Chapter 13

Energy, Heat, and Chemical Change

The conservation of energy, put forth as the first law of thermodynamics, forms the principal theme of Chapter 13. The second law, governing the disposition of energy and the attendant maximization of entropy, is taken up in Chapter 14.

Issues addressed here include the interplay of heat and work in equilibrium thermodynamics, the role of the enthalpy function, and the rationale behind standard thermochemical calculations. Earlier discussions of classical mechanics (Chapter I) and the ideal gas (Chapter 10) support the treatment throughout. Relevant experimental data are collected in Table C-l 6 of Appendix C (PoC, *pages A85–A92).*

The opening questions aim to probe some of the underlying concepts and justifications of the thermodynamic argument.

1. An *intensive* property, independent of the amount of material, has a value at every point in a sample. An *extensive* property varies with the amount of material and requires the entire system for its definition.

PROPERTY	DEFINITION	CLASSIFICATION
(a) pressure	force *per unit area*	intensive
(b) temperature	average thermal energy *per particle*	intensive
(c) number of moles	*total* amount of substance	extensive
(d) volume	*total* capacity of substance	extensive
(e) concentration	amount *per unit volume*	intensive
(f) density	mass *per unit volume*	intensive
(g) molar volume	volume *per mole*	intensive

See also pages 7–8, 468–469, and Example 13-4 in *PoC*.

2. Macroscopic properties emerge as average values arising from the behavior of exceedingly complex microscopic systems. Thermodynamics therefore makes sense only if a system derives its properties from large numbers of constituents. When we speak of an intensive property, we mean a property that is smooth and uniform within any given small volume of a sample-a volume small enough to qualify practically as a "point" but large enough to contain a sufficient number of particles.

3. Let there be N atoms and n moles of helium within each volume. Then use $PV = nRT$ and Avogadro's number

$$N_0 = \frac{6{,}022 \times 1\ 0^{23}\,\text{atoms}}{\text{mol}}$$

to determine the number density, N/V, at STP:

$$\frac{N}{v} = \frac{n}{V} \times N_0$$

$$= \frac{P}{RT} \times N_0$$

$$= \frac{1.00\ \text{atm}}{(0.08206\ \text{atm L mol}^{-1}\ \text{K}^{-1})(273\ \text{K})} \times \frac{6.022 \times 10^{23}\ \text{atoms}}{\text{mol}}$$

$$= \frac{2.69 \times 10^{22}\ \text{atoms}}{\text{L}}$$

(a) A volume of 1 cm^3 is equal to 1 mL, or 10^{-3} L:

NUMBER DENSITY	VOLUME	NUMBER OF ATOMS

$$\frac{2.69 \times 10^{22}\ \text{atoms}}{\text{L}} \times \left(1\ \text{cm}^3 \times \frac{1\ \text{mL}}{\text{cm}^3} \times \frac{1\ \text{L}}{1000\ \text{mL}}\right) = 2.69 \times 10^{\text{''}}\ \text{atoms}$$

(b) A volume of 1 mm^3, equal to 10^{-6} L, contains 2.69×10^{16} atoms:

$$1\ \text{mm}^3 = \left(1\ \text{m m x}\ \frac{\text{lm}}{1000\ \text{mm}}\right)^3 \times \frac{1\ \text{L}}{0.001\ \text{m}^3} = 10^{-6}\ \text{L}$$

$$\frac{2.69 \times 10^{22}\ \text{atoms}}{\text{L}} \times 10^{-6}\ \text{L} = 2.69 \times 10^{16}\ \text{atoms}$$

(c) Convert the volume from cubic microns ($1 \ \mu m^3 = 1 \ \mu m \ x \ 1 \ \mu m \ x \ 1 \ \mu m$) into liters:

$$1 \ \mu m^3 = \left(1 \ \mu m \times \frac{1m}{10^6 \ \mu m}\right)^3 \times \frac{1 \ L}{`0.001 \ m^3} = 10^{-15} \ L$$

$$\frac{2.69 \ x \ 10^{22} \ atoms}{L} \ x \ 10^{-15} \ L = 2.69 \ x \ 10^7 \ atoms$$

(d) A cube with an edge of 10 nm has a volume of $10^{-21} \ L$:

$$10 \ nm \times 10 \ nm \times 10 \ nm = \left(10 \ nm \times \frac{1m}{10^9 \ nm}\right)^3 \times \frac{1 \ L}{0.001 \ m^3} = 10^{-21} \ L$$

$$\frac{2.69 \ x \ 10^{22} \ atoms}{L} \ x \ 10^{-21} \ L = 26.9 \ atoms \approx 27 \ atoms$$

4. Thermodynamic arguments fail when the dimensions of a system become comparable to the size of the particles. The system under study must contain a sufficiently large number of particles for statistical laws to be valid.

   A 10 nm x 10 nm x 10 nm volume, for example, is clearly inadequate to support a thermodynamic treatment of helium gas: 27 particles constitute too small a sample. A space of 1 μm x 1 μm x 1 μm, by contrast, contains nearly 27 million atoms and is likely to be governed by the "law of large numbers."

5. A *function of state* is determined only by the current equilibrium condition of a system, as specified by a set of state variables. A *function of path* varies with the history and preparation of a system. See pages 467–468, 480–481, and R13.4–R13.12 in *PoC*.

(a) *Internal energy:* function of state. The internal energy of an ideal gas, for example, depends only on temperature and amount:

$$E = \frac{3}{2} nRT$$

QUESTION: Why doesn't E depend on, say, the volume or density of an ideal gas?

ANSWER: Since, by definition, the particles of an ideal gas do not interact, their potential energy is independent of distance. A change in volume or density will alter the interparticle spacings, but there will be no attendant change in the internal energy.

QUESTION: The internal energy of an ideal gas depends on both an extensive variable *(n)* and an intensive variable *(T)*. Is E itself an intensive or extensive property?

ANSWER: The total internal energy, $\frac{3}{2}nRT$, scales with the amount of substance and is thus considered an extensive property. One mole of gas has an internal energy of $\frac{3}{2}RT$. Two moles have an energy of 2 x $\frac{3}{2}RT$. Three moles have an energy of 3 x $\frac{3}{2}RT$.

The *molar* internal energy, however, states the value of E per unit amount and is therefore an intensive property:

$$\frac{E}{n} = \frac{3}{2}RT$$

For related examples, see Exercise 1.

(b) *Enthalpy:* function of state. Enthalpy is constructed from a state function (internal energy) and two state variables (pressure and volume):

$$H = E + PV$$

The product of pressure and volume has dimensions of work (equivalently, energy):

$$\text{Pressure x volume} \sim \frac{\text{force}}{(\text{length})^2} \text{ x } (\text{length})^3 = \text{force x length} = \text{work}$$

(c) Heat: function of path. According to the first law of thermodynamics, the same change in internal energy-a function of state-can be realized by infinitely many combinations of heat *(q)* and work *(w)*:

$$\Delta E = q + w$$

Neither heat nor work, individually, is a function of state.

(d) *Work:* function of path. See above, part (c).

(e) *Distance traveled between two cities:* function of path. Different routes produce different distances:
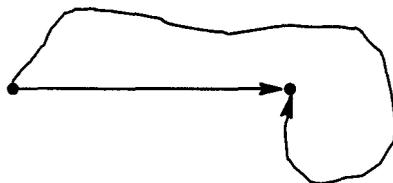
(f) *Minimum distance traveled between two cities:* function of state. The minimum distance in Euclidean space (measured along a straight line, "as the crow flies") is determined entirely by the positions of the two endpoints. There is one and only one possible value. See the sketch in (e).

6. The first law of thermodynamics requires that energy be conserved-specifically, that any local variation in a system's energy be accounted for by an exchange of heat *(q)* and work (w) with the surroundings:

$$\Delta E = q + w$$

If either *q* or w is zero, then the remaining quantity becomes equal to ΔE and thus acts as a function of state:

$\Delta E = q$ if w = 0 (for example, a process at constant volume)

$\Delta E = w$ if *q* = 0 (whenever work is done without the exchange of heat)

The following exercises begin to probe the concepts of heat flow and thermal equilibrium, a subject that will come to-fruition in Section 14-9 (where we shall understand that thermal equilibrium, like all other states of equilibrium, represents the culmination of a statistical drive toward maximum entropy).

7. The internal energy of our ideal gas is given by

$$E = \frac{3}{2} nRT$$

$$= \frac{3}{2} (1.00 \text{ mol})(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{K}^{-1})(1000 \text{ K})$$

$$= 12.5 \text{ kJ}$$

where *n* is the number of moles (here, 1 .OO mol) and *T* is the absolute temperature (here, 1000 K).

