Video Tutor Solutions

Temperature and temperature scales: Two bodies in thermal equilibrium must have the same temperature. A conducting material between two bodies permits them to interact and come to thermal equilibrium; an insulating material impedes this interaction.

The Celsius and Fahrenheit temperature scales are based on the freezing ($0°C = 32°F$) and boiling ($100°C = 212°F$) temperatures of water. One Celsius degree equals $\frac{9}{5}$ Fahrenheit degrees. (See Example 17.1.)

The Kelvin scale has its zero at the extrapolated zero-pressure temperature for a gas thermometer, $-273.15°C = 0$ K. In the gas-thermometer scale, the ratio of two temperatures T_1 and T_2 is defined to be equal to the ratio of the two corresponding gas-thermometer pressures p_1 and p_2.
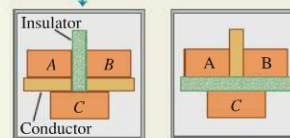
$$T_F = \tfrac{9}{5}T_C + 32° \quad (17.1)$$

$$T_C = \tfrac{5}{9}(T_F - 32°) \quad (17.2)$$

$$T_K = T_C + 273.15 \quad (17.3)$$

$$\frac{T_2}{T_1} = \frac{p_2}{p_1} \quad (17.4)$$

If systems A and B are each in thermal equilibrium with system C …

… then systems A and B are in thermal equilibrium with each other.

Thermal expansion and thermal stress: A temperature change ΔT causes a change in any linear dimension L_0 of a solid body. The change ΔL is approximately proportional to L_0 and ΔT. Similarly, a temperature change causes a change ΔV in the volume V_0 of any solid or liquid; ΔV is approximately proportional to V_0 and ΔT. The quantities α and β are the coefficients of linear expansion and volume expansion, respectively. For solids, $\beta = 3\alpha$. (See Examples 17.2 and 17.3.)

When a material is cooled or heated and held so it cannot contract or expand, it is under a tensile stress F/A. (See Example 17.4.)

$$\Delta L = \alpha L_0\, \Delta T \quad (17.6)$$

$$\Delta V = \beta V_0\, \Delta T \quad (17.8)$$

$$\frac{F}{A} = -Y\alpha\, \Delta T \quad (17.12)$$

$$L = L_0 + \Delta L$$
$$= L_0(1 + \alpha\, \Delta T)$$
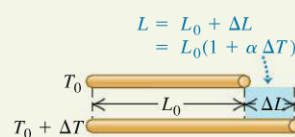
Heat, phase changes, and calorimetry: Heat is energy in transit from one body to another as a result of a temperature difference. Equations (17.13) and (17.18) give the quantity of heat Q required to cause a temperature change ΔT in a quantity of material with mass m and specific heat c (alternatively, with number of moles n and molar heat capacity $C = Mc$, where M is the molar mass and $m = nM$). When heat is added to a body, Q is positive; when it is removed, Q is negative. (See Examples 17.5 and 17.6.)

To change a mass m of a material to a different phase at the same temperature (such as liquid to vapor), a quantity of heat given by Eq. (17.20) must be added or subtracted. Here L is the heat of fusion, vaporization, or sublimation.
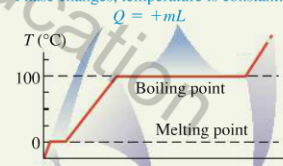
In an isolated system whose parts interact by heat exchange, the algebraic sum of the Q's for all parts of the system must be zero. (See Examples 17.7–17.10.)

$$Q = mc\, \Delta T \quad (17.13)$$

$$Q = nC\, \Delta T \quad (17.18)$$

$$Q = \pm mL \quad (17.20)$$

Phase changes, temperature is constant:
$Q = +mL$

Temperature rises, phase does not change:
$Q = mc\, \Delta T$

Conduction, convection, and radiation: Conduction is the transfer of heat within materials without bulk motion of the materials. The heat current H depends on the area A through which the heat flows, the length L of the heat-flow path, the temperature difference $(T_H - T_C)$, and the thermal conductivity k of the material. (See Examples 17.11–17.13.)
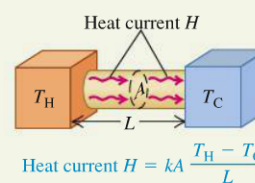
Convection is a complex heat-transfer process that involves mass motion from one region to another.

