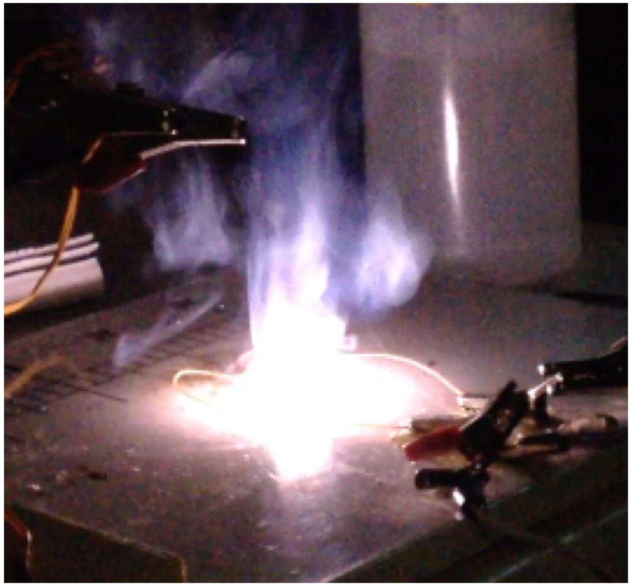
Chapter Six



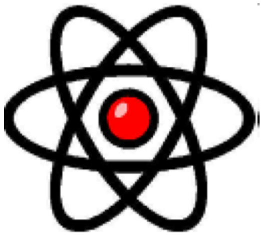
Energy Relationships in Chemical Reactions

Energy (U): Capacity to Do Work

Some types of energy:

Energy = force x distance
= N x m
= kg m^2 / s^2
= kg m^2 s^{-2}
= Joule (J)

- **Radiant**
  - Energy from the sun
- **Nuclear**
  - Energy stored in the nucleus of an atom



- **Thermal**
  - Energy associated with temperature
  - Type of kinetic energy: due to molecular movement

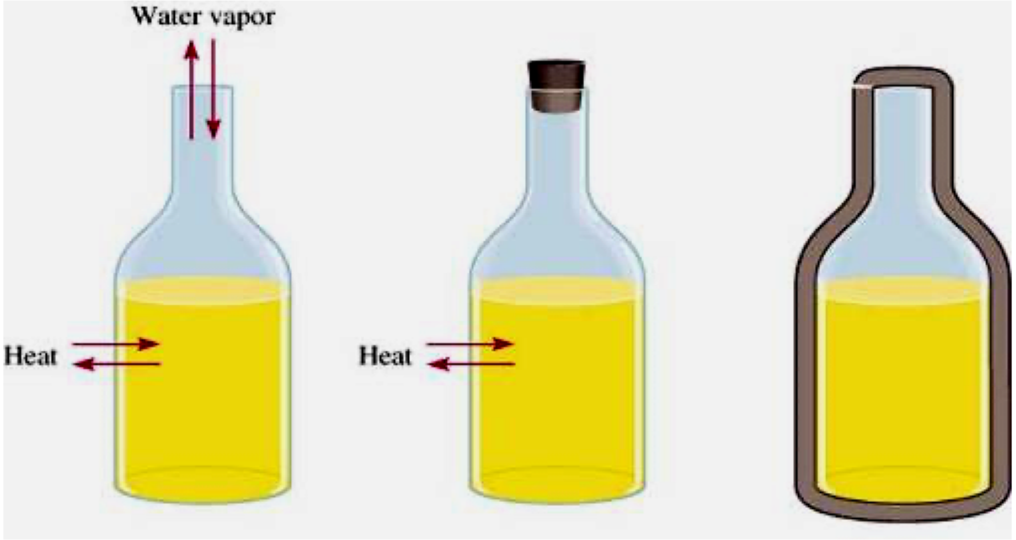
- **Chemical**
  - Energy stored in chemical bonds
  - Type of potential energy: due to position of an object

Thermochemistry

Study of heat change in chemical reactions

System: The part of the universe being studied

- **Open**: Energy & matter exchange with surroundings
- **Closed**: **Only energy exchange with surroundings**
- **Isolated**: No energy or matter exchange – rare



Surroundings: Part of the universe not being studied

Heat Transfer in a System

Heat (q): Transfer of energy due to temp. difference

Exothermic Reaction: System gives off heat (Exiting)

Ex: Methane Burning: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Bonds stronger in $CO_2 + H_2O$ than in $CH_4 + O_2$

- Energy is absorbed when bonds break & released when bonds form
- In this case more energy released than absorbed
- Heat goes from system to surroundings

Endothermic Reaction: System gains heat (Entering)

Ex: Ice Melting: $H_2O\ (s) \rightarrow H_2O\ (l)$

- Need energy to disrupt attractions between H_2O molecules
- Heat goes from surroundings into the system

Thermodynamics – Study of the conversions between heat & energy

State vs. Path Functions

State of a system:

Δ = change

- Describes specific conditions/macroscopic properties
- Composition, temp., pressure, energy, volume

ex: Potential energy of ball at the top of the mountain

State functions:

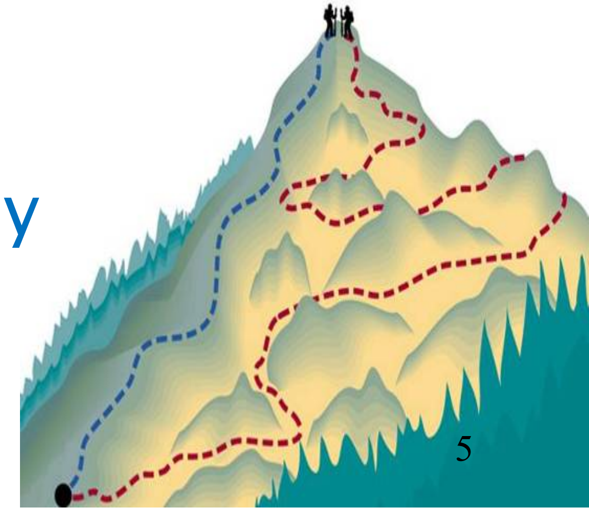
- Properties defined by Δ = final – initial values only
  → process doesn't matter

ex: Height of mountain

Path functions:

- change in values varies by process

ex: the actual distance travelled by ball on its trip to the bottom of the mountain.