Isolated from the surroundings, with no exchange of heat or work, the system will maintain its internal energy of 12.5 kJ indefinitely:

$$q = o \qquad w = o \qquad \Delta E = q + w = 0$$

The temperature, directly proportional to the molar internal energy, therefore is fixed at 1000 K, the same in the year 3000 as it is today. Since *n, T,* and *V* all remain constant (there being no exchanges of matter, heat, or work), the pressure is unchanged as well:

$$P = \frac{nRT}{V} = 100 \text{ atm}$$

(c) With the amount of material constant, the change in internal energy is determined entirely by the change in temperature:

$$\Delta E = E_2 - E_1 = \frac{3}{2}nR(T_2 - T_1)$$

$$= \frac{3}{2}(1.00 \text{ mol})(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(273 \text{ K} - 173 \text{ K}) = 1.25 \text{ kJ}$$

The final energy of the gas is greater than the initial energy.

(d) Average energy and speed are both higher at the higher temperature. More internal energy is shared by the same number of particles.

(e) See pages 374-378 in *PoC* for a discussion of root-mean-square speed:

$$v_{rms} = \sqrt{\frac{3RT}{m}}$$

The symbol m represents the molar mass, expressed in units of kg mol^{-1}.

Before (at $T_1 = 173$ K):

$$v_{rms} = \sqrt{\frac{3(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(173 \text{ K})}{4.0026 \times 10^{-3} \text{ kg mol}^{-1}}}$$

$$= \sqrt{\frac{3(8.3145 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1})(173 \text{ K})}{4.0026 \times 10^{-3} \text{ kg mol}^{-1}}}$$

$$= 1.04 \times 10^3 \text{ m s}^{-1}$$

After (at $T_2 = 273$ K):

$$v_{rms} = \sqrt{\frac{3(8.3145 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1})(273 \text{ K})}{4.0026 \times 10^{-3} \text{ kg mol}^{-1}}} = 1.30 \times 10^3 \text{ m s}^{-1}$$

(f) Substitute the molar mass of neon ($m = 0.02018$ kg mol^{-1}) into the defining equation,

$$v_{rms} = \sqrt{\frac{3RT}{m}}$$

and obtain the following root-mean-square speeds:

$$v_{rms}(173 \text{ K}) = 4.62 \text{ x } 1 \ 0^2 \text{ m s}^{-1}$$

$$v_{rms}(273 \text{ K}) = 5.81 \text{ x } 10^2 \text{ m s}^{-1}$$

The neon atoms, more massive than helium, develop a lower speed given the same amount of kinetic energy ($\frac{1}{2}mv^2$).

10. Total thermal energy is an extensive property, scaling with the number of molecules. The average thermal energy per molecule, an intensive property, is independent of total amount and is reflected by the temperature.

(a) The Atlantic Ocean, vastly larger than a swimming pool, surely has more thermal energy overall-more energy than even a swimming pool at a higher temperature. The average energy per molecule, however, is greater in the swimming pool at 80°F than in the ocean at 33°F. An intensive property does not depend on the quantity of matter.
      In sum, although average thermal energy per molecule is greater in the system at higher temperature (the swimming pool), the system containing *more* molecules (the ocean) has the higher total energy.

(b) For equal volumes of water, total thermal energy is greater in the system at the higher temperature: 100°C. The average energy per molecule is greater as well.

(c) For two systems of water at the same temperature, the one with the larger volume (1 L) has the larger number of molecules and thus the larger total thermal energy-but the average thermal energy per molecule is the same for both.

(d) One liter of water, however high the temperature, makes up only an infinitesimally small part of the universe. The total thermal energy of the universe is unimaginably greater, even though the *average* thermal energy per particle-dependent on temperature-is greater in the small system at 1000 K.

11. A net flow of heat occurs only between bodies at different temperatures. The direction of the flow is from high temperature to low, and the exchange continues until the temperature is uniform and intermediate throughout.

(a) Heat flows from the swimming pool at 80°F to the ocean at 33°F. It is the difference in *temperature,* not the difference in total thermal energy, that determines the direction of flow.

(b) Heat is transferred from water at 100°C to water at 0°C, from high temperature to low.

(c) No heat passes between two systems at the same temperature (10°C).

(d) Heat flows from the system at high temperature (1000 K) out to the rest of the universe. The gas cools.

12. See page 48.5 in *PoC* for a discussion of the enthalpy of vaporization.

(a) Water vapor at 100°C has a higher enthalpy than liquid water at the same temperature. The difference is the *enthalpy of vaporization.*
      The internal energy is higher as well. See Exercise 13.

(b) The enthalpy of vaporization brings about a disruption of intermolecular interactions as the liquid expands into a gas.

Exercises 13 through 16 highlight the similarities and differences between the internal energy and the enthalpy, both extensive functions of state.

13. The enthalpy function, H, is related to the internal energy by the following definition:

$$H = E + PV$$

See Section 13-3 in *PoC* and also Examples 13-1, 13-2, 13-6, and 13-7.

(a) For the gas, we use $PV = nRT$ to calculate the volume per mole:

$$\frac{V_g}{n} = \frac{RT}{P} = \frac{(0.0820578 \text{ atm L mol}^{-1}\text{K}^{-1})(373.15 \text{ K})}{1.0000 \text{ atm}} = 30.620 \text{ L mol}^{-1}$$

For the liquid, we transform the reciprocal density from milliliters per gram into liters per mole:

$$\frac{V_\ell}{n} = \frac{1 \text{ mL}}{0.95840 \text{ g}} \times \frac{18.0153 \text{ g}}{\text{mol}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.018797 \text{ L mol}^{-1}$$

(b) Since the boiling transition occurs at constant pressure $(P = 1 \text{ atm})$, we establish first that **ΔH** and **ΔE** differ by the term $P\,\Delta V$ (where $\Delta V = V_g - V_\ell$):

$$\Delta H = H_g - H_\ell = (E_g + PV_g) - (E_\ell + PV_\ell)$$

$$= (E_g - E_\ell) + P(V_g - V_\ell)$$

$$= \Delta E + P\,\Delta V$$

Rearrangement of the equation then yields the change in molar internal energy:

$$\Delta E = \Delta H - P \Delta V$$

$$= 40.7 \text{ kJ mol}^{-1}$$

$$- (1.0000 \text{ atm})\left(30.620 \text{ L mol}^{-1} - 0.018797 \text{ L mol}^{-1}\right) \times \frac{8.3145 \times 10^{-3} \text{ kJ}}{0.0820578 \text{ atm L}}$$

$$= 37.6 \text{ kJ mol}^{-1}$$

Note that the conversion

$$8.3145 \times 10^{-3} \text{ kJ} = 0.0820578 \text{ atm L}$$

is implicit in the various representations of *R,* the universal gas constant:

$$R = 8.3145 \text{ J mol}^{-1} \text{K}^{-1} = 8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{K}^{-1} = 0.0820578 \text{ atm L mol}^{-1} \text{K}^{-1}$$

QUESTION: Is our result for ΔE consistent with the first law of thermodynamics?

ANSWER: Yes, the definition of enthalpy guarantees that ΔH (the first term in $\Delta E = \Delta H - P \Delta V$) is the heat transferred at constant pressure. Further, the term $-P \Delta V$ represents the work done by the gas expanding against a fixed external pressure:

$$\Delta E = q + w = \Delta H - P \Delta V = 37.6 \text{ kJ mol}^{-1}$$

The change in internal energy is equal to the heat and work exchanged between system and surroundings.

(c) Condensation and vaporization are reverse processes. Any corresponding functions of state are equal in magnitude and opposite in sign:

$$\Delta E_{con} = -\Delta E_{vap} = -37.6 \text{ kJ mol}^{-1}$$

(d) The difference between ΔE and ΔH during condensation derives from a *reduction* in volume, such that

$$\Delta V = V_f - V_g < 0$$

Accordingly, the contribution of $P \Delta V$ to the expression

$$\Delta H = \Delta E + P \Delta V$$

is negative for the gas-to-liquid transition, and hence AH,,, is *more negative* than ΔE_{con}. The enthalpy of condensation, AH,,,,, has the larger absolute value:

$$\left|\Delta E_{con}\right| = \left|-37.6 \text{ kJ mol}^{-1}\right| = 37.6 \text{ kJ mol}^{-1}$$

$$\text{AH,,,} = \left|-40.7 \text{ kJ mol}^{-1}\right| = 40.7 \text{ kJ mol}^{-1}$$

14. The method is the same as in the preceding exercise.

(a) Use the reciprocal density to obtain the molar volume of each phase:

Liquid: $V_{\ell} = \dfrac{1 \text{ mL}}{0.99984 \text{ g}} \times \dfrac{18.0153 \text{ g}}{\text{mol}} \times \dfrac{1 \text{ L}}{1000 \text{ mL}} = 0.018018 \text{ L mol}^{-1}$

Solid: $V_{s} = \dfrac{1 \text{ mL}}{0.917 \text{ g}} \times \dfrac{18.0153 \text{ g}}{\text{mol}} \times \dfrac{1 \text{ L}}{1000 \text{ mL}} = 0.019646 \text{ L mol}^{-1} = 0.0196 \text{ L mol}^{-1}$

The molar volume of the solid is larger. Water expands upon freezing.