Radiation is energy transfer through electromagnetic radiation. The radiation heat current H depends on the surface area A, the emissivity e of the surface (a pure number between 0 and 1), and the Kelvin temperature T. Here σ is the Stefan–Boltzmann constant. The *net* radiation heat current H_{net} from a body at temperature T to its surroundings at temperature T_s depends on both T and T_s. (See Examples 17.14 and 17.15.)

$$H = \frac{dQ}{dt} = kA\frac{T_H - T_C}{L} \quad (17.21)$$

$$H = Ae\sigma T^4 \quad (17.25)$$

$$H_{net} = Ae\sigma(T^4 - T_s^4) \quad (17.26)$$

Heat current H

Heat current $H = kA\dfrac{T_H - T_C}{L}$

Video Tutor
Solutions

Equations of state: The pressure p, volume V, and absolute temperature T of a given quantity of a substance are related by an equation of state. This relationship applies only for equilibrium states, in which p and T are uniform throughout the system. The ideal-gas equation of state, Eq. (18.3), involves the number of moles n and a constant R that is the same for all gases. (See Examples 18.1–18.4.)

$$pV = nRT \qquad (18.3)$$
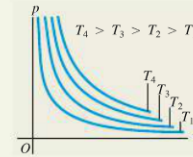
Molecular properties of matter: The molar mass M of a pure substance is the mass per mole. The mass m_{total} of a quantity of substance equals M multiplied by the number of moles n. Avogadro's number N_A is the number of molecules in a mole. The mass m of an individual molecule is M divided by N_A. (See Example 18.5.)

$$m_{total} = nM \qquad (18.2)$$

$$M = N_A m \qquad (18.8)$$

Kinetic-molecular model of an ideal gas: In an ideal gas, the total translational kinetic energy of the gas as a whole (K_{tr}) and the average translational kinetic energy per molecule $[\frac{1}{2}m(v^2)_{av}]$ are proportional to the absolute temperature T, and the root-mean-square speed of molecules is proportional to the square root of T. These expressions involve the Boltzmann constant $k = R/N_A$. (See Examples 18.6 and 18.7.) The mean free path λ of molecules in an ideal gas depends on the number of molecules per volume (N/V) and the molecular radius r. (See Example 18.8.)

$$K_{tr} = \tfrac{3}{2}nRT \qquad (18.14)$$

$$\tfrac{1}{2}m(v^2)_{av} = \tfrac{3}{2}kT \qquad (18.16)$$

$$v_{rms} = \sqrt{(v^2)_{av}} = \sqrt{\frac{3kT}{m}} \qquad (18.19)$$

$$\lambda = v t_{mean} = \frac{V}{4\pi\sqrt{2}\,r^2 N} \qquad (18.21)$$
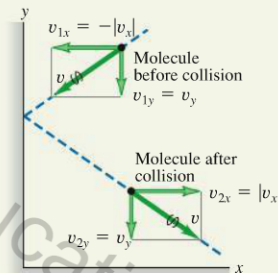
Heat capacities: The molar heat capacity at constant volume C_V is a simple multiple of the gas constant R for certain idealized cases: an ideal monatomic gas [Eq. (18.25)]; an ideal diatomic gas including rotational energy [Eq. (18.26)]; and an ideal monatomic solid [Eq. (18.28)]. Many real systems are approximated well by these idealizations.

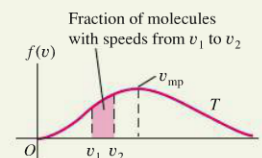$$C_V = \tfrac{3}{2}R \quad \text{(monatomic gas)} \qquad (18.25)$$

$$C_V = \tfrac{5}{2}R \quad \text{(diatomic gas)} \qquad (18.26)$$

$$C_V = 3R \quad \text{(monatomic solid)} \qquad (18.28)$$
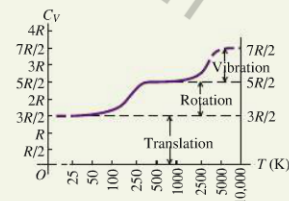

Molecular speeds: The speeds of molecules in an ideal gas are distributed according to the Maxwell–Boltzmann distribution $f(v)$. The quantity $f(v)\,dv$ describes what fraction of the molecules have speeds between v and $v + dv$.

$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

$$(18.32)$$

Phases of matter: Ordinary matter exists in the solid, liquid, and gas phases. A phase diagram shows conditions under which two phases can coexist in phase equilibrium. All three phases can coexist at the triple point. The vaporization curve ends at the critical point, above which the distinction between the liquid and gas phases disappears.
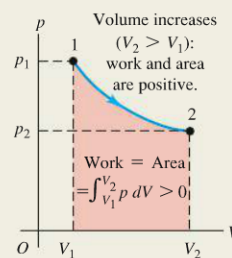
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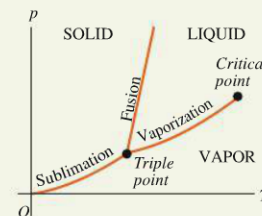
Heat and work in thermodynamic processes: A thermodynamic system has the potential to exchange energy with its surroundings by heat transfer or by mechanical work. When a system at pressure p changes volume from V_1 to V_2, it does an amount of work W given by the integral of p with respect to volume. If the pressure is constant, the work done is equal to p times the change in volume. A negative value of W means that work is done on the system. (See Example 19.1.)
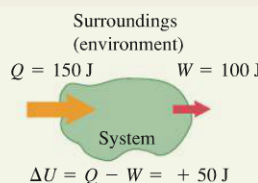
In any thermodynamic process, the heat added to the system and the work done by the system depend not only on the initial and final states, but also on the path (the series of intermediate states through which the system passes).