First Law of Thermodynamics

Energy can be converted from 1 form to another but cannot be created or destroyed

$$\Delta U_{system} = U_{final} - U_{initial}$$

Internal Energy of System: $U_{system} = U_{kinetic} + U_{potential}$

Kinetic energy: Amount of molecular motion
Associated with temperature

Potential energy: Energy stored in bonds
Strength of chemical bonds

When studying a reaction, cannot separate kinetic & potential energy – measure total energy instead

For chemical reactions: $\Delta U_{reaction} = U_{products} - U_{reactants}$

Internal Energy & Enthalpy

Bettmann/Getty Images

Internal Energy: Work and Heat

Energy transfer – caused by changes in heat & work in a system

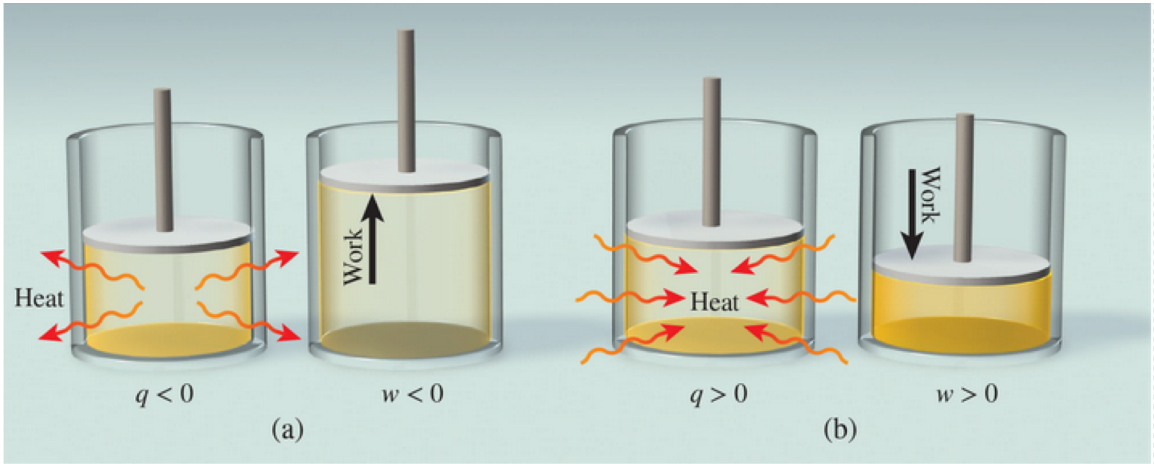
$$\Delta U_{system} = q + w$$

$$\text{Work } (w) = \text{force x distance} = -P\Delta V$$

Work is needed to expand a system against its surroundings

Negative work (–w): System loses energy to surroundings

Positive work (+w): System gains energy from surroundings



$$\text{Work } (w) = -P\Delta V$$

$$\Delta V = V_f - V_i$$

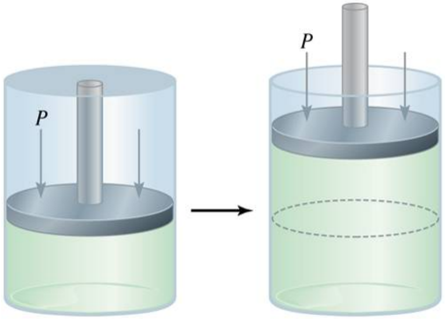
For this situation:
$+ \Delta V$

Therefore: $-w$

1 L x atm = 101.32 J

Work and Heat

A gas expands in volume from 2.000 L to 4.000 L at STP. 350.0 J of energy are needed to maintain the new conditions.



a. Calculate work (J) done against a vacuum & against a pressure of 1.000atm. (A = 0.000J, -202.6J)

*Note that work is reported in J, not L x atm.

b. Calculate the heat required for each system.

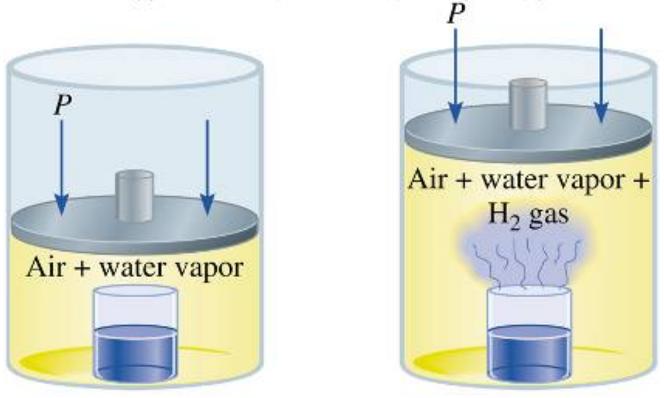
(A = 350.0 J; 552.6 J)

Enthalpy of Chemical Reactions

For systems at constant pressure (usually ~1atm):

