Chapter 5
Thermochemistry

Buffalo State
State University of New York

Jamie Kim
Department of Chemistry
Buffalo State College

Goal: estimation of energy change during chemical reaction

Thermochemistry

- Study of energies released or absorbed during chemical reactions.
- Energy: Ability to work

Kinetic Energy (KE): motion of the particle

  - Depends on speed (v) and mass (m)
  - **KE = $\frac{1}{2}mv^2$**

Potential Energy (PE): Position/location

  - Depends on location or position

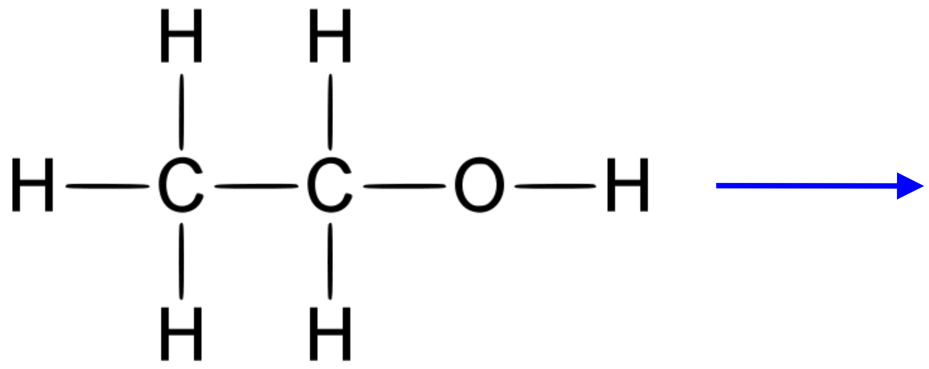
Law of Conservation of Energy

- Energy can neither be created nor destroyed
- Can only be converted from one form to another
- Total energy of universe is constant

Total Energy = Potential Energy + Kinetic Energy

Chemical Energy (PE)

- Potential energy (PE) possessed by chemical compounds
- Stored in chemical bonds
- Breaking bonds
- Forming bonds



$$CH_3CH_2OH \longrightarrow CO_2 + H_2O + \text{energy}$$

ethanol

Units of Energy

Joule (J)

- KE possessed by 2 kg object moving at speed of 1 m/s (**KE = ½mv² **)

$$1J = \frac{1}{2}(2kg)\left(\frac{1m}{1s}\right)^2 \qquad 1J = \frac{1kg \cdot m^2}{s^2}$$

- If calculated value is greater than 1000 J, use kJ
- 1 kJ = 1000 J

Units of Energy

calorie (cal)

- Energy needed to raise temperature of 1 g H_2O by 1 °C
  - **1 cal = 4.184 J (exactly)**
  - 1 kcal = 1000 cal
  - 1 kcal = 4.184 kJ
  - e.g., for 100 g water from 20 to 30 °C, 100 X 10 = 1000 cal or 1 kcal is required

Internal Energy (E)

