The First Law of Thermodynamics

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Topics

- **Heat and Internal Energy**
- **Specific Heat and Calorimetry**
- **Latent Heat**
- Work and Heat in Thermodynamic Processes
- The First Law of Thermodynamics
- Some Applications of the First Law of Thermodynamics
- Energy Transfer Mechanisms in Thermal Processes

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Internal Energy

- Internal energy is all the energy of a system that is associated with its microscopic components - atoms and molecules - when viewed from a reference frame at rest with respect to the center of mass of the system.
- The last part of this sentence ensures that any bulk kinetic energy of the system due to its motion through space is not included in internal energy.
- Internal energy includes:
  - kinetic energy of random translational, rotational, and vibrational motion of molecules
  - vibrational potential energy associated with forces between atoms in molecules
  - electric potential energy associated with forces between molecules.

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Heat

- Heat is defined as a process of transferring energy across the boundary of a system because of a temperature difference between the system and its surroundings. It is also the amount of energy Q transferred by this process.
- When you *heat* a substance, you are transferring energy into it by placing it in contact with surroundings that have a higher temperature.
- Heat is *not* in the following common quotes
  - Heat is *not* energy in a hot substance
  - Heat is *not* radiation
  - Heat is *not* warmth of an environment

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- The work done on a system is a measure of the amount of energy transferred to the system from its surroundings
- The mechanical energy (kinetic energy plus potential energy) of a system is a consequence of the motion and configuration of the system.
- When a person does work on a system, energy is transferred from the person to the system. It makes no sense to talk about the work of a system.
- It makes no sense to talk about the heat of a system; one can refer to heat only when energy has been transferred as a result of a temperature difference.
- Both heat and work are ways of transferring energy between a system and its surroundings.

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Units of Heat

- Calorie (cal), which is defined as the amount of energy transfer necessary to raise the temperature of 1 g of water from 14.5°C to 15.5°C.
- British thermal unit (Btu), which is defined as the amount of energy transfer required to raise the temperature of 1 lb of water from 63°F to 64°F.
- The joule has already been defined as an energy unit based on mechanical processes

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The Mechanical Equivalent of Heat

- Various experiments show that this mechanical energy does not simply disappear but is transformed into internal energy.
- You can perform such an experiment at home by hammering a nail into a scrap piece of wood. Some of it is now in the nail as internal energy, as demonstrated by the nail being measurably warmer.
- This connection between mechanical and internal energy was first suggested by Benjamin Thompson.
- It was James Prescott Joule who established the equivalence of the decrease in mechanical energy and the increase in internal energy.

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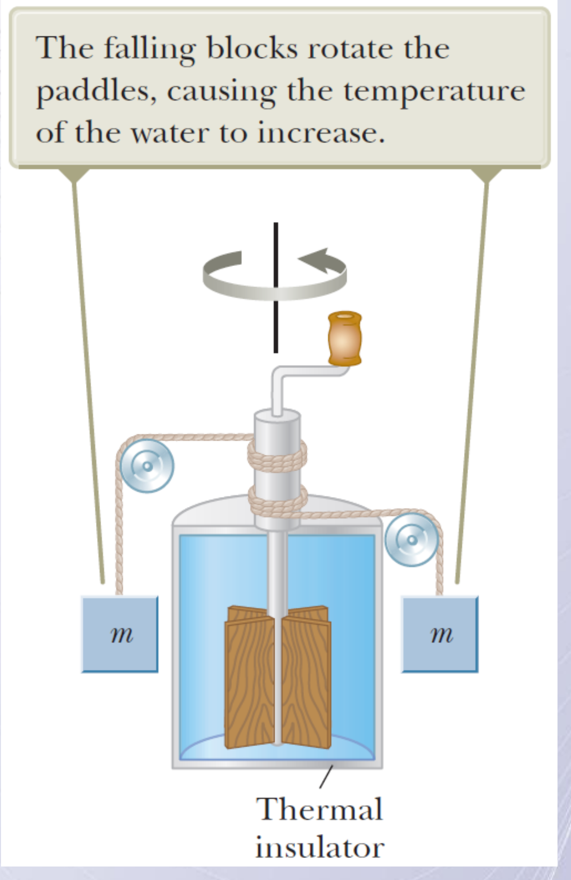
- The system of interest is the Earth, the two blocks, and the water in a thermally insulated container.
- Work is done within the system on the water by a rotating paddle wheel, which is driven by heavy blocks falling at a constant speed.
- If the energy transformed in the bearings and the energy passing through the walls by heat are neglected, the decrease in potential energy of the system as the blocks fall equals the work done by the paddle wheel on the water and, in turn, the increase in internal energy of the water.



