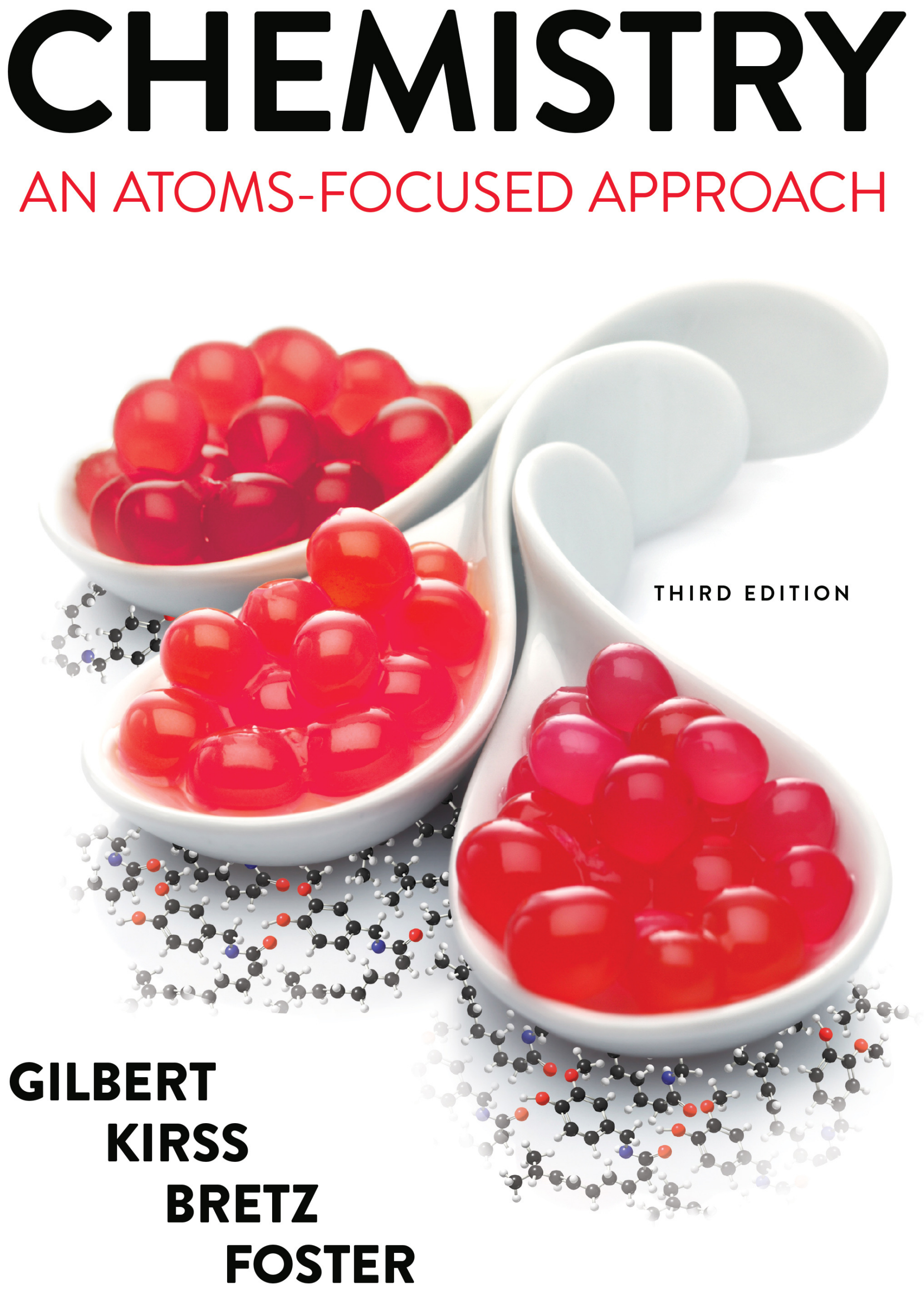


CHEMISTRY

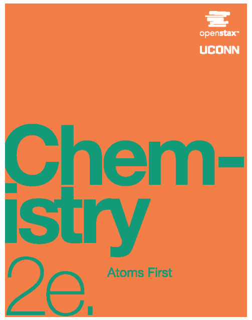
AN ATOMS-FOCUSED APPROACH

THIRD EDITION

GILBERT
KIRSS
BRETZ
FOSTER

Thermochemistry: Energy Changes in Chemical Reactions

Including material from *Atoms First*, [Openstax]

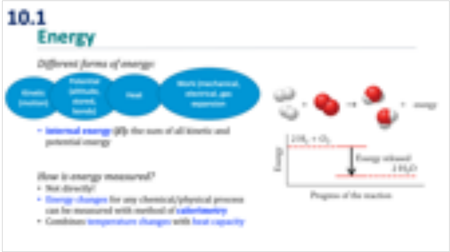


openstax
UCONN
Chem-istry 2e.
Atoms First

openstax™

Outline

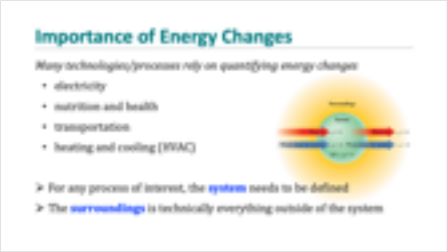
Summary


10.1
Energy

Different forms of energy:

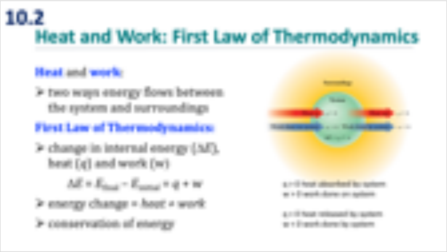
- internal energy (E): the sum of all kinetic and potential energy

How is energy measured?
- Not directly!
- Energy changes for any chemical/physical process can be measured with method of calorimetry
- Combines temperature changes with heat capacity


Importance of Energy Changes

Many technologies/processes rely on quantifying energy changes:
- electricity
- nutrition and health
- transportation
- heating and cooling (HVAC)

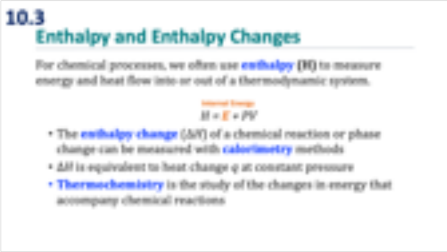
- For any process of interest, the system needs to be defined
- The surroundings is technically everything outside of the system


10.2
Heat and Work: First Law of Thermodynamics

Heat and work:
- two ways energy flows between the system and surroundings

First Law of Thermodynamics:
- change in internal energy (ΔE), heat (q) and work (w)

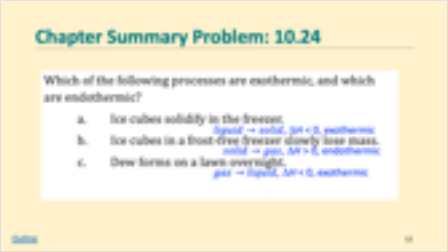
$\Delta E = E_{final} - E_{initial} = q + w$
- energy change = heat + work
- conservation of energy


10.3
Enthalpy and Enthalpy Changes

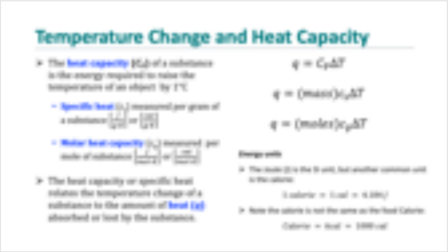
For chemical processes, we often use enthalpy (H) to measure energy and heat flow into or out of a thermodynamic system.

$H = E + PV$

- The enthalpy change (ΔH) of a chemical reaction or phase change can be measured with calorimetry methods
- ΔH is equivalent to heat change q at constant pressure
- Thermochemistry is the study of the changes in energy that accompany chemical reactions


Chapter Summary Problem: 10.24

Which of the following processes are exothermic, and which are endothermic?
a. Ice cubes solidify in the freezer. liquid → solid, $\Delta H < 0$, exothermic
b. Ice cubes in a frost-free freezer slowly lose mass. solid → gas, $\Delta H > 0$, endothermic
c. Dew forms on a lawn overnight. gas → liquid, $\Delta H < 0$, exothermic


Temperature Change and Heat Capacity

- The heat capacity (C_s) of a substance is the energy required to raise the temperature of an object by 1°C

$q = C_s\Delta T$

$q = (mass)c_s\Delta T$

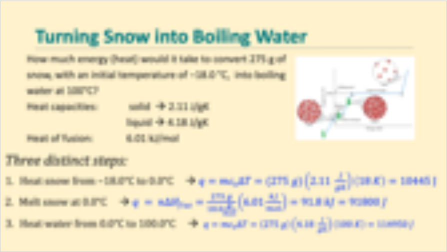
$q = (moles)c_m\Delta T$

1 calorie = 1 cal = 4.184 J

Calorie = kcal = 1000 cal


Tabulated Heat Capacities

Both of these heat capacities are intensive properties and depend on the physical state of the substance

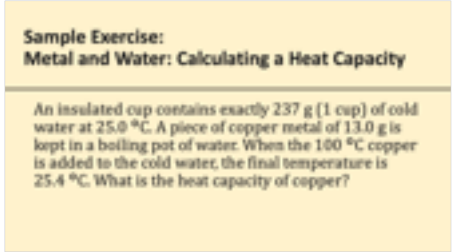

Turning Snow into Boiling Water

How much energy (heat) would it take to convert 275 g of snow, with an initial temperature of −18.0 °C, into boiling water at 100°C?

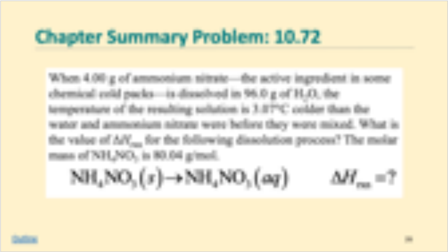
Heat capacities: solid → 2.11 J/gK; liquid → 4.18 J/gK

Heat of fusion: 6.01 kJ/mol

Three distinct steps:
1. Heat snow from −18.0°C to 0.0°C → $q = mc_s\Delta T$ = 10445 J
2. Melt snow at 0.0°C → $q = n\Delta H_{fus}$ = 91.8 kJ = 91800 J
3. Heat water from 0.0°C to 100.0°C → $q = mc_s\Delta T$ = 114950 J

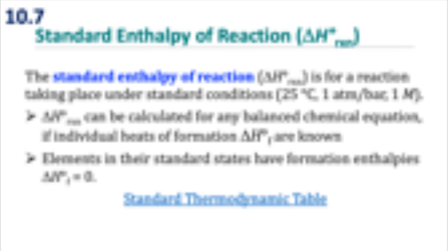

Sample Exercise:
Metal and Water: Calculating a Heat Capacity

An insulated cup contains exactly 237 g (1 cup) of cold water at 25.0 °C. A piece of copper metal of 13.0 g is kept in a boiling pot of water. When the 100 °C copper is added to the cold water, the final temperature is 25.4 °C. What is the heat capacity of copper?