(b) The difference between AH and AE at constant pressure is determined by the change in volume:

$$\Delta E = \Delta H - P\Delta V = \Delta H - P\left(V_{\ell} - V_{s}\right)$$

$$= 6.0 \text{ kJ mol}^{-1}$$

$$- (1.0000 \text{ atm})(0.018018 \text{ L mol}^{-1} - 0.019646 \text{ L mol}^{-1}) \times \dfrac{8.3145 \times 10^{-3} \text{ kJ}}{0.0820578 \text{ atm L}}$$

$$= 6.0 \text{ kJ mol}^{-1} + 0.000165 \text{ kJ mol}^{-1} \approx 6.0 \text{ kJ mol}^{-1}$$

(c) The change during freezing is equal in magnitude and opposite in sign:

$$\Delta E_{freeze} = -\Delta E_{melt} = -(6.0 + 0.000165) \text{ kJ mol}^{-1} \approx -6.0 \text{ kJ mol}^{-1}$$

(d) Although $\left|\Delta E_{freeze}\right|$ is slightly greater than $\left|\Delta H_{freeze}\right|$, the values are nearly the same since the *P AV* term is so small in comparison to 6.0 kJ:

$$\left|\Delta E_{freeze}\right| = \left|-(6.0 + 0.000\ 165) \text{ kJ mol}^{-1}\right| \approx 6.0 \text{ kJ mol}^{-1}$$

$$\Delta H_{freeze} = \left|-6.0 \text{ kJ mol}^{-1}\right| = 6.0 \text{ kJ mol}^{-1}$$

15. The difference in volume between liquid and vapor is usually far greater than the difference in volume between liquid and solid. Hence the $P \, \Delta V$ term contributes comparatively less to the enthalpy change

$$\Delta H = \Delta E + P \, \Delta V$$

during the liquid-solid transition.

16. We continue to explore the relationship between enthalpy and internal energy:

$$H = E + PV$$

See Section 13-3 and Examples 13-1, 13-2, 13-6, and 13-7.

(a) We stipulate that volume decreases during the freezing transition, so as to make $AV < 0$. Given that AE $=$ -100 J at constant pressure, we then inspect the equation

$$\Delta H = \Delta E + P \, \Delta V$$

to determine that AH is equal to *-100* J plus a *negative* number *(P ΔV)*. The only acceptable value from the list is -101 J.

(b) Since melting is the reverse of freezing, the two enthalpies are related by a minus sign: $\Delta H_{melt} = -\Delta H_{freeze} = 10 \ 1$ J.

17. Recall that pressure is equal to force per unit area:

$$\frac{\text{force x length}}{\text{pressure}} = \frac{\text{force x length}}{\text{force / area}} = \text{length x area} = (\text{length})^3 = \text{volume}$$

(a) We derive the conversion factor

$$0.08206 \ \text{atm} \ \text{L} = 8.3 \ 145 \ \text{J}$$

by noting the relationship between two equivalent formulations of the universal gas constant:

$$R = 0.08206 \ \text{atm L mol}^{-1} \text{K}^{-1} = 8.3145 \ \text{J mol}^{-1} \text{K}^{-1}$$

With that, we have only to recognize that 1 J is equal to 1 N m:

$$\frac{1 \, \text{N m}}{\text{atm}} \times \frac{1 \, \text{J}}{\text{N m}} \times \frac{0.08206 \ \text{atm L}}{8.3 \, 145 \ \text{J}} = 9.870 \ \text{x} \ 10^{-3} \ \text{L}$$

See Sections 1-4, 1-7, and 13-1 in *PoC*, as well as Table C-2 (page A63), for a review of newtons and joules.

(b) Same as (a). Expressed in base SI units of mass, length, and time, the joule (or newton-meter) has dimensions of kg m^2 s^{-2}:

$$\frac{1 \text{ kg m}^2 \text{s}^{-2}}{\text{atm}} \times \frac{1 \text{ J}}{\text{kg m}^2 \text{s}^{-2}} \times \frac{0.08206 \text{ atm L}}{8.3145 \text{ J}} = 9.870 \text{ x } 10^{-3} \text{ L}$$

(c) Convert grams and centimeters into kilograms and meters, and convert torr into atmospheres:

$$\frac{1 \text{ g cm}^2 \text{ s}^{-2}}{\text{torr}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^2 \times \frac{760 \text{ torr}}{\text{atm}} \times \frac{0.08206 \text{ atm L}}{8.3145 \text{ kg m}^2 \text{ s}^{-2}} = 7.501 \times 10^{-7} \text{ L}$$

Note that 1 J = 1 N m = 1 kg m^{2}s^{-2}.

(d) One pascal is equal to one newton per square meter, and one joule is equal to one newton-meter:

$$\frac{1 \text{ J}}{\text{Pa}} \text{ x } \frac{1 \text{ N m}}{\text{J}} \text{ X } \frac{1 \text{ Pa}}{\text{N m}^{-2}} \times \frac{1 \text{ L}}{0.001 \text{ m}^3} = 1000 \text{ L}$$

The next group of exercises, focusing exclusively on ideal gases, should help clarify the ins and outs of heat and work in simple systems. Familiarity with both the macroscopic theory of the ideal gas (Section 1 O-2) and the kinetic theory of gases (Section I O-3) will prove useful throughout. Note that the kinetic theory, a particle-based statistical model, is a nonthermodynamic formulation.

18. For a gas at constant temperature ($\Delta E = 0$), the first law ensures that work and heat are equal in magnitude and opposite in sign:

$$\Delta E = q + w = 0$$

$$q = -w$$

(a) To expand isothermally, the gas must absorb heat from its surroundings to do the work of expansion. Such absorption, however, is impossible here since the gas (300 K) is at a higher temperature than the surroundings (270 K). Heat flows naturally from a body at higher temperature to a body at lower temperature, not the other way around.

(b) An isothermal contraction is possible under the prescribed conditions. The work of compression done *on* the system (the gas) is balanced by an outflow of heat from system to surroundings.

19. Here we keep track of *w*, *q*, AE, and ΔH during an isothermal expansion of a gas.

(a) A system does work on its surroundings when it expands against a constant pressure:

$$w = -P\,\Delta V < 0 \quad \text{i} \quad \text{f} \quad \Delta V > 0$$

Work is required to increase the volume against a resisting force.

(b) Our convention, evidenced in the equation $w = -P\,\text{A}\,V$, is to treat work done *by* the system as negative: $w = -100$ J.

(c) Work done by the system makes a negative contribution to AE and thus lowers the internal energy:

$$\text{AE} = q + w = q + \text{negative contribution}$$

(d) Since the gas expands isothermally (AT= 0), there is no change in internal energy despite the work done on the surroundings. To maintain constant energy, the first law of thermodynamics demands that a flow of heat come *from* the surroundings into the system:

$$\Delta E = q + w = 0$$

$$q = -w$$

The sign of *q* is positive.

(e) The influx of heat (considered positive) raises the internal energy of the system by precisely the amount lost owing to the mechanical work of expansion:

$$q = -w = -(-100 \text{ J}) = 100 \text{ J}$$

(f) The change in energy, dependent only on the temperature, is zero for both system (gas) and surroundings because AT $= 0$. The change in enthalpy for the system is equal to the heat absorbed under constant pressure, q_P. For the surroundings, any change in a state function is equal in magnitude but opposite in sign:

	ΔE (J)	$\Delta H = q_P$ (J)
System:	0	100
Surroundings:	0	-100

The total changes in *E* and *H* are both zero for system and surroundings combined.

20. We continue with the gaseous system introduced in the preceding exercise, subjecting it now to an isothermal compression rather than expansion.

(a) This time, the surroundings do work *on* the system to force the isothermal compression. The work is considered positive, and there is a compensating outflow of heat from the system in order to maintain AE = 0. The heat, q = -100 J, has a negative sign.

