i>			<i>Carbon monoxide, CO</i>		
250	1.003	0.716	1.401	0.791	0.602	1.314	1.039	0.743	1.400
300	1.005	0.718	1.400	0.846	0.657	1.288	1.040	0.744	1.399
350	1.008	0.721	1.398	0.895	0.706	1.268	1.043	0.746	1.398
400	1.013	0.726	1.395	0.939	0.750	1.252	1.047	0.751	1.395
450	1.020	0.733	1.391	0.978	0.790	1.239	1.054	0.757	1.392
500	1.029	0.742	1.387	1.014	0.825	1.229	1.063	0.767	1.387
550	1.040	0.753	1.381	1.046	0.857	1.220	1.075	0.778	1.382
600	1.051	0.764	1.376	1.075	0.886	1.213	1.087	0.790	1.376
650	1.063	0.776	1.370	1.102	0.913	1.207	1.100	0.803	1.370

- $u$  and  $h$  data for a number of gases have been tabulated
- These tables are obtained by choosing an arbitrary reference point and performing the integrations by treating state 1 as the reference state
- Table A-17. In the preparation of ideal-gas tables, 0 K is chosen as the reference temperature

**TABLE A-17**

Ideal-gas properties of air

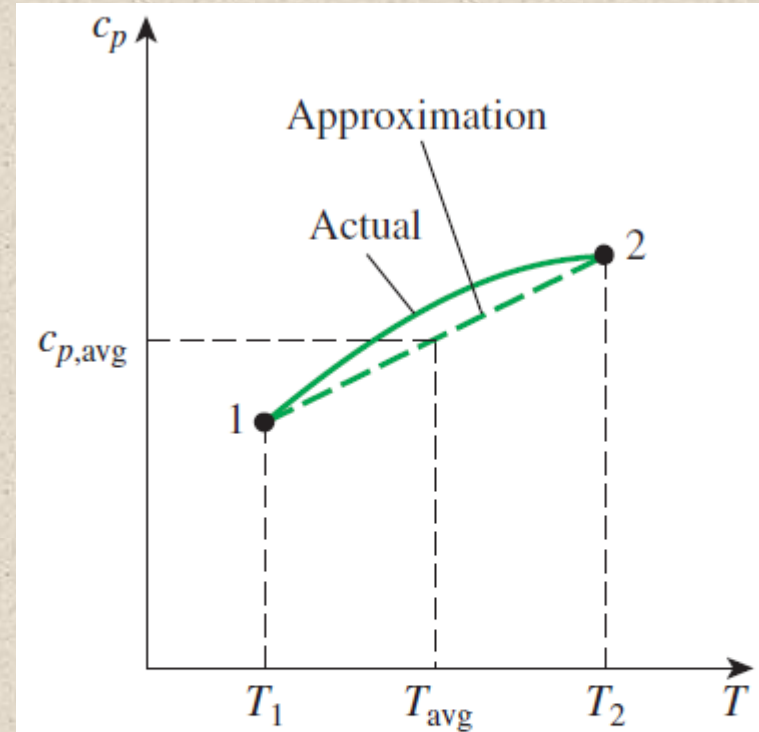
$T$ K	$h$ kJ/kg	$P_r$	$u$ kJ/kg	$v_r$	$s^\circ$ kJ/kg·K	$T$ K	$h$ kJ/kg	$P_r$	$u$ kJ/kg	$v_r$	$s^\circ$ kJ/kg·K
200	199.97	0.3363	142.56	1707.0	1.29559	580	586.04	14.38	419.55	115.7	2.37348
210	209.97	0.3987	149.69	1512.0	1.34444	590	596.52	15.31	427.15	110.6	2.39140
220	219.97	0.4690	156.82	1346.0	1.39105	600	607.02	16.28	434.78	105.8	2.40902
230	230.02	0.5477	164.00	1205.0	1.43557	610	617.53	17.30	442.42	101.2	2.42644
240	240.02	0.6355	171.13	1084.0	1.47824	620	628.07	18.36	450.09	96.92	2.44356
250	250.05	0.7329	178.28	979.0	1.51917	630	638.63	19.84	457.78	92.84	2.46048
260	260.09	0.8405	185.45	887.8	1.55848	640	649.22	20.64	465.50	88.99	2.47716
270	270.11	0.9590	192.60	808.0	1.59634	650	659.84	21.86	473.25	85.34	2.49364
280	280.13	1.0889	199.75	738.0	1.63279	660	670.47	23.13	481.01	81.89	2.50985
285	285.14	1.1584	203.33	706.1	1.65055	670	681.14	24.46	488.81	78.61	2.52589

Internal energy and enthalpy change when specific heat is taken constant at an average value

$$u_2 - u_1 = c_{v,avg}(T_2 - T_1)$$

$$h_2 - h_1 = c_{p,avg}(T_2 - T_1)$$

One can use the specific heat values at a representative average temperature and use it as a constant value of  $c_{v,avg}$  or  $c_{p,avg}$



**FIGURE 4-26**

For small temperature intervals, the specific heats may be assumed to vary linearly with temperature.

