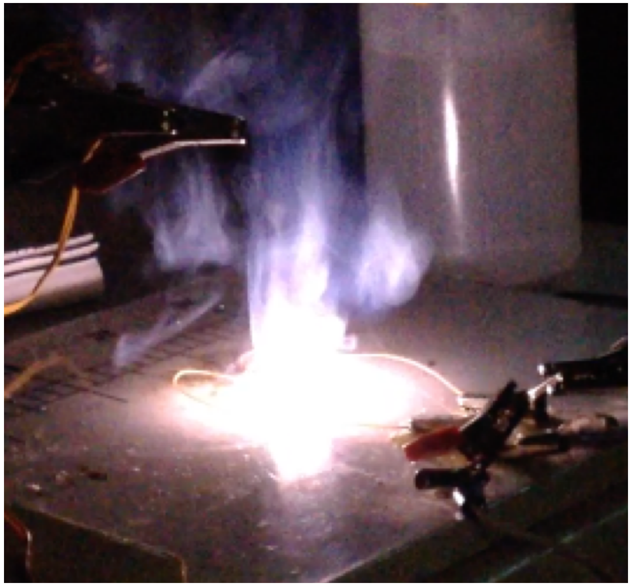
Chapter Six



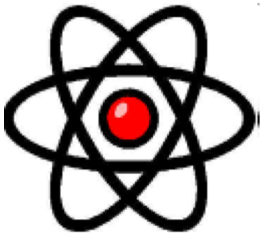
Energy Relationships in Chemical Reactions

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

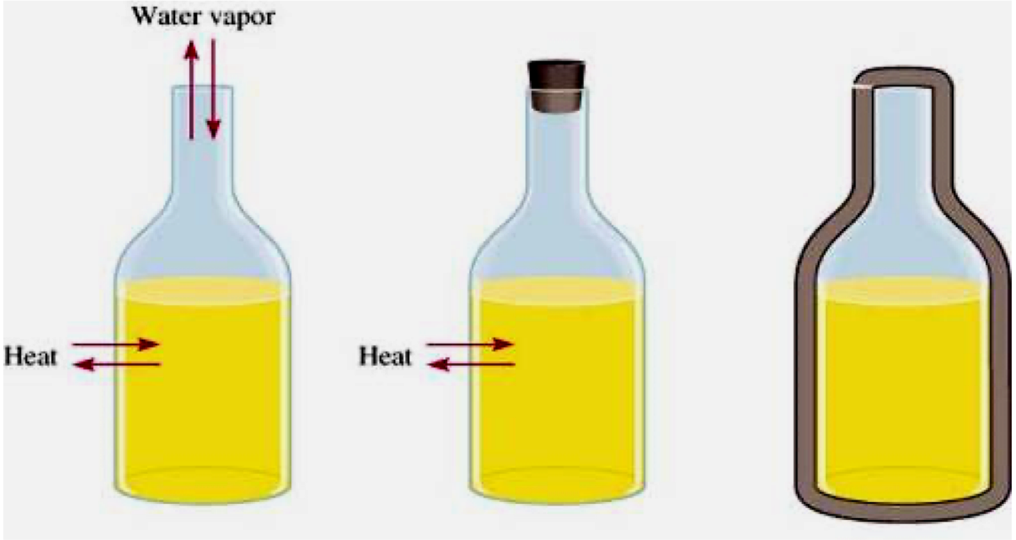
Study of heat change in chemical reactions

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) → 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

