

Chapter 19 First Law of Thermodynamics

When two bodies at different temperatures (T_1 and T_2) are placed in thermal contact, they ultimately reach a common temperature (T_f) somewhere between the two initial temperature ($T_1 < T_f < T_2$ or $T_1 > T_f > T_2$). We say that **heat** has flowed from the hotter to the colder body.

In the eighteenth century heat was believed to be an invisible, massless fluid called “**caloric**”. However, the caloric theory failed to explain the generation of heat by friction.

Until the middle of the eighteenth century, the term heat and temperature had essentially the same meaning.

The relationship between heat and internal energy is embodied in the first law of thermodynamics.

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19.1 Specific Heat (I)

Black was the first person to realize the rise in temperature of a body could be used to determine the quantity of heat absorbed by it.

If a quantity of heat ΔQ produces a change in temperature ΔT in a body, its **heat capacity** is defined as: $\text{heat capacity} = \Delta Q / \Delta T$

A commonly used (non-SI) unit of heat is calorie, which is used to be defined as the quantity of heat required to raise the temperature of 1 g of water from 14.5°C to 15.5°C.

$$1 \text{ calorie} = 4.186 \text{ J}$$

The *British thermal unit* (BTU) is the quantity of heat required to raise the temperature of 1 lb of water from 63°F to 64°F.

$$1 \text{ BTU} = 454 \times 100 / 180 = 252.2 \text{ calorie} = 1055.8 \text{ J}$$

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19.1 Specific Heat (II)

The quantity of heat ΔQ required to produce a change in temperature ΔT is proportional to the mass of the sample m , and to ΔT . $\Delta Q = mc\Delta T$, where c is called the **specific heat** of the material.

The SI unit of the specific heat is $\text{J/kg}\cdot\text{K}$ (although the unit $\text{cal/g}\cdot\text{K}$ is often used).

Specific heat is a property of a given substance, whereas heat capacity refers to a given sample of material.

$$c = \frac{1}{m} \frac{\Delta Q}{\Delta T}$$

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19.1 Specific Heat (III)

Molar specific heat: It is sometimes convenient to work with the number of moles n of a substance rather than its mass.

$$C = \frac{1}{n} \frac{\Delta Q}{\Delta T}$$

C is the molar specific heat, measured in $\text{J/mol}\cdot\text{K}$ or $(\text{cal/mol}\cdot\text{K})$. Since $n = m/M$, where M is the molecular mass, we have $C = Mc$.

表19.1 比熱 (20°C及1atm時之值)

	c ($\text{J/kg}\cdot\text{K}$)	C ($\text{J/mole}\cdot\text{K}$)
鋁	900	24.3
銅	385	24.4
金	130	25.6
銅/鐵	450	25.0
鉛	130	26.8
汞 (水銀)	140	28.0
水	4190	75.4
冰 (-10°C)	2100	38

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19.1 Specific Heat (IV)

The Method of Mixtures

The *method of mixtures*, first employed by Black, is used to determine the final equilibrium temperature. Since there is no heat exchanged with the surroundings, the heat transferred to the colder body is equal to the heat transferred from the hotter body.

$$\Delta Q_1 + \Delta Q_2 = 0$$

$$m_1 c_1 \Delta T_1 + m_2 c_2 \Delta T_2 = 0$$

Where $\Delta T_1 = T_f - T_1$ and $\Delta T_2 = T_f - T_2$.

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Example 19.1

A steel ball of mass $m_1=80$ g has an initial temperature $T_1 = 200$ °C. It is immersed in $m_2=250$ g of water in a copper cup of mass $m_3=100$ g. The initial temperature of the water and cup is $T_2=20$ °C. Find the final temperature when the system reaches the thermal equilibrium, where $c_1=450$ (J/kg·K), $c_2=4190$ (J/kg·K), and $c_3=385$ (J/kg·K).