## Three ways of calculating $\Delta u$ and $\Delta h$

1. By using the tabulated  $u$  and  $h$  data (Table A-17). This is the easiest and **most accurate** (if tables are available)
2. By using the  $c_v$  or  $c_p$  relations (Table A-2c) as a function of temperature and performing the integrations. This is very inconvenient for hand calculations but quite desirable for computerized calculations (results obtained are **very accurate**)
3. By using average specific heats. This is very simple and certainly very convenient when property tables are not available. The results obtained are **reasonably accurate** if the temperature interval is not very large

Three ways of  
calculating  $\Delta u$

$$\Delta u = u_2 - u_1 \text{ (table)}$$

$$\Delta u = \int_1^2 c_v(T) dT$$

$$\Delta u \cong c_{v,\text{avg}} \Delta T$$



# Specific Heat Relations of Ideal Gases

$h = u + RT$  (for ideal gas)      The relationship between  $c_p$ ,  $c_v$  and  $R$

$$c_p = c_v + R \quad (\text{kJ/kg} \cdot \text{K})$$

$$dh = du + R dT$$

On a molar basis

$$dh = c_p dT \text{ and } du = c_v dT$$

$$\bar{c}_p = \bar{c}_v + R_u \quad (\text{kJ/kmol} \cdot \text{K})$$

Air at 300 K

$$\left. \begin{array}{l} c_v = 0.718 \text{ kJ/kg} \cdot \text{K} \\ R = 0.287 \text{ kJ/kg} \cdot \text{K} \end{array} \right\} c_p = 1.005 \text{ kJ/kg} \cdot \text{K}$$

or

$$\left. \begin{array}{l} \bar{c}_v = 20.80 \text{ kJ/kmol} \cdot \text{K} \\ R_u = 8.314 \text{ kJ/kmol} \cdot \text{K} \end{array} \right\} \bar{c}_p = 29.114 \text{ kJ/kmol} \cdot \text{K}$$

# Specific Heat Ratio

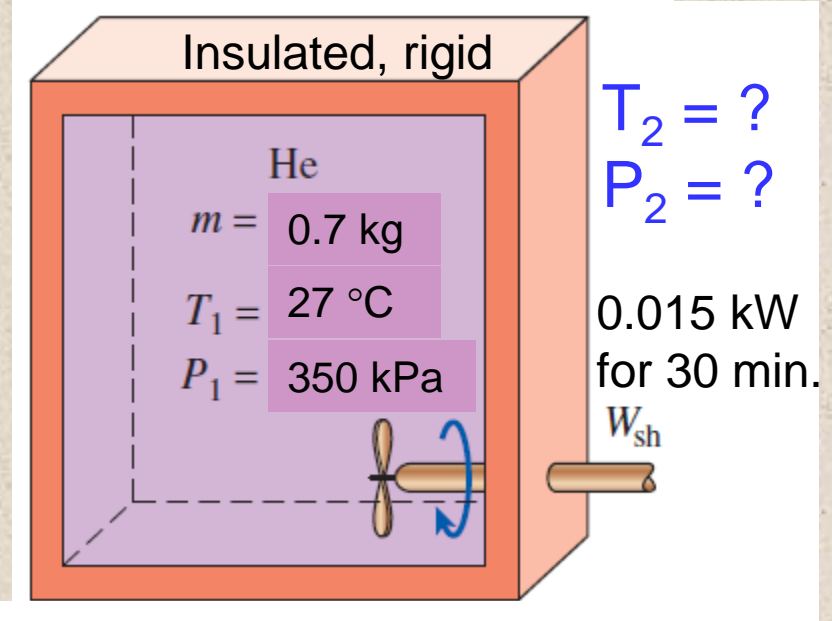
$$k = \frac{c_p}{c_v}$$

Specific  
heat ratio

- The specific heat ratio varies with temperature, but this variation is very mild
- For monatomic gases (helium, argon, etc.), its value is essentially constant at 1.667
- Many diatomic gases, including air, have a specific heat ratio of about 1.4 at room temperature

# Example: Heating of a Gas in a Tank by Stirring

An insulated rigid tank initially contains 0.7 kg of helium at 27 °C and 350 kPa. A paddle wheel with a power rating of 0.015 kW is operated within the tank for 30 min. Determine (a) the final temperature and (b) the final pressure of the helium gas