Chapter Summary Problem: 10.72

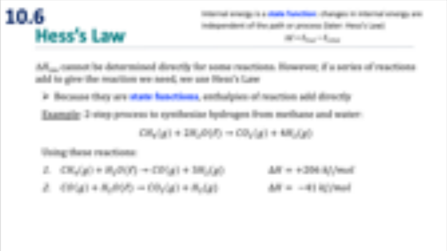
When 4.00 g of ammonium nitrate—the active ingredient in some chemical cold packs—is dissolved in 96.0 g of H_2O, the temperature of the resulting solution is 3.07°C colder than the water and ammonium nitrate were before they were mixed. What is the value of ΔH_{rxn} for the following dissolution process? The molar mass of NH_4NO_3 is 80.04 g/mol.

$NH_4NO_3(s) \rightarrow NH_4NO_3(aq) \qquad \Delta H_{rxn} = ?$


10.7
Standard Enthalpy of Reaction (ΔH°_{rxn})

The standard enthalpy of reaction (ΔH°_{rxn}) is for a reaction taking place under standard conditions (25 °C, 1 atm/bar, 1 M).
- ΔH°_{rxn} can be calculated for any balanced chemical equation, if individual heats of formation ΔH°_f are known
- Elements in their standard states have formation enthalpies $\Delta H^\circ_f = 0$.

Standard Thermodynamic Table


10.6
Hess's Law

Internal energy is a state function: changes in internal energy are independent of the path or process (later: Hess's Law)

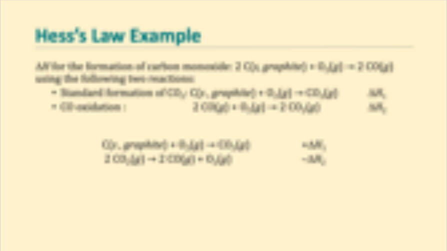
$\Delta E = E_{final} - E_{initial}$

ΔH_{rxn} cannot be determined directly for some reactions. However, if a series of reactions add to give the reaction we need, we use Hess's Law
- Because they are state functions, enthalpies of reaction add directly

Example: 2-step process to synthesize hydrogen from methane and water:

$CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 4H_2(g)$

Using these reactions:
1. $CH_4(g) + H_2O(l) \rightarrow CO(g) + 3H_2(g) \qquad \Delta H = +206$ kJ/mol
2. $CO(g) + H_2O(l) \rightarrow CO_2(g) + H_2(g) \qquad \Delta H = -41$ kJ/mol


Hess's Law Example

ΔH for the formation of carbon monoxide: $2\,C(s, graphite) + O_2(g) \rightarrow 2\,CO(g)$ using the following two reactions:
- Standard formation of CO_2: $C(s, graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_1$
- CO oxidation: $2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g) \qquad \Delta H_2$

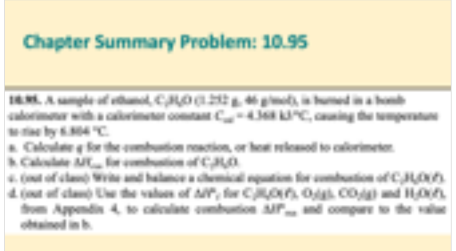
$C(s, graphite) + O_2(g) \rightarrow CO_2(g) \qquad +\Delta H_1$

$2\,CO_2(g) \rightarrow 2\,CO(g) + O_2(g) \qquad -\Delta H_2$

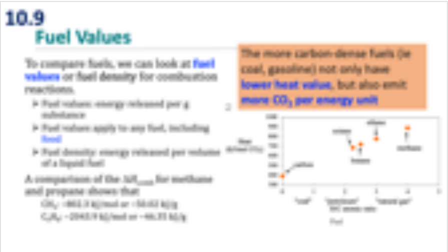

10.5
Calorimetry

The methods of calorimetry are for experimental determination of changes in enthalpy (or internal energy):
- phase changes
- chemical reactions

In order to use a calorimeter, we first standardize it to find how much heat the instrument, or reaction surroundings, absorbs. Standardization yields a calorimeter constant, or heat capacity of the calorimeter C_{cal}.


Chapter Summary Problem: 10.95

10.95. A sample of ethanol, C_2H_6O (1.252 g, 46 g/mol), is burned in a bomb calorimeter with a calorimeter constant C_{cal} = 4.368 kJ/°C, causing the temperature to rise by 6.804 °C.
a. Calculate q for the combustion reaction, or heat released to calorimeter.
b. Calculate ΔH_{rxn} for combustion of C_2H_6O.
c. (out of class) Write and balance a chemical equation for combustion of $C_2H_6O(l)$.
d. (out of class) Use the values of ΔH°_f for $C_2H_6O(l)$, $O_2(g)$, $CO_2(g)$ and $H_2O(l)$, from Appendix 4, to calculate combustion ΔH°_{rxn} and compare to the value obtained in b.


10.9
Fuel Values

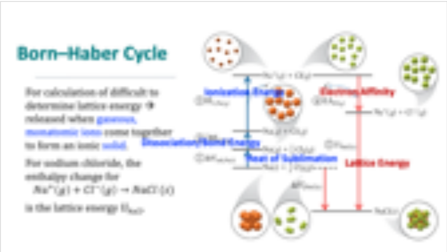
To compare fuels, we can look at fuel values or fuel density for combustion reactions.
- Fuel values: energy released per g of substance
- Fuel values apply to any fuel, including food
- Fuel density: energy released per volume of a liquid fuel

A comparison of the ΔH_{comb} for methane and propane shows that:

CH_4: −802.3 kJ/mol or −50.02 kJ/g

C_3H_8: −2043.9 kJ/mol or −46.35 kJ/g

The more carbon-dense fuels (ie coal, gasoline) not only have lower heat value, but also emit more CO_2 per energy unit


Born–Haber Cycle

For calculation of difficult to determine lattice energy → released when gaseous, monatomic ions come together to form an ionic solid.

For sodium chloride, the enthalpy change for

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

is the lattice energy U_{NaCl}


REMINDERS

Reminders:
- Final Exam: Tuesday, April 30, 8:00-10:30 AM
- Study Session: Tuesday, April 23, 1:30-3:00 PM, Sims 112
- Course Evaluations: no later than T Apr 23, 11:59 PM
  - you will need your Winthrop ID "W12345678"

CRN 21710

10.1

Energy

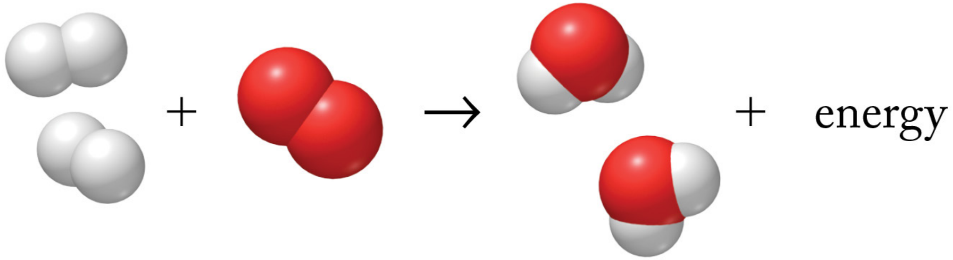
Different forms of energy:

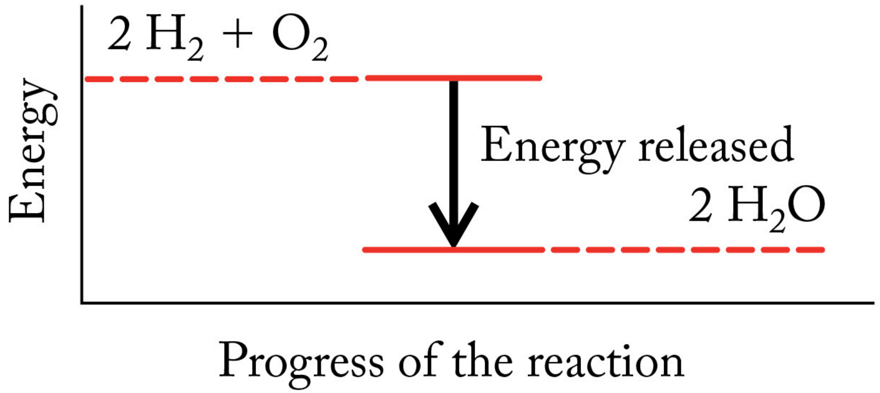
- Kinetic (motion)
- Potential (altitude, stored, bonds)
- Heat
- Work (mechanical, electrical, gas expansion

- **internal energy** (***E***)**:** the sum of all kinetic and potential energy

How is energy measured?

- Not directly!
- Energy changes for any chemical/physical process can be measured with method of **calorimetry**
- Combines temperature changes with heat capacity

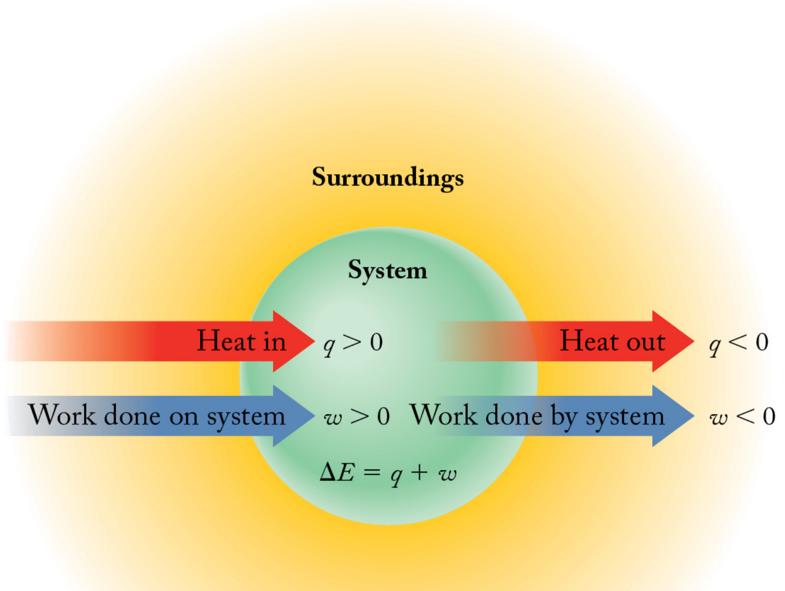




Importance of Energy Changes

Many technologies/processes rely on quantifying energy changes

- electricity
- nutrition and health
- transportation
- heating and cooling (HVAC)