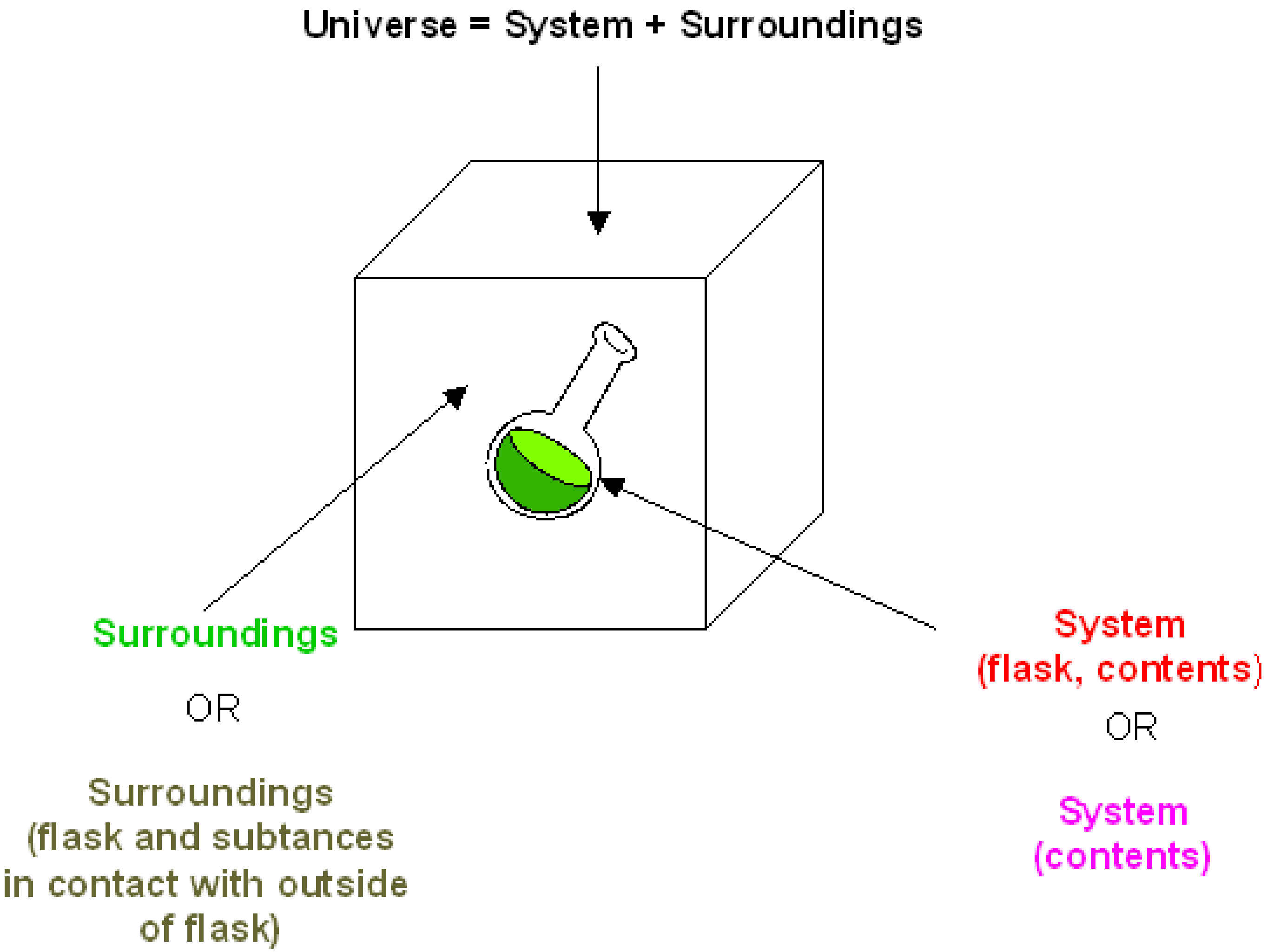
- Sum of energies of all particles in a system
  - $\boldsymbol{E}$ = Total energy of a system
  - $\boldsymbol{E}$ = Potential + Kinetic **= *PE + KE***

Change in Internal Energy

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

- **–** Δ means change
- – final – initial
- – ***$\Delta E > 0$ (energy was absorbed: Endothermic)***
- – ***$\Delta E < 0$ (energy was released: Exothermic)***

Universe, System, and Surroundings



Universe = System + Surroundings

Surroundings

OR

Surroundings
(flask and subtances
in contact with outside
of flask)

System
(flask, contents)

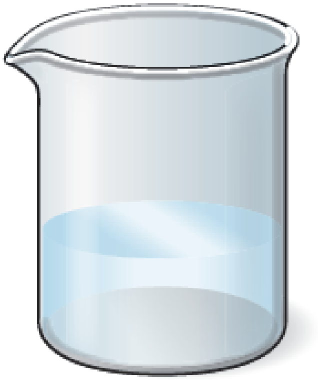
OR

System
(contents)

Three Types of Systems

1. Open System

- Open to atmosphere
- Gain or lose mass and energy across boundary
- Most reactions done in open systems



Open system

2. Closed System

- Not open to atmosphere
- Energy can cross boundary, but mass **cannot**

Closed system

Three Types of Systems

3. Isolated System

- No energy or matter can cross boundary
- Energy and mass are constant

Isolated system

Heat (*q*)

- Heat (***q***) gained or lost by an object
  - Directly proportional to temperature change (Δt) it undergoes
  - Adding heat, increases temperature
  - Removing heat, decreases temperature
- Measure changes in temperature to quantify amount of heat transferred

$$q = C \times \Delta t$$

- **C** = heat capacity

Learning Check: Heat Capacity

A cup of water is used in an experiment. Its heat capacity is known to be 720 J/°C. How much heat will it absorb if the experimental temperature changed from 19.2 °C to 23.5 °C? $q = C \times \Delta t$

Specific Heat (s)