System: Contents of the rigid tank

**Assumptions** 1 Helium is an ideal gas since it is at a very high temperature relative to its critical-point value of  $-451^\circ\text{F}$ . 2 Constant specific heats can be used for helium. 3 The system is stationary and thus the kinetic and potential energy changes are zero,  $\Delta KE = \Delta PE = 0$  and  $\Delta E = \Delta U$ . 4 The volume of the tank is constant, and thus there is no boundary work. 5 The system is adiabatic and thus there is no heat transfer.

$$\underbrace{E_{in} - E_{out}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{\Delta E_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}}$$

$$W_{sh,in} = \Delta U = m(u_2 - u_1) = mc_{v,avg}(T_2 - T_1)$$

# Example: Heating of a Gas in a Tank by Stirring

$$W_{sh,in} = \dot{W}_{sh}\Delta t = 27 \text{ kJ}$$

$$c_v = 3.1156 \frac{\text{kJ}}{\text{kg-K}} \text{ (Table A-2a)}$$

$$m = 0.7 \text{ kg}$$

$$T_2 - T_1 = 12.4 \text{ }^\circ\text{C}$$

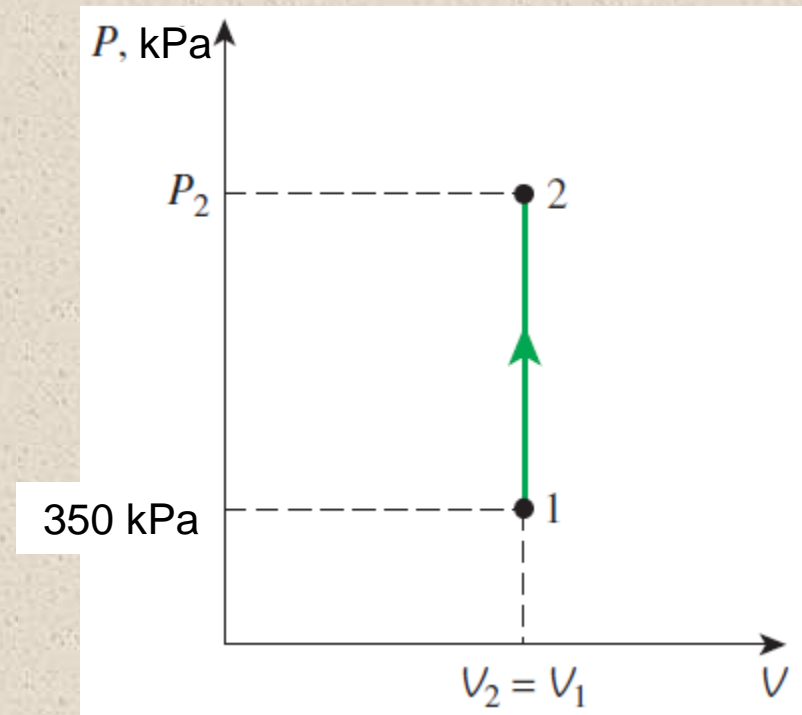
$$T_1 = 27 \text{ }^\circ\text{C}$$

$$T_2 = 39.4 \text{ }^\circ\text{C}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_1 = V_2$$