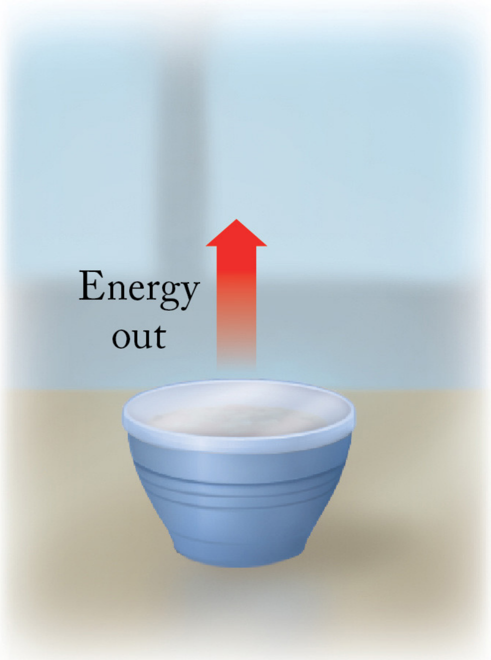


- For any process of interest, the **system** needs to be defined
- The **surroundings** is technically everything outside of the system

Thermodynamic Systems

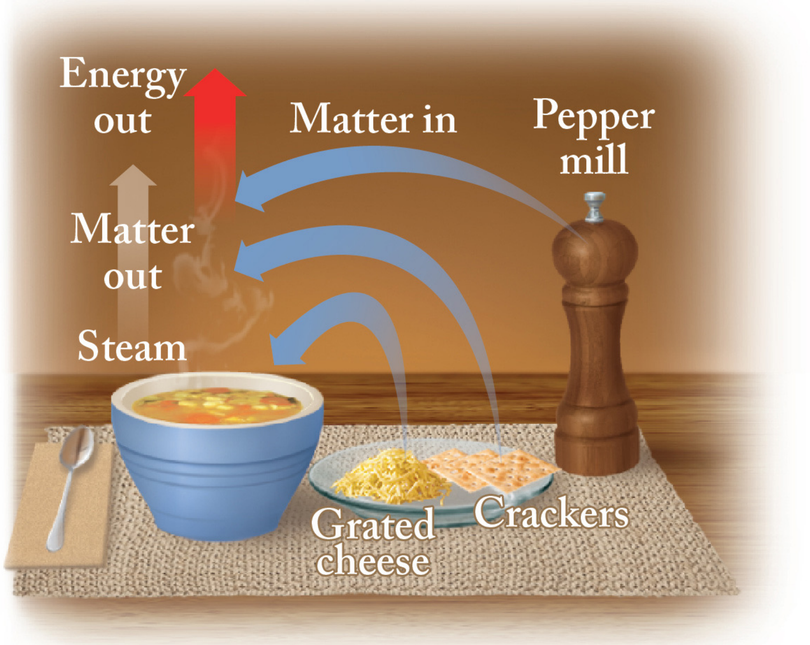
Isolated system: A thermos bottle containing hot soup with the lid screwed on tightly

→ No matter or energy can be exchanged



Closed system: A cup of hot soup with a lid

→ Energy can be exchanged, but not matter



Open system: An open cup of hot soup

→ Energy and matter can be exchanged

10.2

Heat and Work: First Law of Thermodynamics

Heat and **work**:

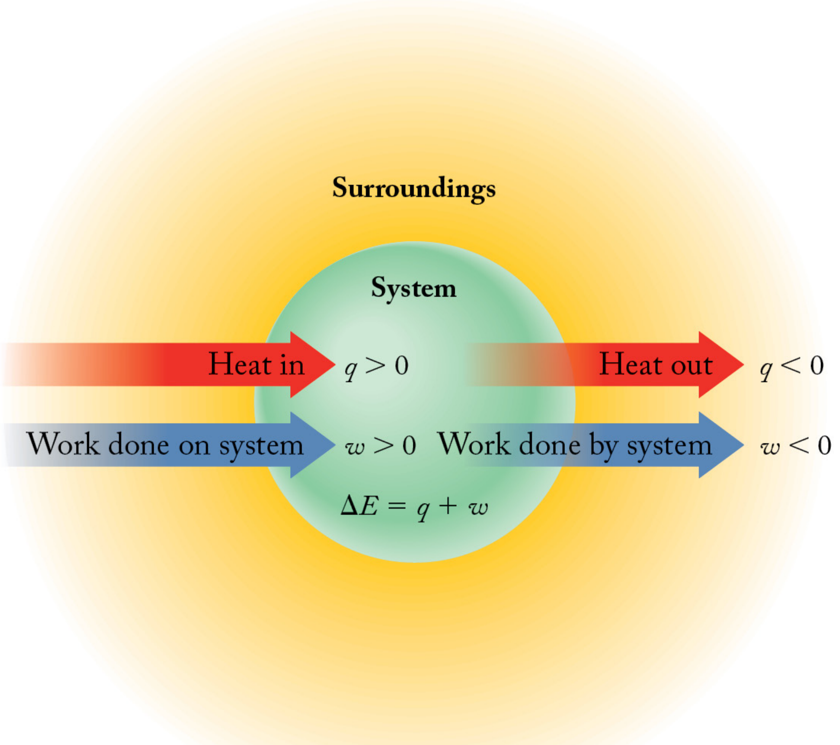
- two ways energy flows between the system and surroundings

First Law of Thermodynamics:

- change in internal energy (ΔE), heat (q) and work (w)

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = q + w$$

- energy change = *heat + work*
- conservation of energy



q > 0 heat absorbed by system
w > 0 work done on system

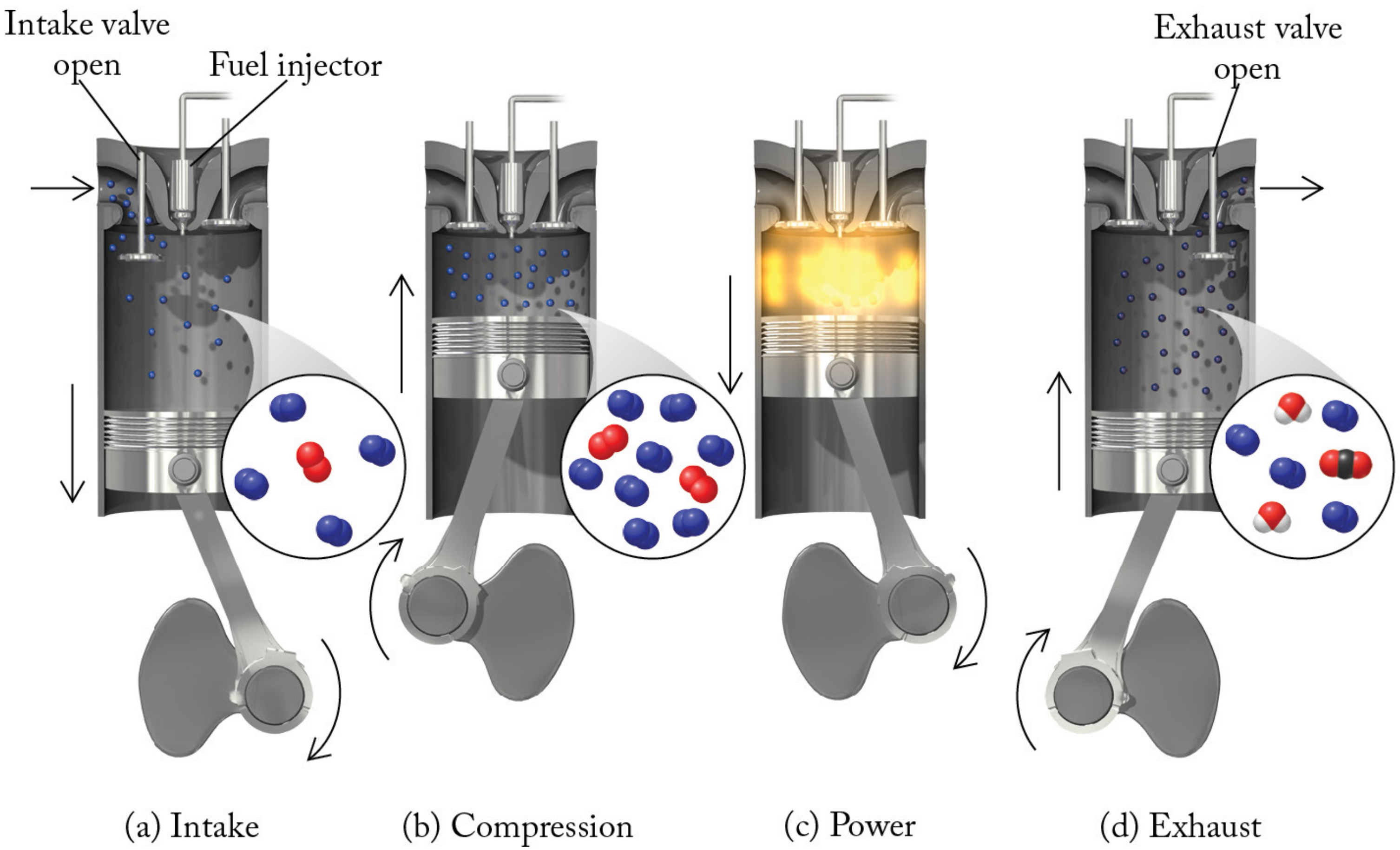
q < 0 heat released by system
w < 0 work done by system

Pressure-Volume Work ~ Gases

Work for gases that expand or get compressed under external pressure (*P*):

$$w = -P\Delta V$$

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



Expansion:	w < 0 (gas does work)
Compression:	w > 0 (work done on the gas)

10.3

Enthalpy and Enthalpy Changes

For chemical processes, we often use **enthalpy** **(H)** to measure energy and heat flow into or out of a thermodynamic system.