$\Delta U = q + w = q_p - P\Delta V$

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



Enthalpy: (H) Experimentally measured & tabulated

- Can think of as heat of a reaction

At constant pressure: $\Delta H = \Delta U + P\Delta V$

Assume negligible volume change: $\Delta H = \Delta U = q_p$

There will be slight differences between ΔH and ΔU, but in many cases they are small enough to be considered negligible

Ways of Calculating Enthalpy/Heat/Energy exchange

$$q = ms\Delta T$$

Experimental

$$q = C\Delta T$$

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

$$\Delta U_{system} = q + w$$

Theoretical

$$\Delta U_{system} = U_{final} - U_{initial}$$

$$\Delta H_{reaction} = \Sigma\Delta H_{products} - \Sigma\Delta H_{reactants}$$

$$\Delta H_{reaction} = \Delta H_1 + \Delta H_2 + \Delta H_3 + ...$$

To determine which formula to use – look at information given in the problem!

Enthalpy of Reaction ($\Delta H = q_{rxn}/mol$)

Amount of heat exchanged between system and surroundings during a chemical reaction

$$\Delta H_{reaction} = \Sigma\Delta H_{products} - \Sigma\Delta H_{reactants}$$

Exothermic Reactions

- Temperature increases in an isolated system.
- Heat released to surroundings is treated as a product
- **Δ H is negative**

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) + 197.8kJ \quad \Delta H = -197.8kJ$

Endothermic Reaction

- Temperature decreases in an isolated system.
- Heat absorbed by system is treated as a reactant
- **Δ H is positive**

$197.8kJ + 2SO_3 \rightarrow 2SO_2(g) + O_2(g) \quad \Delta H = +197.8kJ$

State function: Independent of path

Rules for Working with Heat and Enthalpy

1. Make same changes to enthalpy as to # moles

If decrease or increase reactants & products, do the same for ΔH

$2SO_2\,(g) + O_2(g) \rightarrow 2SO_3\,(g)$ $\qquad \Delta H = -197.8\text{kJ}$

$1SO_2\,(g) + 1/2O_2(g) \rightarrow 1SO_3\,(g)$ $\quad \Delta H = -197.8\text{kJ}/2 = -98.9\text{kJ}$

$\Delta H = -197.8$ kJ /2 mol $SO_3(g)$ $\qquad$ **$\Delta H = -98.9$ kJ /1 mol $SO_3(g)$**

2. Reverse the reaction, reverse sign of ΔH

$2SO_3 \rightarrow 2SO_2\,(g) + O_2(g)$ $\qquad \Delta H = +197.8\text{kJ}$

These rules will allow you to calculate the ΔH for any amount of product or reactant

Calculate how much heat is required to decompose 15.0g $NO_2(g)$ according to this reaction:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H = -114$ kJ

Info Provided:

Calculate molar mass of NO_2 – convert mass to moles NO_2.

Use coefficient & moles NO_2 present to find ΔH for 15.0 g.

A = +18.6 kJ

Calorimetry

parrinst.com

Calculating ΔH Via Experiment: Calorimetry

Calorimetry: Measurement of heat changes

Calorimeter: Device to measure heat (ΔT) produced by a chemical reaction

- $\Delta T = T_{final} - T_{initial}$
- Units: generally °C

Specific Heat (s): Heat needed to raise T of 1 **gram** by 1°C.

- $s = q/(m \times \Delta T)$
- Units: J/g°C or cal/g°C

s_{water} = 4.184 J/g°C
= 1 cal/g°C

Heat capacity (C): Quantity of heat needed to raise T by 1°C

- $C = m \times s$
- Units: J/°C or J/K

Heat of Reaction (q_{rxn})

- $q = m \times s \times \Delta T$ (Const. Volume)
- $q = C\ \Delta T$ (Const. Pressure)
- Units: J

