

Chapter 3 The First Law of Thermodynamics: Closed Systems

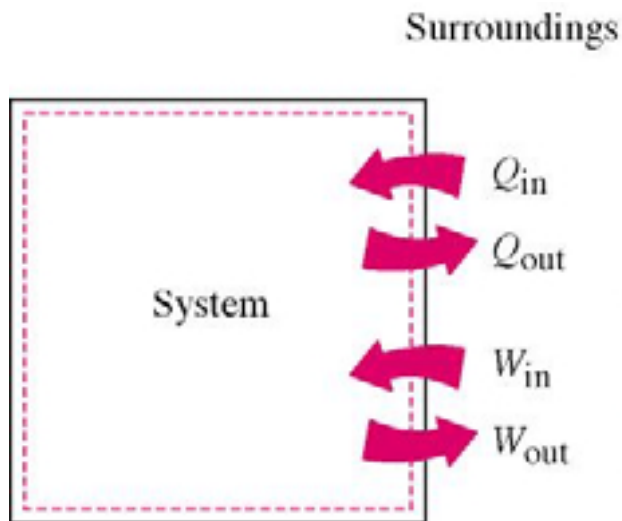
The first law of thermodynamics is an expression of the conservation of energy principle. Energy can cross the boundaries of a closed system in the form of heat or work. Energy transfer across a system boundary due solely to the temperature difference between a system and its surroundings is called heat.

Work energy can be thought of as the energy expended to lift a weight.

Sign Convention

A sign convention is required for heat and work energy transfers, and the classical sign convention is selected for these notes. According to the classical sign convention, heat transfer to a system and work done by a system are positive; heat transfer from a system and work done on a system are negative. The system shown below has heat supplied to it and work done by it.

In these notes we will use the concept of net heat and net work.



Heat Transfer

Recall that heat is energy in transition across the system boundary solely due to the temperature difference between the system and its surroundings. The net heat transferred to a system is defined as

$$Q_{net} = \sum Q_{in} - \sum Q_{out}$$

Here, Q_{in} and Q_{out} are the magnitudes of the heat transfer values. In most thermodynamics texts, the quantity Q is meant to be the net heat transferred to the system, Q_{net} . Since heat transfer is process dependent, the differential of heat transfer δQ is called inexact. We often think about the heat transfer per unit mass of the system, Q .

$$q = \frac{Q}{m}$$

Heat transfer has the units of energy joules (we will use kilojoules, kJ) or the units of energy per unit mass, kJ/kg.

Since heat transfer is energy in transition across the system boundary due to a temperature difference, there are three modes of heat transfer at the boundary that depend on the temperature difference between the boundary surface and the surroundings. These are conduction, convection, and radiation. However, when solving problems in thermodynamics involving heat transfer to a system, the heat transfer is usually given or is calculated by applying the first law, or the conservation of energy, to the system.

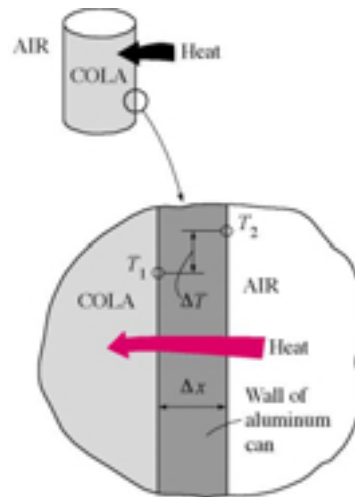
An **adiabatic** process is one in which the system is perfectly insulated and the heat transfer is zero.

For those of us who do not have the opportunity to have a complete course in heat transfer theory and applications, the following is a short introduction to the basic mechanisms of heat transfer. Those of us who have a complete course in heat transfer theory may elect to omit this material at this time.

Heat transfer is energy in transition due to a temperature difference. The three modes of heat transfer are conduction, convection, and radiation.

Conduction through Plane Walls

Conduction heat transfer is a progressive exchange of energy between the molecules of a substance.



Fourier's law of heat conduction is

$$\dot{Q}_{cond} = -A k_t \frac{dT}{dx}$$

here

- \dot{Q}_{cond} = heat flow per unit time (W)
- k_t = thermal conductivity (W/m·K)
- A = area normal to heat flow (m²)
- $\frac{dT}{dx}$ = temperature gradient in the direction of heat flow (°C/m)

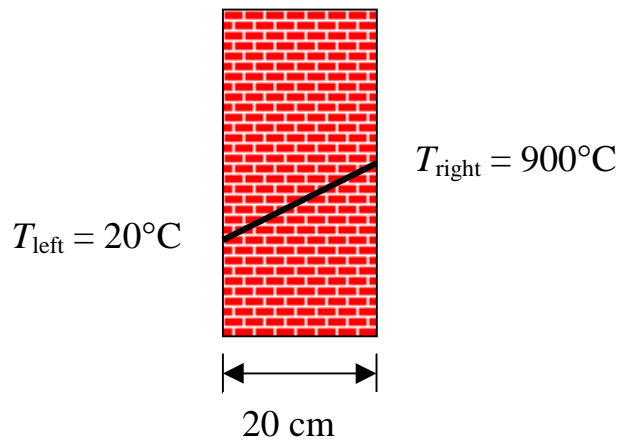
Integrating Fourier's law

$$\dot{Q}_{cond} = kA \frac{\Delta T}{\Delta x}$$

Since $T_2 > T_1$, the heat flows from right to left in the above figure.

Example 3-1

A flat wall is composed of 20 cm of brick ($k_t = 0.72 \text{ W/m}\cdot\text{K}$, see Table 3-1). The right face temperature of the brick is 900°C , and the left face temperature of the brick is 20°C . Determine the rate of heat conduction through the wall per unit area of wall.



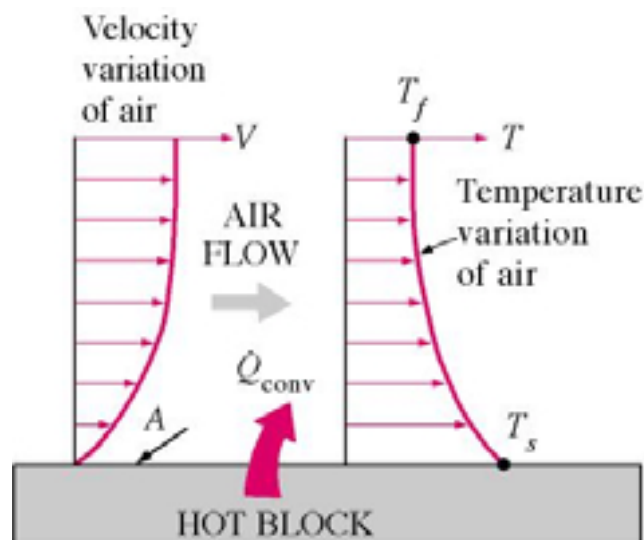
$$\dot{Q}_{cond} = k_t A \frac{\Delta T}{\Delta x}$$

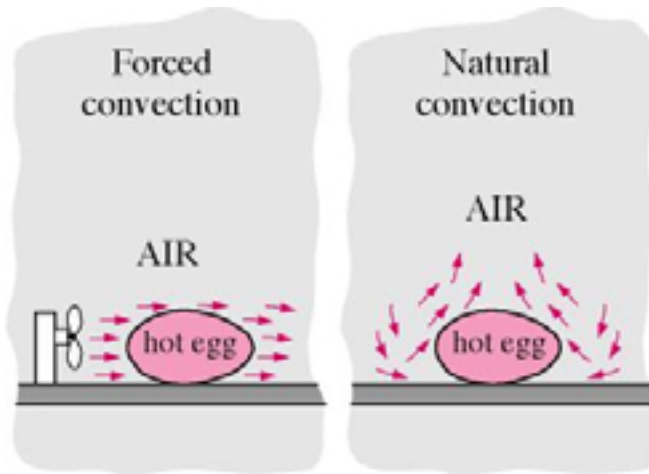
$$\frac{\dot{Q}_{cond}}{A} = k_t \frac{\Delta T}{\Delta x} = 0.72 \frac{W}{m \cdot K} \left(\frac{(900 - 20) K}{0.2 m} \right)$$

$$= 3168 \frac{W}{m^2}$$

Convection Heat Transfer

Convection heat transfer is the mode of energy transfer between a solid surface and the adjacent liquid or gas that is in motion, and it involves the combined effects of conduction and fluid motion.





The rate of heat transfer by convection \dot{Q}_{conv} is determined from Newton's law of cooling, expressed as

$$\dot{Q}_{conv} = h A (T_s - T_f)$$

here

\dot{Q}_{conv} = heat transfer rate (W)

A = heat transfer area (m²)

h = convective heat transfer coefficient (W/m²·K)

T_s = surface temperature (K)

T_f = bulk fluid temperature away from the surface (K)

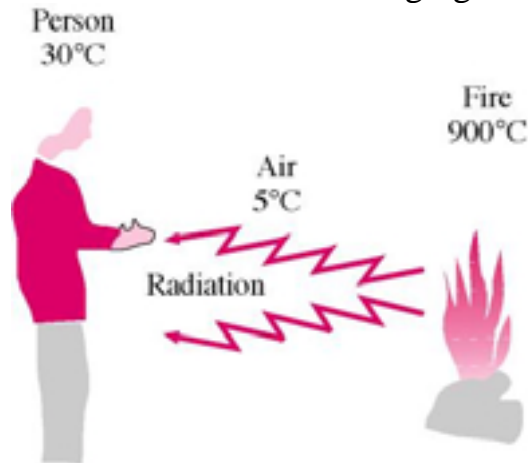
The convective heat transfer coefficient is an experimentally determined parameter that depends upon the surface geometry, the nature of the fluid motion, the properties of the fluid, and the bulk fluid velocity. Ranges of the convective heat transfer coefficient are given below.

h W/m²·K

free convection of gases	2-25
free convection of liquids	50-100
forced convection of gases	25-250
forced convection of liquids	50-20,000
convection in boiling and condensation	2500-100,000

Radiative Heat Transfer

Radiative heat transfer is energy in transition from the surface of one body to the surface of another due to electromagnetic radiation. The radiative energy transferred is proportional to the difference in the fourth power of the absolute temperatures of the bodies exchanging energy.