- Amount of heat needed to raise 1 °C of 1 g substance

$$s = \frac{C(\text{heat capacity})}{\text{mass (g)}}$$

- **Intensive property (doest not depend on mass)**
- Unique to each substance
- Large specific heat means substance needs large amount of heat as it is warmed

Learning Check

- Calculate the specific heat of water if it the heat capacity of 100 g of water is 418 J/°C.

$$\boldsymbol{s} = \frac{\boldsymbol{C}}{\boldsymbol{m}} \qquad \boldsymbol{s} = \frac{418\ \text{J}/^{\circ}\text{C}}{100.\ \text{g}} = \mathbf{4.18\ J/(g\cdot{}^{\circ}C)}$$

- What is the specific heat of water if heat capacity of 1.00 g of water is 4.18 J/°C?

$$\boldsymbol{s} = \frac{4.18\ \text{J}/^{\circ}\text{C}}{1.00\ \text{g}} = \mathbf{4.18\ J/(g\cdot{}^{\circ}C)}$$

- Thus, heat capacity is independent of amount (**intrinsic property**)

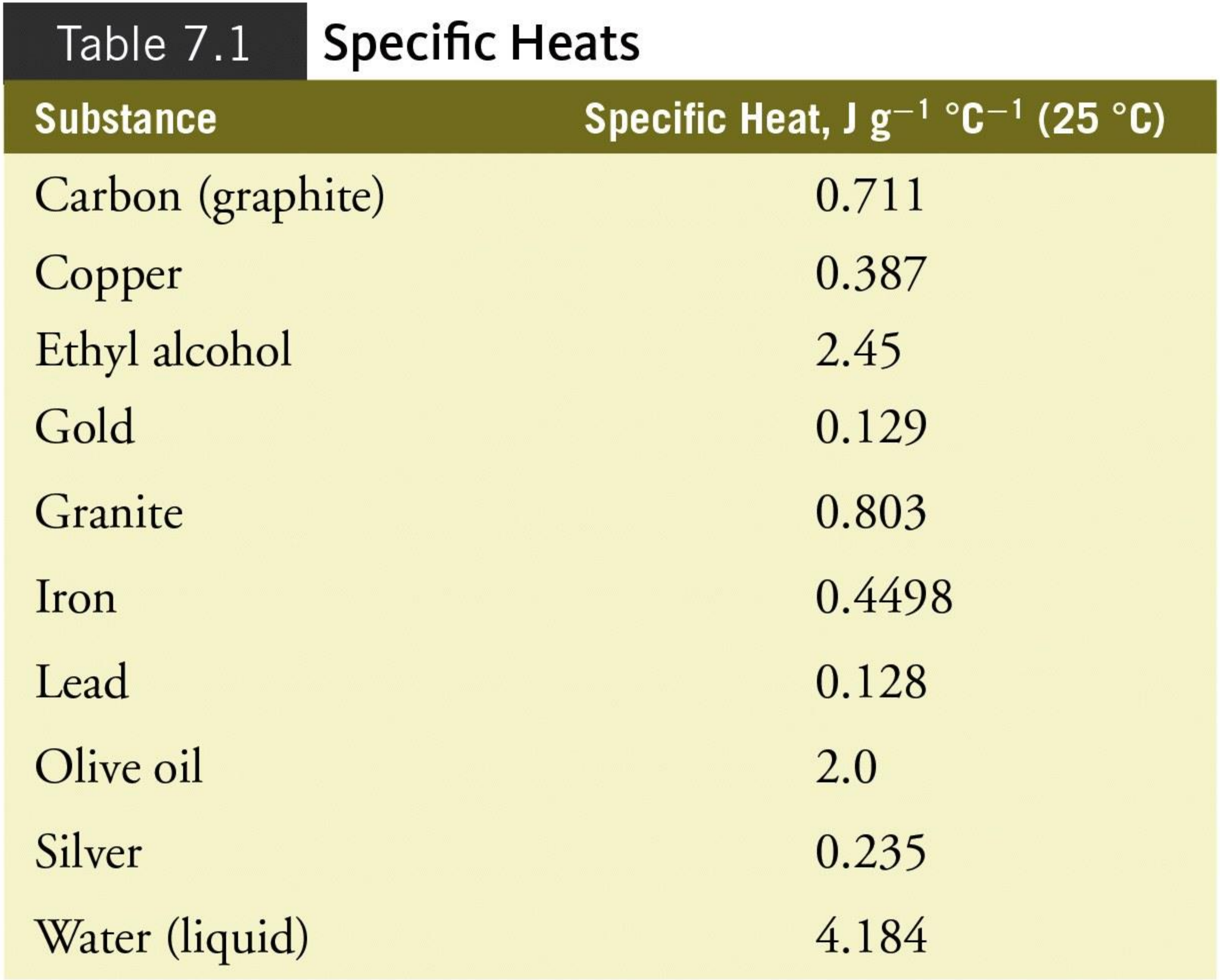


Table 7.1 Specific Heats

Substance	Specific Heat, $\mathrm{J\ g^{-1}\ {}^\circ C^{-1}}$ (25 °C)
Carbon (graphite)	0.711
Copper	0.387
Ethyl alcohol	2.45
Gold	0.129
Granite	0.803
Iron	0.4498
Lead	0.128
Olive oil	2.0
Silver	0.235
Water (liquid)	4.184