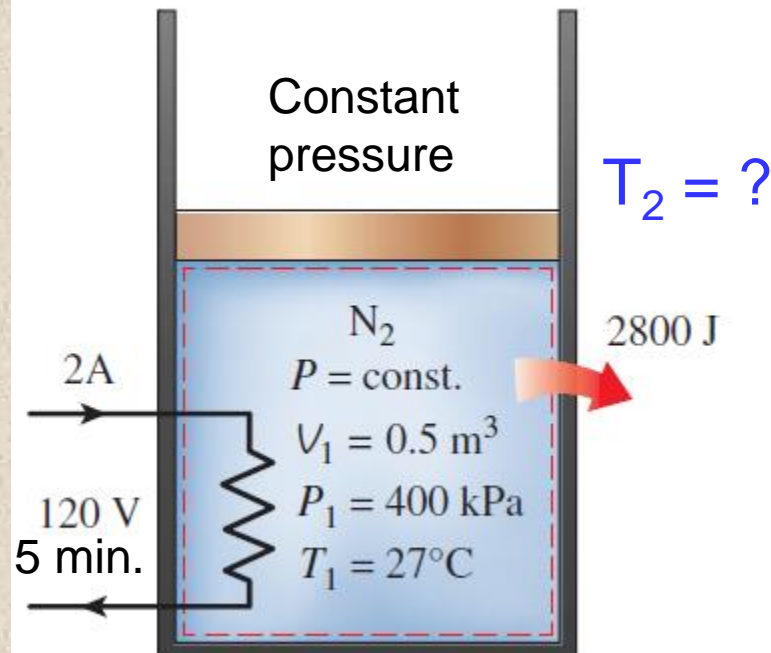
$$P_2 = 364 \text{ kPa}$$





# Example: Heating of a Gas by a Resistance Heater

A piston–cylinder device initially contains 0.5 m<sup>3</sup> of nitrogen gas at 400 kPa and 27 °C. An electric heater within the device is turned on and is allowed to pass a current of 2 A for 5 min from a 120-V source. Nitrogen expands at constant pressure, and a heat loss of 2800 J occurs during the process. Determine the final temperature of nitrogen.



System: Nitrogen inside the piston/cylinder

**Assumptions** 1 Nitrogen is an ideal gas since it is at a high temperature and low pressure relative to its critical-point values of  $-147^{\circ}\text{C}$ , and 3.39 MPa. 2 The system is stationary and thus the kinetic and potential energy changes are zero,  $\Delta KE = \Delta PE = 0$  and  $\Delta E = \Delta U$ . 3 The pressure remains constant during the process and thus  $P_2 = P_1$ . 4 Nitrogen has constant specific heats at room temperature.

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{\Delta E_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}}$$

$$W_{e,\text{in}} - Q_{\text{out}} - W_{b,\text{out}} = \Delta U$$

$$W_{e,\text{in}} - Q_{\text{out}} = \Delta H = m(h_2 - h_1) = mc_p(T_2 - T_1) \quad 49$$

# Example: Heating of a Gas by a Resistance Heater

$$W_{e,in} - Q_{out} = mc_p(T_2 - T_1)$$

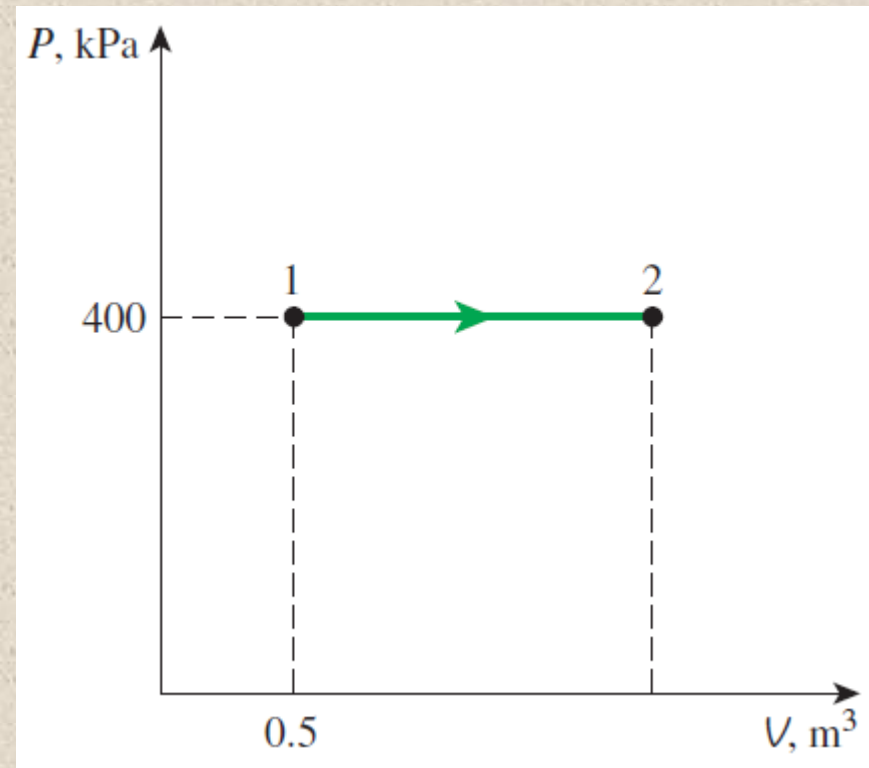
$$W_{e,in} = VI\Delta t = 72 \text{ kJ}$$

$$m = \frac{P_1 V_1}{RT_1} = 2.245 \text{ kg}$$

$$c_p = 1.039 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \text{ (Table A-2a)}$$