The net exchange of radiative heat transfer between a body surface and its surroundings is given by

$$\dot{Q}_{rad} = \epsilon \sigma A (T_s^4 - T_{surr}^4)$$

here

\dot{Q}_{rad} = heat transfer per unit time (W)

A = surface area for heat transfer (m^2)

σ = Stefan-Boltzmann constant, $5.67 \times 10^{-8} \text{ W/m}^2 \text{K}^4$
and $0.1713 \times 10^{-8} \text{ BTU/h ft}^2 \text{R}^4$

ϵ = emissivity

T_s = absolute temperature of surface (K)

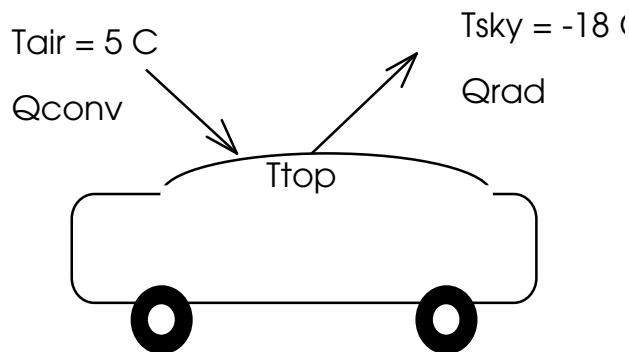
T_{surr} = absolute temperature of surroundings (K)

Example 3-2

A vehicle is to be parked overnight in the open away from large surrounding objects. It is desired to know if dew or frost may form on the vehicle top. Assume the following:

- Convection coefficient h from ambient air to vehicle top is $6.0 \text{ W/m}^2\cdot^\circ\text{C}$.
- Equivalent sky temperature is -18°C .
- Emissivity of vehicle top is 0.84 .
- Negligible conduction from inside vehicle to top of vehicle.

Determine the temperature of the vehicle top when the air temperature is 5°F . State which formation (dew or frost) occurs.



Under steady-state conditions, the energy convected to the vehicle top is equal to the energy radiated to the sky.

$$\dot{Q}_{\text{conv}} = \dot{Q}_{\text{rad}}$$

The energy convected from the ambient air to the vehicle top is

$$\dot{Q}_{\text{conv}} = A_{\text{top}} h (T_{\text{air}} - T_{\text{top}})$$

The energy radiated from the top to the night sky is

$$\dot{Q}_{rad} = \varepsilon \sigma A_{top} (T_{top}^4 - T_{sky}^4)$$

Setting these two heat transfers equal gives

$$A_{top} h (T_{air} - T_{top}) = \varepsilon \sigma A_{top} (T_{top}^4 - T_{sky}^4)$$

$$h (T_{air} - T_{top}) = \varepsilon \sigma (T_{top}^4 - T_{sky}^4)$$

$$\begin{aligned} 6.0 \frac{W}{m^2 K} [(5 + 273) - T_{top}] K \\ = (0.84) \left(5.67 \times 10^{-8} \frac{W}{m^2 K^4} \right) [T_{top}^4 - (-18 + 273)^4] K^4 \end{aligned}$$

Write the equation for T_{top} in °C ($T\text{ K} = T^\circ\text{C} + 273$)

$$(5 - T_{top}) = \frac{(0.84)(5.67)}{6.0} \left[\left(\frac{T_{top} + 273}{100} \right)^4 - (2.55)^4 \right]$$

Using the EES software package

$$T_{top} = -3.38^\circ\text{C}$$

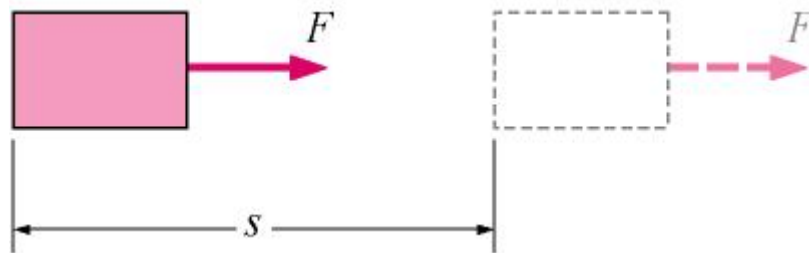
Since T_{top} is below the triple point of water, 0.01°C , the water vapor in the air will form frost on the car top (see Chapter 13).

Extra Problem

Explore what happens to T_{top} as you vary the convective heat transfer coefficient. On a night when the atmosphere is particularly still and cold and has a clear sky, why do fruit growers use fans to increase the air velocity in their fruit groves?

Work

Work is energy expended by a force acting through a distance. Thermodynamic work is defined as energy in transition across the system boundary and is done by a system if the sole effect external to the boundaries could have been the raising of a weight.



Mathematically, the differential of work is expressed as

$$\delta W = \vec{F} \cdot d\vec{s} = F ds \cos \Theta$$

here Θ is the angle between the force vector and the displacement vector. As with the heat transfer, the Greek δ means that work is a path-dependent function and has an inexact differential. If the angle between the force and the displacement is zero, the work done between two states is

$$W_{12} = \int_1^2 \delta W = \int_1^2 F ds$$

Work has the units of energy force times displacement or newton times meter or joule (we will use kilojoules). Work per unit mass of a system is measured in kJ/kg.

Common Types of Work Energy

The net work done by the system may be in two forms. First, there can be work crossing the system boundary in the form of a rotating shaft or electrical work. We will call shaft work and electrical work “other” work, that is, work not associated with a moving boundary. In thermodynamics electrical energy is normally considered to be work energy rather than heat energy, but the placement of the system boundary dictates whether to include electrical energy as work or heat. Second, the system may do work on its surroundings because of moving boundaries.

The net work done by a closed system is defined by

$$W_{net} = \left(\sum W_{out} - \sum W_{in} \right)_{other} + W_b$$

Here, W_{out} and W_{in} are the magnitudes of the other work forms crossing the boundary. W_b is the work due to the moving boundary and will be positive or negative depending upon the process.

Or

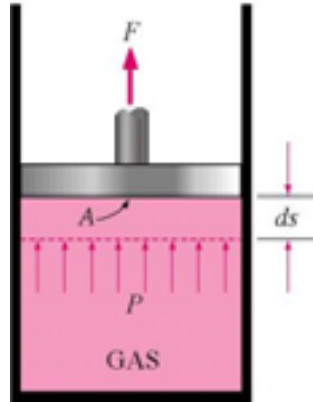
$$W_{net} = \left(W_{net} \right)_{other} + W_b$$

Several types of “other” work (shaft work, electrical work, etc.) are discussed in the text.

Boundary Work

Work is energy expended when a force acts through a displacement. Boundary work occurs because the mass of the substance contained within the system boundary causes a force, the pressure times the surface area, to

act on the boundary surface and make it move. This is what happens when steam, the “gas” in the figure below, contained in a piston-cylinder device expands against the piston and forces the piston to move; thus, boundary work is done by the steam on the piston. Boundary work is then calculated from



$$W_b = \int_1^2 \delta W_b = \int_1^2 F ds = \int_1^2 \frac{F}{A} A ds$$

$$= \int_1^2 P dV$$

Since the work is process dependent, the differential of boundary work δW_b is

$$\delta W_b = P dV$$

is called inexact. The above equation for W_b is valid for a quasi-equilibrium process and gives the maximum work done during expansion and the minimum work input during compression.

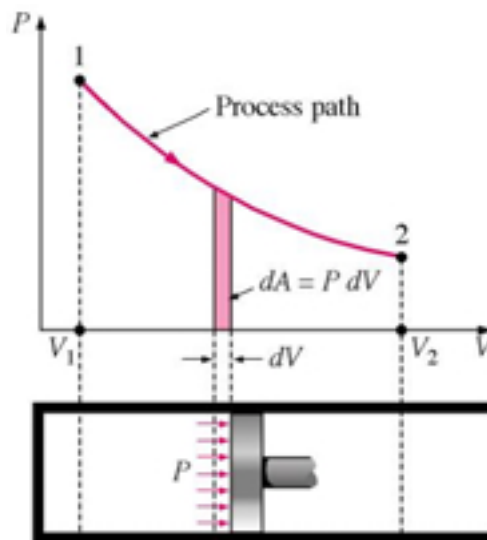
To calculate the boundary work, the process by which the system changed states must be known. Once the process is determined, the pressure-volume relationship for the process can be obtained and the integral in the

boundary work equation can be performed. For each process we need to determine

$$P = f(V)$$

So as we work problems, we will be asking, “What is the pressure-volume relationship for the process?” Remember that this relation is really the force-displacement function.