How much heat is absorbed by a copper penny with mass 3.10 g whose temperature rises from −8.0 °C to 37.0 °C?, specific heat of copper: 0.387

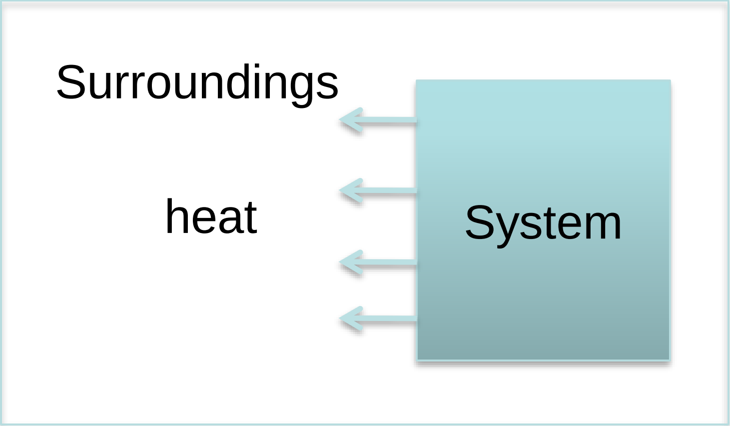
Chemical Reactions

Involves breaking chemical bonds in reactants and formation of chemical bonds in products

Forming Bonds: release energy (heat)

Breaking Bonds: requires energy (heat)

Exothermic Reaction

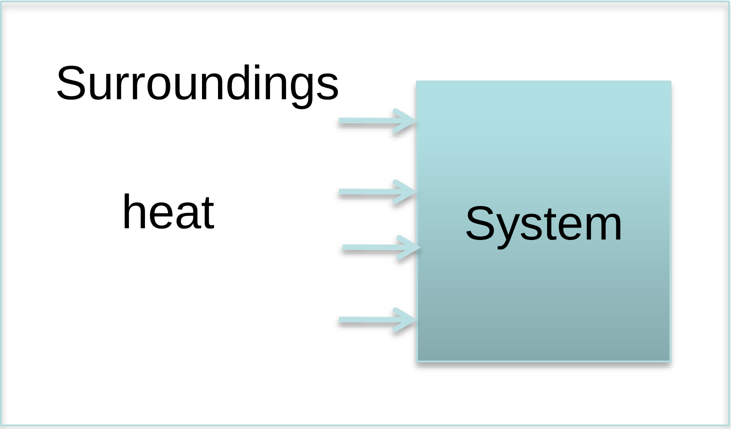


- Reaction releases heat to surroundings
- Surrounding temperature is raised (↑T)
- You feel warm

Ex.

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ + heat

Endothermic Reaction



- Reaction absorbs heat from surroundings
- Surrounding temperature is lowered (↓T)
- You feel cool

Ex. Photosynthesis

$$6CO_2(g) + 6H_2O(g) + \text{solar energy (heat)} \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

Change in Internal Energy (ΔE) via Chemical Reaction

From explosion (chemical reaction),
q = heat
w = work (expansion of air, sounds, destruction of building, etc)

$$\Delta E = q + w$$

If the burning of the fuel in a potato cannon performs 855 J of work on the potato and produces 1422 J of heat, what is ΔE for the burning of the fuel?