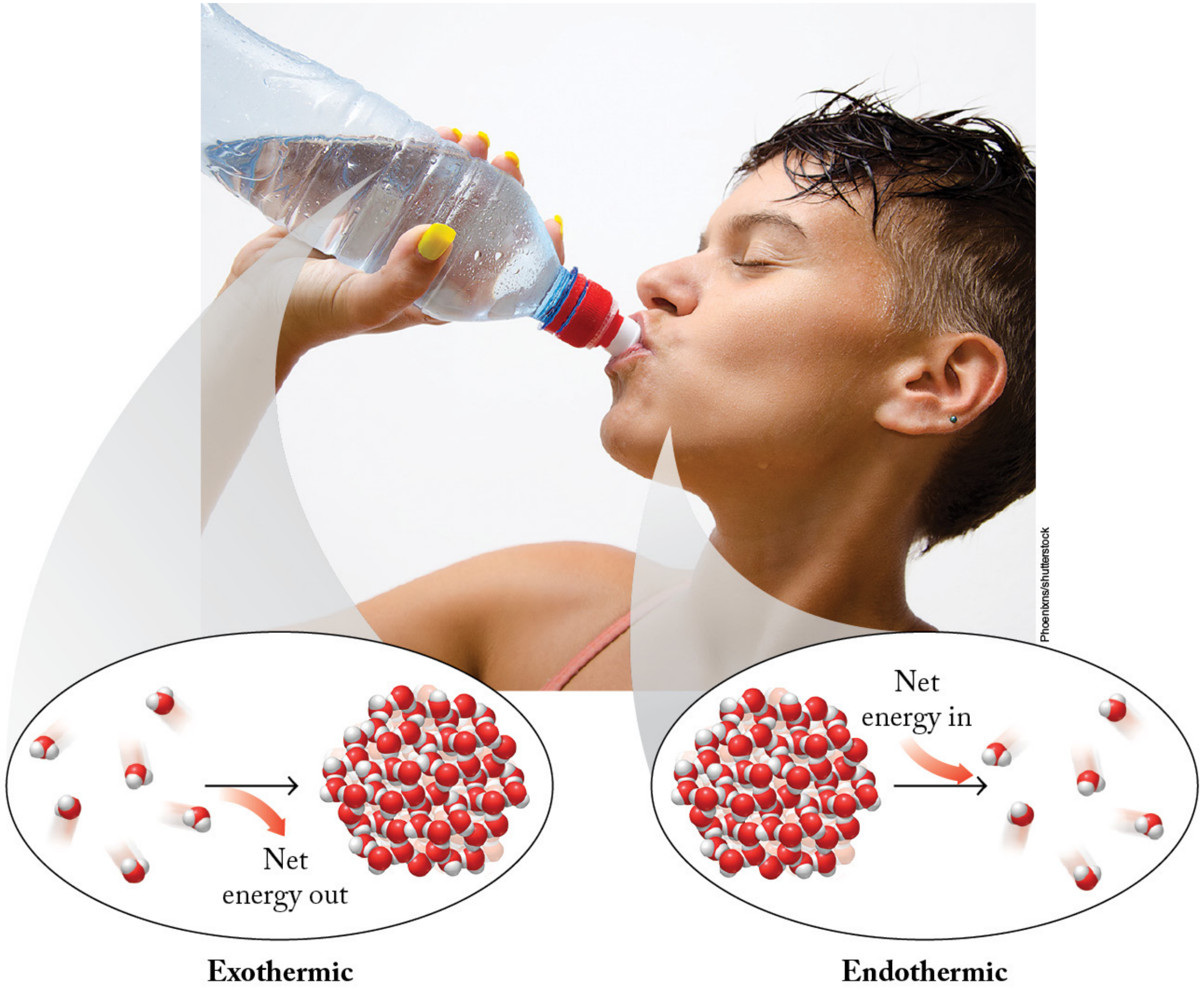
$$H = \overset{\text{Internal Energy}}{\boldsymbol{E}} + PV$$

- The **enthalpy change** (ΔH) of a chemical reaction or phase change can be measured with **calorimetry** methods
- ΔH is equivalent to heat change q at constant pressure
- **Thermochemistry** is the study of the changes in energy that accompany chemical reactions

Exothermic and Endothermic Processes

Reactions are classified as **exothermic** or **endothermic** according to heat flow:

- **Exothermic**: Energy released from system to surroundings
  - **$\Delta H < 0$ (q < 0)**
  - *surroundings gets hot*
- **Endothermic**: Energy absorbed into a system from surroundings
  - **$\Delta H > 0$ (q > 0)**
  - *surroundings gets cold*



Phase Change Enthalpies

- Phase change enthalpies are for changes in state:
  - **Enthalpy of fusion** (ΔH_{fus}): solid to liquid conversion at the freezing point
  - **Enthalpy of vaporization** (ΔH_{vap}): liquid to vapor conversion at the boiling point
- Enthalpy values are reported per mole (or g) of substance, and

$$q = (moles)\Delta H \quad [\text{or } (mass)\Delta H]$$

- Fusion and vaporization (and $s \rightarrow g$ **sublimation**) are inherently endothermic, absorbing heat

TABLE 10.2 Enthalpies of Fusion and Vaporization

Compound and Molecular Structure	$\mathcal{M}$ (g/mol)	ΔH_{fus} (kJ/mol)	ΔH_{vap} (kJ/mol)
Methane	16.04	0.94	8.2
Ethane	30.07	2.86	14.7
Propane	44.10	3.53	15.7
Butane	58.12	4.66	21.0
Methanol	32.04	3.18	35.3
Ethanol	46.07	5.02	38.6
Acetone	58.08	5.69	31.3
Ammonia	17.03	5.65	23.4
Water	18.02	6.01	44.0 at 25°C 43.5 at 40°C 42.5 at 60°C 41.6 at 80°C 40.7 at 100°C

Chapter Summary Problem: 10.24

Which of the following processes are exothermic, and which are endothermic?

a. Ice cubes solidify in the freezer.

$liquid \rightarrow solid, \Delta H < 0$, exothermic

b. Ice cubes in a frost-free freezer slowly lose mass.

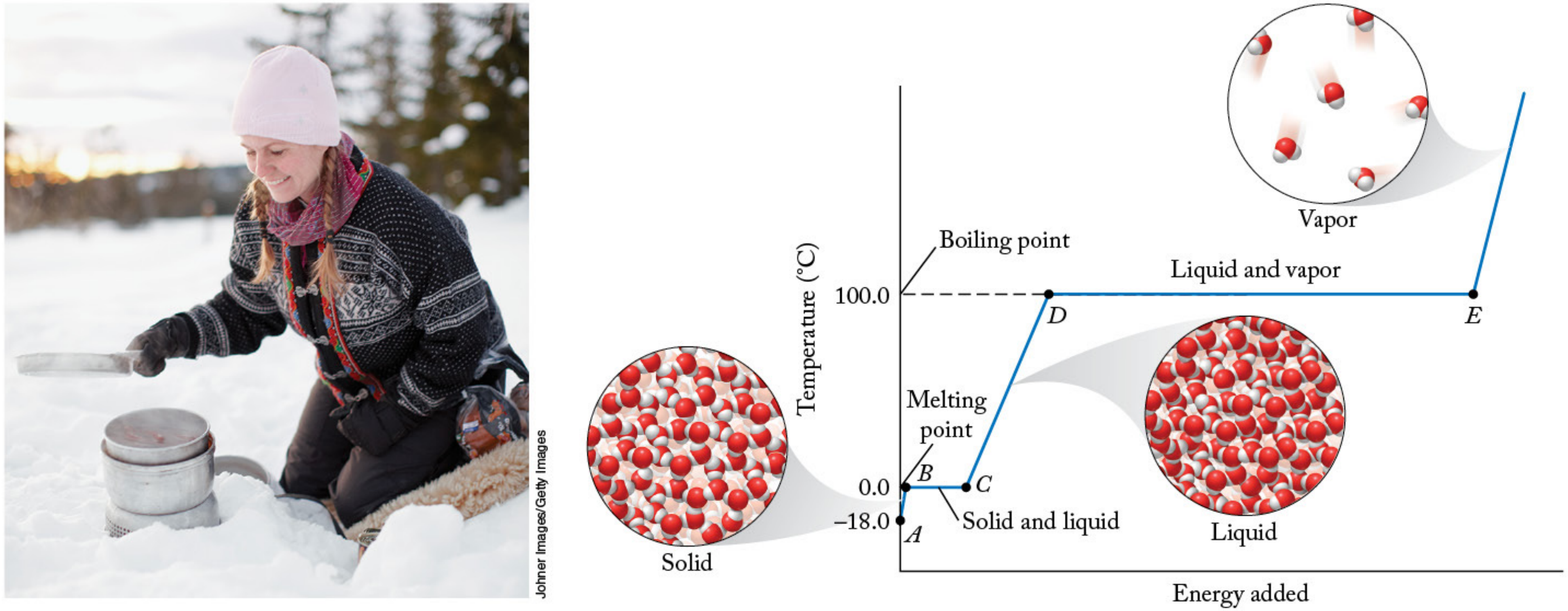
$solid \rightarrow gas, \Delta H > 0$, endothermic

c. Dew forms on a lawn overnight.

$gas \rightarrow liquid, \Delta H < 0$, exothermic

10.4
Heating Curves

- Below are changes in temperature and physical states as water goes from snow at −18°C into boiling water.
- During a phase transition, temperature is constant



Johner Images/Getty Images

(a) (b)

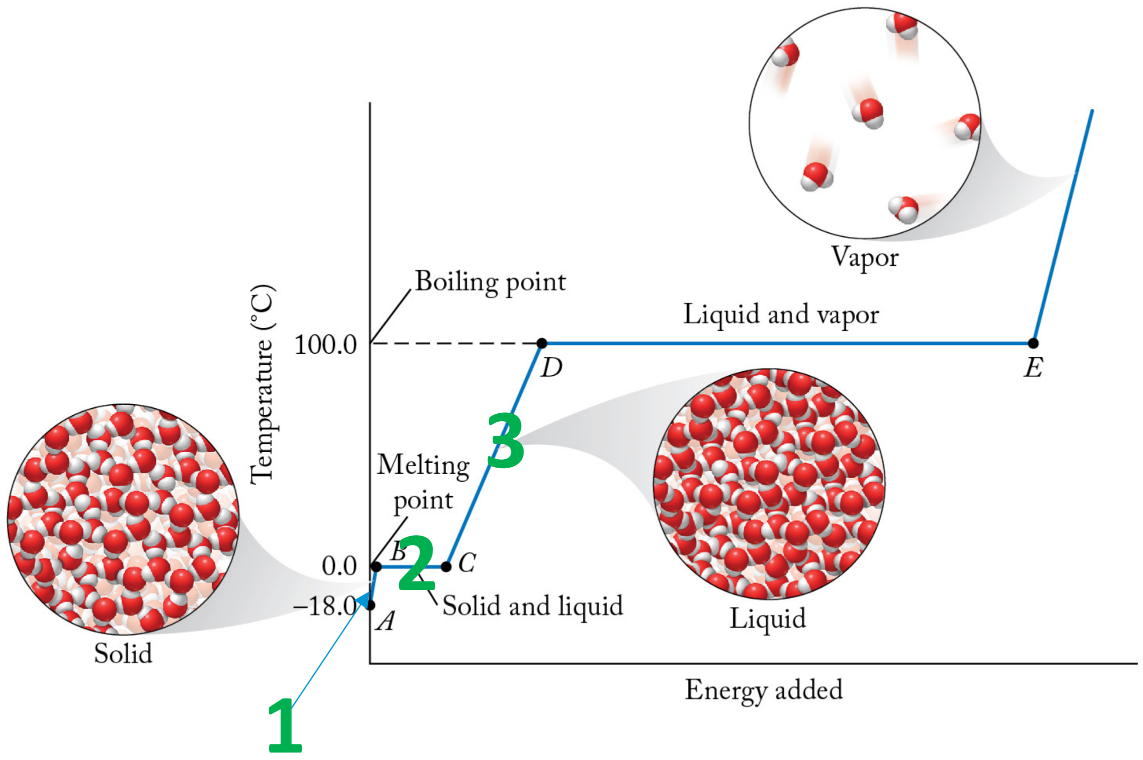
Turning Snow into Boiling Water

How much energy (heat) would it take to convert 275 g of snow, with an initial temperature of −18.0 °C, into boiling water at 100°C?