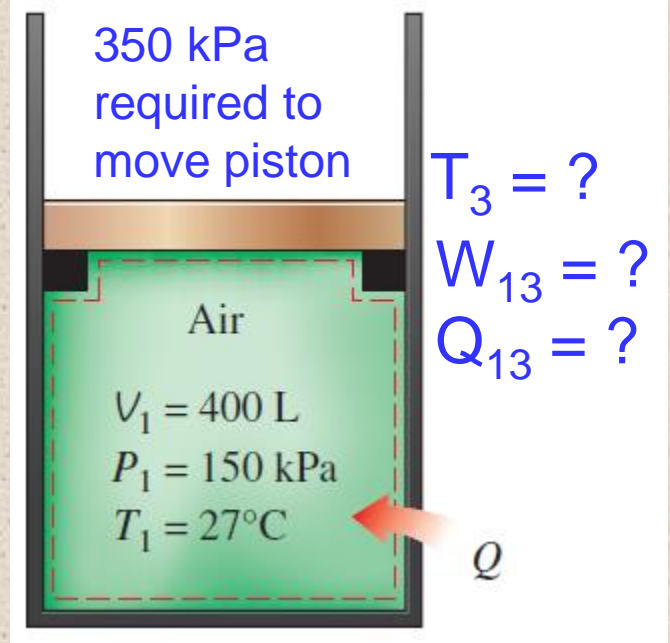
$$T_2 - T_1 = 29.7 \text{ }^\circ\text{C}$$

$$T_2 = 56.7 \text{ }^\circ\text{C}$$



# Example: Heating of a Gas at Constant Volume and Constant Pressure

A piston–cylinder device initially contains air at 150 kPa and 27 °C. At this state, the piston is resting on a pair of stops, as shown in Fig., and the enclosed volume is 400 L. The mass of the piston is such that a 350-kPa pressure is required to move it. The air is now heated until its volume has doubled. Determine (a) the final temperature, (b) the work done by the air, and (c) the total heat transferred to the air.



System: Air inside the piston/cylinder

**Assumptions** 1 Air is an ideal gas since it is at a high temperature and low pressure relative to its critical-point values. 2 The system is stationary and thus the kinetic and potential energy changes are zero,  $\Delta KE = \Delta PE = 0$  and  $\Delta E = \Delta U$ . 3 The volume remains constant until the piston starts moving, and the pressure remains constant afterwards. 4 There are no electrical, shaft, or other forms of work involved.

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{\Delta E_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}}$$

$$Q_{\text{in}} - W_{b,\text{out}} = \Delta U = m(u_3 - u_1)$$

# Example: Heating of a Gas at Constant Volume and Constant Pressure

$$Q_{\text{in}} - W_{b,\text{out}} = m(u_3 - u_1)$$

$$m = \frac{P_1 V_1}{RT_1} = 0.697 \text{ kg}$$

$W_{13} = \text{area under the process curve}$

$$W_{13} = W_{b,\text{out}} = (V_3 - V_2)P_2 = 140 \text{ kJ}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_3 V_3}{T_3}$$