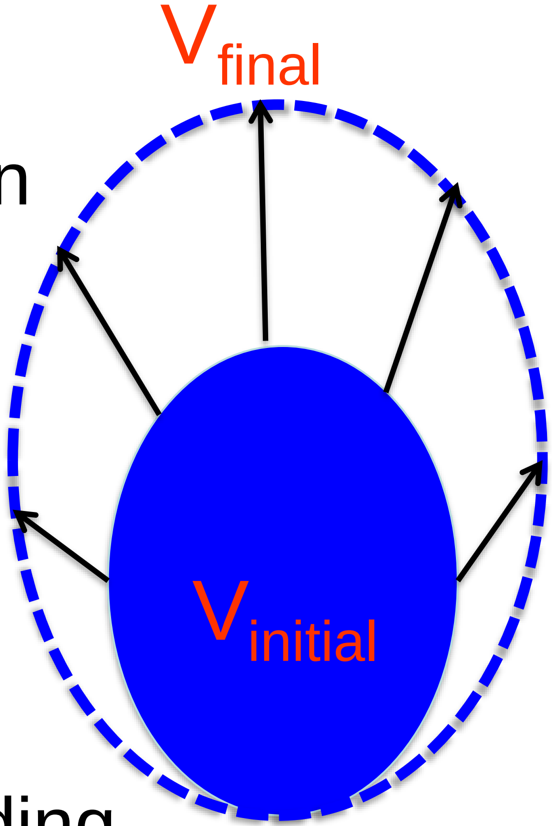
Heats of Reaction (q)

- Amount of heat absorbed or released in chemical reaction
- Calorimeter
  - Instrument used to measure temperature changes (Δt)
  - $q = C\Delta t$
- Can be measured under two different conditions
  - Constant volume, q_V (limited case)
    - Closed, rigid container
  - Constant pressure, q_P (general case)
    - Open to atmosphere

Work (w)

Work = –P×ΔV

- **P** = pressure (always positive)
- **ΔV** = change in volume after reaction
- **ΔV** = $V_{final} – V_{initial}$
- Expansion of ballon
  - Since $V_{final} > V_{initial}$
  - **ΔV** must be positive
  - So expansion work is negative
  - Work done **by** system to surrounding
  - to convert the units to joules use 101.3 J = 1 atm·L



First Law of Thermodynamics

- In an isolated system, energy can be transformed, i.e. changed from one form to another, but cannot be created nor destroyed.
- $\Delta E = q + w$

q is (+)	Heat **absorbed** by system (IN)
q is (–)	Heat **released** by system (OUT)
w is (+)	Work done **on** system (IN)
w is (–)	Work done **by** system (OUT)

Your Turn!

A gas releases 3.0 J of heat and then performs 12.2 J of work. What is the change in internal energy of the gas?

A. –15.2 J

B. 15.2 J

C. –9.2 J

D. 9.2 J

E. 3.0 J

ΔE = q + w

ΔE = – 3.0 J + (–12.2 J)

If a balloon is inflated from 0.100 L to 1.85 L against an external pressure of 1.00 atm, how much work is done? (101.3 J = 1 atm·L)

Enthalpy (*H*)

- Chemists usually do NOT run reactions at constant ***V***
- Usually do reactions in open containers
  - Open to atmosphere; constant ***P***
- Heat of reaction at constant pressure ($\boldsymbol{q_p}$) is defined as enthalpy (H)

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Enthalpy Change (ΔH)

- $\Delta H = H_{\text{final}} - H_{\text{initial}}$
- For chemical reaction,
- $\Delta H = H_{\text{products}} - H_{\text{reactants}}$
- Significance of sign of ΔH

Endothermic reaction ($\Delta H > 0$)

  - System absorbs energy from surroundings
  - $\Delta H > 0$

Exothermic reaction

  - System loses energy to surroundings
  - $\Delta H < 0$

ΔH in Chemical Reactions

Standard condition

Standard Heat of Reaction ($\Delta H°$)

– Enthalpy change for reaction at 1 atm and 25 °C

Ex.

$$N_2(g) + 3H_2(g) \longrightarrow 2\,NH_3(g)$$

1.000 mol   3.000 mol   2.000 mol

- 1 mole N_2 and 3 moles of H_2 react to form NH_3 at 25 °C and 1 atm
- 92.38 kJ released (exothermic)
- $\Delta H = -92.38$ kJ

Thermochemical Equation

- Write Δ***H***° immediately after equation

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta H° = -92.38\ \text{kJ}$

$2N_2(g) + 6H_2(g) \rightarrow 4NH_3(g) \quad \Delta H° = ?$

$3N_2(g) + 9H_2(g) \rightarrow 6NH_3(g) \quad \Delta H° = ?$

$\tfrac{1}{2}N_2(g) + {}^{3}/2H_2(g) \rightarrow NH_3(g) \quad \Delta H° = ?$

Learning Check:

Consider the following reaction:

$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$

$\Delta E = -2511\ \text{kJ}$

The reactants (acetylene and oxygen) have 2511 kJ more energy than products. How many kJ are released for 1 mol C_2H_2?