Solution:

$$m_1 c_1 (T_f - T_1) + (m_2 c_2 + m_3 c_3) (T_f - T_2) = 0$$

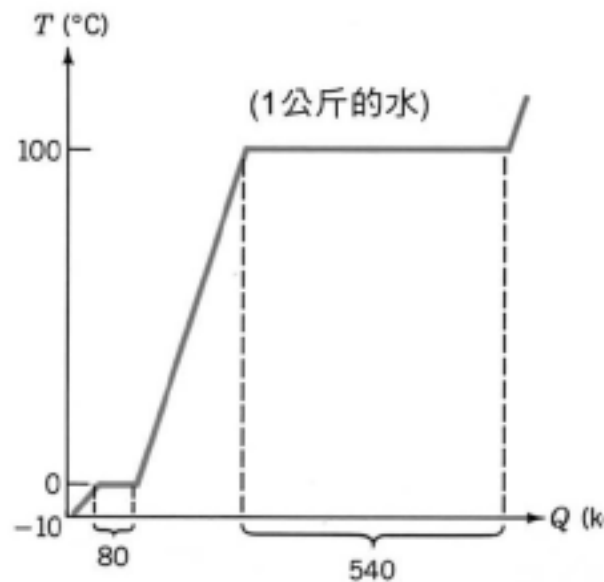
$$36(T_f - 200) + (1047 + 39)(T_f - 20) = 0$$

$$T_f = 25.8^\circ\text{C}$$

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19.2 Latent Heat (I)

Black recognized that adding heat to a system does not always result in a change in its temperature. The temperature remains constant when a substance changes its **phase** --- for example ice-water.



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19.2 Latent Heat (II)

Latent heat of fusion L_f : from solid to liquid.

Latent heat of vaporization L_v : from liquid to vapor.

$$L = \frac{\Delta Q}{m}$$

表19.2 潛熱 (在1atm下)

	熔點	熔解潛熱 (J/kg)	沸點	汽化潛熱 (J/kg)
	°C		°C	
鋁	660	24.5×10^3	2450	11390×10^3
銅	1083	134×10^3	1187	5065×10^3
金	1063	64.5×10^3	2660	1580×10^3
鉛	327	24.5×10^3	1750	870×10^3
水	0	334×10^3	100	2260×10^3
	K		K	
氫	3.5	5.23×10^3	4.2	20.9×10^3
氮	13.8	58.6×10^3	20.3	452×10^3
氧	63.2	25.5×10^3	77.3	201×10^3
汞 (水銀)	234	11.8×10^3	630	272×10^3

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Example 19.2

A 2-kg chunk of ice at -10°C is added to 5 kg of liquid water at 45°C . What is the final temperature of the system.

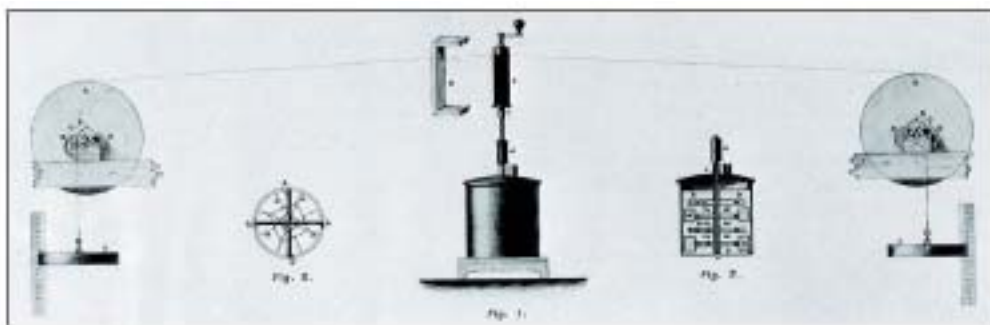
Solution:

$$\begin{aligned}2 \cdot 2100 \cdot 10 + 2 \cdot 334000 + 2 \cdot 4190 \cdot T_f \\= 5 \cdot 4190 \cdot (45 - T_f) \\T_f = 7.93^{\circ}\text{C}\end{aligned}$$

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19.3 The Mechanical Equivalent of Heat: Joule's Experiment

Mechanical energy can transfer to **heat** which was demonstrated through Joule's experiment. Heat was identified as another form of energy.