The boundary work is equal to the area under the process curve plotted on the pressure-volume diagram.



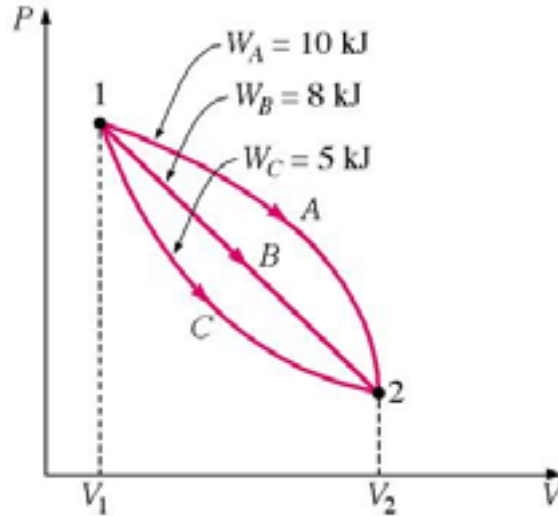
Note:

P is the absolute pressure and is always positive.

When dV is positive, W_b is positive.

When dV is negative, W_b is negative.

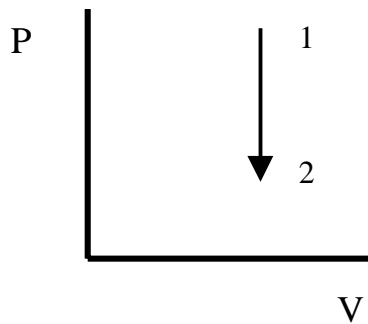
Since the areas under different process curves on a P - V diagram are different, the boundary work for each process will be different. The next figure shows that each process gives a different value for the boundary work.



Some Typical Processes

Constant volume

If the volume is held constant, $dV = 0$, and the boundary work equation becomes

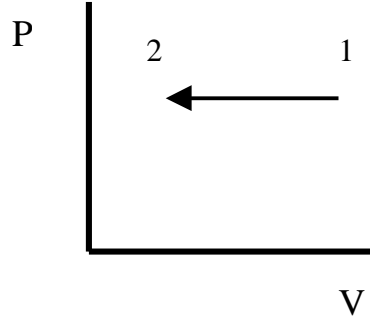


P - V diagram for $V = \text{constant}$

$$W_b = \int_1^2 P dV = 0$$

If the working fluid is an ideal gas, what will happen to the temperature of the gas during this constant volume process?

Constant pressure



P-V diagram for $P = \text{constant}$

If the pressure is held constant, the boundary work equation becomes

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

For the constant pressure process shown above, is the boundary work positive or negative and why?

Constant temperature, ideal gas

If the temperature of an ideal gas system is held constant, then the equation of state provides the pressure-volume relation

$$P = \frac{mRT}{V}$$

Then, the boundary work is

$$\begin{aligned} W_b &= \int_1^2 P dV = \int_1^2 \frac{mRT}{V} dV \\ &= mRT \ln \left(\frac{V_2}{V_1} \right) \end{aligned}$$

Note: The above equation is the result of applying the ideal gas assumption for the equation of state. For real gases undergoing an isothermal (constant temperature) process, the integral in the boundary work equation would be done numerically.

The polytropic process

The polytropic process is one in which the pressure-volume relation is given as

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

The exponent n may have any value from minus infinity to plus infinity depending on the process. Some of the more common values are given below.

Process	Exponent n
Constant pressure	0
Constant volume	∞
Isothermal & ideal gas	1
Adiabatic & ideal gas	$k = C_p/C_v$

Here, k is the ratio of the specific heat at constant pressure C_p to specific heat at constant volume C_v . The specific heats will be discussed later.

The boundary work done during the polytropic process is found by substituting the pressure-volume relation into the boundary work equation. The result is

$$\begin{aligned}W_b &= \int_1^2 P dV = \int_1^2 \frac{Const}{V^n} dV \\&= \frac{P_2 V_2 - P_1 V_1}{1 - n}, \quad n \neq 1 \\&= PV \ln \left(\frac{V_2}{V_1} \right), \quad n = 1\end{aligned}$$

For an ideal gas under going a polytropic process, the boundary work is

$$\begin{aligned}W_b &= \int_1^2 P dV = \int_1^2 \frac{Const}{V^n} dV \\&= \frac{mR(T_2 - T_1)}{1 - n}, \quad n \neq 1 \\&= mRT \ln \left(\frac{V_2}{V_1} \right), \quad n = 1\end{aligned}$$

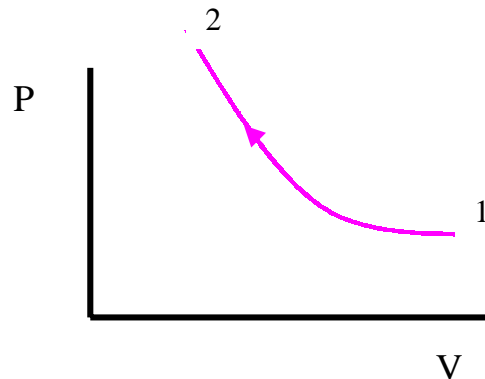
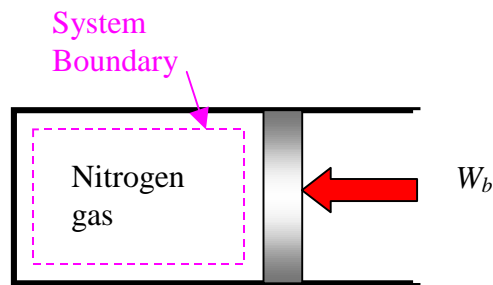
Notice that the results we obtained for an ideal gas undergoing a polytropic process when $n = 1$ are identical to those for an ideal gas undergoing the isothermal process.

Example 3-3

Three kilograms of nitrogen gas at 27°C and 0.15 MPa are compressed isothermally to 0.3 MPa in a piston-cylinder device. Determine the minimum work of compression, in kJ.

System: Nitrogen contained in a piston-cylinder device.

Process: Constant temperature



P-V diagram for $T = \text{constant}$

Property Relation: Check the reduced temperature and pressure for nitrogen. The critical state properties are found in Table A-1.

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{(27 + 273)\text{ K}}{126.2\text{ K}} = 2.38 = T_{R2}$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{0.15\text{ MPa}}{3.39\text{ MPa}} = 0.044$$

$$P_{R2} = 2P_{R1} = 0.088$$

Since $P_R \ll 1$ and $T > 2T_{cr}$, nitrogen is an ideal gas, and we use the ideal gas equation of state as the property relation.

$$PV = mRT$$

Work Calculation:

$$W_{net,12} = (W_{net})_{other,12} + W_{b,12}$$

$$\begin{aligned} W_{b,12} &= \int_1^2 P dV = \int_1^2 \frac{mRT}{V} dV \\ &= mRT \ln \left(\frac{V_2}{V_1} \right) \end{aligned}$$

For an ideal gas in a closed system (mass = constant), we have

$$\begin{aligned} m_1 &= m_2 \\ \frac{P_1 V_1}{RT_1} &= \frac{P_2 V_2}{RT_2} \end{aligned}$$

Since the R 's cancel and $T_2 = T_1$,

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

$$\begin{aligned}
 W_{b,12} &= mRT \ln\left(\frac{P_1}{P_2}\right) \\
 &= (3 \text{ kg}) \left(0.2968 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \right) (300 \text{ K}) \ln\left(\frac{0.15 \text{ MPa}}{0.30 \text{ MPa}}\right) \\
 &= -184.5 \text{ kJ}
 \end{aligned}$$

The net work is

$$W_{net,12} = 0 + W_{b,12} = -184.5 \text{ kJ}$$

On a per unit mass basis

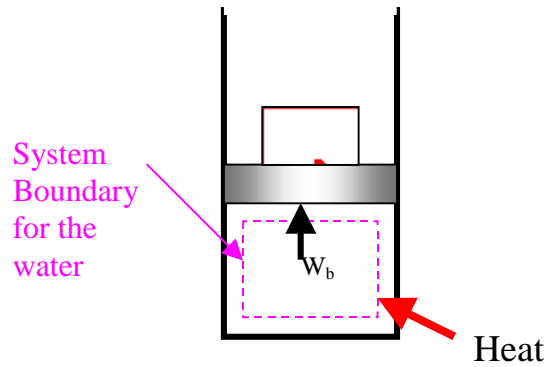
$$w_{net,12} = \frac{W_{net,12}}{m} = -61.5 \frac{\text{kJ}}{\text{kg}}$$

The net work is negative because work is done **on** the system during the compression process. Thus, the work into the system is 184.5 kJ, or 184.5 kJ of work energy is required to compress the nitrogen.