Your Turn!

Based on the reaction

$CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(g) + 4HCl(g)$

$\Delta H = -434$ kJ/mol CH_4

What energy change occurs when 1.2 moles of methane reacts?

A. -3.6×10^2 kJ

B. $+5.2 \times 10^2$ kJ

C. -4.3×10^2 kJ

D. $+3.6 \times 10^2$ kJ

E. -5.2×10^2 kJ

$\Delta H = -434$ kJ/mol × 1.2 mol

$\Delta H = -5\underline{2}0.8$ kJ

Running Thermochemical Equations in Reverse

Consider

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

$\Delta H^\circ = -\ 802.3\ \text{kJ}$

- Reverse thermochemical equation
- Must change sign of ΔH

$CO_2(g)\ +\ 2H_2O(g)\ \rightarrow\ CH_4(g)\ +\ 2O_2(g)$

$\Delta H^\circ = 802.3\ \text{kJ}$

Multiple Paths; Same ΔH°

Hess's Law of Heat Summation

- For any reaction that can be written into steps, value of ΔH° for reactions = sum of ΔH° values of each individual step

Step 1: $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta H° = –110.5$ kJ

Step 2: $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H° = –283.0$ kJ

Step 1 + Step 2

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = ?$

$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$ $\Delta H° =$?

Step 1: $N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H° = 180.$ kJ

Step 2: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H° = –112$

Given the following information:

$Cu(s) + Cl_2(g) \rightarrow CuCl_2(s) \qquad \Delta H^\circ = -206\ kJ$

$2\ Cu(s) + Cl_2(g) \rightarrow 2\ CuCl(s) \qquad \Delta H^\circ = -\ 36\ kJ$

Calculate the ΔH° for the reaction below:

$Cu(s) + CuCl_2(s) \rightarrow 2\ CuCl(s) \qquad \Delta H^\circ = ?\ kJ$

Your Turn!

Which of the following is a statement of Hess's Law?

A. ΔH for a reaction in the forward direction is equal to Δ H for the reaction in the reverse direction.

B. ΔH for a reaction depends on the physical states of the reactants and products.

C. If a reaction takes place in steps, ΔH for the reaction will be the sum of ΔHs for the individual steps.

D. If you multiply a reaction by a number, you multiply ΔH by the same number.

E. ΔH for a reaction in the forward direction is equal in magnitude and opposite in sign to ΔH for the reaction in the reverse direction.

Standard State

- Most stable form and physical state of element at 1 atm (1 bar) and 25 °C (298 K)

element	**Standard state**
O	$O_2(g)$
C	$C_{gr}(s)$
H	$H_2(g)$
Al	$Al(s)$
Ne	$Ne(g)$

Note: **All $\Delta H_f°$ of elements in their std states = 0**

Forming element from itself.