$$W = \int_{V_1}^{V_2} p \, dV \qquad (19.2)$$

$$W = p(V_2 - V_1) \qquad (19.3)$$
(constant pressure only)

The first law of thermodynamics: The first law of thermodynamics states that when heat Q is added to a system while the system does work W, the internal energy U changes by an amount equal to $Q - W$. This law can also be expressed for an infinitesimal process. (See Examples 19.2, 19.3, and 19.5.)
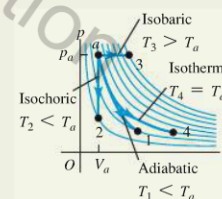
The internal energy of any thermodynamic system depends only on its state. The change in internal energy in any process depends only on the initial and final states, not on the path. The internal energy of an isolated system is constant. (See Example 19.4.)

$$\Delta U = Q - W \qquad (19.4)$$

$$dU = dQ - dW \qquad (19.6)$$
(infinitesimal process)

Important kinds of thermodynamic processes:

- Adiabatic process: No heat transfer into or out of a system; $Q = 0$.
- Isochoric process: Constant volume; $W = 0$.
- Isobaric process: Constant pressure; $W = p(V_2 - V_1)$.
- Isothermal process: Constant temperature.

Thermodynamics of ideal gases: The internal energy of an ideal gas depends only on its temperature, not on its pressure or volume. For other substances the internal energy generally depends on both pressure and temperature.

The molar heat capacities C_V and C_p of an ideal gas differ by R, the ideal-gas constant. The dimensionless ratio of heat capacities, C_p/C_V, is denoted by γ. (See Example 19.6.)

$$C_p = C_V + R \qquad (19.17)$$

$$\gamma = \frac{C_p}{C_V} \qquad (19.18)$$
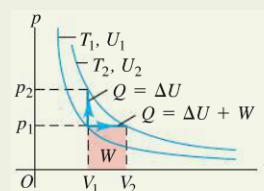
Adiabatic processes in ideal gases: For an adiabatic process for an ideal gas, the quantities $TV^{\gamma-1}$ and pV^γ are constant. The work done by an ideal gas during an adiabatic expansion can be expressed in terms of the initial and final values of temperature, or in terms of the initial and final values of pressure and volume. (See Example 19.7.)

$$W = nC_V(T_1 - T_2)$$

$$= \frac{C_V}{R}(p_1V_1 - p_2V_2) \qquad (19.25)$$

$$= \frac{1}{\gamma - 1}(p_1V_1 - p_2V_2) \qquad (19.26)$$
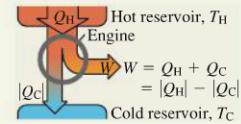
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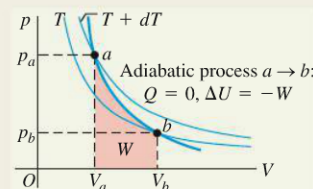
Reversible and irreversible processes: A reversible process is one whose direction can be reversed by an infinitesimal change in the conditions of the process, and in which the system is always in or very close to thermal equilibrium. All other thermodynamic processes are irreversible.

Irreversible:
Metal, 70°C — Ice at 0°C ⇒ 40°C Water, 40°C

Reversible:
Metal, 0°C — Ice at 0°C ⇔ 0°C Water, 0°C
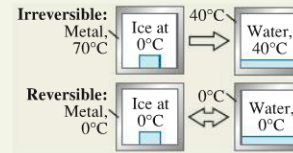
Heat engines: A heat engine takes heat Q_H from a source, converts part of it to work W, and discards the remainder $|Q_C|$ at a lower temperature. The thermal efficiency e of a heat engine measures how much of the absorbed heat is converted to work. (See Example 20.1.)

$$e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \left| \frac{Q_C}{Q_H} \right| \quad (20.4)$$

Hot reservoir, T_H
Engine
$W = Q_H + Q_C = |Q_H| - |Q_C|$
Cold reservoir, T_C

The Otto cycle: A gasoline engine operating on the Otto cycle has a theoretical maximum thermal efficiency e that depends on the compression ratio r and the ratio of heat capacities γ of the working substance.

$$e = 1 - \frac{1}{r^{\gamma-1}} \quad (20.6)$$

Otto cycle
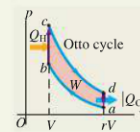
Refrigerators: A refrigerator takes heat Q_C from a colder place, has a work input $|W|$, and discards heat $|Q_H|$ at a warmer place. The effectiveness of the refrigerator is given by its coefficient of performance K.