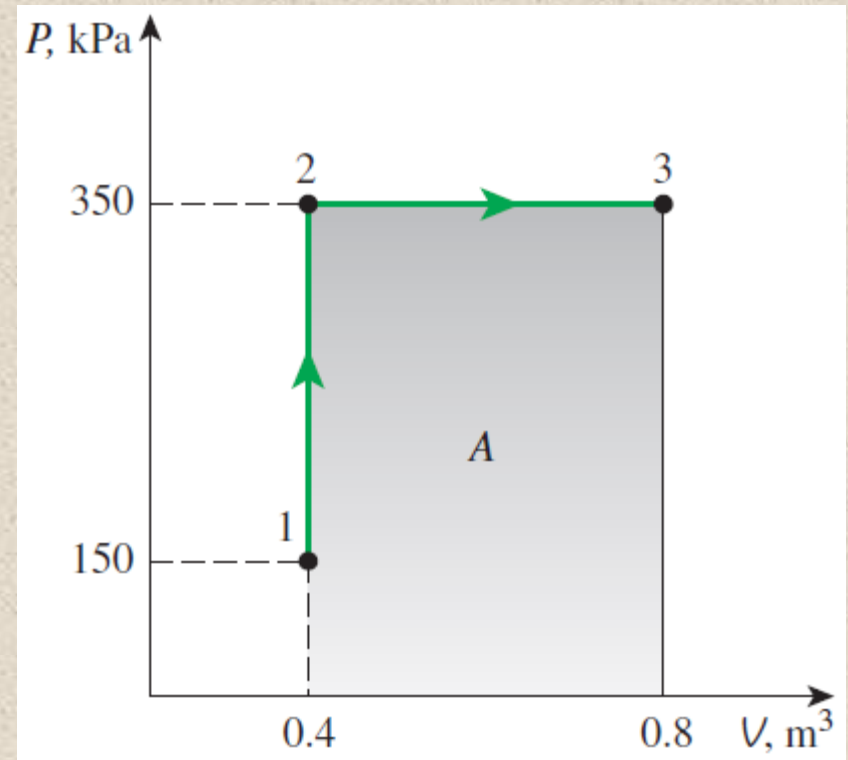
$$T_3 = 1400 \text{ K}$$

$$u_1 = u_{@300\text{K}} = 214.07 \text{ kJ/kg}$$

$$u_2 = u_{@1400\text{K}} = 1113.52 \text{ kJ/kg}$$

Table A-17

$$Q_{13} = Q_{\text{in}} = 767 \text{ kJ}$$





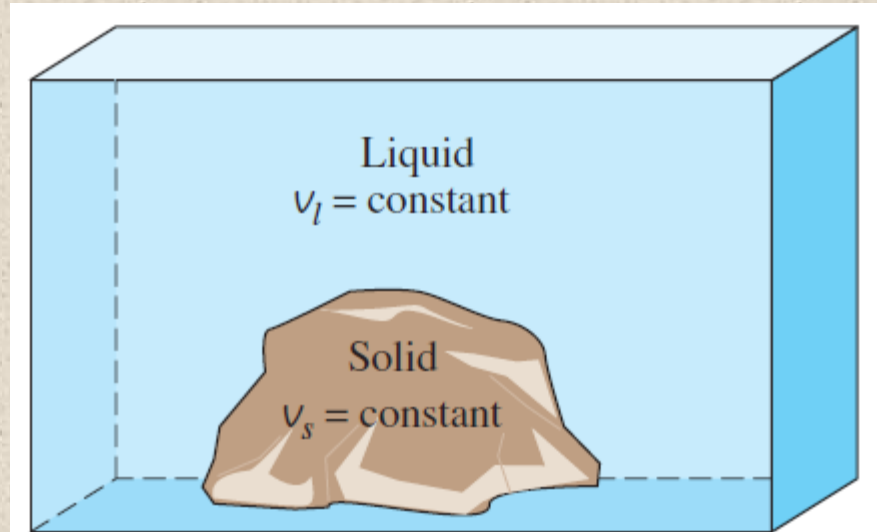
# INTERNAL ENERGY, ENTHALPY, AND SPECIFIC HEATS OF SOLIDS AND LIQUIDS

## Incompressible substance:

A substance whose specific volume (or density) is constant

**Solids and liquids** can be approximated as incompressible substances without sacrificing much accuracy

The constant volume assumption should be taken to imply that the energy associated with the volume change is negligible with other forms of energy

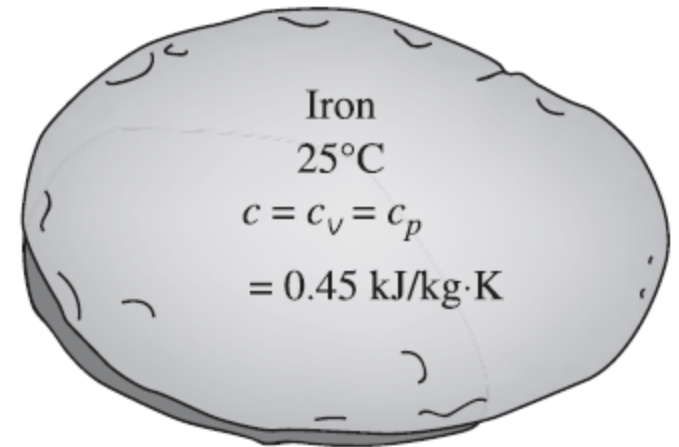


**FIGURE 4–33**

The specific volumes of incompressible substances remain constant during a process.

# INTERNAL ENERGY, ENTHALPY, AND SPECIFIC HEATS OF SOLIDS AND LIQUIDS

- It can be mathematically shown that *constant-volume and constant-pressure specific heats are identical for incompressible substances*
- The difference between the two specific heats is very small and is usually disregarded for substances that are *nearly* incompressible, such as liquids and solids
- Therefore, for solids and liquids, the subscripts on  $c_p$  and  $c_v$  can be dropped and both specific heats can be represented by a single symbol  $c$  ( $c = c_p = c_v$ )



**FIGURE 4–34**

The  $c_v$  and  $c_p$  values of incompressible substances are identical and are denoted by  $c$ .