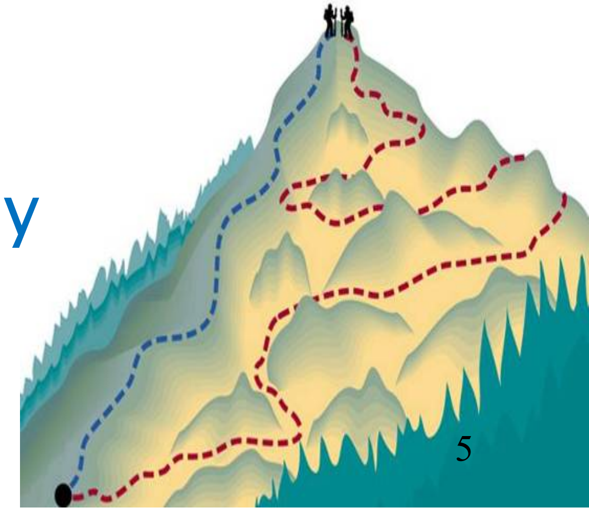
→ process doesn't matter

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

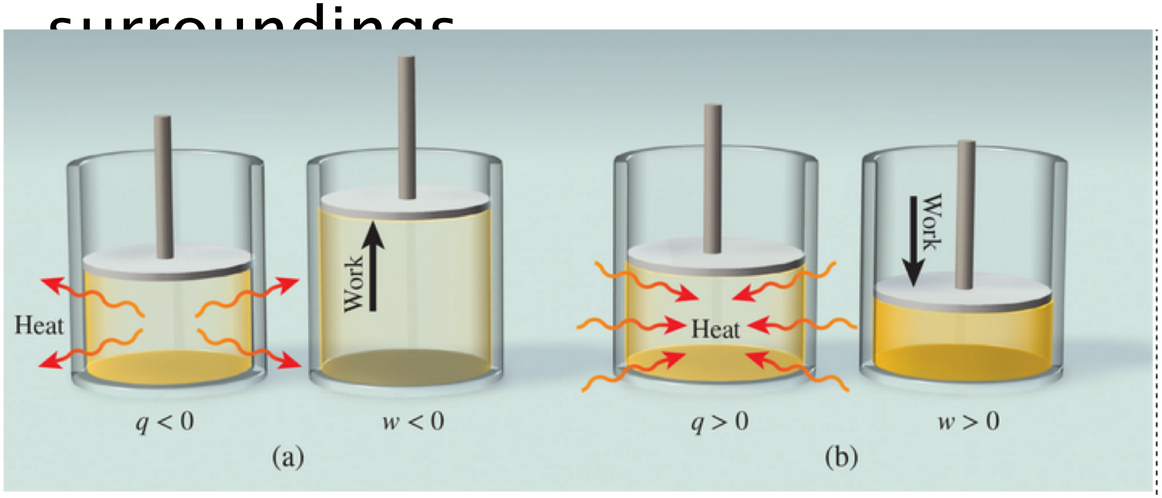
$$\Delta U_{system} = q + w$$

Work (w) = 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



Work (w) = $-P\Delta V$

$\Delta V = V_f - V_i$

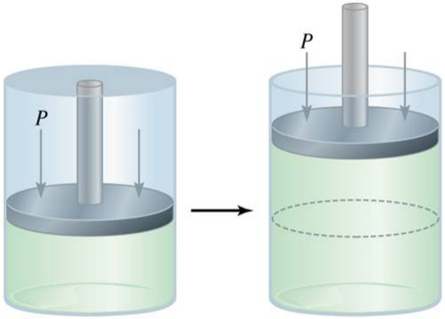
For this situation: $+\Delta V$

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.

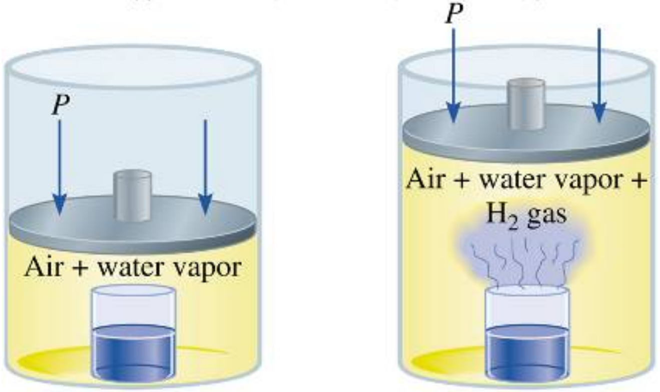
(A = 350.0 J; 552.6 J)