Heat is energy transferred between two bodies as a consequence of a temperature difference between them.

How to convert heat back to mechanical energy?

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19.4 Work in Thermodynamics

Thermodynamics is concerned with the work done by a system and the heat it exchanges with its surrounding.

Heat reservoir: a extremely large heat capacity.

Quasistatic: The thermodynamic valuables (P , V , T , n , etc.) of the system and its surroundings change infinitely slowly. Thus the system is *always arbitrarily close to an equilibrium state*.

The work done by the gas is

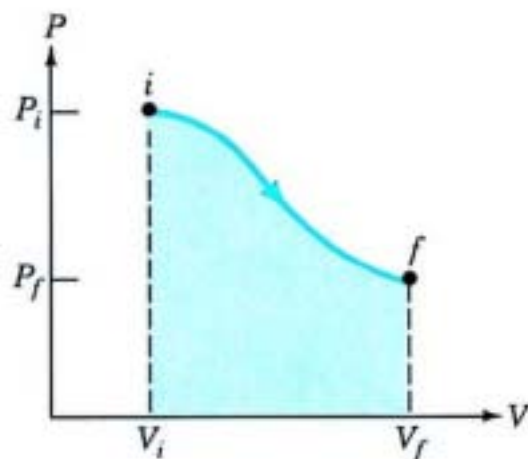
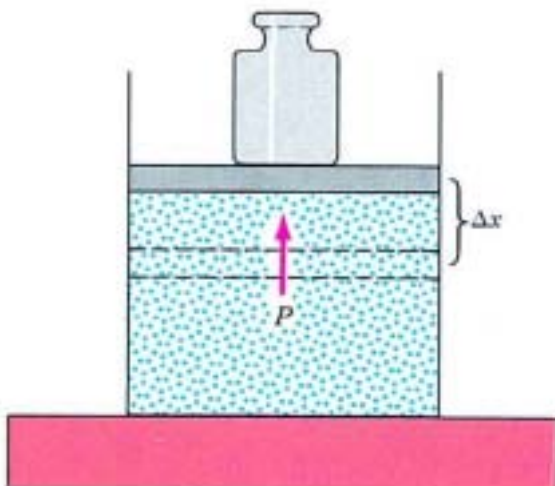
$$dW = Fdx = PAdx = PdV$$

$$W = \int_{V_i}^{V_f} PdV$$

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19.4 Work in Thermodynamics: Quasistatic

Quasistatic: The thermodynamic valuables (P , V , T , n , etc.) of the system and its surroundings change infinitely slowly. Thus the system is *always arbitrarily close to an equilibrium state*.

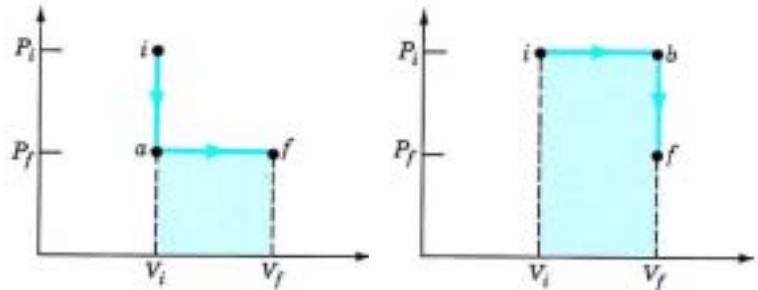


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19.4 Work in Thermodynamics: Isobaric Work

In an **isobaric** process the expansion or compression occurs at constant pressure.