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|} \quad (20.9)$$

Outside air, T_H
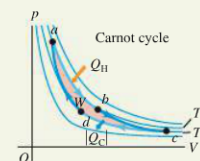Refrigerator
$|W|$
Inside of refrigerator, T_C
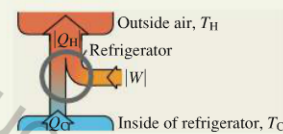
The second law of thermodynamics: The second law of thermodynamics describes the directionality of natural thermodynamic processes. It can be stated in several equivalent forms. The *engine* statement is that no cyclic process can convert heat completely into work. The *refrigerator* statement is that no cyclic process can transfer heat from a colder place to a hotter place with no input of mechanical work.

T_H
$Q_H - |Q_C|$ 100%-efficient engine
Impossible W
T_C
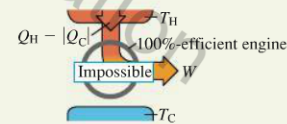
The Carnot cycle: The Carnot cycle operates between two heat reservoirs at temperatures T_H and T_C and uses only reversible processes. Its thermal efficiency depends only on T_H and T_C. An additional equivalent statement of the second law is that no engine operating between the same two temperatures can be more efficient than a Carnot engine. (See Examples 20.2 and 20.3.)

A Carnot engine run backward is a Carnot refrigerator. Its coefficient of performance depends only on T_H and T_C. Another form of the second law states that no refrigerator operating between the same two temperatures can have a larger coefficient of performance than a Carnot refrigerator. (See Example 20.4.)

$$e_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} \quad (20.14)$$

$$K_{\text{Carnot}} = \frac{T_C}{T_H - T_C} \quad (20.15)$$

Carnot cycle

Entropy: Entropy is a quantitative measure of the disorder of a system. The entropy change in any reversible process depends on the amount of heat flow and the absolute temperature T. Entropy depends only on the state of the system, and the change in entropy between given initial and final states is the same for all processes leading from one state to the other. This fact can be used to find the entropy change in an irreversible process. (See Examples 20.5–20.10.)

$$\Delta S = \int_1^2 \frac{dQ}{T} \quad (20.19)$$
(reversible process)

Calorimetric calculations:

$dQ = mcdT$ or $dQ = nCdT$ (*specific heat*)

$Q = mL$ (*latent heat*)

General Formulas applicable to ALL processes in an Ideal Gas:

$PV = nRT$

$dU = dQ - dW$

$dW = PdV$

$dU = nC_V dT$

$C_V = \dfrac{3}{2}R$ (*monoatomic*)

$C_P = C_V + R$

Specific Processes:

Isothermal: T=constant → dT = 0 → dU =0 → dQ=dW

$$W = \int_i^f PdV = \int_i^f \frac{nRT}{V} dV = nRT \ln\left(\frac{V_f}{V_i}\right)$$

Adiabatic: dQ=0 → dU= -dW

$$dW = -dU \quad \rightarrow \quad W = -\int_i^f nC_V dT = -nC_V\left(T_f - T_i\right)$$

$$PV^\gamma = const$$

$$TV^{\gamma-1} = const$$

Isobaric: P=constant

$$\rightarrow W = \int_i^f PdV = P\left(V_f - V_i\right)$$

Isochroic: V=constant → dV=0 → dW=0 → dU=dQ

Entropy:

General Reversible Processes: dS=dQ/T

$$\rightarrow \Delta S = nC_V \ln\left(T_f/T_i\right) + nR\ln\left(V_f/V_i\right)$$

Calorimetric Processes:

$(specific\ heat): dQ = mcdT \quad or \quad dQ = nCdT$

$$\rightarrow \quad dS = mc\frac{dT}{T} \quad or \quad = nC\frac{dT}{T}$$

$$\rightarrow \quad \Delta S = mc\ln\left(\frac{T_f}{T_i}\right) \quad or \quad = nC\ln\left(\frac{T_f}{T_i}\right)$$

$(latent\ heat): Q = mL$

$$\rightarrow \quad \Delta S = \frac{\pm mL}{T}\left[T \text{ remains constant at phase change}\right]$$

Non Reversible Processes: (one *cannot* write dS=dQ/T for the process)

But one can use a surrogate reversible process with the same initial and final states to calculate ΔS.

2nd Law of Thermodynamics:

$$\Delta S_{tot} = \Delta S_{system} + \Delta S_{environment} \geq 0$$