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- If the two blocks fall through a distance *h*, the decrease in potential energy of the system is $2mgh$, where m is the mass of one block; this energy causes the temperature of the water to increase.
- By varying the conditions of the experiment, Joule found that the decrease in mechanical energy is proportional to the product of the mass of the water and the increase in water temperature.
- Mechanical equivalent of heat (**equivalence between mechanical energy and internal energy**)
  - 1 cal = 4.186 J

Specific Heat and Calorimetry

- Generally, when energy is added to a system and there is no change in the kinetic or potential energy of the system, the temperature of the system usually rises.
- If the system consists of a sample of a substance, we find that the quantity of energy required to raise the temperature of a given mass of the substance by some amount varies from one substance to another.
- The heat capacity C of a particular sample is defined as the amount of energy needed to raise the temperature of that sample by 1°C.
- From this definition, we see that if energy Q produces a change ΔT in the temperature of a sample, then
  - $Q = C \Delta T$

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Table 20.1 Specific Heats of Some Substances at 25°C and Atmospheric Pressure

Substance	Specific Heat (J/kg · °C)	Substance	Specific Heat (J/kg · °C)
Elemental solids		*Other solids*	
Aluminum	900	Brass	380
Beryllium	1 830	Glass	837
Cadmium	230	Ice (−5°C)	2 090
Copper	387	Marble	860
Germanium	322	Wood	1 700
Gold	129	*Liquids*	
Iron	448	Alcohol (ethyl)	2 400
Lead	128	Mercury	140
Silicon	703	Water (15°C)	4 186
Silver	234	*Gas*	
		Steam (100°C)	2 010

Note: To convert values to units of cal/g · °C, divide by 4 186.

- The specific heat c of a substance is the heat capacity per unit mass.

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- Therefore, if energy Q transfers to a sample of a substance with mass m and the temperature of the sample changes by ΔT, the specific heat of the substance is

$$c \equiv \frac{Q}{m\Delta T}$$

- Specific heat is essentially a measure of how thermally insensitive a substance is to the addition of energy.
- The greater a material's specific heat, the more energy must be added to a given mass of the material to cause a particular temperature change.
- From this definition, we can relate the energy Q transferred between a sample of mass m of a material and its surroundings to a temperature change ΔT as
  - $Q = mc\,\Delta T$

- Notice that when the temperature increases, Q and ΔT are taken to be positive and energy transfers into the system.
- When the temperature decreases, Q and ΔT are negative and energy transfers out of the system.
- We can identify $mc\,\Delta T$ as the change in internal energy of the system if we ignore any thermal expansion or contraction of the system.
- The internal energy of the system can be changed by transferring energy into the system by any mechanism.
- Specific heat varies with temperature.
- If temperature intervals are not too great, the temperature variation can be ignored and c can be treated as a constant.