(b) Apply the first law:

$$\Delta E = q + w = 0$$

$$w = -q = -(-100 \text{ J}) = 100 \text{ J}$$

(c) The change in internal energy is zero, because the temperature remains constant:

$$\Delta E_{sys} = -\Delta E_{surr} = 0$$

The change in enthalpy for the system is equal to the heat exchanged under constant pressure, determined above in (a):

$$\Delta H_{sys} = q_P = \text{-100 J}$$

The corresponding change for the surroundings is equal in magnitude and opposite in sign:

$$\Delta H_{surr} = \text{-AH,,,} = 100 \text{ J}$$

21. We examine further the relationships connecting AE, q, w, and AH, again using a gas as an illustrative model system. See Example 13-1 in *PoC*.

(a) The internal energy of an ideal gas is proportional to temperature and amount:

$$\Delta E = \frac{3}{2} nR \, \Delta T = \frac{3}{2} nR \left(T_2 - T_1\right)$$

$$= \frac{3}{2}(1.00 \text{ mol})\left(8.3\,145 \text{ J mol}^{-1}\text{K}^{-1}\right)\left(298 \text{ K} - 273 \text{ K}\right)$$

$$= 312 \text{ J}$$

See pages 374-376 of *PoC*, as well as Examples 10-8, 10-9, and 13-5.

(b) Given the change in internal energy ($\Delta E = 312$ J) and an accompanying transfer of heat *(q = 520 J)*, we use the first law of thermodynamics to calculate the necessary work:

$$\Delta E = q + w$$

$$w = \Delta E - q = 312 \text{ J} - 520 \text{ J} = -208 \text{ J}$$

(c) Since w is negative, we know that the work is done *by* the system expanding against a constant external pressure of 1 atm. The volume goes up, in agreement with our definition of pressure-volume work:

$$w = -P_{ext} \Delta V$$

$$\Delta V = -\frac{w}{P_{ext}} = -\left(\frac{-208 \text{ J}}{1.00 \text{ atm}}\right) \times \frac{0.08206 \text{ atm L}}{8.3145 \text{ J}} = 2.05 \text{ L}$$

According to the ideal gas law as well, we expect the volume to increase in direct proportion to the rise in temperature:

$$\Delta V = V_2 - V_1 = \frac{nR(T_2 - T_1)}{P}$$

$$= \frac{(1.00 \text{ mol})(0.08206 \text{ atm L mol}^{-1}\text{K}^{-1})(298 \text{ K} - 273 \text{ K})}{1.00 \text{ atm}}$$

$$= 2.05 \text{ L}$$

The results obtained by the two methods are consistent, as they must be.

(d) The change in enthalpy, ΔH, is equal to the heat absorbed at constant pressure: 520 J, the value already given. No further calculation is necessary.

For confirmation and additional practice, however, we shall use the change in volume to compute ΔH explicitly:

$$\Delta H = \Delta E + P \Delta V = 312 \text{ J} + (1.00 \text{ atm})(2.05 \text{ L}) \times \frac{8.3145 \text{ J}}{0.08206 \text{ atm L}}$$

$$= 312 \text{ J} + 208 \text{ J}$$

$$= 520 \text{ J}$$

(e) The reaction is endothermic, since $\Delta H > 0$. Heat flows into the system.

22. The wording of the problem enables us to specify *P, V, T,* and *n* for both the initial and final states:

$$P_1 = 1.00 \text{ atm} \qquad V_1 = 22.4 \text{ L} \qquad T_1 = 273 \text{ K} \qquad n_1 = 1.00 \text{ mol}$$

$$P_2 = \textbf{1.0916 atm} \qquad V_2 = 22.4 \text{ L} \qquad T_2 = 298 \text{ K} \qquad n_2 = 1.00 \text{ mol}$$

Recall here that the molar volume of an ideal gas at STP is 22.4 L (*PoC*, page 367), and so we have $V_1 = V_2 = 22.4$ L for the rigid container. Observe also that pressure inside the container increases during the process, going from 1 atm at 273 K to 1.09 atm at 298 K:

$$P_2 = P_1 \times \frac{T_2}{T_1} = 1.00 \text{ atm} \times \frac{298 \text{ K}}{273 \text{ K}} = 1.0916 \text{ atm}$$

We shall retain extra digits in P_2 to avoid round-off error.

(a) Similar to Example 13-2. First, use the equation

$$E = \frac{3}{2} nRT$$

to calculate the change in internal energy for the monatomic gas:

$$\text{AE} = \frac{3}{2} \left(1.00 \text{ mol} \right) \left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \right) \left(298 \text{ K-273 K} \right) = 312 \text{ J}$$

Second, realize that the system undergoes no change in volume and therefore no mechanical work: w = 0.

Next, use the first law of thermodynamics to determine *q*:

$$q = \Delta E - w = 312 \text{ J} - 0 = 312 \text{ J}$$

Finally, compute AH given the definition of enthalpy *(H = E + PV)*

$$\Delta H = \Delta E + \Delta(PV)$$

$$= \Delta E + \left(P_2 V_2 - P_1 V_1 \right)$$

$$= \Delta E + V_1 \left(P_2 - P_1 \right)$$

$$= 312 \text{ J} + \left(22.4 \text{ L} \right) \left(1.0916 \text{ atm} - 1.00 \text{ atm} \right) \times \frac{8.3145 \text{ J}}{0.08206 \text{ atm L}} = 520 \text{ J}$$

Note that the applicable pressure is the *internal* pressure, and note further that the volume remains constant in this example: $V_1 = V_2$. Compare the process with the one in Exercise 2 1.

ALTERNATIVE SOLUTION: For an ideal gas, we can substitute

$$\Delta(nRT) = \Delta(PV)$$

and solve for AH based on the change in temperature:

$$AH = AE + A(\ PV)$$

$$= \Delta E + A(nRT)$$

$$= \Delta E + nR\left(T_2 - T_1\right)$$

$$= 3\ 12\ J + (1.00\ mol)\left(8.3\ 145\ J\ mol^{-1}\ K^{-1}\right)\left(298\ K - 273\ K\right)$$

$$= 520\ J$$

(b) The sign of q is positive. Heat flows from the surroundings into the system.

23. Internal energy is a state function. The history or preparation of a system has no effect on the value of AE.

(a) There is no net change in internal energy, because both the temperature $(T_1 = T_2 = 273\ K)$ and amount of substance $(n_1 = n_2)$ are the same at the beginning and at the end:

$$\Delta E = \frac{3}{2} R\left(n_2 T_2 - n_1 T_1\right) = 0$$

Only the initial and final states are relevant. We ignore everything that happens in between.

(b) The change is irreversible, owing to the abrupt and turbulent steps in the process. A transformation is considered reversible (or *quasi-static)* only if it proceeds in a series of vanishingly small steps, remaining infinitesimally close to equilibrium at each stage. See pages 471-474 in *PoC*.

The remaining problems deal with various practical aspects of thermochemistry, focusing principally on heat capacity and calorimetry (Exercises 24 through 31, 41, 42) and Hess 's law (Exercises 32 through 40).

24. Heat capacity is covered in Section 13-3 and illustrated in Examples 13-5, 13-6, and 13-8.

(a) Substance X has a constant-pressure heat capacity, c_P, equal to 50 J mol^{-1}K^{-1} at all temperatures:

$$q = c_P \Delta T = c_P(T_2 - T_1) \quad \text{(per mole)}$$

$$= (50 \text{ J mol}^{-1}\text{K}^{-1})(300 \text{ K} - 100 \text{ K})$$

$$= 10,000 \text{ J mol}^{-1}$$

(b) For substance Y, the heat capacity $c_P(T)$ varies with temperature:

$$c_P(T) = 50 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{for} \quad T < 200 \text{ K}$$

$$c_P(T) = 100 \text{ J mol}^{-1}\text{K}^{-1} \quad \text{for} \quad T \geq 200 \text{ K}$$

We obtain the total heat absorbed as the sum of two separate contributions, one from each region where $c_P(T)$ is constant:

$$q = (50 \text{ J mol}^{-1} \text{ K}^{-1})(200 \text{ K} - 100 \text{ K}) + (100 \text{ J mol}^{-1}\text{K}^{-1})(300 \text{ K} - 200 \text{ K})$$

$$= 5000 \text{ J mol}^{-1} + 10,000 \text{ J mol}^{-1}$$

$$= 15,000 \text{ J mol}^{-1}$$

25. The heat capacity of a substance (c_P) determines the change in temperature for a given flow of heat (q):

$$\Delta T = \frac{q}{nc_P}$$

The smaller the heat capacity, the larger is the change in temperature imposed on some fixed molar amount n. See Section 13-3 and Examples 13-5, 13-6, and 13-8.

(a) Substance X, with $c_P = 100$ J mol^{-1} K^{-1}, undergoes a larger change in temperature when it absorbs the same amount of heat as substance Y ($c_P = 200$ J mol^{-1}K^{-1}).