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

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

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

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

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**

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

Endothermic Reaction

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

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

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

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

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

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

2. Reverse the reaction, reverse sign of ΔH

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

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

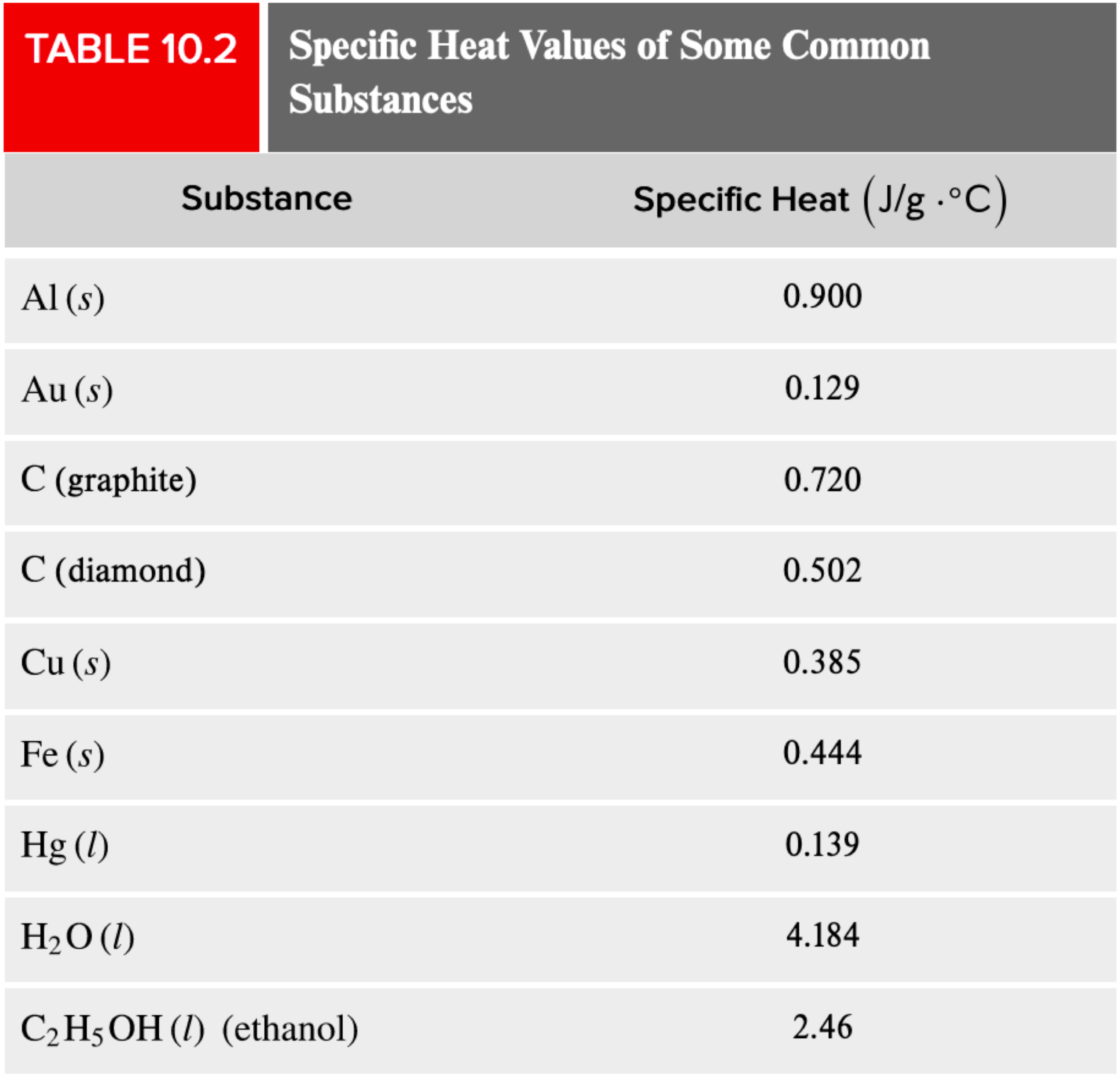


TABLE 10.2 **Specific Heat Values of Some Common Substances**

Substance	Specific Heat $(\text{J/g}\cdot{}^\circ\text{C})$
$Al(s)$	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)

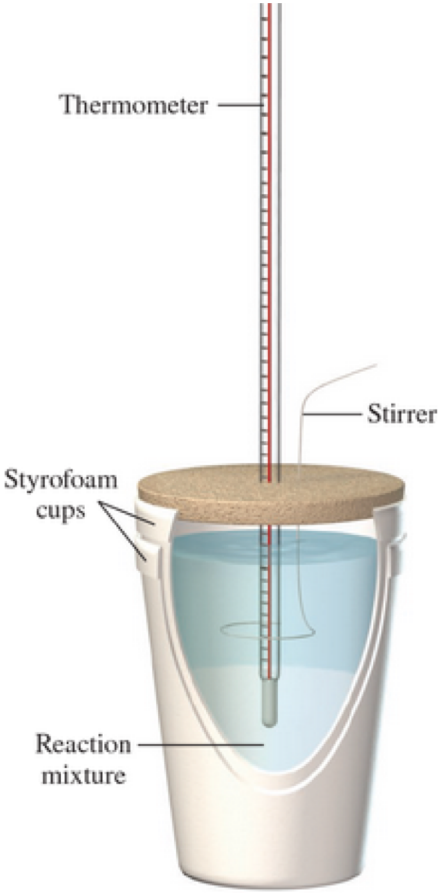
1. Measure ΔT of water in calorimeter
2. Use **$q = ms\Delta T$** to calculate the heat gained or lost by the water
3. Heat gained by the water in the calorimeter is lost by the system; heat heat lost by the water is gained by the system: $-q_{rxn} = q_{cal}$
4. Use q_{rxn} to determine information about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