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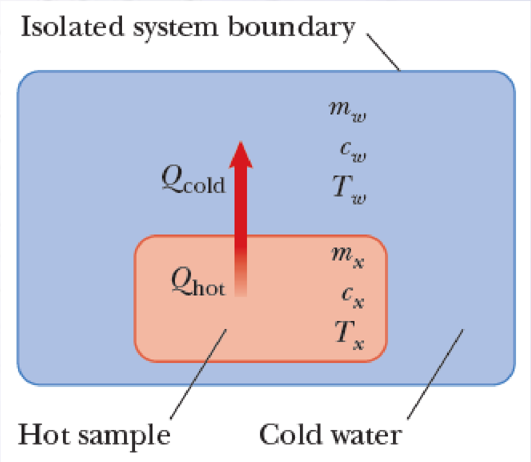
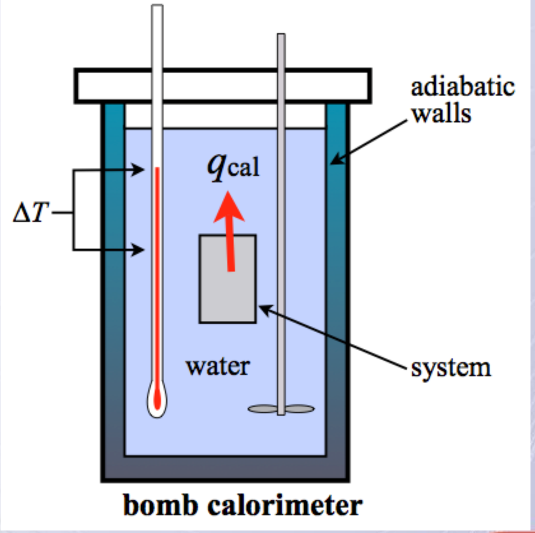
Calorimetry

- One technique for measuring specific heat involves heating a sample to some known temperature T_x, placing it in a vessel containing water of known mass and temperature $T_w < T_x$, and measuring the temperature of the water after equilibrium has been reached.
- If the system of the sample and the water is isolated, the principle of conservation of energy requires that the amount of energy Q_{hot} that leaves the sample (of unknown specific heat) equal the amount of energy Q_{cold} that enters the water.





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- Conservation of energy allows us to write the mathematical representation of this energy statement as
  - $Q_{\mathrm{cold}} = - Q_{\mathrm{hot}}$
- Suppose m_x is the mass of a sample of some substance whose specific heat we wish to determine. Let's call its specific heat c_x and its initial temperature T_x.
- Let m_w, c_w, and T_w represent corresponding values for the water. T_f is the final temperature after the system comes to equilibrium.
  - $m_w c_w (T_f - T_w) = - m_x c_x (T_f - T_x)$

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Latent Heat

- The transfer of energy does not result in a change in temperature when the physical characteristics of the substance change from one form to another (phase change).
- Two common phase changes are from solid to liquid (melting) and from liquid to gas (boiling).
- All such phase changes involve a change in the system's internal energy but no change in its temperature.
- The increase in internal energy in boiling, for example, is represented by the breaking of bonds between molecules in the liquid state; this bond breaking allows the molecules to move farther apart in the gaseous state, with a corresponding increase in intermolecular potential energy.

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- Different substances respond differently to the addition or removal of energy as they change phase because their internal molecular arrangements vary.
- When discussing two phases of a material, we will use the term higher-phase material to mean the material existing at the higher temperature.
- We define the **latent heat** for this phase change as

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

- The value of L for a substance depends on the nature of the phase change as well as on the properties of the substance.

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Table 20.2 Latent Heats of Fusion and Vaporization

Substance	Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)
Helium[a]	−272.2	5.23×10^3	−268.93	2.09×10^4
Oxygen	−218.79	1.38×10^4	−182.97	2.13×10^5
Nitrogen	−209.97	2.55×10^4	−195.81	2.01×10^5
Ethyl alcohol	−114	1.04×10^5	78	8.54×10^5
Water	0.00	3.33×10^5	100.00	2.26×10^6
Sulfur	119	3.81×10^4	444.60	3.26×10^5
Lead	327.3	2.45×10^4	1 750	8.70×10^5
Aluminum	660	3.97×10^5	2 450	1.14×10^7
Silver	960.80	8.82×10^4	2 193	2.33×10^6
Gold	1 063.00	6.44×10^4	2 660	1.58×10^6
Copper	1 083	1.34×10^5	1 187	5.06×10^6

[a]Helium does not solidify at atmospheric pressure. The melting point given here corresponds to a pressure of 2.5 MPa.

- If the entire amount of the lower-phase material undergoes a phase change, the change in mass Δm of the higher-phase material is equal to the initial mass of the lower-phase material.

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- From the definition of latent heat, and again choosing heat as our energy transfer mechanism, the energy required to change the phase of a pure substance is
    - $Q = L\,\Delta m$
- When energy enters a system, causing melting or vaporization, the amount of the higher-phase material increases, so Δm is positive and Q is positive.
- When energy is extracted from a system, causing freezing or condensation, the amount of the higher-phase material decreases, so Δm is negative and Q is negative.
- Δm always refers to the higher-phase material.