Three distinct steps:

1. Heat snow from −18.0°C to 0.0°C
2. Melt snow at 0.0°C
3. Heat water from 0.0°C to 100.0°C

- How can each of these heats be calculated?



Temperature Change and Heat Capacity

- The **heat capacity** **(C_P)** of a substance is the energy required to raise the temperature of an object by 1°C
  - **Specific heat** (c_s) measured per gram of a substance $\left[\frac{J}{g \cdot K}\right]$ or $\left[\frac{cal}{g \cdot K}\right]$
  - **Molar heat capacity** (c_p) measured per mole of substance $\left[\frac{J}{mol \cdot K}\right]$ or $\left[\frac{cal}{mol \cdot K}\right]$
- The heat capacity or specific heat relates the temperature change of a substance to the amount of **heat (q)** absorbed or lost by the substance.

$$q = C_\mathrm{P}\Delta T$$

$$q = (mass)c_\mathrm{s}\Delta T$$

$$q = (moles)c_\mathrm{p}\Delta T$$

Energy units

- The Joule (J) is the SI unit, but another common unit is the calorie:

$$1\ calorie = 1\ cal = 4.184\ J$$

- Note the calorie is not the same as the food Calorie:

$$Calorie = kcal = 1000\ cal$$

Tabulated Heat Capacities

Both of these heat capacities are intensive properties and depend on the physical state of the substance

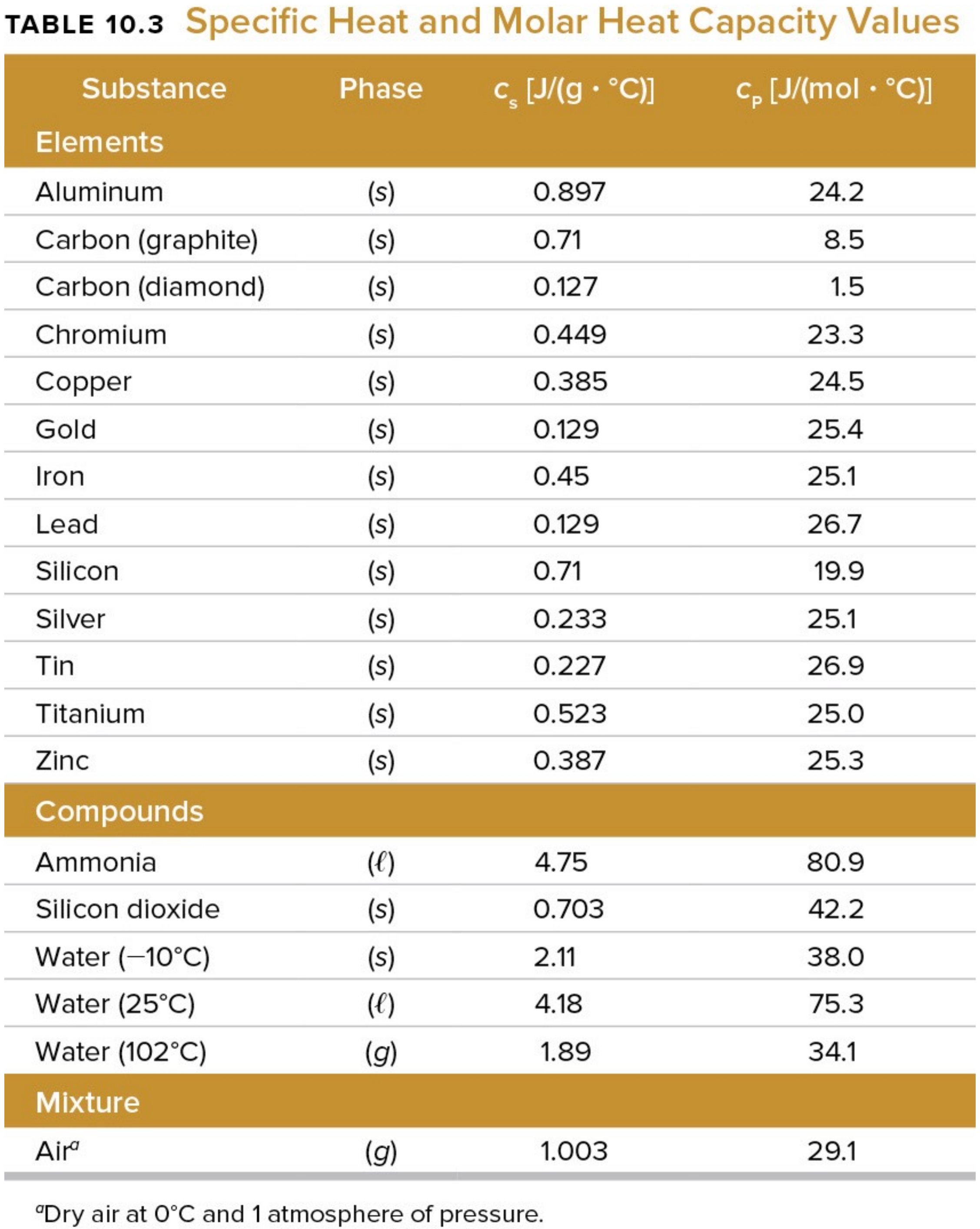


TABLE 10.3 Specific Heat and Molar Heat Capacity Values

Substance	Phase	c_s [J/(g · °C)]	c_P [J/(mol · °C)]
Elements			
Aluminum	(*s*)	0.897	24.2
Carbon (graphite)	(*s*)	0.71	8.5
Carbon (diamond)	(*s*)	0.127	1.5
Chromium	(*s*)	0.449	23.3
Copper	(*s*)	0.385	24.5
Gold	(*s*)	0.129	25.4
Iron	(*s*)	0.45	25.1
Lead	(*s*)	0.129	26.7
Silicon	(*s*)	0.71	19.9
Silver	(*s*)	0.233	25.1
Tin	(*s*)	0.227	26.9
Titanium	(*s*)	0.523	25.0
Zinc	(*s*)	0.387	25.3
Compounds			
Ammonia	(ℓ)	4.75	80.9
Silicon dioxide	(*s*)	0.703	42.2
Water (−10°C)	(*s*)	2.11	38.0
Water (25°C)	(ℓ)	4.18	75.3
Water (102°C)	(*g*)	1.89	34.1
Mixture			
Air[a]	(*g*)	1.003	29.1

[a] Dry air at 0°C and 1 atmosphere of pressure.

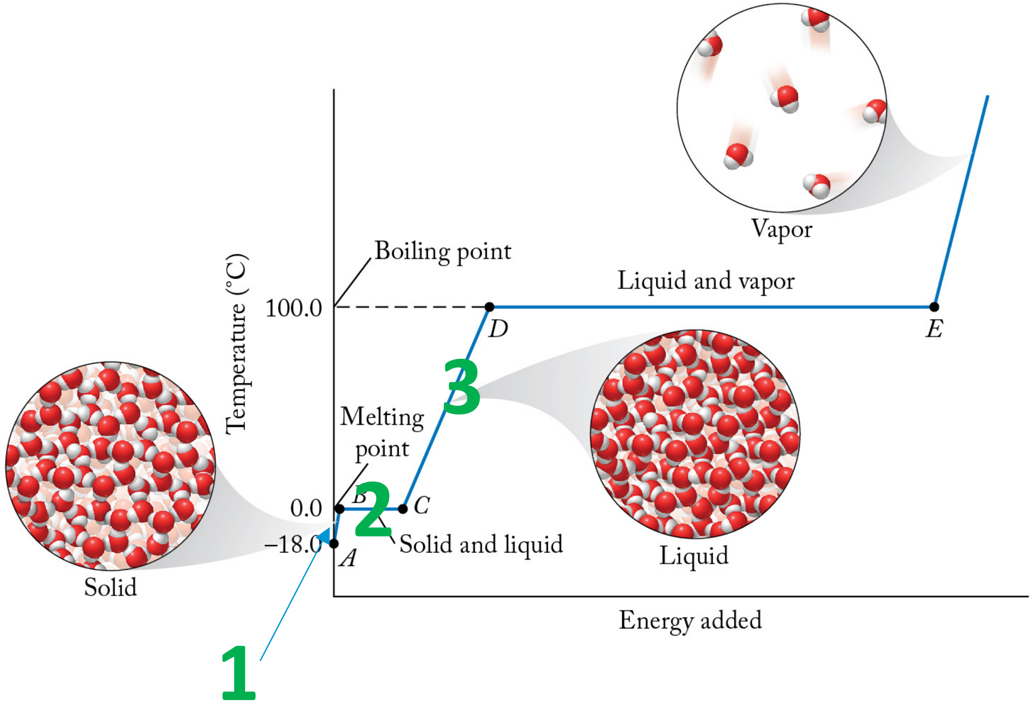
Turning Snow into Boiling Water

How much energy (heat) would it take to convert 275 g of snow, with an initial temperature of −18.0 °C, into boiling water at 100°C?

Three distinct steps:

1. Heat snow from −18.0°C to 0.0°C
2. Melt snow at 0.0°C
3. Heat water from 0.0°C to 100.0°C

- ➢ How can each of these heats be calculated?