Commonly Used Specific Heats

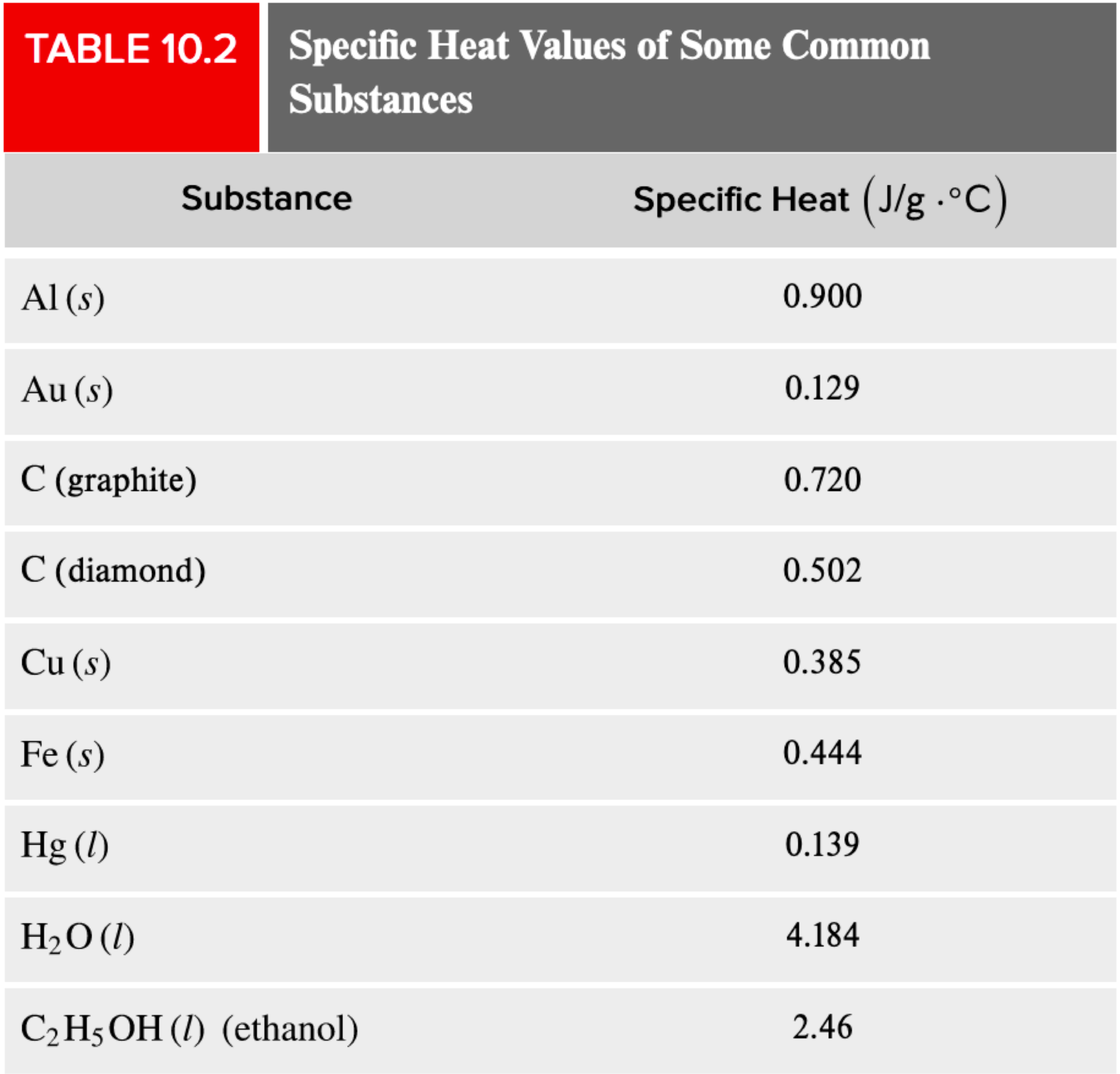


TABLE 10.2 **Specific Heat Values of Some Common Substances**

Substance	Specific Heat (J/g ·°C)
Al (s)	0.900
Au (s)	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu (s)	0.385
Fe (s)	0.444
Hg (l)	0.139
H_2O (l)	4.184
C_2H_5OH (l) (ethanol)	2.46

Constant Pressure Calorimetry Experiments

During the experiment, heat is transferred from the reaction (system) to the water (surroundings)

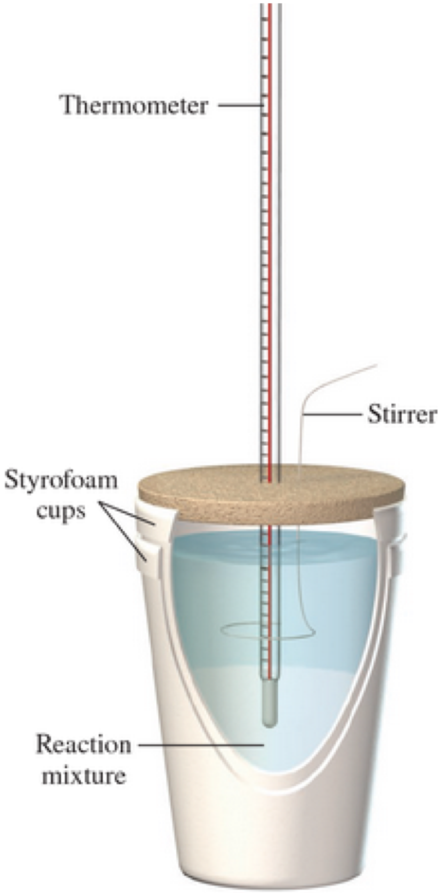
1. Measure ΔT of water in calorimeter
2. Use **$q = ms\Delta T$** to calculate the heat gained or lost by the water
3. Heat gained by the water in the calorimeter is lost by the system; heat heat lost by the water is gained by the system: **$-q_{rxn} = q_{cal}$**
4. Use q_{rxn} to determine information about system variables:

$$q_{rxn} = m_{sys} \times s_{sys} \times \Delta T_{sys}$$

Always have 2 sets of variables!

1 for water (surroundings)

1 for reaction (system)



A 30.0g sample of metal is heated to 100.0°C by placing it in a boiling water bath. The metal is removed from the boiling water, and placed in 25.0g of water at 22.0°C. The final temp was 27.6°C, what is the specific heat of the metal? S_{H2O} = 4.184 J/g°C

What is your equation?

What info is provided?

Solve for q_{cal} ($q_{cal} = -q_{metal}$)

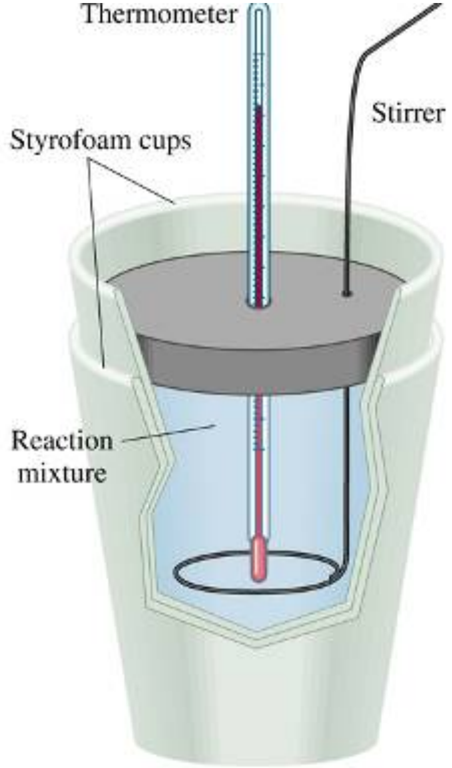
Use formula for q_{metal} to solve for s_{metal}