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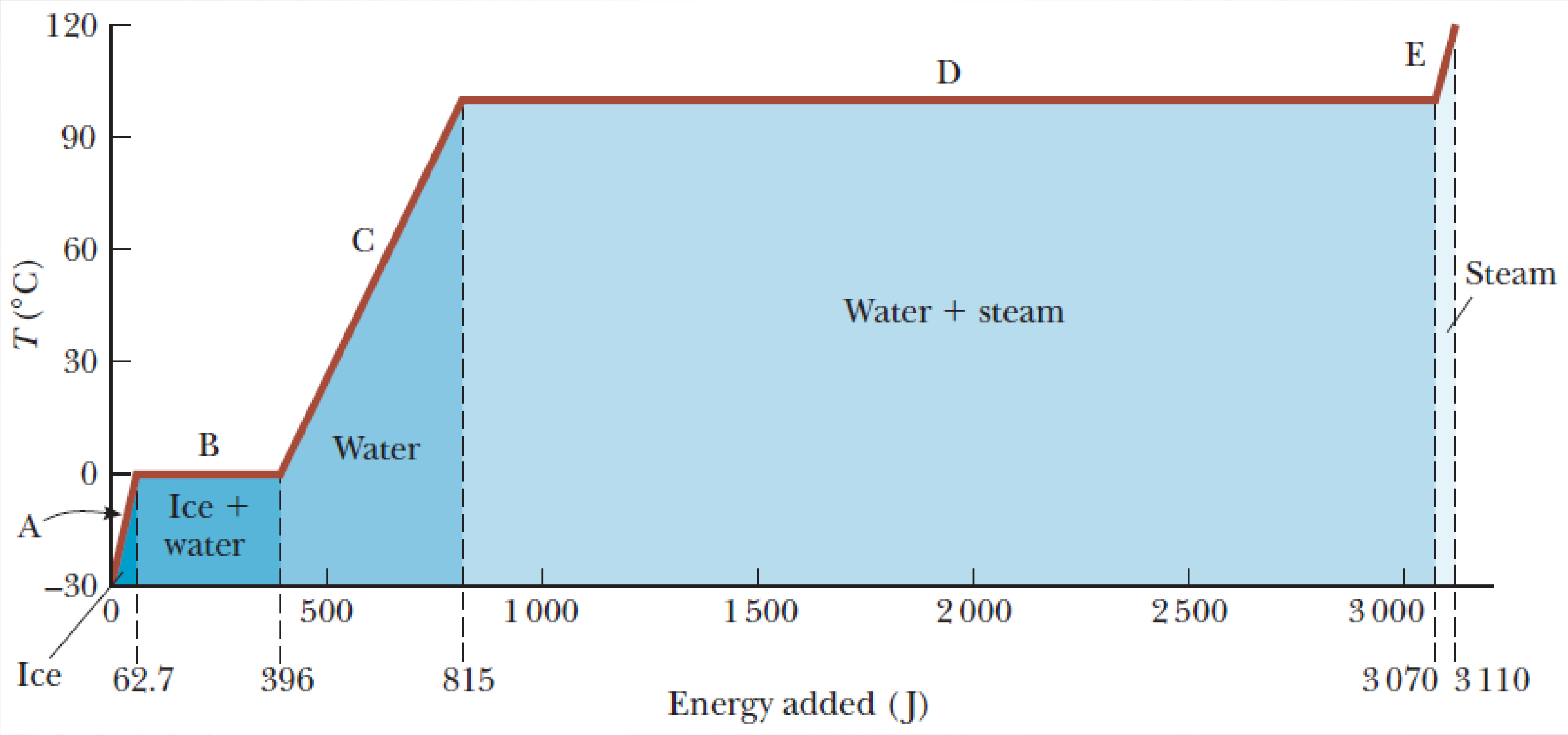
120
90
60
30
0
–30
T (°C)
A
B
C
D
E
Ice + water
Water
Water + steam
Steam
Ice
0
500
1 000
1 500
2 000
2 500
3 000
62.7
396
815
3 070
3 110
Energy added (J)