(b) Heat is distributed into a system's microscopic degrees of freedom-translations, rotations, vibrations, electronic excitations. Different substances have different internal modes and therefore different "capacities" to absorb and store thermal energy.

(c) Monatomic gases possess only the ability to translate and thus have access to only three degrees of freedom. There are no differences in the internal modes available to one such gas and another, provided we ignore electronic excitations and interparticle interactions (as we do for systems considered ideal).

26. The substance with the greater number and variety of internal modes should have the higher heat capacity. For experimental values, see Table C-l 6 in PoC (pages A85–A92).

(a) C_3H_8 can vibrate and rotate in additibn to undergoing translational motion. Its heat capacity is higher than that of He, which can only translate.

(b) C_8H_{18}, with more atoms and more bonds than CH_4, has the higher heat capacity. It has more rotational, vibrational, and electronic degrees of freedom.

(c) Cl_2, a diatomic molecule, is able to rotate, vibrate, and translate. Monatomic Ne can only translate. Cl_2 has the higher heat capacity.

(d) Enormously large and complex, DNA has a higher heat capacity than H_2O.

(e) NH; has more atoms and more bonds than H_2—and hence the higher heat capacity.

27. See Examples 13-5 and 13-6 for details about the molar heat capacity of a monatomic gas.

(a) Since no pressure-volume work is done at constant volume,

$$w = -PAV = 0$$

we note first that the change in internal energy is determined entirely by the flow of heat:

$$\Delta E = q + w = q + 0 \equiv q_V$$

Next, given the internal energy of an ideal gas (AE $= \frac{3}{2}nR$ AT), we establish that c_V is equal to $\frac{3}{2}R$:

$$c_V = \frac{q_V}{n\,\Delta T} = \frac{\Delta E}{n\,\Delta T} = \frac{3}{2}\frac{nRAT}{n\,\Delta T} = \frac{3}{2}R$$

The heat transferred at constant volume follows directly:

$$q_V = nc_V\,\Delta T = n\left(\frac{3}{2}R\right)\Delta T$$

$$= \left(100.\ \text{g Ne} \times \frac{1\ \text{mol Ne}}{20.18\ \text{g Ne}}\right)\left(\frac{3}{2} \times 0.0083\ 145\ \text{kJ mol}^{-1}\,\text{K}^{-1}\right)(100\ \text{K})$$

$$= 6.18\ \text{kJ}$$

(b) The heat transferred at constant pressure, q_P, is registered as a change in enthalpy:

$$\Delta H = \Delta E + P\,\Delta V \equiv q_P$$

We then use the ideal gas relationships

$$\Delta E = \frac{3}{2} nR\,\Delta T \qquad \text{and} \qquad PAV = nRAT$$

to equate c_P with $\frac{5}{2}R$:

$$\Delta H = \Delta E + P\,\Delta V = q_P$$

$$= \frac{3}{2} nR\,\Delta T + nR\,\Delta T$$

$$= \frac{5}{2} nR\,\Delta T$$

$$c_P = \frac{q_P}{n\,\Delta T} = \frac{5}{2} R$$

For a sample containing 100 g Ne, a 100-K rise in temperature thus requires the absorption of 10.3 kilojoules at constant pressure:

$$q_P = nc_P\,\Delta T = n\left(\frac{5}{2} R\right)\Delta T$$

$$= \left(1OO.\text{gNex} \frac{1\ \text{mol Ne}}{20.18\ \text{g Ne}}\right)\left(\frac{5}{2} \times 0.0083\,145\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)(100\ \text{K})$$

$$= 10.3\ \text{kJ}$$

28. See Section l-7 in *PoC* for a discussion of work and energy in general. Examples l-l through l-3 treat the specific case of gravitational potential energy.

See also Example 13-8 (beginning on page R13.17) for an illustration of a typical calorimetric   calculation.

(a) The potential energy of a body subject to terrestrial gravity is given by the equation

$$E = mgh$$

where m is the mass (in kilograms), g is the acceleration due to gravity (9.81 m s^{-2}), and h is the height of the body (in meters) close to the earth's surface. The energy is thus expressed in kg m^2 s^{-2}, or joules:

$$E = (1.00\ \text{kg})(9.81\,\text{m s}^{-2})(10.0\ \text{m}) = 98.1\ \text{kg m}^2\ \text{s}^{-2} = 98.1\ \text{J}$$

We assume that this potential energy, converted into kinetic energy, is absorbed fully by the water as heat (q_P, at constant pressure):

$$q_P = nc_P \, \Delta T$$

$$\Delta T = \frac{q_P}{nc_P} = \frac{98.1 \text{ J}}{\left(1.00 \text{ L} \times \dfrac{1000 \text{ mL}}{\text{L}} \times \dfrac{1.00 \text{ g } H_2O}{\text{mL}} \times \dfrac{1 \text{ mol}}{18.015 \text{ g } H_2O}\right)\left(75.3 \text{ J mol}^{-1} K^{-1}\right)}$$

$$= 0.0235 \text{ K}$$

(b) Use the same method as in (a), but this time substitute 0.100 L H_2O in place of 1.00 L. The tenfold reduction in volume leads to a tenfold increase in ΔT:

$$\Delta T = 0.235 \text{ K}$$

Absorbed by a smaller mass of water, the same quantity of heat produces a proportionally greater rise in temperature.

29. Except for the use of ethanol instead of water, the method is the same as in Exercise 28:

$$q_P = nc_P \, \Delta T = mgh$$

$$\Delta T = \frac{q_P}{nc_P} = \frac{mgh}{nc_P}$$

The heat capacity and density of C_2H_5OH at 25°C are given as 111.5 J mol^{-1} K^{-1} and 0.789 g mL^{-1}, respectively:

$$n = 1.00 \text{ L} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{0.789 \text{ g } C_2H_5OH}{\text{mL}} \times \frac{1 \text{ mol}}{46.069 \text{ g } C_2H_5OH} = 17.126 \text{ mol}$$

$$\Delta T = \frac{mgh}{nc_P} = \frac{(1.00 \text{ kg})(9.81 \text{ m s}^{-2})(10.0 \text{ m}) \times \dfrac{1 \text{ J}}{\text{kg m}^2 \text{ s}^{-2}}}{(17.126 \text{ mol})(111.5 \text{ J mol}^{-1} K^{-1})} = 0.0514 \text{ K}$$

30. The specific heat, c_s, denotes the heat capacity expressed per gram of substance. See pages 477 and R13.19 in *PoC*.

(a) Use the molar mass to convert moles into grams:

$$c_s = \frac{81.6 \text{ J}}{\text{mol K}} \times \frac{1 \text{ mol}}{32.042 \text{ g } CH_3OH} = 2.55 \text{ J g}^{-1} K^{-1}$$

(b) The temperature of a l-g sample rises by 1 K for every 2.55 J absorbed. Here the total mass proves to be 105 g:

$$q = mc_s \, \Delta T$$

$$m = \frac{q}{c_s \, \Delta T} = \frac{3135}{(2.55 \text{ J g}^{-1} \text{K}^{-1})(1.17 \text{ K})} = 105 \text{ g}$$

Remember that the Celsius degree and the kelvin have the same magnitude.

31. In general, the relationship between heat and temperature is determined by the quantity of matter and the heat capacity:

Heat = quantity of matter x heat capacity x change in temperature

(a) If 1 gram of silver has a heat capacity of 0.235 J K^{-1}, then a lo-gram mass has a heat capacity of 2.35 J K^{-1}. The quantity of heat scales in proportion to the mass:

$$\frac{0.235 \smile \text{J}}{\text{g K}} \times 10.0 \text{ g} = 2.35 \text{ J K}^{-1} \quad \text{(per 10 g Ag)}$$

(b) Given the mass *(m),* specific heat (c,), and change in temperature (AT), we have **sufficient** information to calculate the quantity of heat:

$$q = mc, \text{ AT} = (10.0 \text{ g})(0.235 \text{ J g}^{-1}\text{K}^{-1})(10.3 \text{ K}) = 24.2 \text{ J}$$

Note that the change in temperature

$$\text{AT} = T_2 - T_1 = 30.3°\text{C} - 20.0°\text{C} = 10.3°\text{C} = 10.3 \text{ K}$$

is the same whether expressed in kelvins or degrees Celsius. The size of a degree is identical in both scales.

32. Hess's law, applicable to any function of state, allows us to calculate the standard change in enthalpy for an arbitrary chemical reaction:

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$
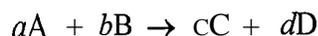
$$\text{AH"} = c \, \Delta H_f^\circ(\text{C}) + d \, \Delta H_f^\circ(\text{D}) - a \, \Delta H_f^\circ(\text{A}) - b \, \Delta H_f^\circ(\text{B})$$

The standard enthalpy of formation, ΔH_f°, is zero for any element in its standard state under standard conditions. See Section 13-4 and Examples 13-9 through 13-11 in *PoC*

for similar calculations. Standard enthalpies of formation are collected in Table C-16 of Appendix C (pages A85–A92).