# Internal Energy Changes for Incompressible Substances

- It can be mathematically shown that the *internal energy* and *specific heat* of incompressible substances depend on temperature only. i.e.  $u = u(T)$  and  $c_v = c = c(T)$

$$du = c_v dT = c(T) dT$$

$$\Delta u = u_2 - u_1 = \int_1^2 c(T) dT \quad (\text{kJ/kg})$$

$$\Delta u \cong c_{\text{avg}}(T_2 - T_1) \quad (\text{kJ/kg})$$

# Enthalpy Changes

$$h = u + Pv$$

$$v = \text{constant.}$$

Note that *enthalpy* of incompressible substances depends on both temperature and pressure

$$dh = du + v dP + P dv \overset{0}{=} du + v dP$$

$$\Delta h = \Delta u + v \Delta P \cong c_{\text{avg}} \Delta T + v \Delta P \quad (\text{kJ/kg})$$

For *solids*, the term  $v \Delta P$  is insignificant and thus  $\Delta h = \Delta u \cong c_{\text{avg}} \Delta T$ . For *liquids*, two special cases are commonly encountered:

1. *Constant-pressure processes*, as in heaters ( $\Delta P = 0$ ):  $\Delta h = \Delta u \cong c_{\text{avg}} \Delta T$
2. *Constant-temperature processes*, as in pumps ( $\Delta T = 0$ ):  $\Delta h = v \Delta P$

$$h_2 - h_1 = v(P_2 - P_1) \quad \text{Isothermal process}$$

$$h_{@P,T} \cong h_{f@T} + v_{f@T}(P - P_{\text{sat}@T})$$

The enthalpy of a compressed liquid

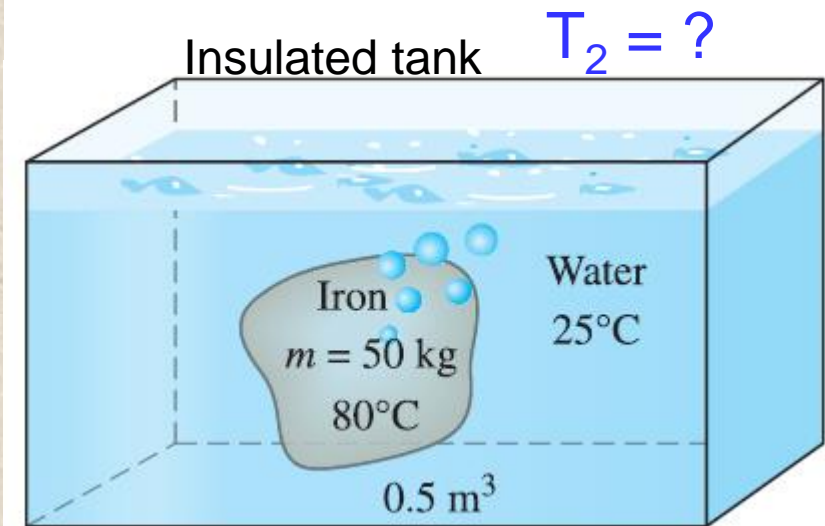
Usually a more accurate relation than

$$h_{@P,T} \cong h_{f@T}$$



# Example: Cooling of an Iron Block by Water

A 50-kg iron block at 80 °C is dropped into an insulated tank that contains 0.5 m<sup>3</sup> of liquid water at 25°C. Determine the temperature when thermal equilibrium is reached.



System: Contents of the tank

**Assumptions**

- 1 Both water and the iron block are incompressible substances.
- 2 Constant specific heats at room temperature can be used for water and the iron.
- 3 The system is stationary and thus the kinetic and potential energy changes are zero,  $\Delta KE = \Delta PE = 0$  and  $\Delta E = \Delta U$ .
- 4 There are no electrical, shaft, or other forms of work involved.
- 5 The system is well-insulated and thus there is no heat transfer.

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{\Delta E_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}}$$

$$0 = \Delta U$$

$$\Delta U_{\text{sys}} = \Delta U_{\text{iron}} + \Delta U_{\text{water}} = 0$$

$$[mc(T_2 - T_1)]_{\text{iron}} + [mc(T_2 - T_1)]_{\text{water}} = 0$$

## Example: Cooling of an Iron Block by Water

$$[mc(T_2 - T_1)]_{\text{iron}} + [mc(T_2 - T_1)]_{\text{water}} = 0$$

$$m_{\text{water}} = \frac{V}{v} = 500 \text{ kg} \quad m_{\text{iron}} = 50 \text{ kg}$$

$$c_{\text{iron}} = 0.45 \frac{\text{kJ}}{\text{kg-K}} \quad (\text{Table A-3})$$