A = 0.269 J/g°C

Heat Evolved During a Chemical Reaction

Reaction conducted in a Styrofoam cup calorimeter

- The calorimeter does not absorb or give off heat.
- Heat absorbed by the solution in the calorimeter (q_{cal}) is the heat that has been given off by the chemical reaction ($-q_{rxn}$)



Two solutions are mixed in the calorimeter

40.0 mL of 1.00 M KOH(aq)
40.0mL of 1.00M H_2S0_4(aq)
T_i of both solutions = 21.00°C

Data on final solution

Density:	1.02 g/mL	Volume:	80.0 mL
S.H.:	4.00 J/g°C	Temp.:	27.85°C

Question: Calculate the enthalpy change of this reaction per mole of acid used.

Calculate the enthalpy change, ΔH, of this reaction per mole of acid used.

1. What is the chemical reaction?

$$2\ KOH + H_2SO_4 \rightarrow K_2SO_4(aq) + 2H_2O$$

$$\Delta H_{rxn} = q_{rxn} = -q_{cal}$$

$$q = m \times s \times \Delta T$$

2. What information is given?

Initial Information:	Final information:
40.0 mL of 1.00 M KOH(aq)	Density: 1.02 g/mL
40.0 mL of 1.00 M H_2S0_4(aq)	Volume: 80.0 mL
T_i of both solutions = 21.00°C	S.H.: 4.00 J/g°C (not just H_2O)
	Temp: 27.85°C

Note: ΔH calculated from calorimetry is heat that was transferred into the solution in the **CALORIMETER**, not water from the chemical reaction!!!

Calculating the ΔH per mole H_2O, con’t

3. Calculate heat absorbed by the solution in the calorimeter q_{cal}). Need mass of solution for this.

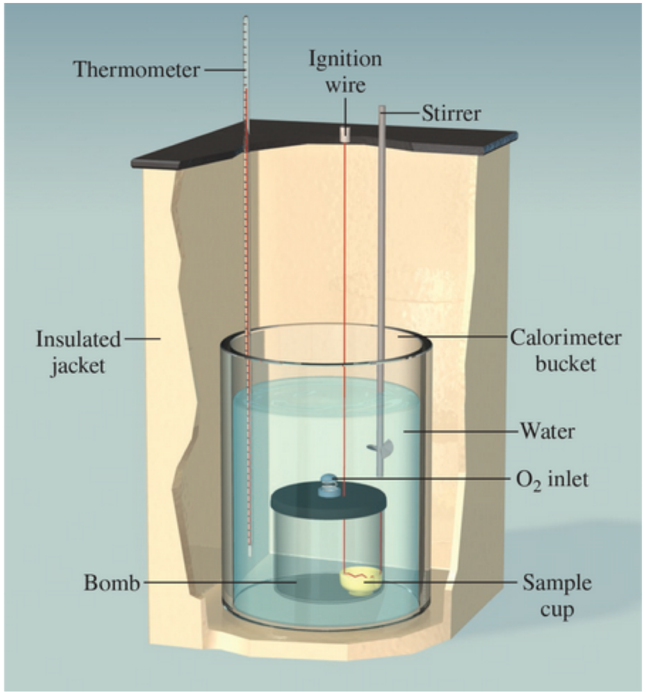
4. Calculate the # of moles of acid used in the reaction. Need to find LR!

Calculate ΔH per 1 mole of acid used. Remember that $q_{cal} = -q_{rxn}$.

A = -55.9 kJ/mol

Constant Volume ”bomb” Calorimetry

1. Heat is still transferred from the reaction to the water bath surroundings, and the relationship **$-q_{rxn} = q_{cal}$** remains the same.
2. Since the reaction takes place in the “bomb” rather than in the water bath, combustion and other reactions that cannot take place in solution can be studied.
3. The equation **$q = C\Delta T$** is used, where C is the heat capacity of the calorimeter.
4. C is generally determined by burning a material with a well known Δ**H** of combustion, then using q and ΔT to determine C.