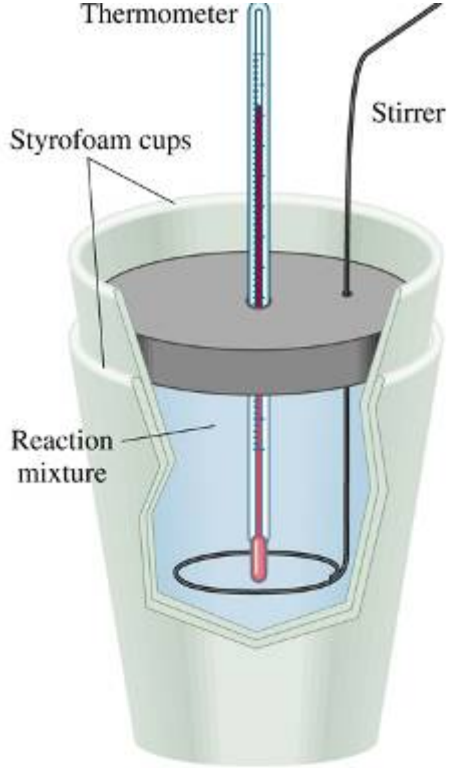
Use formula for q_{metal} to solve for s_{metal}

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 <u>per mole of acid</u> 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:

40.0 mL of 1.00 M KOH(aq)

40.0 mL of 1.00 M H_2S0_4(aq)

T_i of both solutions = 21.00˚C

Final information:

Density: 1.02 g/mL

Volume: 80.0 mL

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 **<u>CALORIMETER</u>**, 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 $q_{cal} = -q_{rxn}$.

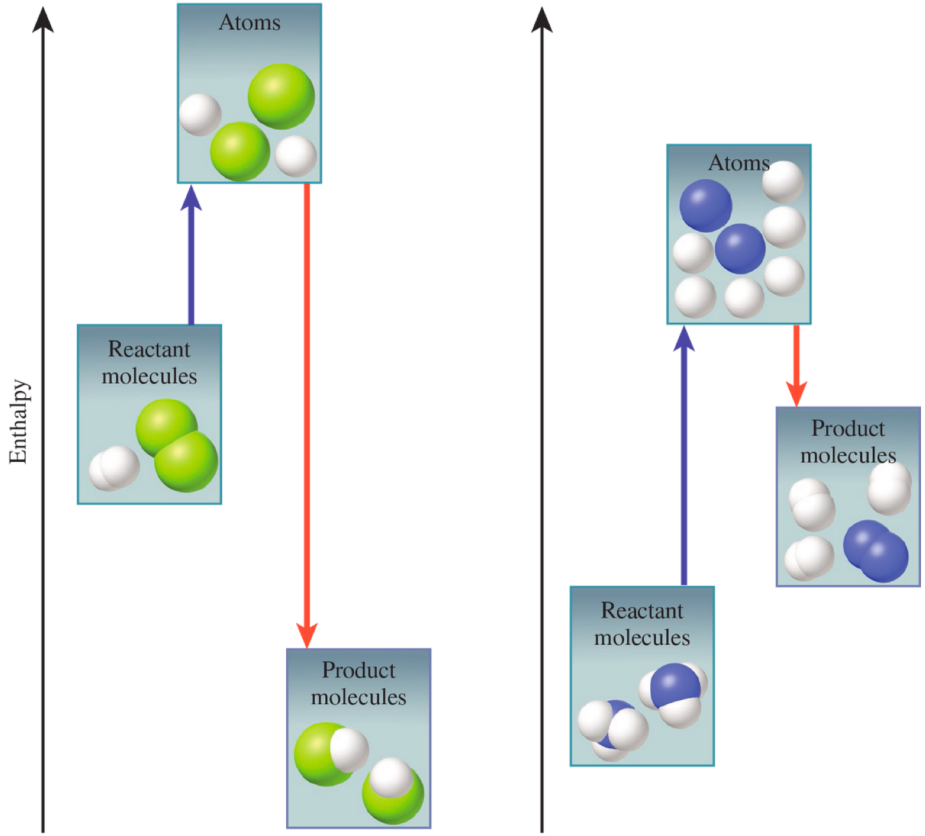
A = -55.9 kJ/mol

Constant Volume 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



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

$\Delta H° = -184.7$ kJ/mol

(a)