(a) The sublimation of potassium metal is endothermic (AH" > 0). Heat must be absorbed if atoms are to be liberated from the solid:

$$K(s) \rightarrow K(g)$$
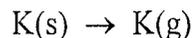
$$AH" = \Delta H_f^\circ \left[K(g) \right] - \Delta H_f^\circ \left[K(s) \right]$$

$$= \left(\frac{89.0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right)$$

$$= 89.0 \text{ kJ (endothermic)}$$

(b) The precipitation of magnesium chloride is endothermic:

$$Mg^{2+}(aq) + 2Cl^-(aq) \rightarrow MgCl_2(s)$$
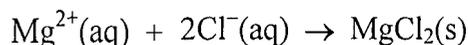
$$AH" = \Delta H_f^\circ \left[MgCl_2(s) \right] - \Delta H_f^\circ \left[Mg^{2+}(aq) \right] - 2\,\Delta H_f^\circ \left[Cl^-(aq) \right]$$

$$= \left(-\frac{641.3 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right) - \left(-\frac{466.9 \text{ kJ}}{11101} \times 1 \text{ mol} \right) - \left(-\frac{167.2 \text{ kJ}}{\text{mol}} \times 2 \text{ mol} \right)$$

$$= 160.0 \text{ kJ (endothermic)}$$

(c) The dissolution of sodium hydroxide is exothermic (AH" < 0):

$$NaOH(s) \rightarrow Na^+(aq) + OH\text{-}(aq)$$
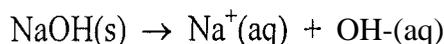
$$AH" = \Delta H_f^\circ \left[Na^+(aq) \right] + \Delta H_f^\circ \left[OH^-(aq) \right] - \Delta H_f^\circ \left[NaOH(s) \right]$$

$$= \left(-\frac{240.1 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right) + \left(-\frac{230.0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right) - \left(-\frac{425.6 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right)$$

$$= -44.5 \text{ kJ (exothermic)}$$

Note that we have no qualitatively reliable way to predict whether a particular dissolution-precipitation reaction will be endothermic or exothermic. See pages 543-550 in *PoC* and also Examples 15-8 through 15-l 2 for the role played by enthalpy, entropy, and free energy in solution equilibria.

(d) The complete combustion of methane to carbon dioxide and water is strongly exothermic:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$
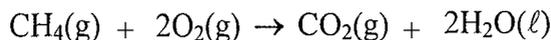
$$AH" = \Delta H_f^\circ\left[CO_2(g)\right] + 2\Delta H_f^\circ\left[H_2O(\ell)\right] - \Delta H_f^\circ\left[CH_4(g)\right] - 2\Delta H_f^\circ\left[O_2(g)\right]$$

$$= \left(-\frac{393.5 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) + \left(-\frac{285.8 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right)$$

$$- \left(-\frac{74.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right)$$

$$= -890.3 \text{ kJ (exothermic)}$$

(e) The synthesis of ammonia, discussed in Section 12-6, is exothermic:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
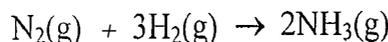
$$\Delta H^\circ = 2\Delta H_f^\circ\left[NH_3(g)\right] - \Delta H_f^\circ\left[N_2(g)\right] - 3\Delta H_f^\circ\left[H_2(g)\right]$$

$$= \left(-\frac{46.1 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 3 \text{ mol}\right)$$

$$= -92.2 \text{ kJ (exothermic)}$$

(f) The decomposition of hydrogen peroxide is exothermic:

$$H_2O_2(\ell) \rightarrow H_2O(\ell) + \tfrac{1}{2}O_2(g)$$
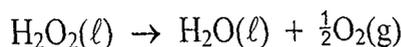
$$\Delta H^\circ = \Delta H_f^\circ\left[H_2O(\ell)\right] + \frac{1}{2}\Delta H_f^\circ\left[O_2(g)\right] - \Delta H_f^\circ\left[H_2O_2(\ell)\right]$$

$$= \left(-\frac{285.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) + \left(\frac{0 \text{ kJ}}{\text{mol}} \times \frac{1}{2} \text{ mol}\right) - \left(-\frac{187.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right)$$

$$= -98.0 \text{ kJ (exothermic)}$$

33. Use the same method as in the preceding exercise.

(a) The process shown is the formation reaction for sulfur dioxide:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$
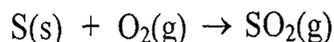
$$\Delta H" = \Delta H_f^\circ[SO_2(g)] - \Delta H_f^\circ[S(s)] - \Delta H_f^\circ[O_2(g)]$$

$$= \left(-\frac{296.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right)$$

$$= -296.8 \text{ kJ (exothermic)}$$

(b) The neutralization of hydronium and hydroxide ions is exothermic:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$$
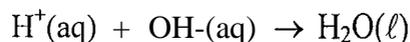
$$\Delta H" = \Delta H_f^\circ[H_2O(\ell)] - \Delta H_f^\circ[H^+(aq)] - \Delta H_f^\circ[OH^-(aq)]$$

$$= \left(-\frac{285.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(-\frac{230.0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right)$$

$$= -55.8 \text{ kJ (exothermic)}$$

(c) The decomposition of methane into its constituent elements is the reverse of the formation reaction. We find, accordingly, that AH" is equal to $-\Delta H_f^\circ$ [CH, (g)] :

$$CH_4(g) \rightarrow C(s) + 2H_2(g)$$
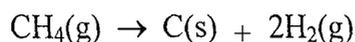
$$\Delta H" = \Delta H_f^\circ[C(s)] + 2\,\Delta H_f^\circ[H_2(g)] - \Delta H_f^\circ[CH_4(g)]$$

$$= \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) + \left(\frac{0 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) - \left(-\frac{74.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right)$$

$$= 74.8 \text{ kJ} = -\Delta H_f^\circ[CH_4(g)] \quad \text{(endothermic)}$$

(d) Similar to (c)-the decomposition of a substance, water, into its constituent elements:

$$H_2O(g) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$
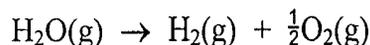
$$\Delta H^\circ = \Delta H_f^\circ\left[H_2(g)\right] + \frac{1}{2}\Delta H_f^\circ\left[O_2(g)\right] - \Delta H_f^\circ\left[H_2O(g)\right]$$

$$= \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) + \left(\frac{0 \text{ kJ}}{\text{mol}} \times \frac{1}{2} \text{ mol}\right) - \left(-\frac{241.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right)$$

$$= 241.8 \text{ kJ} = -\Delta H_f^\circ\left[H_2O(g)\right] \quad \text{(endothermic)}$$

(e) Another decomposition of a substance (here, ozone) into its component elements:

$$2O_3(g) \rightarrow 3O_2(g)$$
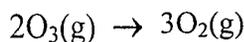
$$AH" = 3\Delta H_f^\circ\left[O_2(g)\right] - 2\Delta H_f^\circ\left[O_3(g)\right]$$

$$= \left(\frac{0 \text{ kJ}}{\text{mol}} \times 3 \text{ mol}\right) - \left(\frac{142.7 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right)$$

$$= -285.4 \text{ kJ (exothermic)}$$

(f) The formation of two moles of fluorine atoms from one mole of elemental fluorine is endothermic. Energy is needed to break the F-F bond:

$$F_2(g) \rightarrow 2F(g)$$
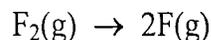
$$AH" = 2\Delta H_f^\circ\left[F(g)\right] - \Delta H_f^\circ\left[F_2(g)\right]$$

$$= \left(\frac{79.4 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right)$$

$$= 158.8 \text{ kJ (endothermic)}$$

34. Phase transitions. The transformation is endothermic in the direction

$$\text{order} \rightarrow \text{disorder}$$

and exothermic in the direction

$$\text{disorder} \rightarrow \text{order}$$

(a) The evaporation of butane is endothermic:
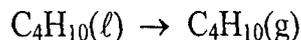
$$C_4H_{10}(\ell) \rightarrow C_4H_{10}(g)$$

$$\Delta H^\circ = \Delta H_f^\circ\left[C_4H_{10}(g)\right] - \Delta H_f^\circ\left[C_4H_{10}(\ell)\right]$$

$$= \left(-\frac{124.7 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(-\frac{147.6 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right)$$

$$= 22.9 \text{ kJ (endothermic)}$$

The value computed is the heat of vaporization, per mole.