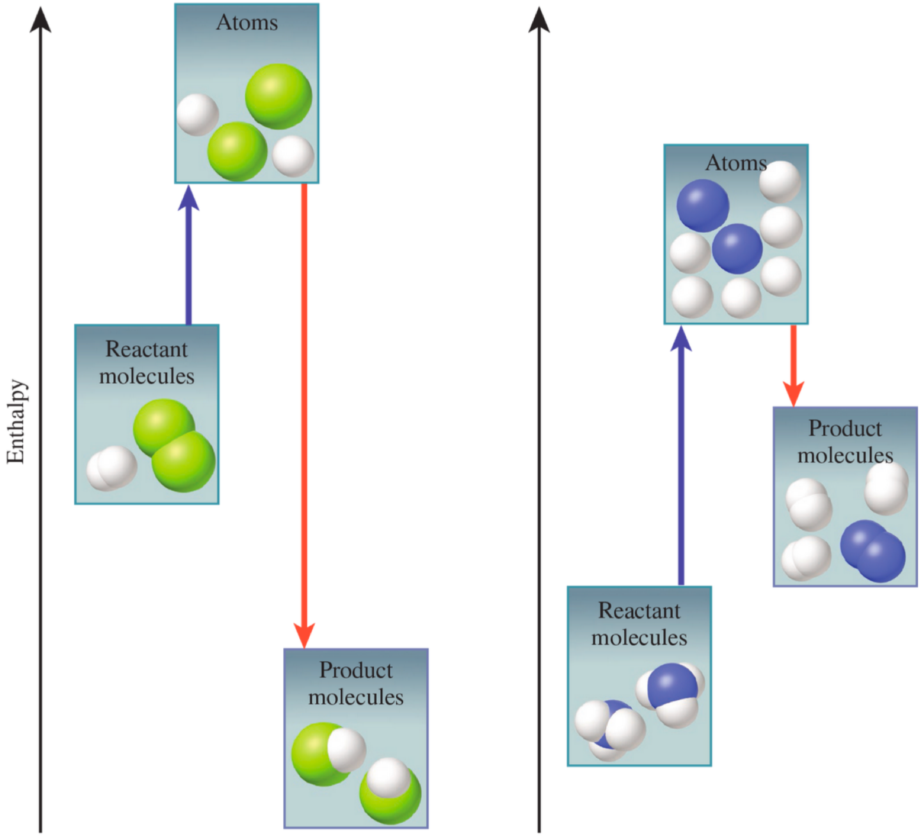


Constant Volume Calorimetry

A 0.2400g sample of nitroguanidine ($CH_4N_4O_2$; 104.07g/mol) was burned in a bomb calorimeter, increasing the temperature of the water bath from 25.000°C to 30.047°C. If the heat capacity of the calorimeter is 39.52J/°C, what is the heat content of nitroguanidine in J/g and kJ/mole?

831.1 J/g; 86.49kJ/mol

Standard Enthalpies, Hess's Law, & Bond Enthalpy



$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

$\Delta H^\circ = -184.7$ kJ/mol

(a)

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

$\Delta H^\circ = 92.6$ kJ/mol

(b)

Calculating ΔH_{rxn} Using Known Values: Standard Enthalpies of Formation ($\Delta H_f°$) & Reaction ($\Delta H_f°_{rxn}$)

The standard state of an element: $\mathbf{\Delta H_f° = 0}$

- Pure element in its most stable form at 1 atm & 20°C
- Solvents in aqueous solution are at a concentration of 1 M

  ex: $H_2(g)$ $N_2(g)$ $O_2(g)$ $Cl_2(g)$ $Br_2(l)$ $Hg(l)$ $Na(s)$

  – all have $\Delta H_f° = 0$

The standard molar enthalpy of formation, $\Delta H_f°$

- ΔH_f for 1 mol substance produced from elements in standard states
- Tabulated for compounds at 1atm and 20°C

  ex: $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_f° = -393.5 kJ/mol$

Calculation of ΔH_{rxn} Using Known Values

Calculating $\Delta H°$ of a chemical reaction

- **$\Delta H°_{rxn} = \Sigma\Delta H_f°$ products – $\Sigma\Delta H_f°$ reactants**
- **ex: $C(s) + O_2(g) \rightarrow CO_2(g)$**
- Multiply each $\Delta H_f°$ by the stoichiometric coefficient for that species. Ex:

$C(s)$ $\Delta H_f° = 1 \times 0 kJ/mol = 0 kJ/mol$

$O_2(g)$ $\Delta H_f° = 1 \times 0 kJ/mol = 0 kJ/mol$

$CO_2(g)$ $\Delta H_f° = 1 \times -393.5 kJ/mol = -393.5 kJ/mol$

$$\Delta H_{rxn}° = \Delta H°_{products} - \Delta H°_{reactants}$$

$$= -393.5 - (0+0) = -393.5 kJ/mol$$

*Note: If there are multiple reactants or products, you add the multiple $\Delta H_f°$ values before subtracting reactants from products.

Calculate ΔH_{rxn}° for the combustion of $C_2H_5OH(l)$ ΔH_f° values are given below

$$C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

ΔH_f° Reactants:

C_2H_5OH (l): –277.7 kJ/mol

O_2: 0 kJ/mol

Total reactants =

ΔH_f° Products

$CO_2(g)$: –393.5 kJ/mol

$H_2O(l)$: –285.8 kJ/mol

Total products =

ΔH° = products – reactants

A = –1366.7 kJ

Hess's Law Of Constant Heat Summation: Another way to calculate ΔH

The heat of a reaction, ΔH, is constant, whether the reaction is carried out directly in one step or through a number of steps.

The equation for the overall reaction is the sum of two or more other equations (reaction steps).

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \ldots$$

If you reverse a chemical equation, you reverse the sign of ΔH.

$$\Delta H_{forward} = -\Delta H_{reverse}$$

Hess' Law Example #1

What is ΔH when KOH(s) reacts with H_2S0_4 (aq)?

$2\ KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$

This is a 2-step process – dissolve KOH then neutralize – so need to use Hess' Law

Given information: Styrofoam cup calorimetry was used to determine the following:

Step 1. KOH(s) → KOH(aq)

ΔH_{sol} of KOH(s) = –58.4 kJ/mol

Step 2. Neutralization reaction

ΔH per mole KOH = –55.9 kJ/mol

First: Need **2 mol** KOH in rxn; must double given values.

Then: Add the ΔHs for all steps of the reactions

A = –228.6 kJ

Hess' Law: Using Info From Other Reactions

1. Find each reactant in an equation with known enthalpy
    - Use multiple equations if necessary to find all reactants
2. Find each product in an equation with known enthalpy
    - Use multiple equations if necessary to find all products
3. Add reactions to get the reaction you are looking for
    - Cross out items that are both products & reactants
        - stoichiometry matters, might not cross out all
    - Add multiples
4. Check final equation to make sure it matches the equation of interest.