- See Appendix in back of textbook

Uses of Standard Enthalpy (Heat) of Formation, $\Delta H_f°$

From definition of $\Delta H_f°$, can write balanced equations directly

$\Delta H_f°$ of $C_2H_5OH(\ell)$: from table 7-2

$2C(s, gr) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(\ell)$

$\Delta H_f° = –277.03$ kJ/mol

$\Delta H_f°$ of $Fe_2O_3(s)$: from table 7-2

$2Fe(s) + {}^3/_2O_2(g) \rightarrow Fe_2O_3(s)$ $\Delta H_f° = – 822.2$ kJ/mol

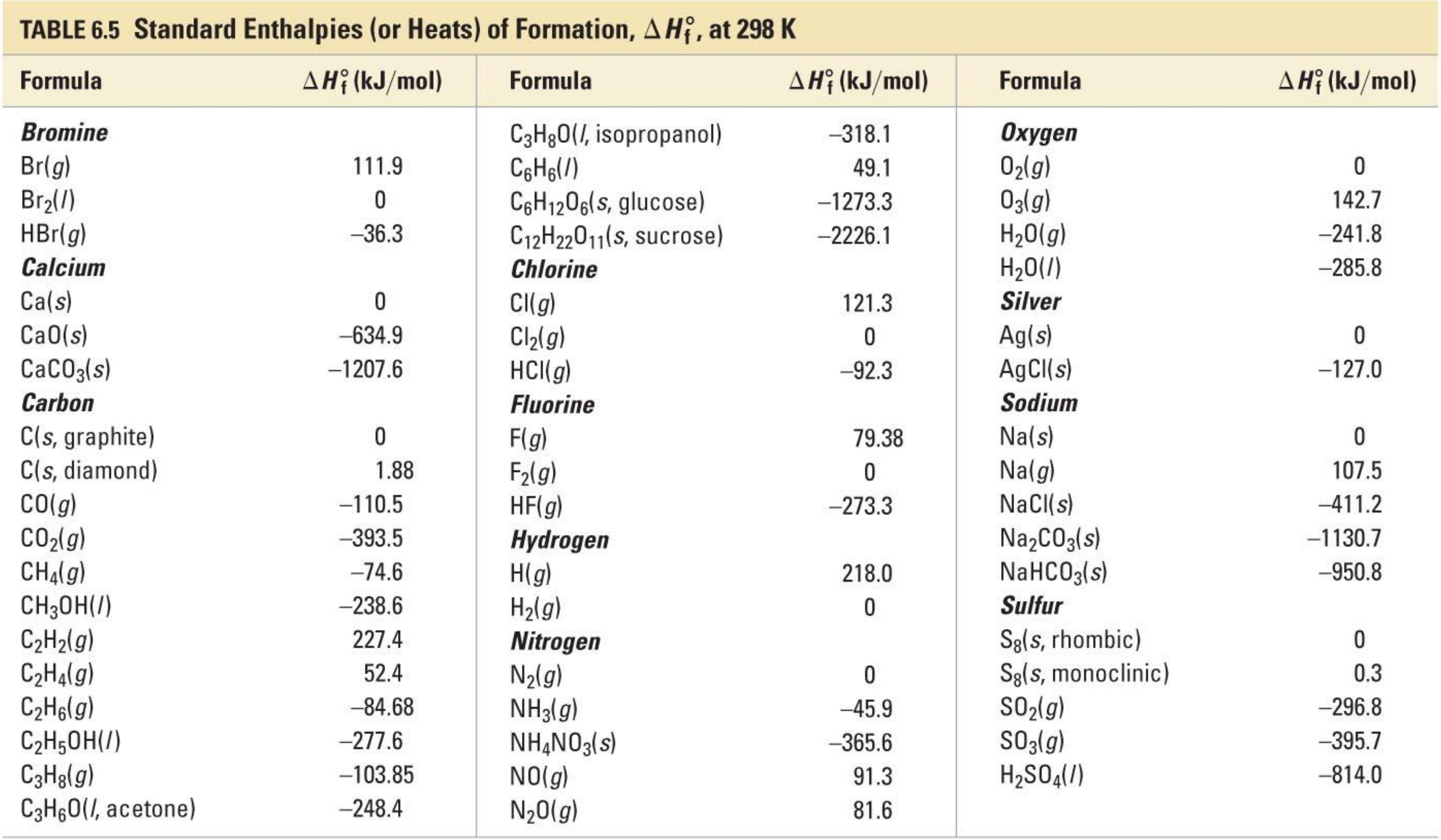


TABLE 6.5 Standard Enthalpies (or Heats) of Formation, ΔH_f°, at 298 K

Formula	ΔH_f° (kJ/mol)	Formula	ΔH_f° (kJ/mol)	Formula	ΔH_f° (kJ/mol)
Bromine		C_3H_8O(*l*, isopropanol)	–318.1	***Oxygen***	
$Br(g)$	111.9	$C_6H_6(l)$	49.1	$O_2(g)$	0
$Br_2(l)$	0	$C_6H_{12}O_6$(*s*, glucose)	–1273.3	$O_3(g)$	142.7
$HBr(g)$	–36.3	$C_{12}H_{22}O_{11}$(*s*, sucrose)	–2226.1	$H_2O(g)$	–241.8
Calcium		***Chlorine***		$H_2O(l)$	–285.8
$Ca(s)$	0	$Cl(g)$	121.3	***Silver***	
$CaO(s)$	–634.9	$Cl_2(g)$	0	$Ag(s)$	0
$CaCO_3(s)$	–1207.6	$HCl(g)$	–92.3	$AgCl(s)$	–127.0
Carbon		***Fluorine***		***Sodium***	
C(*s*, graphite)	0	$F(g)$	79.38	$Na(s)$	0
C(*s*, diamond)	1.88	$F_2(g)$	0	$Na(g)$	107.5
$CO(g)$	–110.5	$HF(g)$	–273.3	$NaCl(s)$	–411.2
$CO_2(g)$	–393.5	***Hydrogen***		$Na_2CO_3(s)$	–1130.7
$CH_4(g)$	–74.6	$H(g)$	218.0	$NaHCO_3(s)$	–950.8
$CH_3OH(l)$	–238.6	$H_2(g)$	0	***Sulfur***	
$C_2H_2(g)$	227.4	***Nitrogen***		S_8(*s*, rhombic)	0
$C_2H_4(g)$	52.4	$N_2(g)$	0	S_8(*s*, monoclinic)	0.3
$C_2H_6(g)$	–84.68	$NH_3(g)$	–45.9	$SO_2(g)$	–296.8
$C_2H_5OH(l)$	–277.6	$NH_4NO_3(s)$	–365.6	$SO_3(g)$	–395.7
$C_3H_8(g)$	–103.85	$NO(g)$	91.3	$H_2SO_4(l)$	–814.0
C_3H_6O(*l*, acetone)	–248.4	$N_2O(g)$	81.6		