(b) Compare the process here to the one considered in (a). Condensation is the reverse of vaporization:
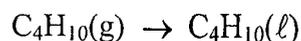
$$C_4H_{10}(g) \rightarrow C_4H_{10}(\ell)$$

$$\Delta H^\circ = \Delta H_f^\circ\left[C_4H_{10}(\ell)\right] - \Delta H_f^\circ\left[C_4H_{10}(g)\right]$$

$$= \left(-\frac{147.6 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(-\frac{124.7 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right)$$

$$= -22.9 \text{ kJ (exothermic)}$$

The heat of condensation is equal in magnitude and opposite in sign to the heat of vaporization.

(c) The evaporation of benzene is endothermic:

$$C_6H_6(\ell) \rightarrow C_6H_6(g)$$
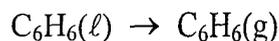
$$\Delta H^\circ = \Delta H_f^\circ\left[C_6H_6(g)\right] - \Delta H_f^\circ\left[C_6H_6(\ell)\right]$$

$$= \left(\frac{82.9 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{49.0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right)$$

$$= 33.9 \text{ kJ (endothermic)}$$

(b) The equation represents the formation of one mole of gaseous ethylene from its elements:

$$2C(s) + 2H_2(g) \rightarrow C_2H_4(g)$$
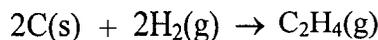
Consulting Table C- 16 for the standard enthalpy of formation, we have AH" without any explicit   calculation:

$$\Delta H^\circ = \Delta H_f^\circ \left[C_2 H_4(g) \right] = \frac{52.3 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} = 52.3 \text{ kJ}$$

(c) The reaction

$$SO_3(g) \rightarrow S(s) + \tfrac{3}{2}O_2(g)$$
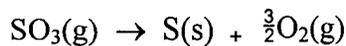
brings about the decomposition of one mole of gaseous SO3 into elemental sulfur and oxygen. To obtain ΔH°, we look up $\Delta H_f^\circ \left[SO_3(g) \right]$ and reverse the sign:

$$\Delta H^\circ = -\Delta H_f^\circ \left[SO_3(g) \right] = -\left(-\frac{395.7 \text{ kJ}}{\text{mol}} \right) \times 1 \text{ mol} = 395.7 \text{ kJ}$$

(d) Here we have the decomposition of two moles of sodium chloride into elemental sodium and chlorine:

$$2NaCl(s) \rightarrow 2Na(s) + Cl_2(g)$$

$$\Delta H^\circ = -2\Delta H_f^\circ \left[NaCl(s) \right] = -\left(-\frac{411.2 \text{ kJ}}{\text{mol}} \times 2 \text{ mol} \right) = 822.4 \text{ kJ}$$

37. Use the molar mass to convert kilojoules per mole into kilojoules per gram.

(a) We calculated in the previous exercise that AH" = -546.6 kJ for the formation of two moles of HF(g):

$$H_2(g) + F_2(g) \rightarrow 2HF(g) \qquad \Delta H^\circ = \text{-546.6 kJ}$$
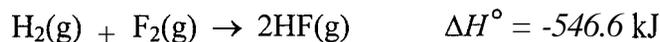
The value corresponding to the formation of 1 .OO g is computed as follows:

$$-\frac{546.6 \text{ kJ}}{2 \text{ mol HF}} \times \frac{1 \text{ mol HF}}{20.0063 \text{ g HF}} \times 1.00 \text{ g} = \text{-13.7 kJ}$$

(b) The endothermic formation of one mole of ethylene requires 52.3 kilojoules. Scaled down, the formation of one gram requires 1.86:

$$\frac{52.3 \text{ kJ}}{\text{mol } C_2H_4} \times \frac{1 \text{ mol } C_2H_4}{28.054 \text{ g } C_2H_4} \times 1.00 \text{ g} = 1.86 \text{ kJ}$$

(c) The reaction as written,

$$S(s) + \tfrac{3}{2}O_2(g) \rightarrow SO_3(g)$$
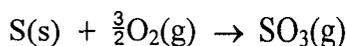
is the reverse of the process considered in Exercise 36(c). The change in enthalpy is therefore opposite in sign:

$$- \frac{395.7 \text{ kJ}}{\text{mol } SO_3} \times \frac{1 \text{ mol } SO_3}{80.064 \text{ g } SO_3} \times 1.00 \text{ g} = -4.94 \text{ kJ}$$

(d) Similar. The reaction as written,

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$
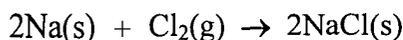
is the reverse of the process considered in Exercise 36(d). The change in enthalpy is opposite in sign:

$$- \frac{822.4 \text{ kJ}}{2 \text{ mol } NaCl} \times \frac{1 \text{ mol } NaCl}{58.443 \text{ g } NaCl} \times 1.00 \text{ g} = -7.04 \text{ kJ}$$

38. We can systematically derive a balanced equation for the complete combustion of any alkane (a hydrocarbon with general formula C_nH_{2n+2}):

$$\_\_ C_nH_{2n+2} + \_\_ O_2 \rightarrow \_\_ CO_2 + \_\_ H_2O \qquad \text{(unbalanced)}$$

$$C_nH_{2n+2} + \_\_ O_2 \rightarrow nCO_2 + \_\_ H_2O \qquad \text{(C is balanced)}$$

$$C_nH_{2n+2} + \_\_ O_2 \rightarrow nCO_2 + (n + 1)H_2O \qquad \text{(H is balanced)}$$

$$C_nH_{2n+2} + \frac{3n+1}{2} O_2 \rightarrow nCO_2 + (n + 1)H_2O \qquad \text{(0 is balanced)}$$
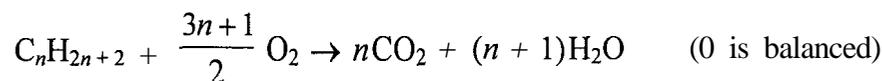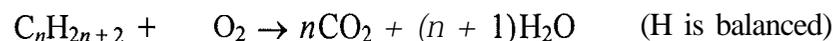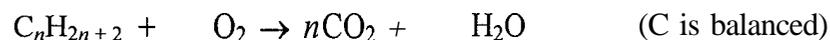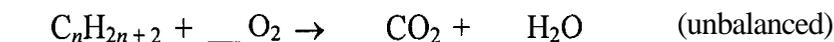
(a) Applied to propane ($n = 3$), the generalized equation quickly gives us a balanced reaction:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(\ell)$$
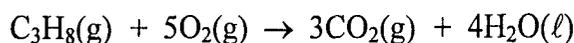
After that, we apply Hess's law to calculate $\Delta H°$:

$$\Delta H° = 3\,\Delta H_f°\left[CO_2\,(g)\right] + 4\,\Delta H_f°\left[H_2O(\ell)\right] - \Delta H_f°\left[C_3H_8(g)\right] - 5\,\Delta H_f°\left[O_2\,(g)\right]$$

$$= \left(-\frac{393.5\ kJ}{mol} \times 3\ mol\right) + \left(-\frac{285.8\ kJ}{mol} \times 4\ mol\right)$$

$$-\left(-\frac{103.9\ kJ}{mol} \times 1\ mol\right) - \left(\frac{0\ kJ}{mol} \times 5\ mol\right)$$

$$= -2219.8\ kJ$$

(b) Convert moles into grams:

$$-\frac{2219.8\ kJ}{mol\ C_3H_8} \times \frac{1\ mol\ C_3H_8}{44.097\ g\ C_3H_8} \times 1.00\ g\ C_3H_8 = -50.3\ kJ$$

39. Use the same method as in the preceding exercise.

(a) Inserting $n = 4$ into the general combustion formula for an alkane,

$$C_nH_{2n+2} + \frac{3n+1}{2}\ O_2 \rightarrow nCO_2 + (n + 1)H_2O$$
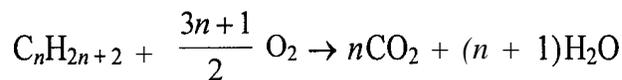
we have a balanced equation for butane:

$$C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(\ell)$$
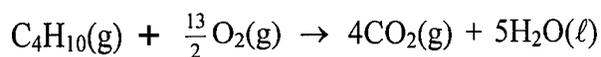
The corresponding enthalpy of reaction, per mole of C_4H_{10}, is -2878.3 kJ:

$$\Delta H° = 4\,\Delta H_f°\left[CO_2\,(g)\right] + 5\,\Delta H_f°\left[H_2O(\ell)\right] - \Delta H_f°\left[C_4H_{10}(g)\right] - \frac{13}{2}\,\Delta H_f°\left[O_2\,(g)\right]$$

$$= \left(-\frac{393.5\ kJ}{mol} \times 4\ mol\right) + \left(-\frac{285.8\ kJ}{mol} \times 5\ mol\right)$$

$$-\left(-\frac{124.7\ kJ}{mol} \times 1\ mol\right) - \left(\frac{0\ kJ}{mol} \times \frac{13}{2}\ mol\right)$$

$$= -2878.3\ kJ$$

(b) Convert moles into grams:

$$- \frac{2878.3 \text{ kJ}}{\text{mol } C_4H_{10}} \times \frac{1 \text{ mol } C_4H_{10}}{58.123 \text{ g } C_4H_{10}} \times 1.00 \text{ g } C_4H_{10} = -49.5 \text{ kJ}$$

(c) Propane (C_3H_8) yields more enthalpy per gram: -50.3 kJ.