$$W = \int_{V_i}^{V_f} P dV = P(V_f - V_i)$$

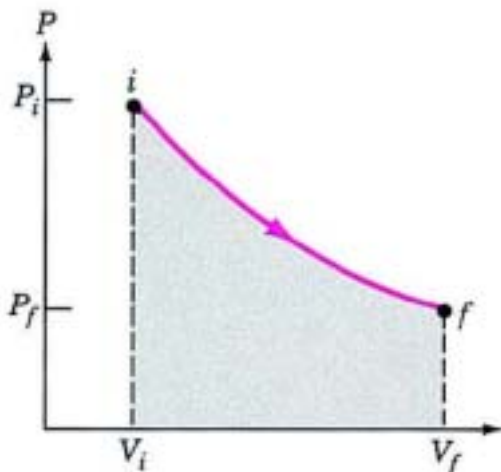


The work done by a system depends on the details of the process that takes it from one equilibrium state to another (**non-conservative force**).

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19.4 Work in Thermodynamics: Isothermal Work

In an **isothermal** process, the system is kept in contact with a single reservoir at temperature T.



$$\begin{aligned} W &= \int_{V_i}^{V_f} P dV \\ &= nRT \int_{V_i}^{V_f} \frac{1}{V} dV \\ &= nRT \ln\left(\frac{V_f}{V_i}\right) \end{aligned}$$

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19.5 First Law of Thermodynamics

The **internal energy** U is a *state function* --- one that depends only on the *thermodynamic state* of the system.

The change in internal energy of the system is

$$\Delta U = Q - W$$

In this definition, Q is positive when heat *enters* the system and W is positive when work is done by the system on its surroundings. * Notice that we can specify only the change in internal energy.

The first law of thermodynamics is a generalization of the results of many experiments, starting with those of Mayer and Joule. It serves as a general definition of heat.

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19.5 First Law of Thermodynamics (II)

The internal energy U is the sum of all possible kinds of energy “stored” in the system --- mechanical, electrical, magnetic, chemical, nuclear, and so on.

It does not include the kinetic and potential energies associated with the **center of mass** of the system.

The kinetic and potential energies associated with the random motion of particles form a part of internal energy called thermal energy.

Where would the heat come from?

Does a heat reservoir possess a large quantity of heat?

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19.5 First Law of Thermodynamics (III)

The physical quantity possessed by a system is internal energy, which is the sum of **all** the kinds of energy in the system.

The internal energy is a *state function* that depends on the equilibrium state of a system, whereas Q and W depend on the thermodynamic path between two equilibrium states. That is, Q and W are associated with processes.

The heat absorbed by a system will increase its *internal energy*, only **some** of which is *thermal energy*.

How is it possible for heat to enter or to leave a system and yet not to be store in it?

Sound energy enters and leaves your bodies, but at any given moment there is no sound stored.

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19.6 Application of The First Law of Thermodynamics (a) Isolated System

There is no heat exchange ($Q=0$) and no work done on the external environment ($W=0$).

$$\Delta U = 0 \text{ or } U = \text{constant}$$

The internal energy of an isolated system is constant.

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19.6 Application of The First Law of Thermodynamics

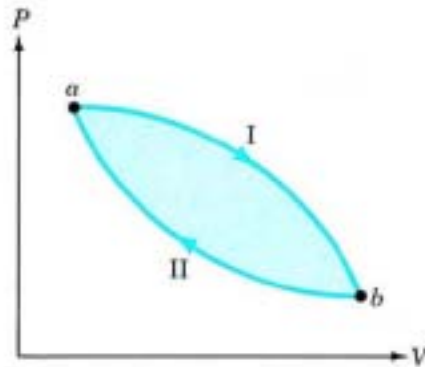
(b) Cyclic Process

Engines operate in cycles, in which the system --- for example, a gas --- periodically returns to its initial state.

Since the system returns to its initial state, the change in the internal energy in one complete cycle is zero; that is, $\Delta U=0$.

From the first law we see that

$$Q = W$$



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19.6 Application of The First Law of Thermodynamics

(c) Constant-Volume Process

In a constant-volume process, the volume of the system stays constant. Consequently, $W=0$.