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

$\Delta H° = 92.6$ 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: **$\Delta H_f° = 0$**

- 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 ΔH° of a chemical reaction

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

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

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

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

$$\Delta H_{rxn}^\circ = \Delta H^\circ_{products} - \Delta H^\circ_{reactants}$$

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

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

Calculate $\Delta H_{rxn}°$ for the combustion of $C_2H_5OH(l)$ $\Delta H_f°$ values are given below

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

$\Delta H_f°$ Reactants:

C_2H_5OH (l): –277.7 kJ/mol

O_2: 0 kJ/mol

Total reactants =

$\Delta H_f°$ Products

CO_2(g): –393.5 kJ/mol

H_2O(l): –285.8 kJ/mol

Total products =

$\Delta H°$ = 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_2SO_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:

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

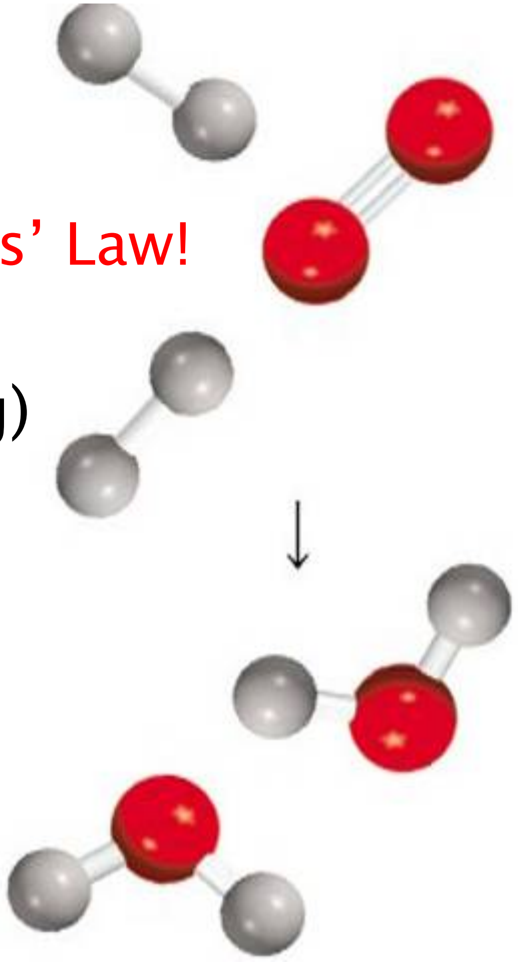
$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g) \qquad \Delta H = -566.0\ kJ$

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

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

$$\begin{aligned}
\Sigma\Delta H_{\text{bond breaking}} &= 2(\Delta H_{\text{H-H}}) + \Delta H_{\text{O=O}} \\
&= 2(436\text{kJ}) + 499\text{kJ} \\
&= 1371\text{kJ (endothermic)}
\end{aligned}$$

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

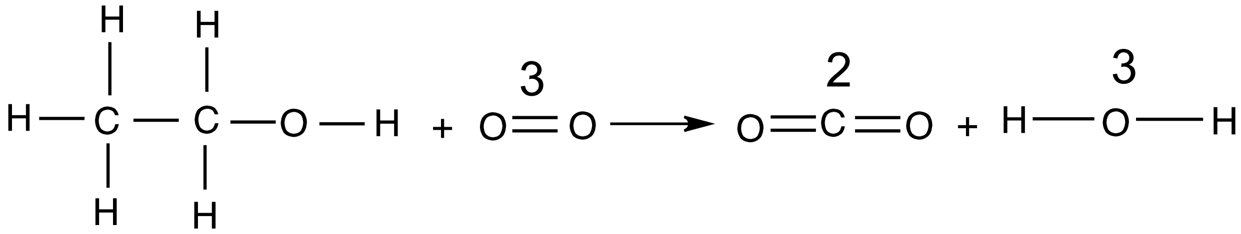
$$\Delta H_{\text{reaction}} = \Sigma\Delta H_{\text{bond breaking}} + \Sigma\Delta H_{\text{bond formation}}$$