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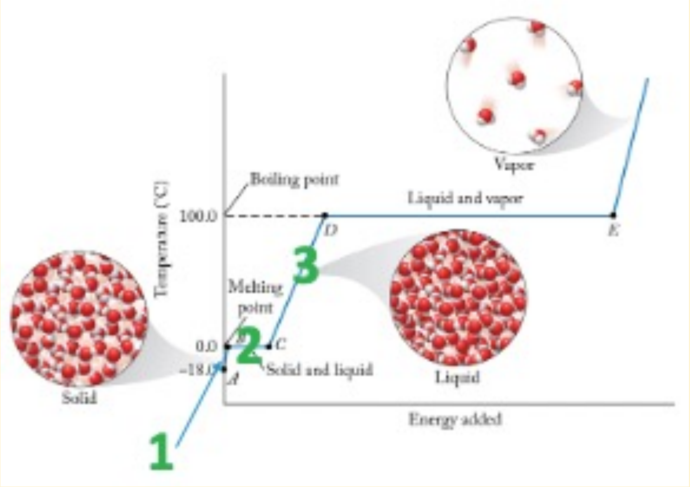
Heat capacities: solid → 2.11 J/gK
liquid → 4.18 J/gK
Heat of fusion: 6.01 kJ/mol



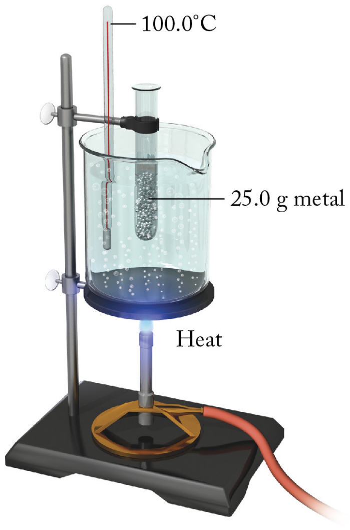
Three distinct steps:

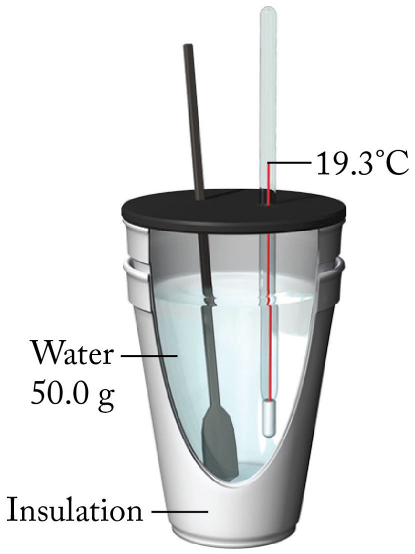
1. Heat snow from −18.0°C to 0.0°C → $q = mc_s\Delta T = (275\ g)\left(2.11\ \frac{J}{gK}\right)(18\ K) = 10445$ J
2. Melt snow at 0.0°C → $q = n\Delta H_{fus} = \frac{275\ g}{18.0\frac{g}{mol}}\left(6.01\ \frac{kJ}{mol}\right) = 91.8\ kJ = 91800\ J$
3. Heat water from 0.0°C to 100.0°C → $q = mc_s\Delta T = (275\ g)\left(4.18\ \frac{J}{gK}\right)(100\ K) = 114950\ J$

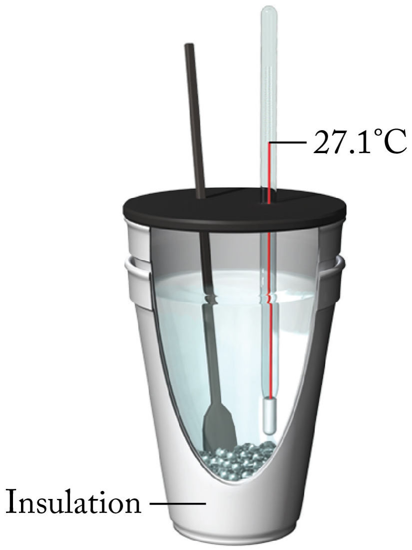
Determining the Specific Heat of a Metal

The specific heat of a metal can be determined by:

1. Heating a known mass of metal (25.0 g) to a particular temperature (100°C).
2. Transferring the metal into an insulated container holding a measured amount of water (50.0 g) at a particular temperature (19.3°C).
3. Allowing the mixture of metal and water to reach its maximum temperature. At this point, the heat lost by the metal will be equal to the heat gained by the water.







$$q_{\text{water}} = -q_{\text{metal}}$$

$$q = mc_s\Delta T$$

Sample Exercise:
Metal and Water: Calculating a Heat Capacity

An insulated cup contains exactly 237 g (1 cup) of cold water at 25.0 °C. A piece of copper metal of 13.0 g is kept in a boiling pot of water. When the 100 °C copper is added to the cold water, the final temperature is 25.4 °C. What is the heat capacity of copper?

Sample Exercise:
Metal and Water: Calculating a Heat Capacity

Solve An insulated cup contains exactly 237 g (1 cup) of cold water at 25.0 °C. A piece of copper metal of 13.0 g is kept in a boiling pot of water. When the 100 °C copper is added to the cold water, the final temperature is 25.4 °C. What is the heat capacity of copper?

What's happening as far as heat flow? After mixing the hot copper and cold water:

- Copper sample **loses heat** to decrease temperature from 100.0 to 25.4 °C.
- The water **gains heat** to increase temperature from 25.0 to 25.4 °C. (heat capacity $= 4.18 \frac{\text{J}}{\text{g}\cdot{}^\circ\text{C}}$)

$$q(Cu) = (mass)c_s\Delta T \rightarrow c_s = \frac{q(Cu)}{(mass)\Delta T} = \frac{q(Cu)}{(13.0\ g)(25.4-100.0)^\circ C} = \frac{q(Cu)}{-970\ g^\circ C}$$

$$q(H_2O) = (mass)c_s\Delta T \rightarrow q(H_2O) = (237\ g)\left(4.18 \frac{J}{g\cdot{}^\circ C}\right)(25.4-25.0)^\circ C = 396\ J$$

Sample Exercise:
Metal and Water: Calculating a Heat Capacity

Solve

An insulated cup contains exactly 237 g (1 cup) of cold water at 25.0 °C. A piece of copper metal of 13.0 g is kept in a boiling pot of water. When the 100 °C copper is added to the cold water, the final temperature is 25.4 °C. What is the heat capacity of copper?

- The heat is transferred from the copper to the water, and importantly,

$$q(Cu) = -q(H_2O)$$

- This is true for <u>any</u> set of system/surroundings: **(heat absorbed) = –(heat released)**

$$q(Cu) = -q(H_2O) = -396\,J$$

$$c_s = \frac{q(Cu)}{-970\ g°C} = \frac{-396\,J}{-970\ g°C} = 0.4\,\frac{J}{g°\mathrm{C}}$$

Enthalpy of Formation

- **Standard enthalpy of formation** ($\Delta H°_{\text{f}}$) is the enthalpy change that takes place at a constant pressure (1 atm/bar) when one mole of a substance is formed from elements in their standard states.
- The **standard state** is the phase (s, ℓ, g) and chemical formula of the element at 25 °C and 1 atm.

➢ For NO(*g*), elements are diatomic nitrogen and diatomic oxygen:

$$\longrightarrow \text{NO}(g)$$

Enthalpy of Formation

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- The **standard state** is the phase (s, ℓ, g) and chemical formula of the element at 25 °C and 1 atm.

➢ For NO(*g*), elements are diatomic nitrogen and diatomic oxygen:

$$N_2(g) + O_2(g) \longrightarrow NO(g)$$

➢ Balance, then ensure 1 mol of product:

$$\tfrac{1}{2} N_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow NO(g) \quad \Delta H°_f = 90.3\ \text{kJ}$$

Enthalpies of Formation: Values

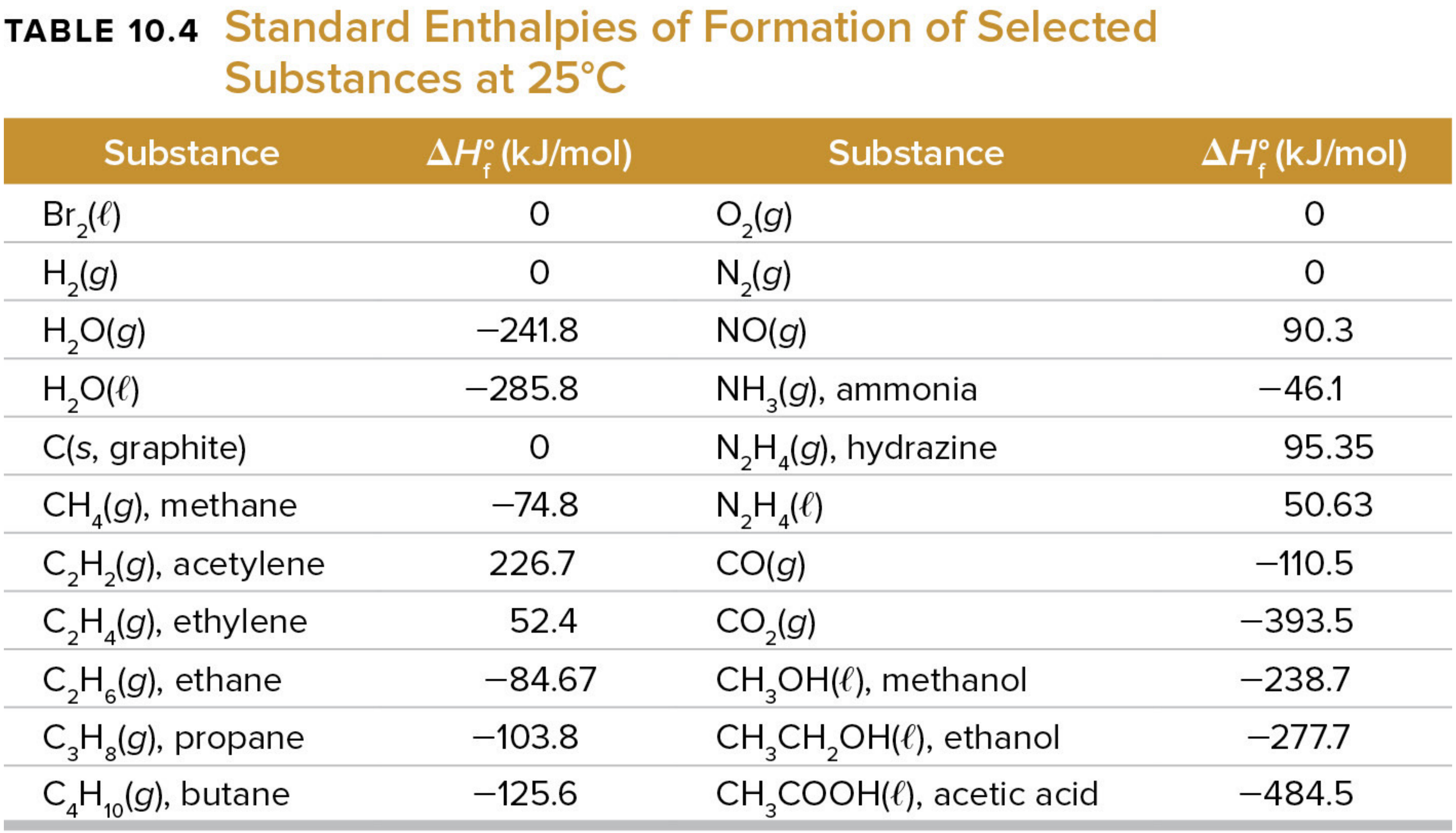

TABLE 10.4 Standard Enthalpies of Formation of Selected Substances at 25°C

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
$Br_2(\ell)$	0	$O_2(g)$	0
$H_2(g)$	0	$N_2(g)$	0
$H_2O(g)$	−241.8	$NO(g)$	90.3
$H_2O(\ell)$	−285.8	$NH_3(g)$, ammonia	−46.1
C(*s*, graphite)	0	$N_2H_4(g)$, hydrazine	95.35
$CH_4(g)$, methane	−74.8	$N_2H_4(\ell)$	50.63
$C_2H_2(g)$, acetylene	226.7	$CO(g)$	−110.5
$C_2H_4(g)$, ethylene	52.4	$CO_2(g)$	−393.5
$C_2H_6(g)$, ethane	−84.67	$CH_3OH(\ell)$, methanol	−238.7
$C_3H_8(g)$, propane	−103.8	$CH_3CH_2OH(\ell)$, ethanol	−277.7
$C_4H_{10}(g)$, butane	−125.6	$CH_3COOH(\ell)$, acetic acid	−484.5