Hess' Law Example #2

What is the enthalpy of the reaction between carbon and oxygen to form carbon monoxide?

$2\ C(graphite) + O_2(g) \rightarrow 2\ CO(g) \qquad \Delta H = ?$

You are given the following reactions with known enthalpies:

$C(graphite) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5\ kJ$

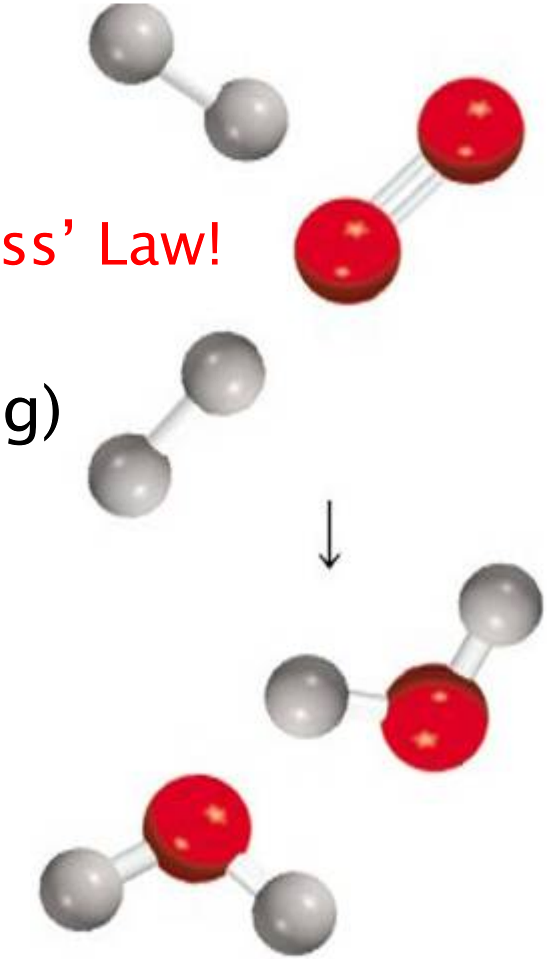
$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g) \qquad \Delta H = -566.0\ kJ$

$2\ C(graphite) + O_2(g) \rightarrow 2\ CO(g) \qquad \Delta H = -221.0\ kJ$

Bond Enthalpy

Bond Enthalpy: reason for energy change during reactions

- Energy required to break a particular bond in a molecule in the **gas** phase.



Enthalpy change for the Reaction (ΔH)

$\Delta H = \Sigma\Delta H_{\text{bond breaking}} + \Sigma\Delta H_{\text{bond formation}}$ Hess' Law!

(Note that bond formation is **negative**)

Enthalpy change: $2H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$

$$\Sigma\Delta H_{\text{bond breaking}} = 2(\Delta H_{\text{H–H}}) + \Delta H_{\text{O=O}}$$
$$= 2(436\text{kJ}) + 499\text{kJ}$$
$$= 1371\text{kJ (endothermic)}$$

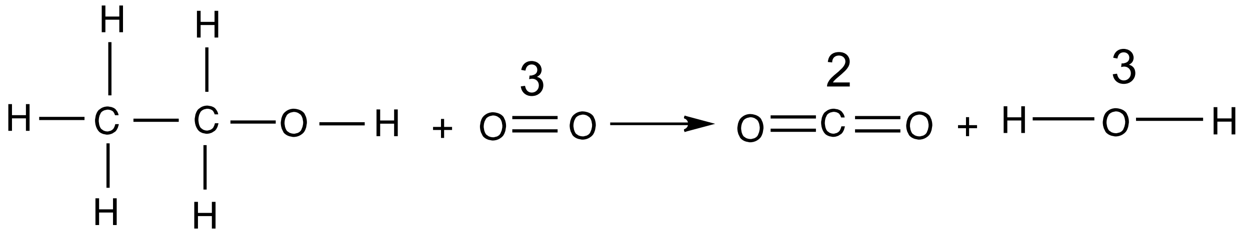
$$\Sigma\Delta H_{\text{formation}} = 4(\Delta H_{\text{H–O}}) = 4(-460\text{kJ})$$
$$= -1840\text{kJ (exothermic)}$$

$$\Delta H_{\text{reaction}} = \Sigma\Delta H_{\text{bond breaking}} + \Sigma\Delta H_{\text{bond formation}}$$
$$\Delta H_{\text{reaction}} = 1371\text{kJ} - 1840\text{kJ} = -469\text{kJ}$$

Just another example – same formula written differently

Theoretical Calculation: $\Delta H = E_{in} - E_{out}$

$$CH_3CH_2OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$$



C–C Bond = 80 kcal/mole

C–H Bond = 100 kcal/mole

C–O Bond = 90 kcal/mole

O=O Bond = 120 kcal/mole

O–H Bond = 110 kcal/mole

C=O Bond = 180 kcal/mole

E_{in}:

1 C-C bond x 80 kcal/mol = 80 kcal/mol
5 C-H bonds x 100 kcal/mol = 500 kcal/mol
1 C-O bond x 90 kcal/mol = 90 kcal/mol
1 O-H bond x 110 kcal/mol = 110 kcal/mol
3 O=O bond x 120 kcal/mol = 360 kcal/mol

1140 kcal/mol

E_{out}:

2x2 C=O bonds x 180 kcal/mol = 720 kcal/mol
3x2 O-H bonds x 110 kcal/mol = 660 kcal/mol

1380 kcal/mol

$\Delta H = E_{in} - E_{out}$
= 1140 kcal/mol – 1380 kcal/mol
= –240 kcal/mol

Estimate the enthalpy change for the combustion of 1 mole of methane

1. Write the reaction: $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$

2. Calculate energy needed to break the bonds in reactants (ΔH_{BB}) and energy produced when the bonds of products form (ΔH_{BF}).