Example 3-4

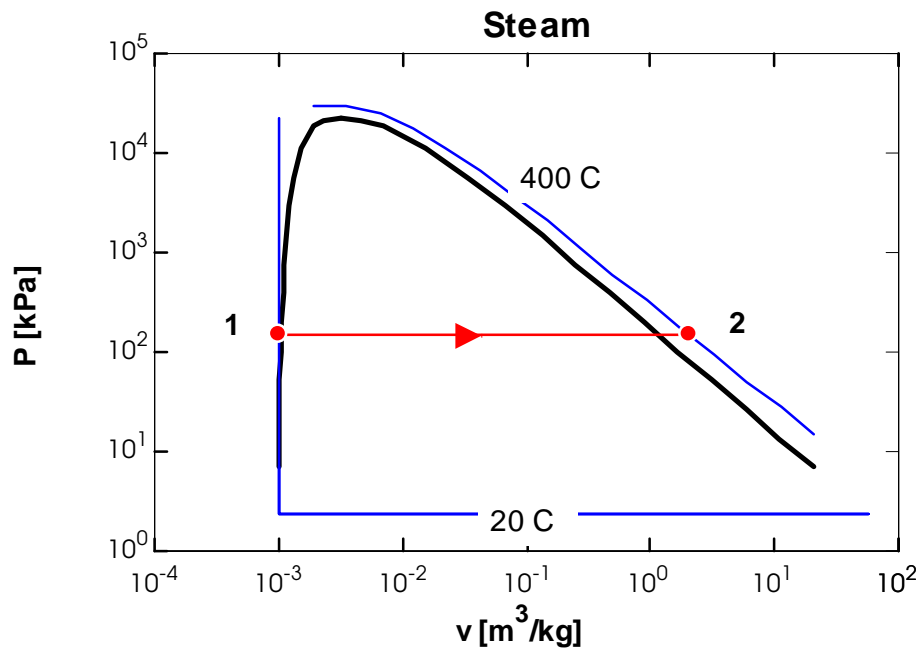
Water is placed in a piston-cylinder device at 20 °C, 0.1 MPa. Weights are placed on the piston to maintain a constant force on the water as it is heated to 400 °C. How much work does the water do on the piston?

System: The water contained in the piston-cylinder device



Property Relation: Steam tables

Process: Constant pressure



Work Calculation:

Since there is no W_{other} mentioned in the problem, the net work is

$$W_{net,12} = W_{b,12} = \int_1^2 P dV = P \int_1^2 dV = P(V_2 - V_1)$$

Since the mass of the water is unknown, we calculate the work per unit mass.

$$w_{b,12} = \frac{W_{b,12}}{m} = \frac{P(V_2 - V_1)}{m} = P(v_2 - v_1)$$

At $T_1 = 20^\circ\text{C}$, $P_{\text{sat}} = 2.339 \text{ kPa}$. Since $P_1 > 2.339 \text{ kPa}$, state 1 is compressed liquid. Thus,

$$v_1 \cong v_f \text{ at } 20^\circ\text{C} = 0.001002 \text{ m}^3/\text{kg}$$

At $P_2 = P_1 = 0.1 \text{ MPa}$, $T_2 > T_{\text{sat}}$ at $0.1 \text{ MPa} = 99.63^\circ\text{C}$.

So, state 2 is superheated. Using the superheated tables,

$$v_2 = 3.103 \text{ m}^3/\text{kg}$$

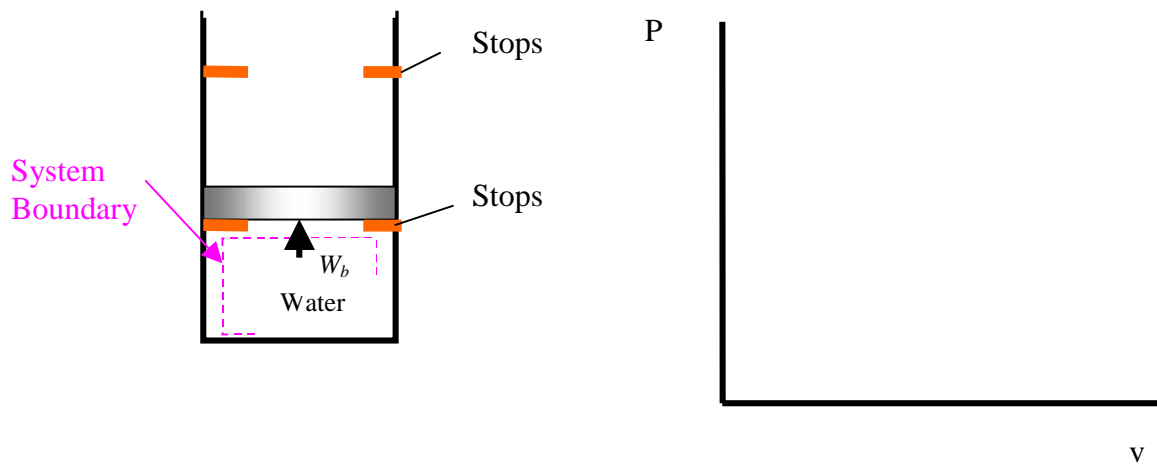
$$\begin{aligned} w_{b,12} &= P(v_2 - v_1) \\ &= 0.1 \text{ MPa}(3.103 - 0.001002) \frac{\text{m}^3}{\text{kg}} \frac{10^3 \text{ kPa}}{\text{MPa}} \frac{\text{kJ}}{\text{m}^3 \text{ kPa}} \\ &= 310.2 \frac{\text{kJ}}{\text{kg}} \end{aligned}$$

The water does work on the piston in the amount of 310.2 kJ/kg.

Example 3-5

One kilogram of water is contained in a piston-cylinder device at 100 °C. The piston rests on lower stops such that the volume occupied by the water is 0.835 m³. The cylinder is fitted with an upper set of stops. When the piston rests against the upper stops, the volume enclosed by the piston-cylinder device is 0.841 m³. A pressure of 200 kPa is required to support the piston. Heat is added to the water until the water exists as a saturated vapor. How much work does the water do on the piston?

System: The water contained in the piston-cylinder device



Property Relation: Steam tables

Process: Combination of constant volume and constant pressure processes to be shown on the P - v diagram as the problem is solved

Work Calculation:

The specific volume at state 1 is

$$v_1 = \frac{V_1}{m} = \frac{0.835 \text{ m}^3}{1 \text{ kg}} = 0.835 \frac{\text{m}^3}{\text{kg}}$$

At $T_1 = 100^\circ\text{C}$,

$$v_f = 0.0010044 \frac{\text{m}^3}{\text{kg}} \quad v_g = 1.6729 \frac{\text{m}^3}{\text{kg}}$$

Therefore, $v_f < v_1 < v_g$ and state 1 is in the saturation region; so $P_1 = 101.35 \text{ kPa}$.

Now let's consider the processes for the water.

Process 1-2: The volume stays constant until the pressure increases to 200 kPa. Then the piston will move.

$$v_2 = v_1 = 0.835 \frac{\text{m}^3}{\text{kg}}$$

Process 2-3: Piston lifts off the bottom stops while the pressure stays constant. Does the piston hit the upper stops before or after reaching the saturated vapor state?

Let's set

$$v_3 = \frac{V_3}{m} = \frac{0.841 \text{ m}^3}{1 \text{ kg}} = 0.841 \frac{\text{m}^3}{\text{kg}}$$

At $P_3 = P_2 = 200 \text{ kPa}$

$$v_f = 0.0010061 \frac{\text{m}^3}{\text{kg}} \quad v_g = 0.8857 \frac{\text{m}^3}{\text{kg}}$$

Thus, $v_f < v_3 < v_g$. So, the piston hits the upper stops before the water reaches the saturated vapor state. Now we have to consider a third process.

Process 3-4: With the piston against the upper stops, the volume remains constant during the final heating to the saturated vapor state and the pressure increases.

Because the volume is constant in process 3-to-4, $v_4 = v_3 = 0.841 \text{ m}^3/\text{kg}$ and v_4 is a saturated vapor state. Interpolating in either the saturation pressure table or saturation temperature table at $v_4 = v_g$ gives

State 4:

$$\left. \begin{array}{l} P_4 = 211.3 \text{ kPa} \\ v_4 = v_g \end{array} \right\} T_4 = 122^\circ \text{C}$$

The net work for the heating process is (the “other” work is zero)

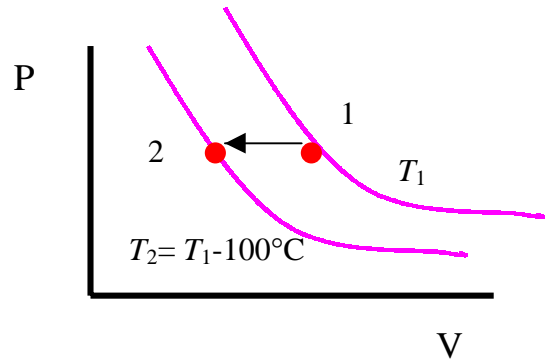
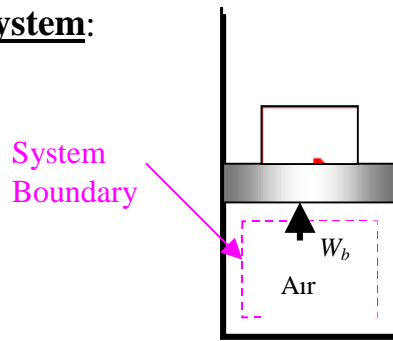
$$\begin{aligned} W_{net,14} &= W_{b,14} = \int_1^4 P dV = \int_1^2 P dV + \int_2^3 P dV + \int_3^4 P dV \\ &= 0 + mP(v_3 - v_2) + 0 \\ &= (1\text{kg})(200\text{kPa})(0.841 - 0.835) \frac{\text{m}^3}{\text{kg}} \frac{\text{kJ}}{\text{m}^3 \text{kPa}} \\ &= 1.2 \text{ kJ} \end{aligned}$$

Later, we will apply the conservation of energy, or the first law of thermodynamics, to this process to determine the amount of heat transfer required.