Chapter Summary Problem: 10.72

When 4.00 g of ammonium nitrate—the active ingredient in some chemical cold packs—is dissolved in 96.0 g of H_2O, the temperature of the resulting solution is 3.07°C colder than the water and ammonium nitrate were before they were mixed. What is the value of ΔH_{rxn} for the following dissolution process? The molar mass of NH_4NO_3 is 80.04 g/mol.

$$NH_4NO_3\left(s\right)\rightarrow NH_4NO_3\left(aq\right) \qquad \Delta H_{\text{rxn}} = ?$$

Outline

10.7

Standard Enthalpy of Reaction ($\Delta H°_{rxn}$)

The **standard enthalpy of reaction** ($\Delta H°_{rxn}$) is for a reaction taking place under standard conditions (25 °C, 1 atm/bar, 1 *M*).

- $\Delta H°_{rxn}$ can be calculated for any balanced chemical equation, if individual heats of formation $\Delta H°_f$ are known
- Elements in their standard states have formation enthalpies $\Delta H°_f = 0$.

Standard Thermodynamic Table

Standard Enthalpy of Reaction (ΔH°_{rxn})

$$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H^\circ_{rxn} = \ ?$$

ΔH°_f (kJ/mol)	–365.6	–132.5	–206.6	(values from tables)

$$\Delta H^\circ_{rxn} = \{product\ \Delta H^\circ_f\} - \{reactant\ \Delta H^\circ_f\}$$

$$= \{(1)(-132.5) + (1)(-206.6)\} - \{(1)(-365.6)\}$$

$$= +26.5\ kJ/mol$$

- The chemical coefficients are included
- This reaction is endothermic

Standard Enthalpy of Reaction

Standard enthalpies of reaction can be used to determine the $\Delta H°_{\text{rxn}}$ for the industrial process that is used to form hydrogen gas from methane and steam.

$$\mathrm{CH_4}(g) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{CO_2}(g) + 4\,\mathrm{H_2}(g) \qquad \Delta H°_{\text{rxn}} = ?$$

$\Delta H°_{\text{f}}$ (kJ/mol) –74.6 –241.8. –393.5 0

multiplied by chemical coefficients

$$\Delta H°_{\text{rxn}} = \{product\ \Delta H°_{\text{f}}\} - \{reactant\ \Delta H°_{\text{f}}\}$$

$$= \{(1)(-393.5) + (4)(0)\} - \{(1)(-74.6) + (2)(-241.8)\}$$

$$= +164.7\ kJ/mol$$

Enthalpies of Reaction

The general expression explicitly includes the coefficients *n* from the balanced equation:

$$\Delta H^\circ_{\mathrm{rxn}} = \sum n_{\mathrm{products}}\, \Delta H^\circ_{\mathrm{f,products}} - \sum n_{\mathrm{reactants}}\, \Delta H^\circ_{\mathrm{f,reactants}}$$

10.6

Hess's Law

Internal energy is a **state function**: changes in internal energy are independent of the path or process (later: Hess's Law)

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

ΔH_{rxn} cannot be determined directly for some reactions. However, if a series of reactions add to give the reaction we need, we use Hess's Law

- Because they are **state functions**, enthalpies of reaction add directly

Example: 2-step process to synthesize hydrogen from methane and water:

$$CH_4(g) + 2H_2O(\ell) \rightarrow CO_2(g) + 4H_2(g)$$

Using these reactions:

1. $CH_4(g) + H_2O(\ell) \rightarrow CO(g) + 3H_2(g)$ $\quad \Delta H = +206\ kJ/mol$
2. $CO(g) + H_2O(\ell) \rightarrow CO_2(g) + H_2(g)$ $\quad \Delta H = -41\ kJ/mol$

10.6

Hess's Law

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Example: 2-step process to synthesize hydrogen from methane and water:

$$CH_4(g) + 2H_2O(\ell) \rightarrow CO_2(g) + 4H_2(g)$$

1. $CH_4(g) + H_2O(\ell) \rightarrow \cancel{CO(g)} + 3H_2(g)$ $\Delta H = +206\ kJ/mol$
2. $\cancel{CO(g)} + H_2O(\ell) \rightarrow CO_2(g) + H_2(g)$ $\Delta H = -41\ kJ/mol$

Adding these reactions gives the equation (and enthalpy change) we need. For the net equation, enthalpies of 2 steps add to give the total enthalpy change.

$$CH_4(g) + 2H_2O(\ell) \rightarrow CO_2(g) + 4H_2(g) \qquad \Delta H = +165\ kJ/mol$$

Hess's Law Example

ΔH for the formation of carbon monoxide: $2\ \mathrm{C}(s, graphite) + \mathrm{O_2}(g) \rightarrow 2\ \mathrm{CO}(g)$ using the following two reactions:

- Standard formation of $\mathrm{CO_2}$: $\mathrm{C}(s\,, graphite) + \mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g)$ $\quad \Delta H_1$
- CO oxidation : $2\ \mathrm{CO}(g) + \mathrm{O_2}(g) \rightarrow 2\ \mathrm{CO_2}(g)$ $\quad \Delta H_2$

$$\mathrm{C}(s\,, graphite) + \mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) \qquad +\Delta H_1$$

$$2\ \mathrm{CO_2}(g) \rightarrow 2\ \mathrm{CO}(g) + \mathrm{O_2}(g) \qquad -\Delta H_2$$

Hess's Law Example

ΔH for the formation of carbon monoxide: $2\ \mathrm{C}(s, graphite) + \mathrm{O_2}(g) \rightarrow 2\ \mathrm{CO}(g)$ using the following two reactions:

- Standard formation of $\mathrm{CO_2}$: $\mathrm{C}(s, graphite) + \mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g)$ $\quad \Delta H_1$
- CO oxidation : $2\ \mathrm{CO}(g) + \mathrm{O_2}(g) \rightarrow 2\ \mathrm{CO_2}(g)$ $\quad \Delta H_2$

$$\left(\mathrm{C}(s, graphite) + \mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) \qquad +\Delta H_1\right)\mathbf{x2}$$

$$2\ \mathrm{CO_2}(g) \rightarrow 2\ \mathrm{CO}(g) + \mathrm{O_2}(g) \qquad -\Delta H_2$$

$$2\ \mathrm{C}(s, graphite) + \mathrm{O_2}(g) \rightarrow 2\ \mathrm{CO}(g) \qquad 2\Delta H_1 - \Delta H_2$$

10.5

Calorimetry

The methods of calorimetry are for experimental determination of changes in enthalpy (or internal energy):

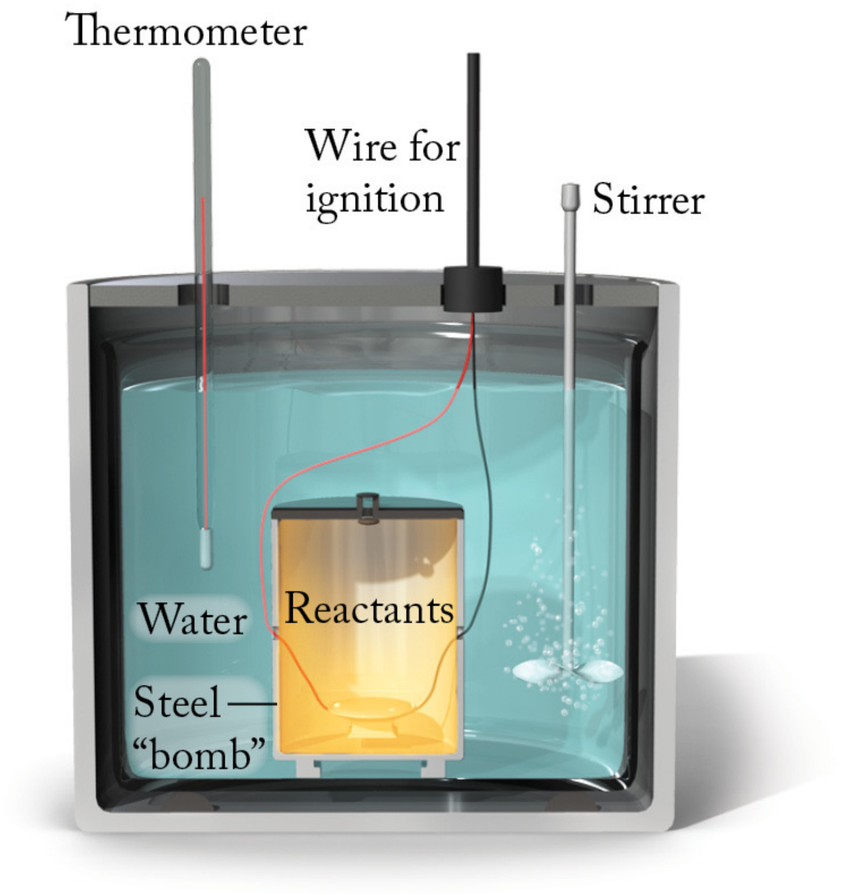
- phase changes
- chemical reactions

In order to use a calorimeter, we first standardize it to find how much heat the instrument, or reaction surroundings, absorbs. Standardization yields a calorimeter constant, or **heat capacity** of the calorimeter C_{cal}.