$$c_{\text{water}} = 4.18 \frac{\text{kJ}}{\text{kg-K}}$$

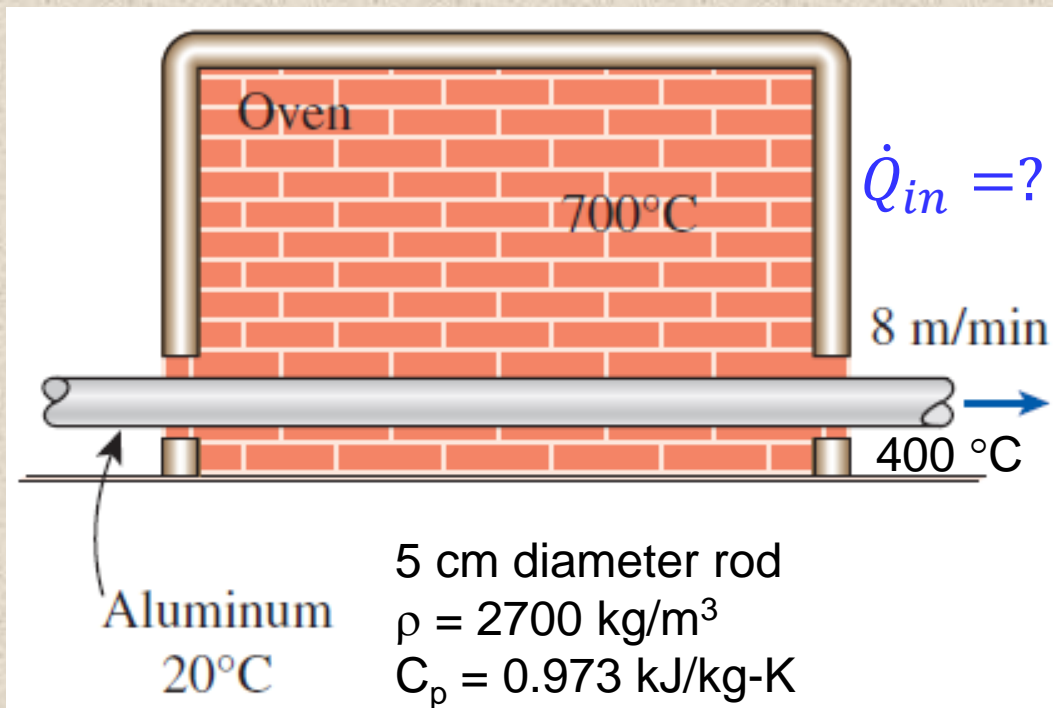
$$T_{1-\text{iron}} = 80^\circ\text{C} \quad T_{1-\text{water}} = 25^\circ\text{C}$$

$$T_{2-\text{iron}} = T_{2-\text{water}} = T_2 \quad \text{at thermal equilibrium}$$

$$T_2 = 25.6^\circ\text{C}$$

# Example: Heating of Aluminum Rods in a Furnace

Long cylindrical aluminum rods ( $\rho = 2700 \text{ kg/m}^3$  and  $c_p = 0.973 \text{ kJ/kg}\cdot\text{K}$ ) of 5-cm diameter are heat treated from  $20^\circ\text{C}$  to an average temperature of  $400^\circ\text{C}$  by drawing them at a velocity of  $8 \text{ m/min}$  through a long oven. Determine the rate of heat transfer to the rods in the oven.



**Assumptions** 1 The thermal properties of the rods are constant. 2 There are no changes in kinetic and potential energies. 3 The rods are at a uniform temperature when they leave the oven.

$$\underbrace{E_{in} - E_{out}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{\Delta E_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}}$$

$$Q_{in} = \Delta U_{\text{rod}} = m(u_2 - u_1)$$

$$Q_{in} = mc(T_2 - T_1)$$

Take the 8 m long section of the rod as the system

# Example: Heating of Aluminum Rods in a Furnace

$$Q_{\text{in}} = mc(T_2 - T_1)$$

Consider 8 m long section of the rod as the system

$$m = \rho V = \rho \frac{\pi D^2}{4} L = 42.41 \text{ kg}$$

$$T_2 = 400 \text{ }^\circ\text{C}, T_1 = 20 \text{ }^\circ\text{C}$$

$$Q_{\text{in}} = 15,680 \text{ kJ}$$

(per 8 m section)

$$\Delta t = 1 \text{ minute} = 60 \text{ s}$$

$$\dot{Q}_{\text{in}} = Q_{\text{in}} / \Delta t$$

$$\dot{Q}_{\text{in}} = 261 \text{ kJ/s}$$



# Summary

- Moving boundary work
  - ✓  $W_b$  for an isothermal process
  - ✓  $W_b$  for a constant-pressure process
  - ✓  $W_b$  for a polytropic process
- Energy balance for closed systems
  - ✓ Energy balance for a constant-pressure expansion or compression process
- Specific heats
  - ✓ Constant-pressure specific heat,  $c_p$
  - ✓ Constant-volume specific heat,  $c_v$
- Internal energy, enthalpy, and specific heats of ideal gases
  - ✓ Specific heat relations of ideal gases
- Internal energy, enthalpy, and specific heats of incompressible substances (solids and liquids)