Example 3-6

Air undergoes a constant pressure cooling process in which the temperature decreases by 100°C . What is the magnitude and direction of the work for this process?

System:



P-V diagram for $T = \text{constant}$

Property Relation: Ideal gas law, $Pv = RT$

Process: Constant pressure

Work Calculation: Neglecting the “other” work

$$\begin{aligned} W_{net,12} &= 0 + W_{b,12} = \int_1^2 P dV = P(V_2 - V_1) \\ &= mR(T_2 - T_1) \end{aligned}$$

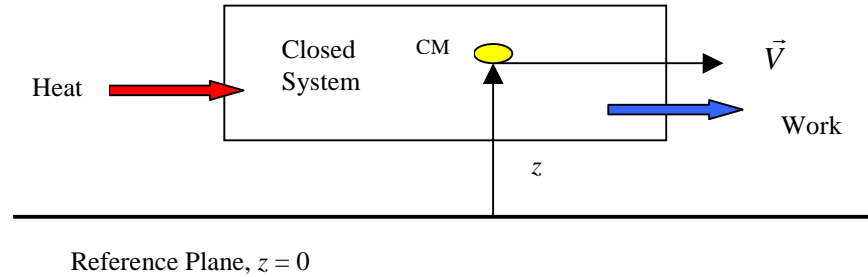
The work per unit mass is

$$\begin{aligned} w_{net,12} &= \frac{W_{net,12}}{m} = R(T_2 - T_1) \\ &= (0.287 \frac{\text{kJ}}{\text{kg} \cdot \text{K}})(-100 \text{ K}) \\ &= -28.7 \frac{\text{kJ}}{\text{kg}} \end{aligned}$$

The work **done on** the air is 28.7 kJ/kg.

Closed System First Law

A closed system moving relative to a reference plane is shown below where z is the elevation of the center of mass above the reference plane and \vec{V} is the velocity of the center of mass.



For the closed system shown above, the **conservation of energy principle** or **the first law of thermodynamics** is expressed as

$$\left(\begin{array}{c} \text{Total energy} \\ \text{entering the system} \end{array} \right) - \left(\begin{array}{c} \text{Total energy} \\ \text{leaving the system} \end{array} \right) = \left(\begin{array}{c} \text{The change in total} \\ \text{energy of the system} \end{array} \right)$$

or

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

According to classical thermodynamics, we consider the energy added to be net heat transfer to the closed system and the energy leaving the closed system to be net work done by the closed system. So

$$Q_{net} - W_{net} = \Delta E_{system}$$

Normally the stored energy, or total energy, of a system is expressed as the sum of three separate energies. The **total energy of the system**, E_{system} , is given as

$$E = \text{Internal energy} + \text{Kinetic energy} + \text{Potential energy}$$

$$E = U + KE + PE$$

Recall that U is the sum of the energy contained within the molecules of the system other than the kinetic and potential energies of the system as a whole and is called the internal energy. The internal energy U is dependent on the state of the system and the mass of the system.

For a system moving relative to a reference plane, the kinetic energy KE and the potential energy PE are given by

$$KE = \int_{\vec{V}=0}^{\vec{V}} m \vec{V} d\vec{V} = \frac{m \vec{V}^2}{2}$$

$$PE = \int_{z=0}^z mg dz = mgz$$

The change in stored energy for the system is

$$\Delta E = \Delta U + \Delta KE + \Delta PE$$

Now the **conservation of energy principle**, or the **first law of thermodynamics for closed systems**, is written as

$$Q_{net} - W_{net} = \Delta U + \Delta KE + \Delta PE$$

If the system does not move with a velocity and has no change in elevation, the conservation of energy equation reduces to

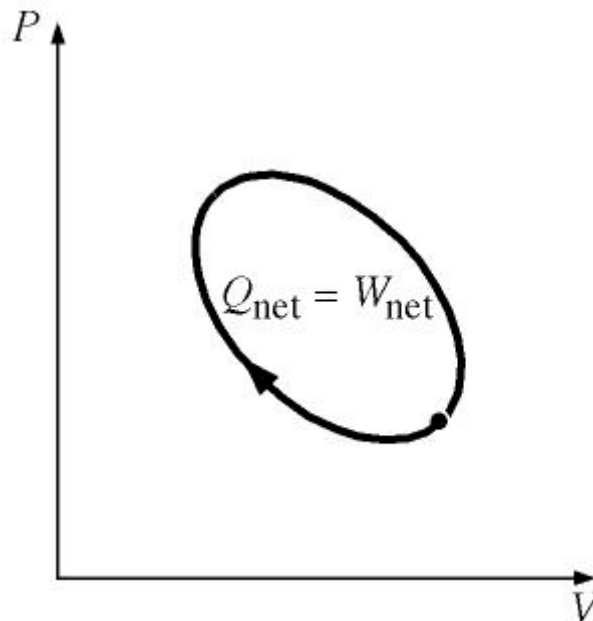
$$Q_{net} - W_{net} = \Delta U$$

We will find that this is the most commonly used form of the first law.
Closed System First Law for a Cycle

Since a thermodynamic cycle is composed of processes that cause the working fluid to undergo a series of state changes through a series of processes such that the final and initial states are identical, the change in internal energy of the working fluid is zero for whole numbers of cycles. The first law for a closed system operating in a thermodynamic cycle becomes

$$Q_{net} - W_{net} = \Delta U_{cycle}^0$$

$$Q_{net} = W_{net}$$



Example 3-7

Complete the table given below for a closed system under going a cycle.

Process	Q_{net} kJ	W_{net} kJ	$U_2 - U_1$ kJ
1-2	+5		-5
2-3	+20	+10	
3-1		-5	
Cycle			

(Answer to above problem) Row 1: +10, Row 2: +10, Row 3: -10, -5

Row 4: +15, +15, 0

Example 3-8

Find the required heat transfer to the water in Example 3-5.

Review the solution procedure of Example 3-5 and then apply the first law to the process.

Conservation of Energy:

$$E_{in} - E_{out} = \Delta E$$
$$Q_{net,14} - W_{net,14} = \Delta U_{14}$$

In Example 3-3 we found that

$$W_{net,14} = 1.2 \text{ kJ}$$

The heat transfer is obtained from the first law as

$$Q_{net,14} = W_{net,14} + \Delta U_{14}$$

where

$$\Delta U_{14} = U_4 - U_1 = m(u_4 - u_1)$$

At state 1, $T_1 = 100^\circ\text{C}$, $v_1 = 0.835 \text{ m}^3/\text{kg}$ and $v_f < v_1 < v_g$ at T_1 . The quality at state 1 is

$$v_1 = v_f + x_1 v_{fg}$$

$$x_1 = \frac{v_1 - v_f}{v_{fg}} = \frac{0.835 - 0.001044}{1.6729 - 0.001044} = 0.499$$

$$\begin{aligned}
 u_1 &= u_f + x_1 u_{fg} \\
 &= 418.94 + (0.499)(2087.6) \\
 &= 1460.26 \frac{kJ}{kg}
 \end{aligned}$$

Because state 4 is a saturated vapor state and $v_4 = 0.841 \text{ m}^3/\text{kg}$, interpolating in either the saturation pressure table or saturation temperature table at $v_4 = v_g$ gives

$$u_4 = 2531.48 \frac{kJ}{kg}$$

So

$$\begin{aligned}
 \Delta U_{14} &= m(u_4 - u_1) \\
 &= (1 \text{ kg})(2531.48 - 1460.26) \frac{kJ}{kg} \\
 &= 1071.22 \text{ kJ}
 \end{aligned}$$

The heat transfer is

$$\begin{aligned}
 Q_{net,14} &= W_{net,14} + \Delta U_{14} \\
 &= 1.2 \text{ kJ} + 1071.22 \text{ kJ} \\
 &= 1072.42 \text{ kJ}
 \end{aligned}$$

Heat in the amount of 1072.42 kJ is added to the water.

Specific Heats, Internal Energy and Enthalpy

Before the first law of thermodynamics can be applied to systems, ways to calculate the change in internal energy of the substance enclosed by the system boundary must be determined. For real substances like water, the property tables are used to find the internal energy change. For ideal gases the internal energy is found by knowing the specific heats. Physics defines the amount of energy needed to raise the temperature of a unit of mass of a substance one degree as the specific heat at constant volume C_V for a constant-volume process, and the specific heat at constant pressure C_P for a constant-pressure process. Recall that enthalpy h is the sum of the internal energy u and the pressure-volume product Pv .

$$h = u + Pv$$

In thermodynamics, the specific heats are defined as

$$C_V = \left(\frac{\partial u}{\partial T} \right)_v \quad \text{and} \quad C_P = \left(\frac{\partial h}{\partial T} \right)_P$$

Simple Substance

The thermodynamic state of a simple, homogeneous substance is specified by giving any two independent, intensive properties. Let's consider the internal energy to be a function of T and v and the enthalpy to be a function of T and P as follows:

$$u = u(T, v) \quad \text{and} \quad h = h(T, P)$$

The total differential of u is

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

or

$$du = C_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

The total differential of h is

$$dh = \left(\frac{\partial h}{\partial T} \right)_P dT + \left(\frac{\partial h}{\partial P} \right)_T dP$$

or

$$dh = C_P dT + \left(\frac{\partial h}{\partial P} \right)_T dP$$

Using thermodynamic relation theory, we could evaluate the remaining partial derivatives of u and h in terms of functions of P, v , and T . These functions depend upon the equation of state for the substance. Given the specific heat data and the equation of state for the substance, we can develop the property tables like the steam tables.