Bonds broken	ΔH	Bonds formed	ΔH

3. Calculate ΔH for the reaction ($\Delta H = \Delta H_{BB} + \Delta H_{BF}$) & divide by coefficient of CH_4.

   $\Delta H_{\text{approx}} =$

A = – 785 kJ/mol methane

Representative Bond Enthalpies

Table 10.4
in your book

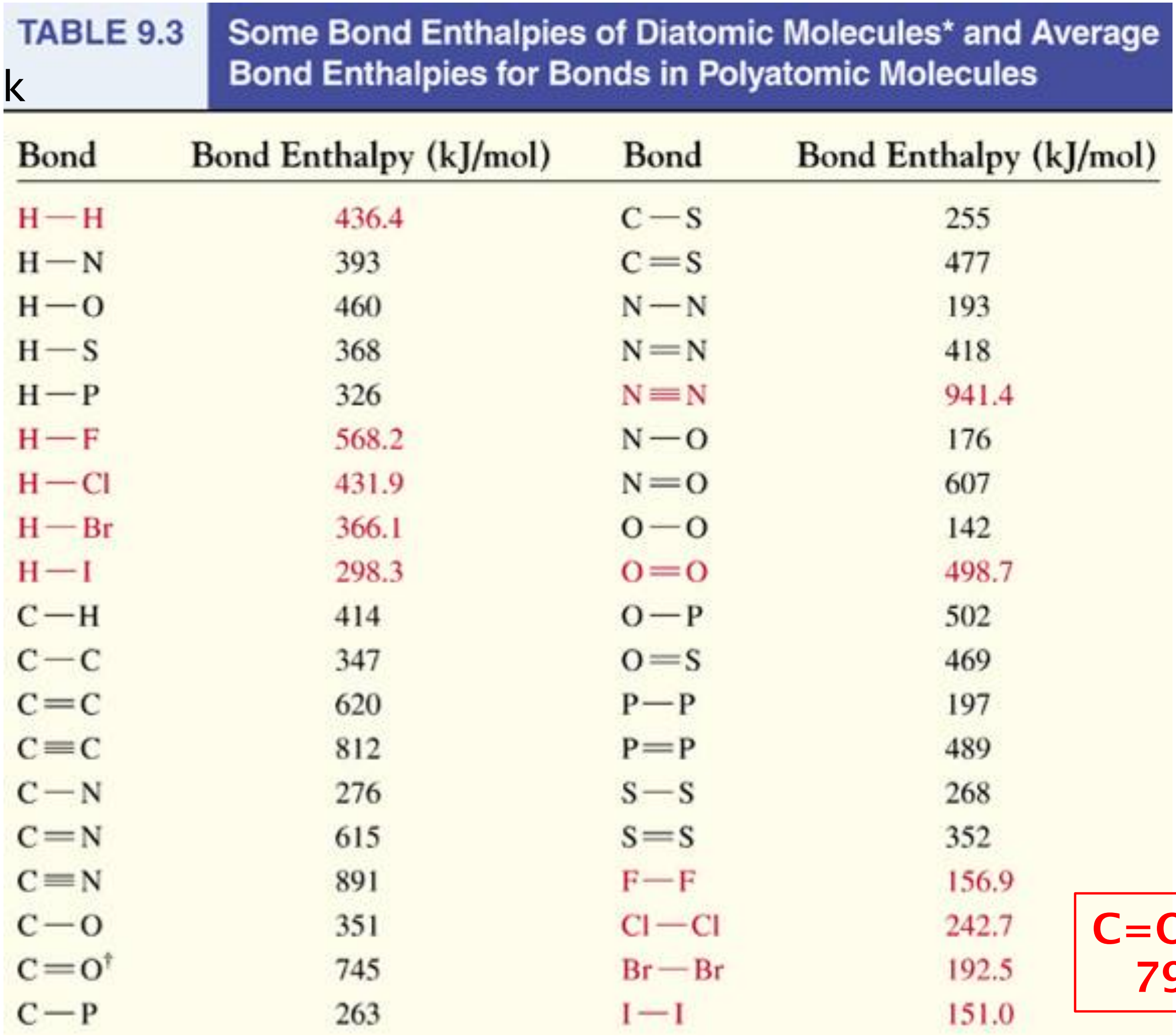


TABLE 9.3 Some Bond Enthalpies of Diatomic Molecules[*] and Average Bond Enthalpies for Bonds in Polyatomic Molecules

Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)
H—H	436.4	C—S	255
H—N	393	C=S	477
H—O	460	N—N	193
H—S	368	N=N	418
H—P	326	N≡N	941.4
H—F	568.2	N—O	176
H—Cl	431.9	N=O	607
H—Br	366.1	O—O	142
H—I	298.3	O=O	498.7
C—H	414	O—P	502
C—C	347	O=S	469
C=C	620	P—P	197
C≡C	812	P=P	489
C—N	276	S—S	268
C=N	615	S=S	352
C≡N	891	F—F	156.9
C—O	351	Cl—Cl	242.7
C=O[†]	745	Br—Br	192.5
C—P	263	I—I	151.0

C=O in CO_2: 799 kJ/mol