$$\Delta H_{\text{reaction}} = 1371\text{kJ} - 1840\text{kJ} = -469\text{kJ}$$

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

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

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

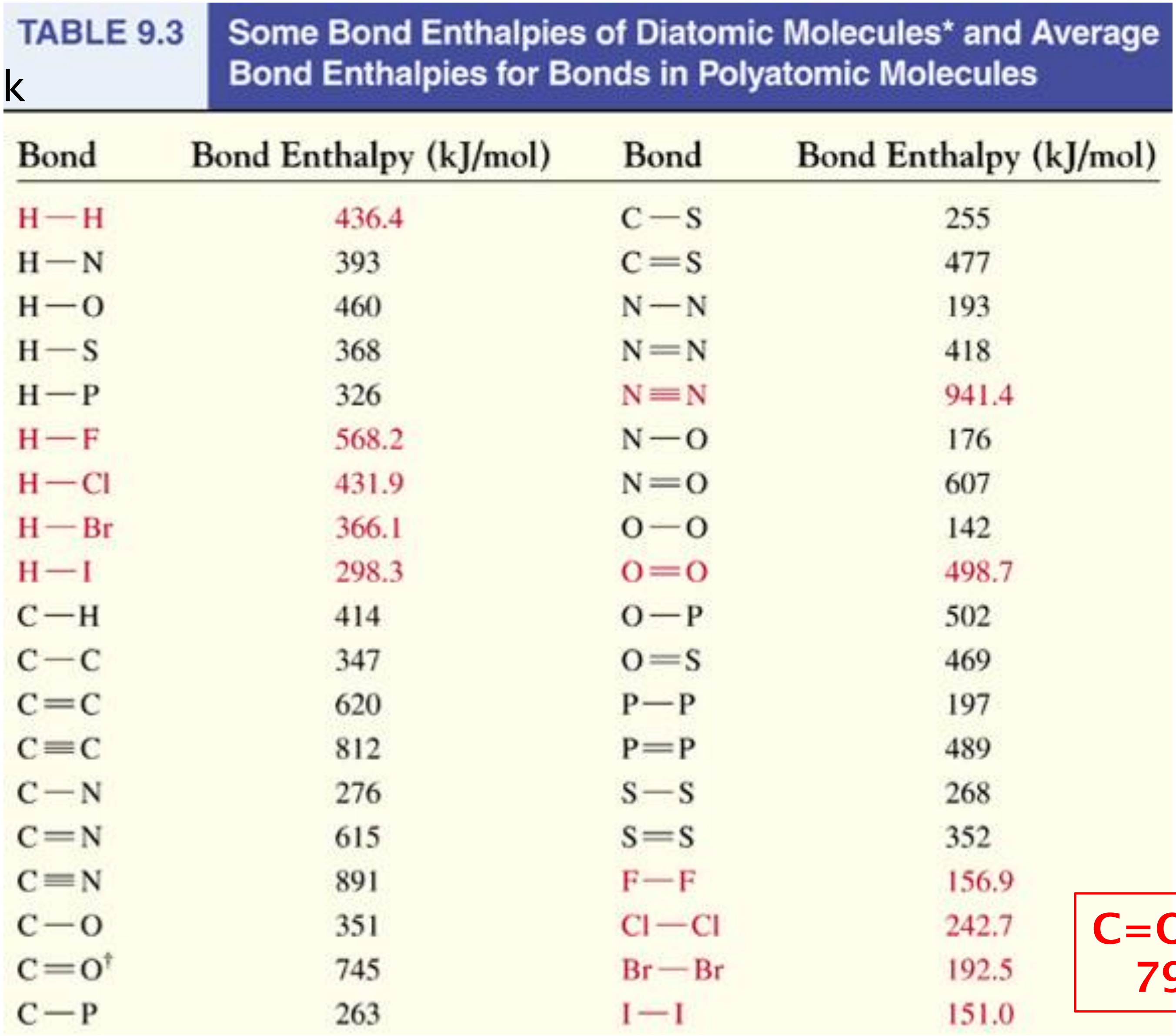


TABLE 9.3 Some Bond Enthalpies of Diatomic Molecules* and Average Bond Enthalpies for Bonds in Polyatomic Molecules

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