Ideal Gases

For ideal gases, we use thermodynamic function relation theory of Chapter 11 and the equation of state ($Pv = RT$) to show that u , h , C_v , and C_P are functions of temperature alone. Then for ideal gases,

$$C_V = C_V(T) \quad \text{and} \quad \left(\frac{\partial u}{\partial v} \right)_T \equiv 0$$

$$C_P = C_P(T) \quad \text{and} \quad \left(\frac{\partial h}{\partial P} \right)_T \equiv 0$$

The ideal gas specific heats are written in terms of ordinary differentials as

$$C_V = \left(\frac{du}{dT} \right)_{ideal\ gas}$$

$$C_P = \left(\frac{dh}{dT} \right)_{ideal\ gas}$$

Using the simple “dumbbell model” for diatomic ideal gases, statistical thermodynamics predicts the molar specific heat at constant pressure as a function of temperature to look like the following

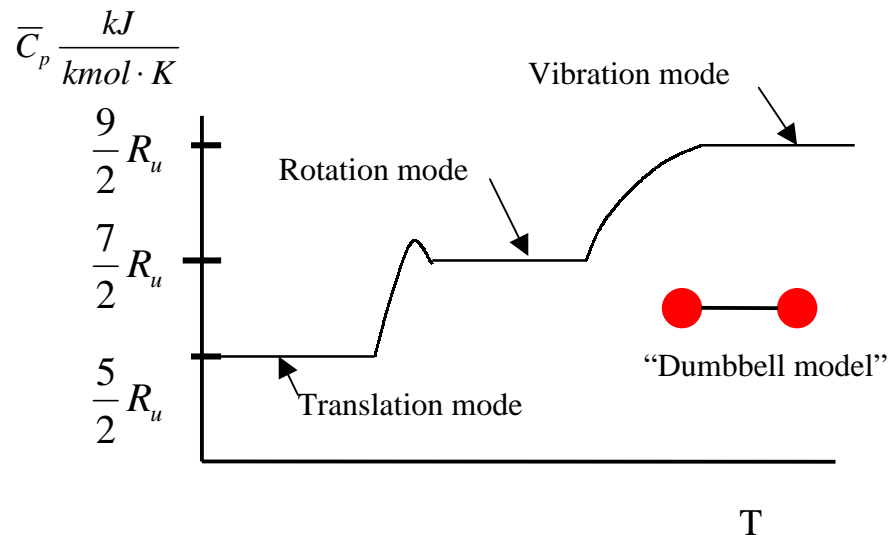
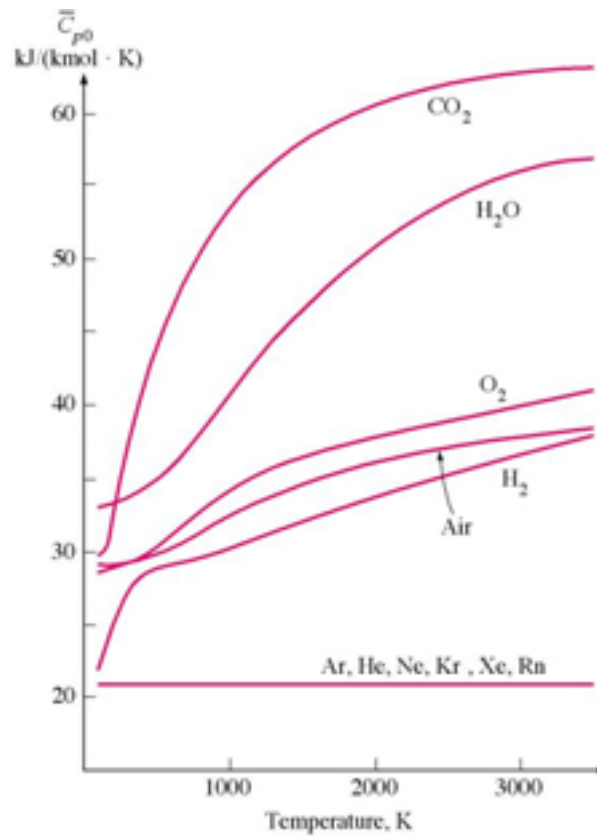


Figure 3-76, page 143 in the text, shows how the molar specific heats vary with temperature for selected ideal gases.



The differential changes in internal energy and enthalpy for ideal gases become

$$du = C_V dT$$

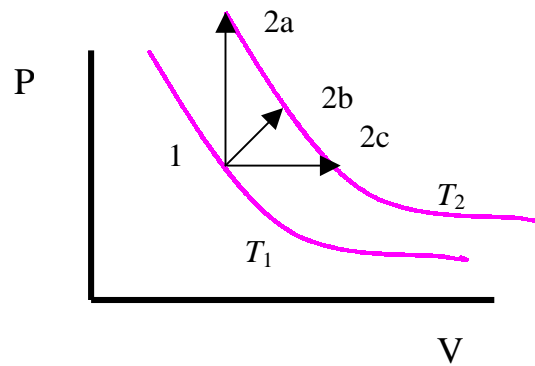
$$dh = C_P dT$$

The change in internal energy and enthalpy of ideal gases can be expressed as

$$\Delta u = u_2 - u_1 = \int_1^2 C_V(T) dT = C_{V,ave} (T_2 - T_1)$$

$$\Delta h = h_2 - h_1 = \int_1^2 C_P(T) dT = C_{P,ave} (T_2 - T_1)$$

where $C_{V,ave}$ and $C_{P,ave}$ are average or constant values of the specific heats over the temperature range. We will drop the **ave** subscript shortly.



P-V diagram for several processes for an ideal gas.

In the above figure an ideal gas undergoes three different process between the same two temperatures.

Process 1-2a: Constant volume

Process 1-2b: $P = a + bV$, a linear relationship

Process 1-2c: Constant pressure

These ideal gas processes have the same change in internal energy and enthalpy because the processes occur between the same temperature limits.

$$\Delta u_a = \Delta u_b = \Delta u_c = \int_1^2 C_V(T) dT$$

$$\Delta h_a = \Delta h_b = \Delta h_c = \int_1^2 C_P(T) dT$$

To find Δu and Δh we often use average, or constant, values of the specific heats. Some ways to determine these values are as follows:

1. The best average value (the one that gives the exact results)

See Table A-2c for variable specific data.

$$C_{v,ave} = \frac{\int_1^2 C_v(T) dT}{T_2 - T_1} \quad \text{and} \quad C_{P,ave} = \frac{\int_1^2 C_P(T) dT}{T_2 - T_1}$$

2. Good average values are

$$C_{v,ave} = \frac{C_v(T_2) + C_v(T_1)}{2} \quad \text{and} \quad C_{P,ave} = \frac{C_P(T_2) + C_P(T_1)}{2}$$

and

$$C_{v,ave} = C_v(T_{ave}) \quad \text{and} \quad C_{P,ave} = C_P(T_{ave})$$

where

$$T_{ave} = \frac{T_2 + T_1}{2}$$

3. Sometimes adequate (and most often used) values are the ones evaluated at 300 K and are given in Table A-2(a).

$$C_{v,ave} = C_v(300K) \quad \text{and} \quad C_{P,ave} = C_P(300K)$$

Let's take a second look at the definition of Δu and Δh for ideal gases. Just consider the enthalpy for now.

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

Let's perform the integral relative to a reference state where
 $h = h_{\text{ref}}$ at $T = T_{\text{ref}}$.

$$\Delta h = h_2 - h_1 = \int_{T_1}^{T_{\text{ref}}} C_P(T')dT' + \int_{T_{\text{ref}}}^{T_2} C_P(T')dT'$$

or

$$\begin{aligned}\Delta h = h_2 - h_1 &= \int_{T_{\text{ref}}}^{T_2} C_P(T')dT' - \int_{T_{\text{ref}}}^{T_1} C_P(T')dT' \\ &= (h_2 - h_{\text{ref}}) - (h_1 - h_{\text{ref}})\end{aligned}$$

At any temperature, we can calculate the enthalpy relative to the reference state as

$$h - h_{\text{ref}} = \int_{T_{\text{ref}}}^T C_P(T')dT'$$

or

$$h = h_{\text{ref}} + \int_{T_{\text{ref}}}^T C_P(T')dT'$$

Similarly, the internal energy change relative to the reference state is

$$u - u_{ref} = \int_{T_{ref}}^T C_V(T') dT'$$

or

$$u = u_{ref} + \int_{T_{ref}}^T C_V(T') dT'$$

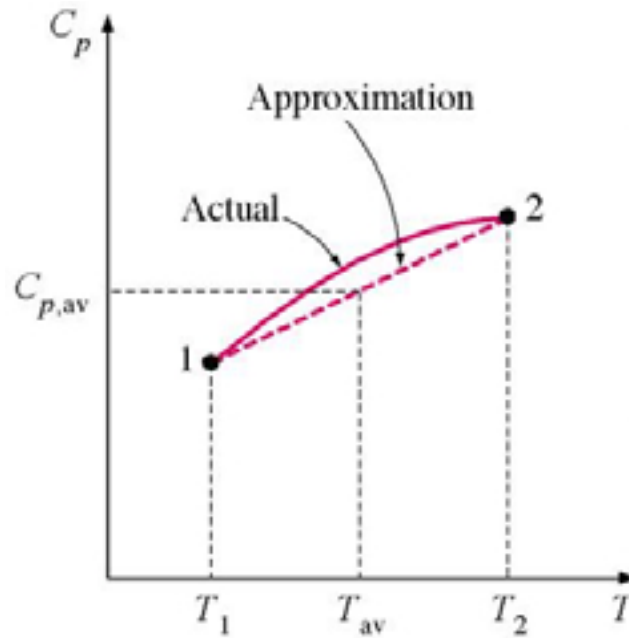
These last two relations form the basis of the air tables (Table A-17 on a mass basis) and the other ideal gas tables (Tables A-18 through A-25 on a mole basis). When you review Table A-17, you will find h and u as functions of T in K. Since the parameters P_r , v_r , and s° apply to air in a particular process, call isentropic, you should ignore these parameters until we study Chapter 6. The reference state for these tables is defined as

$$u_{ref} = 0 \text{ at } T_{ref} = 0K$$

$$h_{ref} = 0 \text{ at } T_{ref} = 0K$$

AIR		
T, K	$u, kJ/kg$	$h, kJ/kg$
0	0	0
.	.	.
300	214.17	300.19
310	221.25	310.24
.	.	.
.	.	.