From the first law we see that

$$\Delta U = Q$$

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19.6 Application of The First Law of Thermodynamics

(d) Adiabatic Process

In an adiabatic process, the system does not change heat with its surrounding; that is, $Q=0$.

From the first law we see that

$$\Delta U = -W$$

In an adiabatic expansion the internal energy decreases. That is usually manifested as a drop in temperature.

Conversely, when a gas is compressed adiabatically, its internal energy increases and the temperature rises.

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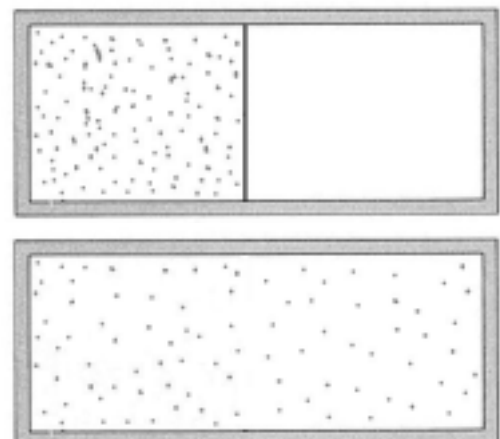
19.6 Application of The First Law of Thermodynamics

(e) Adiabatic Free Expansion

What happens when a gas is allowed to expand adiabatically without doing work?

$$Q = 0 \text{ and } W = 0$$

$$\Delta U = 0$$



This uncontrolled expansion is not quasistatic and cannot be depicted on a PV diagram.

In an adiabatic free expansion, the internal energy does not change.

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Example 19.4

A cylinder with a piston contains 0.2 kg of water at 100 °C. What is the change in internal energy of the water when it is converted to steam at 100 °C at a constant pressure? The density of the water $\rho_w=1000 \text{ kg/m}^3$ and that of steam is $\rho_s=0.6 \text{ kg/m}^3$. The Latent heat of vaporization of water is $L_v=2.26 \times 10^6 \text{ J/kg}$.

Solution:

$$\text{Heat } Q = mL_v = 0.2 \times 2.26 \times 10^6 = 4.52 \times 10^5 \text{ J}$$

$$\text{Work } W = P(V_s - V_w) = 3.36 \times 10^4 \text{ J}$$

The change in internal energy is

$$\Delta U = Q - W = 418 \text{ kJ}$$

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19.7 Ideal Gases: Specific Heat

Heat absorbed at constant volume is $Q_v = nC_v\Delta T$

Since the work done by the gas is zero, we see that $\Delta U = Q_v = nC_v\Delta T$

Heat absorbed at constant pressure is $Q_p = nC_p\Delta T$

The work done by the gas at constant pressure $W=P\Delta V$

$$nC_v\Delta T = nC_p\Delta T - P\Delta V$$

$$P\Delta V = n(C_p - C_v)\Delta T$$

At fixed pressure $P\Delta V = nR\Delta T$,

so the difference between the two specific heats is

$$(C_p - C_v) = R$$

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19.7 Ideal Gases: Adiabatic Quasistatic Process

In an adiabatic process there is no heat exchange with the surroundings, so $dQ=0$. The work done by the gas for an infinitesimal change in volume dV is $dW=PdV$.

$$\Delta U = -W$$

$$nC_v dT = -PdV \quad (19.16)$$

From the equation of state for an ideal gas, $PV=nRT$, we have

$$nRdT = PdV + VdP \quad (19.17)$$

Substituting Eq. 19.16 into Eq. 19.17, and rearranging it, we find

$$P(C_v + R)dV + C_v VdP = 0$$

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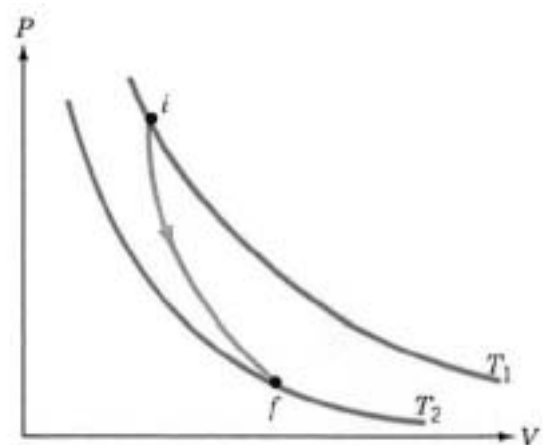
19.7 Ideal Gases: Adiabatic Quasistatic Process