40. We begin with the combustion of sucrose to carbon dioxide and water:

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(\ell) \qquad \Delta H^{\circ} = -5644 \text{ kJ}$$
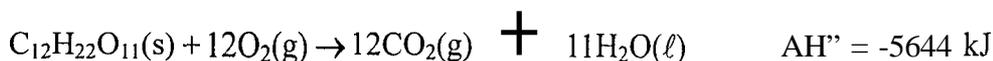
(a) Given the overall enthalpy of reaction ($\Delta H^{\circ} = -5644$ kJ), we rearrange the Hess's law summation

$$\Delta H^{\circ} = 12 \Delta H_f^{\circ}\left[CO_2(g)\right] + 11 \Delta H_f^{\circ}\left[H_2O(\ell)\right] - \Delta H_f^{\circ}\left[C_{12}H_{22}O_{11}(s)\right] - 12 \Delta H_f^{\circ}\left[O_2(g)\right]$$

to obtain the standard enthalpy of formation of $C_{12}H_{22}O_{11}(s)$:

$$\Delta H_f^{\circ}\left[C_{12}H_{22}O_{11}(s)\right] = 12 \Delta H_f^{\circ}\left[CO_2(g)\right] + 11 \Delta H_f^{\circ}\left[H_2O(\ell)\right] - 12 \Delta H_f^{\circ}\left[O_2(g)\right] - \Delta H^{\circ}$$

$$= \left(-\frac{393.5 \text{ kJ}}{\text{mol}} \times 12 \text{ mol}\right) + \left(-\frac{285.8 \text{ kJ}}{\text{mol}} \times 11 \text{ mol}\right)$$

$$- \left(\frac{0 \text{ kJ}}{\text{mol}} \times 12 \text{ mol}\right) - (-5644 \text{ kJ})$$

$$= -2221.8 \text{ kJ}$$

The result, limited to a whole number by the value $\Delta H^{\circ} = -5644$ J, is -2222 kJ mol^{-1}.

(b) Use the molar mass to convert moles into grams:

$$- \frac{2222 \text{ kJ}}{\text{mol } C_{12}H_{22}O_{11}} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.300 \text{ g } C_{12}H_{22}O_{11}} = -6.491 \text{ kJ g}^{-1} \quad \text{(formation)}$$

$$- \frac{5644 \text{ kJ}}{\text{mol } C_{12}H_{22}O_{11}} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.300 \text{ g } C_{12}H_{22}O_{11}} = -16.49 \text{ kJ g}^{-1} \quad \text{(combustion)}$$

41. See Example 13-8 in *PoC* (beginning on page R13.17) for a related sample problem.

(a) We implement a Hess's law summation to calculate the enthalpy of reaction:

$$NaCl(s) \rightarrow Na^+(aq) + Cl\text{-}(aq)$$
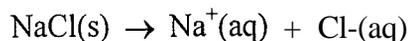
$$AH" = \Delta H_f^\circ\left[Na^+(aq)\right] + \Delta H_f^\circ\left[Cl^-(aq)\right] - \Delta H_f^\circ\left[NaCl(s)\right]$$

$$= \left(-\frac{240.1 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) + \left(-\frac{167.2 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(-\frac{411.2 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right)$$

$$= 3.9 \text{ kJ}$$

The reaction is endothermic. Heat flows from the surroundings into the system, leaving the surroundings at a lower temperature.

(b) At constant pressure, the heat outflow from n moles of water is given by the equation

$$q_P = nc_P \, AT$$

and the corresponding change in temperature is therefore

$$\Delta T = \frac{q_P}{nc_P}$$

We are already provided with the value of c_P for water, and we can calculate the number of moles from the volume and density:

$$n = 50.00 \text{ mL H}_2\text{O} \times \frac{1.00 \text{ g H}_2\text{O}}{\text{mL H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = 2.775 \text{ mol H}_2\text{O}$$

The heat fueling the endothermic dissolution of 10.00 g NaCl follows from the molar ΔH° calculated in (a). Treating water as the calorimetric system, we use a negative sign to indicate the *outflow* of heat from $H_2O(\ell)$ to NaCl(s):

$$q_P = -\frac{3.9 \text{ kJ}}{\text{mol NaCl}} \times \frac{1 \text{ mol NaCl}}{58.443 \text{ g NaCl}} \times 10.00 \text{ g NaCl} \times \frac{1000 \text{ J}}{\text{kJ}} = -667.3 \text{ J}$$

Putting everything together, we obtain the change in temperature:

$$\Delta T = \frac{q_P}{nc_P} = \frac{-667.3 \text{ J}}{(2.775 \text{ mol})(75.3 \text{ J mol}^{-1}\text{K}^{-1})} = -3.2 \text{ K} = -3.2\,^\circ\text{C}$$

Note that the two-digit accuracy of AH" likewise limits AT to two significant figures. The final temperature is 21.8°C:

$$T_2 = T_1 + \Delta T = 25.0°C - 3.2°C = 21.8°C$$

42. Another calorimetric calculation, similar to the preceding exercise.

(a) Realize that the substance $NaNO_3(aq)$ is actually a mixture of $Na^+(aq)$ and NO_3^- (aq) ions. Therefore we write

$$\Delta H_f^o\left[Na^+(aq)\right] + \Delta H_f^o\left[NO_3^-(aq)\right] = \Delta H_f^o\left[NaNO_3(aq)\right]$$

and use the available data to determine ΔH_f^o for the nitrate ion:

$$\Delta H_f^o\left[NO_3^-(aq)\right] = \Delta H_f^o\left[NaNO_3(aq)\right] - \Delta H_f^o\left[Na^+(aq)\right]$$

$$= -445.1 \ kJ\,mol^{-1} - (- 240.1 \ kJ\,mol^{-1})$$

$$= -205.0 \ kJ\,mol^{-1}$$

(b) Apply Hess's law, as demonstrated in Exercise 32:

$$AgNO_3(s) \rightarrow Ag^+(aq) + NO_3^-(aq)$$
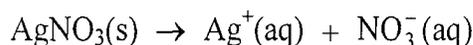
$$AH" = \Delta H_f^o\left[Ag^+(aq)\right] \text{-t } \Delta H_f^o\left[NO_3^-(aq)\right] - \Delta H_f^o\left[AgNO_3(s)\right]$$

$$= \left(\frac{105.6 \ kJ}{mol} \times 1 \ mol\right) + \left(-\frac{205.0 \ kJ}{mol} \times 1 \ mol\right) - \left(-\frac{124.4 \ kJ}{mol} \times 1 \ mol\right)$$

$$= 25.0 \ kJ$$

We have an endothermic reaction. Silver nitrate absorbs heat from the water bath, and the temperature of water in the calorimeter decreases as a result.

(c) Use the same method as in Exercise 41(b). Note that the sign of q_P is negative,

$$q_P = -\frac{25.0 \ kJ}{mol \ AgNO_3} \times \frac{1 \ mol \ AgNO_3}{169.873 \ g \ AgNO_3} \times 10.00 \ g \ AgNO_3 \times \frac{1000 \ J}{kJ} = -1471.7 \ J$$

representing an *outflow* of heat from water to the endothermic $AgNO_3$ reaction:

$$\Delta T = \frac{q_P}{n c_P}$$

$$= \frac{-1471.7 \text{ J}}{\left(200.0 \text{ mL H}_2\text{O} \times \dfrac{1.00 \text{ g H}_2\text{O}}{\text{mL H}_2\text{O}} \times \dfrac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \right) \left(\dfrac{75.3 \text{ J K}^{-1}}{\text{mol H}_2\text{O}} \right)}$$

$$= -1.76 \text{ K} = -1.76 \,^{\circ}\text{C}$$

The final temperature is 23.24°C:

$$T_2 = T_1 + \text{AT} = 25.00^{\circ}\text{C} - 1.76^{\circ}\text{C} = 23.24^{\circ}\text{C}$$