Partial listing of Table A.17 given in Figure 3-77



In the analysis to follow, the “ave” notation is dropped. In most applications for ideal gases, the values of the specific heats at 300 K given in Table A-2 are adequate constants.

Exercise

Determine the average specific heat for air at 305 K.

$$C_{P, ave} =$$

(Answer: 1.005 kJ/kg·K, approximate the derivative of h wrt T as differences)

Relation between C_P and C_V for Ideal Gases

Using the definition of enthalpy ($h = u + Pv$) and writing the differential of enthalpy, the relationship between the specific heats for ideal gases is

$$h = u + Pv$$

$$dh = du + d(RT)$$

$$C_P dT = C_V dT + R dT$$

$$C_P = C_V + R$$

where R is the particular gas constant. The specific heat ratio k (fluids texts often use γ instead of k) is defined as

$$k = \frac{C_P}{C_V}$$

Extra Problem

Show that

$$C_P = \frac{kR}{k-1} \quad \text{and} \quad C_V = \frac{R}{k-1}$$

Example 3-9

Two kilograms of air are heated from 300 to 500 K. Find the change in enthalpy by assuming

- Empirical specific heat data from Table A-2(c).
- Air tables from Table A-17.
- Specific heat at the average temperature from Table A-2(c).
- Use the 300 K value for the specific heat from Table A-2(a).

a. Table A-2(c) gives the molar specific heat at constant pressure for air as

$$\bar{C}_p = 28.11 + 0.1967 \times 10^{-2} T + 0.4802 \times 10^{-5} T^2 - 1.966 \times 10^{-9} T^3 \quad \frac{kJ}{kmol \cdot K}$$

The enthalpy change per unit mole is

$$\begin{aligned} \Delta \bar{h} &= \bar{h}_2 - \bar{h}_1 = \int_1^2 \bar{C}_p(T) dT \\ &= \int_{300K}^{500K} (28.11 + 0.1967 \times 10^{-2} T + 0.4802 \times 10^{-5} T^2 \\ &\quad - 1.966 \times 10^{-9} T^3) dT \\ &= \left(28.11T + \frac{0.1967 \times 10^{-2}}{2} T^2 + \frac{0.4802 \times 10^{-5}}{3} T^3 \right. \\ &\quad \left. - \frac{1.966 \times 10^{-9}}{4} T^4 \right) \Big|_{300K}^{500K} \\ &= 5909.49 \frac{kJ}{kmol} \end{aligned}$$

$$\Delta h = \frac{\Delta \bar{h}}{M} = \frac{5909.49 \frac{kJ}{kmol}}{28.97 \frac{kg}{kmol}} = 203.9 \frac{kJ}{kg}$$

$$\Delta H = m\Delta h = (2 \text{ kg})(203.9 \frac{kJ}{kg}) = 407.98 \text{ kJ}$$

- b. Using the air tables, Table A-17, at $T_1 = 300 \text{ K}$, $h_1 = 300.19 \text{ kJ/kg}$ and at $T_2 = 500 \text{ K}$, $h_2 = 503.02 \text{ kJ/kg}$

$$\Delta H = m\Delta h = (2 \text{ kg})(503.02 - 300.19) \frac{kJ}{kg} = 405.66 \text{ kJ}$$

The results of parts a and b would be identical if Table A-17 had been based on the same specific heat function listed in Table A-2(c).

- c. Let's use a constant specific heat at the average temperature.

$T_{\text{ave}} = (300 + 500)\text{K}/2 = 400 \text{ K}$. At T_{ave} , Table A-2 gives $C_p = 1.013 \text{ kJ/(kg}\cdot\text{K)}$.

For $C_p = \text{constant}$,

$$\begin{aligned} \Delta h &= h_2 - h_1 = C_{p,\text{ave}} (T_2 - T_1) \\ &= 1.013 \frac{kJ}{kg \cdot K} (500 - 300) \text{ K} \\ &= 202.6 \frac{kJ}{kg} \end{aligned}$$

$$\Delta H = m\Delta h = (2 \text{ kg})(202.6) \frac{\text{kJ}}{\text{kg}} = 405.2 \text{ kJ}$$

d. Using the 300 K value from Table A-2(a), $C_p = 1.005 \text{ kJ/kg} \cdot \text{K}$.

For $C_p = \text{constant}$,

$$\begin{aligned}\Delta h &= h_2 - h_1 = C_p (T_2 - T_1) \\ &= 1.005 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} (500 - 300) \text{ K} \\ &= 201.0 \frac{\text{kJ}}{\text{kg}}\end{aligned}$$

$$\Delta H = m\Delta h = (2 \text{ kg})(201.0) \frac{\text{kJ}}{\text{kg}} = 402.0 \text{ kJ}$$

Extra Problem

Find the change in internal energy for air between 300 K and 500 K, kJ/kg.

The Systematic Thermodynamics Solution Procedure

When we apply a methodical solution procedure, thermodynamics problems are relatively easy to solve. Each thermodynamics problem is approached the same way as shown in the following, which is a modification of the procedure given in the text:

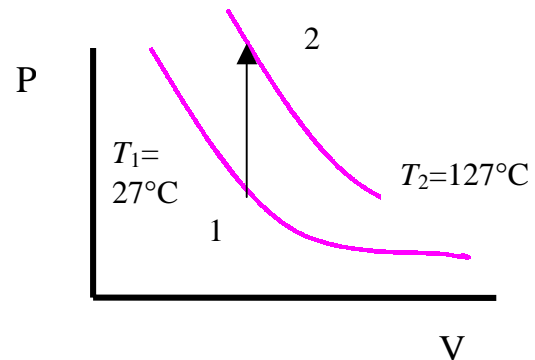
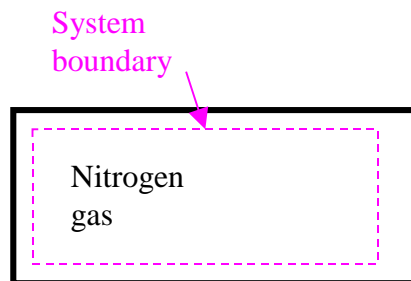
Thermodynamics Solution Method

1. Sketch the system and show energy interactions across the boundaries.
2. Determine the property relation. Is the working substance an ideal gas or a real substance? Begin to set up and fill in a property table.
3. Determine the process and sketch the process diagram. Continue to fill in the property table.
4. Apply conservation of mass and conservation of energy principles.
5. Bring in other information from the problem statement, called physical constraints, such as the volume doubles or the pressure is halved during the process.
6. Develop enough equations for the unknowns and solve.

Example 3-10

A tank contains nitrogen at 27°C. The temperature rises to 127°C by heat transfer to the system. Find the heat transfer and the ratio of the final pressure to the initial pressure.

System: Nitrogen in the tank.



P-V diagram for a constant volume process

Property Relation: Nitrogen is an ideal gas. The ideal gas property relations apply. Let's assume constant specific heats. (You are encouraged to rework this problem using variable specific heat data.)

Process: Tanks are rigid vessels; therefore, the process is constant volume.