Your Turn!

What is the reaction that corresponds to the standard enthalpy of formation of $NaHCO_3(s)$, $\Delta H_f° = – 947.7$ kJ/mol?

a. $Na(s) + \frac{1}{2}H_2(g) + {}^3/_2O_2(g) + C(s, gr) \rightarrow NaHCO_3(s)$

b. $Na^+(g) + H^+(g) + 3O^{2-}(g) + C^{4+}(g) \rightarrow NaHCO_3(s)$

c. $Na^+(aq) + H^+(aq) + 3O^{2-}(aq) + C^{4+}(aq) \rightarrow NaHCO_3(s)$

d. $NaHCO_3(s) \rightarrow Na(s) + \frac{1}{2}H_2(g) + {}^3/_2O_2(g) + C(s, gr)$

e. $Na^+(aq) + HCO_3^-(aq) \rightarrow NaHCO_3(s)$

Calculate $\Delta H°_{rxn}$ Using $\Delta H_f°$

Calculate $\boldsymbol{\Delta H°_{rxn}}$ using $\boldsymbol{\Delta H_f°}$ data for the reaction

$$SO_3(g) \longrightarrow SO_2(g) + \tfrac{1}{2}O_2(g)$$

1. Add $\boldsymbol{\Delta H_f°}$ for each product times its coefficient
2. Subtract $\boldsymbol{\Delta H_f°}$ for each reactant times its coefficient.

$$\Delta H°_{rxn} = \Delta H°_f(SO_2(g)) + \tfrac{1}{2}\Delta H°_f(O_2(g)) - \Delta H°_f(SO_3(g))$$

$$\Delta H°_{rxn} = -297\,\text{kJ/mol} + \tfrac{1}{2}(0\,\text{kJ/mol}) - (-396\,\text{kJ/mol})$$

$\boldsymbol{\Delta H°_{rxn} = 99}$ ***kJ/mol*** **, endothermic**

Learning Check

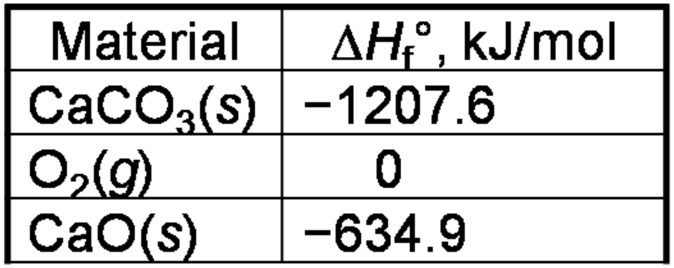
Calculate ΔH for this reaction using ΔH_f° data.

$$\mathrm{CO_2}(g) \;+\; 2\mathrm{H_2O}(\ell) \;\rightarrow\; 2\mathrm{O_2}(g) \;+\; \mathrm{CH_4}(g)$$

$$\Delta H_f^\circ \quad -393.5 \qquad -285.8 \qquad 0 \qquad -74.8$$

Calculate the $\Delta H°$ for decomposing 10.0 g of limestone, $CaCO_3$, under standard conditions.

$$CaCO_3(s) \rightarrow CaO(s) + O_2(g)$$



Material	$\Delta H_f°$, kJ/mol
$CaCO_3(s)$	−1207.6
$O_2(g)$	0
$CaO(s)$	−634.9

Homework

TBA