Bomb Calorimetry

- A bomb calorimeter is used for combustion reactions.
- Calorimeter constant, C_{cal}
  - The energy lost by the reaction mixture in a bomb calorimeter is the energy gained by the calorimeter:

    (heat absorbed) = –(heat released)



Chapter Summary Problem: 10.95

10.95. A sample of ethanol, C_2H_6O (1.252 g, 46 g/mol), is burned in a bomb calorimeter with a calorimeter constant $C_{\mathrm{cal}} = 4.368$ kJ/°C, causing the temperature to rise by 6.804 °C.

a. Calculate q for the combustion reaction, or heat released to calorimeter.

b. Calculate ΔH_{rxn} for combustion of C_2H_6O.

c. (out of class) Write and balance a chemical equation for combustion of $C_2H_6O(\ell)$.

d. (out of class) Use the values of $\Delta H^\circ_{\mathrm{f}}$ for $C_2H_6O(\ell)$, $O_2(g)$, $CO_2(g)$ and $H_2O(\ell)$, from Appendix 4, to calculate combustion $\Delta H^\circ_{\mathrm{rxn}}$ and compare to the value obtained in b.

10.9

Fuel Values

To compare fuels, we can look at **fuel values** or fuel density for combustion reactions.

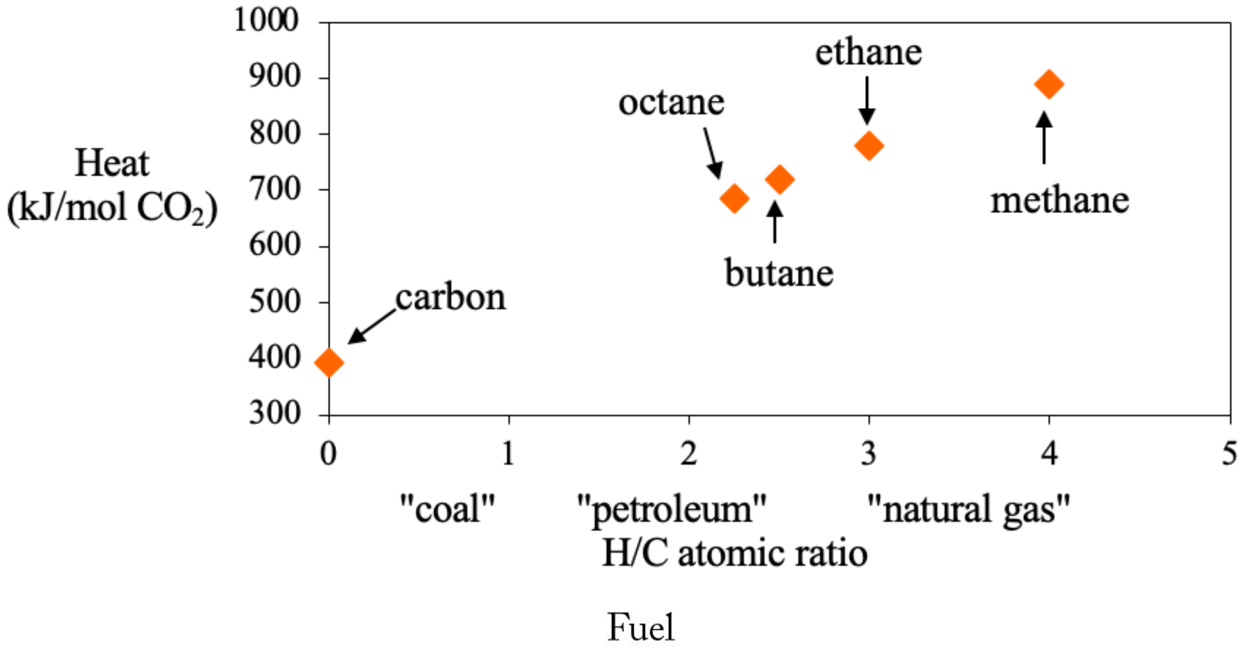
- Fuel values: energy released per g substance
- Fuel values apply to any fuel, including food
- Fuel density: energy released per volume of a liquid fuel

A comparison of the ΔH_{comb} for methane and propane shows that

CH_4: −802.3 kJ/mol or −50.02 kJ/g

C_3H_8: −2043.9 kJ/mol or −46.35 kJ/g

The more carbon-dense fuels (ie coal, gasoline) not only have **lower heat value**, but also emit **more CO_2 per energy unit**



Energy from Food

- Food is fuel of living systems and is converted into energy biochemically.
  - These processes are similar to combustion reactions.
  - The energy content can be determined by bomb calorimetry

$$q_{\text{calorimeter}} = C_{\text{calorimeter}}\,\Delta T$$

- The fuel value of food is usually reported in Calories per gram.
  - Calorie (Cal): 1 Cal = 10^3 cal = 4.184 kJ

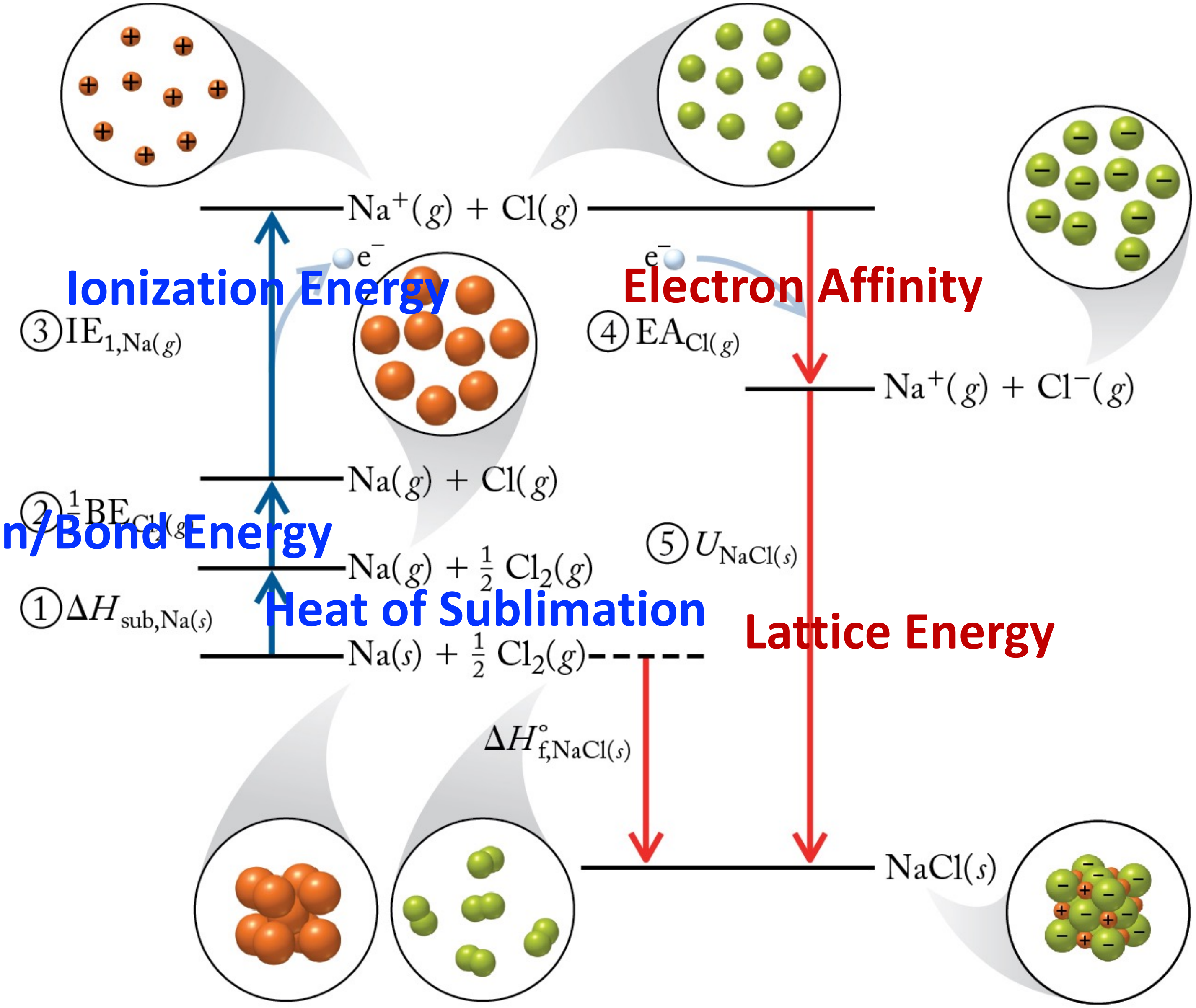
Born–Haber Cycle

For calculation of difficult to determine lattice energy → released when gaseous, monatomic ions come together to form an ionic solid.

For sodium chloride, the enthalpy change for

$$Na^{+}(g) + Cl^{-}(g) \rightarrow NaCl\ (s)$$

is the lattice energy U_{NaCl}.



Lattice Energies from the Born–Haber Cycle

The formation reaction of NaCl can be broken down into five steps, one of which corresponds to the lattice energy for NaCl (step 5).

1. Sublimation of 1 mol Na (endothermic)
2. Breaking covalent bonds of 0.5 mol Cl_2 (endothermic)
3. Ionize 1 mol Na(*g*) atoms to 1 mol Na^+ ions (endothermic)
4. 1 mol Cl atoms acquire 1 mol electrons to form 1 mol Cl^- (exothermic)
5. Form 1 mol NaCl(*s*) from 1 mol Na^+ and 1 mol Cl^- (exothermic)

$$\Delta H^\circ_{\mathrm{f,NaCl}} = \Delta H_{\mathrm{sub,Na}} + \frac{1}{2}\mathrm{BE}_{\mathrm{Cl_2}} + \mathrm{IE}_{\mathrm{1,Na}} + \mathrm{EA}_{\mathrm{Cl}} + U_{\mathrm{NaCl}}$$

$$-411\ \mathrm{kJ} = (108\ \mathrm{kJ}) + \frac{1}{2}(243\ \mathrm{kJ}) + (495\ \mathrm{kJ}) + (-349\ \mathrm{kJ}) + U_{\mathrm{NaCl}}$$

$$U_{\mathrm{NaCl}} = (-411\ \mathrm{kJ}) - (108\ \mathrm{kJ}) - (121.5\ \mathrm{kJ}) - (495\ \mathrm{kJ}) - (-349\ \mathrm{kJ}) = -786\ \mathrm{kJ}$$

REMINDERS

Reminders:

- **Final Exam**: Tuesday, April 30, 8:00-10:30 AM
- **Study Session**: Tuesday, April 23, 1:30-3:00 PM, Sims 112
- **Course Evaluations: no later than T Apr 23, 11:59 PM**
  - ➢ you will need your Winthrop ID “W123456789”

https://winthrop.qualtrics.com/jfe/form/SV_bEDbbk1ElSpRuv4

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