Conservation of Mass:

$$m_2 = m_1$$

Using the ideal gas equation of state,

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

Since R is the particular gas constant, and the process is constant volume,

$$V_2 = V_1$$
$$\frac{P_2}{P_1} = \frac{T_2}{T_1} = \frac{(127 + 273) K}{(27 + 273) K} = 1.333$$

Conservation of Energy:

The first law closed system is

$$E_{in} - E_{out} = \Delta E$$
$$Q_{net} - W_{net} = \Delta U$$

For nitrogen undergoing a constant volume process ($dV = 0$), the net work is ($W_{other} = 0$)

$$W_{net,12} = 0 + W_{b,12} = \int_1^2 P dV = 0$$

Using the ideal gas relations with $W_{net} = 0$, the first law becomes (constant specific heats)

$$Q_{net} - 0 = \Delta U = m \int_1^2 C_V dT = m C_V (T_2 - T_1)$$

The heat transfer per unit mass is

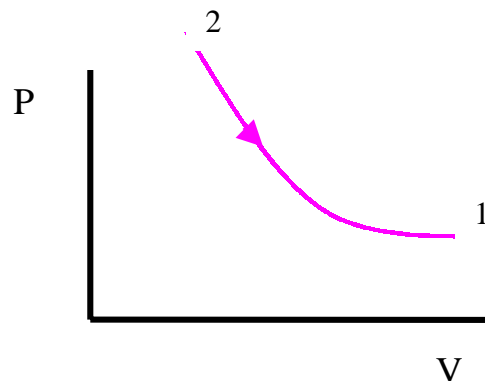
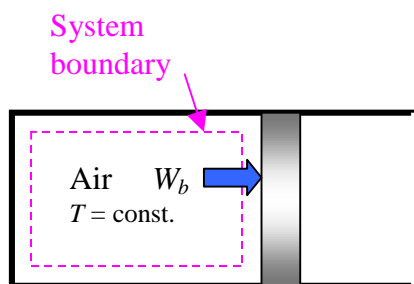
$$\begin{aligned}
 q_{net} &= \frac{Q_{net}}{m} = C_V (T_2 - T_1) \\
 &= 0.743 \frac{kJ}{kg \cdot K} (127 - 27) K \\
 &= 74.3 \frac{kJ}{kg}
 \end{aligned}$$

Example 3-11

Air is expanded isothermally at 100°C from 0.4 MPa to 0.1 MPa. Find the ratio of the final to the initial volume, the heat transfer, and work.

System: Air contained in a piston-cylinder device, a closed system

Process: Constant temperature



P-V diagram for $T = \text{constant}$

Property Relation: Assume air is an ideal gas and use the ideal gas property relations with constant specific heats.

$$PV = mRT$$

$$\Delta u = C_v (T_2 - T_1)$$

Conservation of Energy:

$$E_{in} - E_{out} = \Delta E$$

$$Q_{net} - W_{net} = \Delta U$$

The system mass is constant but is not given and cannot be calculated; therefore, let's find the work and heat transfer per unit mass.

Work Calculation:

$$W_{net,12} = (W_{net})_{other,12} + W_{b,12}$$

$$\begin{aligned} W_{b,12} &= \int_1^2 P dV = \int_1^2 \frac{mRT}{V} dV \\ &= mRT \ln \left(\frac{V_2}{V_1} \right) \end{aligned}$$

Conservation of Mass: For an ideal gas in a closed system (mass = constant), we have

$$\begin{aligned} m_1 &= m_2 \\ \frac{P_1 V_1}{RT_1} &= \frac{P_2 V_2}{RT_2} \end{aligned}$$

Since the R 's cancel and $T_2 = T_1$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{0.4 \text{ MPa}}{0.1 \text{ MPa}} = 4$$

Then the work expression per unit mass becomes

$$\begin{aligned} w_{b,12} &= \frac{W_{b,12}}{m} = RT \ln \left(\frac{V_2}{V_1} \right) \\ w_{b,12} &= \left(0.287 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \right) (100 + 273) \text{ K} \ln(4) \\ &= 148.4 \frac{\text{kJ}}{\text{kg}} \end{aligned}$$

The net work per unit mass is

$$w_{net,12} = 0 + w_{b,12} = 148.4 \frac{\text{kJ}}{\text{kg}}$$

Now to continue with the conservation of energy to find the heat transfer.
Since $T_2 = T_1 = \text{constant}$,

$$\Delta U_{12} = m \Delta u_{12} = m C_V (T_2 - T_1) = 0$$

So the heat transfer per unit mass is

$$\begin{aligned}
 q_{net} &= \frac{Q_{net}}{m} \\
 q_{net} - w_{net} &= \Delta u = 0 \\
 q_{net} &= w_{net} \\
 &= 148.4 \frac{kJ}{kg}
 \end{aligned}$$

The heat transferred **to** the air during an isothermal expansion process equals the work **done**.

Examples Using Variable Specific Heats

Review the solutions in Chapter 3 to the ideal gas examples where the variable specific heat data are used to determine the changes in internal energy and enthalpy.

Extra Problem for You to Try:

An ideal gas, contained in a piston-cylinder device, undergoes a polytropic process in which the polytropic exponent n is equal to k , the ratio of specific heats. Show that this process is adiabatic. You will find that this is an important ideal gas process when we get to Chapter 6.

Solids and Liquids

We treat solids and liquids as incompressible substances. That is, we assume that the density or specific volume of the substance is essentially constant during a process. We can show that the specific heats of incompressible substances (see Chapter 11) are identical.

$$C_P = C_V = C \quad \left(\frac{kJ}{kg \cdot K} \right)$$

The specific heats of incompressible substances depend only on temperature; therefore, we write the differential change in internal energy as

$$du = C_V dT = C dT$$

and assuming constant specific heats, the change in internal energy is

$$\Delta u = C\Delta T = C(T_2 - T_1)$$

Recall that enthalpy is defined as

$$h = u + Pv$$

The differential of enthalpy is

$$dh = du + Pdv + vdP$$

For incompressible substances, the differential enthalpy becomes

$$dv = 0$$

$$dh = du + Pdv^0 + v dP$$

$$dh = du + v dP$$

Integrating, assuming constant specific heats

$$\Delta h = \Delta u + v\Delta P = C\Delta T + v\Delta P$$

For **solids** the specific volume is approximately zero; therefore,

$$\Delta h_{solid} = \Delta u_{solid} + v^0 \Delta P$$

$$\Delta h_{solid} = \Delta u_{solid} \cong C\Delta T$$

For **liquids**, two special cases are encountered:

1. **Constant-pressure processes**, as in heaters ($\Delta P = 0$)

$$\Delta h_{liquid} = \Delta u_{liquid} \cong C\Delta T$$

2. **Constant-temperature processes**, as in pumps ($\Delta T = 0$)

$$\Delta h_{liquid} = \Delta u_{liquid} + v\Delta P \cong C\Delta^0 T + v\Delta P$$

$$\Delta h_{liquid} = v\Delta P$$

We will derive this last expression for Δh again once we have discussed the first law open system and the second law in Chapter 6.

The specific heats of selected liquids and solids are given in Table A-3.

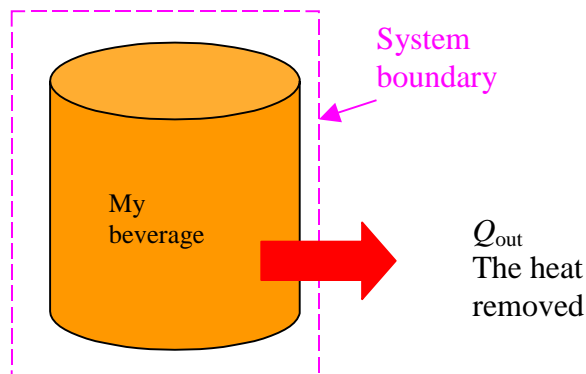
Example 3-12

A two-liter bottle of your favorite beverage has just been removed from the trunk of your car. The temperature of the beverage is 35°C, and you always drink your beverage at 10°C.

- How much heat energy must be removed from your two liters of beverage?
- You are having a party and need to cool 10 of these two-liter bottles in one-half hour. What rate of heat removal, in kW, is required?

Assuming that your refrigerator can accomplish this and that electricity costs 8.5 cents per kW-hr, how much will it cost to cool these 10 bottles?

System: The liquid in the constant volume, closed system container



Property Relation: Incompressible liquid relations, let's assume that the beverage is mostly water and takes on the properties of liquid water. The specific volume is 0.001 m³/kg, $C = 4.184$ kJ/kg·K.

Process: Constant volume

$$V_2 = V_1$$

Conservation of Mass:

$$m_2 = m_1 = m$$

$$m = \frac{V}{v} = \frac{2 \text{ L}}{0.001 \frac{\text{m}^3}{\text{kg}}} \left(\frac{\text{m}^3}{1000 \text{ L}} \right) = 2 \text{ kg}$$

Conservation of Energy:

The first law closed system is

$$E_{in} - E_{out} = \Delta E$$

Since the container is constant volume and there is no “other” work done on the container during the cooling process, we have

$$W_{net} = (W_{net})_{other} + W_b = 0$$

The only energy crossing the boundary is the heat transfer leaving the container. Assuming the container to be stationary, the conservation of energy becomes

$$-E_{out} = \Delta E$$

$$-Q_{out} = \Delta U = mC\Delta T$$

$$-Q_{out} = (2 \text{ kg})(4.181 \frac{\text{kJ}}{\text{kg} \cdot \text{K}})(10 - 35) \text{ K}$$

$$-Q_{out} = -209.2 \text{ kJ}$$

$$Q_{out} = 209.2 \text{ kJ}$$

The heat transfer rate to cool the 10 bottles in one-half hour is

$$\begin{aligned} \dot{Q}_{out} &= \frac{(10 \text{ bottles})(209.2 \frac{\text{kJ}}{\text{bottle}})}{0.5 \text{ hr}} \left(\frac{1 \text{ hr}}{3600 \text{ s}} \right) \left(\frac{\text{kW}}{\frac{\text{kJ}}{\text{s}}} \right) \\ &= 1.162 \text{ kW} \end{aligned}$$

$$\begin{aligned} \text{Cost} &= (1.162 \text{ kW})(0.5 \text{ hr}) \frac{\$0.085}{\text{kW} \cdot \text{hr}} \\ &= \$0.05 \end{aligned}$$