With the definition $\gamma = C_p / C_v$

we have
$$\gamma \frac{dV}{V} + \frac{dP}{P} = 0$$

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

This equation applies to a quasistatic adiabatic process involving an ideal gas.



The slope of the adiabatic curve is steeper than that of an isothermal curve.

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Example 19.5

An ideal monatomic gas, for which $\gamma=5/3$, undergoes a quasistatic expansion to one-third of its initial pressure. Find the ratio of the final volume to the initial volume if the process is (a) isothermal; (b) adiabatic.

Solution:

(a) isothermal $PV = \text{constant}$.

$$\frac{V_f}{V_i} = \frac{P_i}{P_f} = 3$$

(b) adiabatic $PV^\gamma = \text{constant}$

$$\frac{V_f}{V_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1}{\gamma}} = 3^{3/5} = 1.9$$

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Example 19.6

Find the work done by an ideal gas when its state change adiabatically (a) from P_1 and V_1 to P_2 and V_2 , and (b) from T_1 to T_2 .

Solution:

$$W = \int P dV$$

(a) adiabatic $(P_1, V_1) \rightarrow (P_2, V_2)$

$$W = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} K \frac{dV}{V^\gamma} = \frac{K}{\gamma-1} \left(\frac{1}{V_1^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}} \right) = \frac{1}{\gamma-1} \left(\frac{1}{P_1 V_1} - \frac{1}{P_2 V_2} \right)$$

(b) adiabatic from T_1 to T_2

$$W = -nC_c \int_{T_1}^{T_2} dT = -nC_v(T_2 - T_1)$$

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19.9 Heat Transport

Heat transfer occurs by three mechanisms:

1. In **conduction** heat is transferred by collisions between molecules, and in case of metal, by “free electrons”.
2. In **convection** heat transport is associated with movement of warm and cold parts of a fluid.
3. **Radiation** is the transfer of energy without intervening medium. A warm body radiates to its cooler surrounding.

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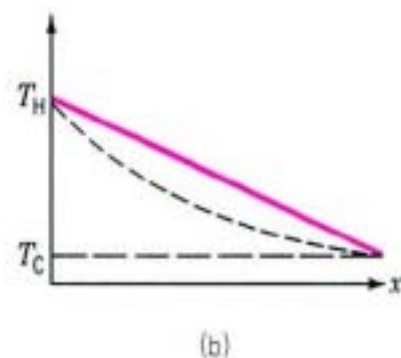
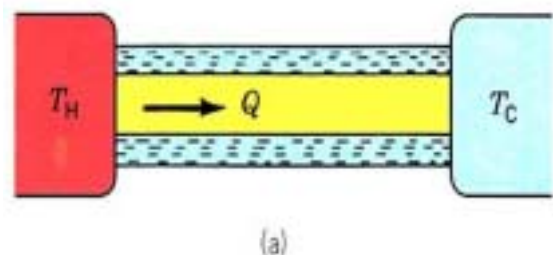
19.9 Heat Transport: Conduction

The rate of transfer of heat through conduction, dQ/dt , is proportional to the cross-section area, A , and to the temperature gradient, dT/dx .

$$\frac{dQ}{dt} = -\kappa A \frac{dT}{dx}$$

The constant κ , called the thermal conductivity, is a measure of the ability of a material to conduct heat.

What is the **thermal resistance**?



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19.9 Heat Transport: Convection

A glider can gain altitude by entering a rising column of warm air called a “thermal.”



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Exercises and Problems

Ch.19:

Ex. 13, 24, 32, 36, 43, 45, 50

Prob. 3, 8, 9

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