Chapter 5 - Thermochemistry

Study of energy changes that
accompany chemical rx's.

I) Nature of Energy

Energy ≡ Capacity to do work

Mechanical Work

$$w = F \times d$$

Heat energy

- energy used to cause the
  temperature of an object to inc.

A) Units of Energy

$$w = F \text{ x } d$$

$$= (\, m \text{ x } a) \text{ x } d$$

$$= (\text{kg} \times \text{m/s}^2) \times \text{m}$$

$$\Downarrow$$

$$= (\text{kg} \bullet \text{m}^2)/\ \text{s}^2 \quad = \text{N} \times \text{m}$$

$$= \text{ joule, } \quad \text{J} \quad (\text{SI unit})$$

calorie (cal)

original def: amt. of energy reg. to raise temp. of 1g of water by 1 °C, from 14.5 °C to 15.5 °C

1 cal = 4.184 J

Cal - nutritional calorie

1 kcal

B) Kinetic & Potential Energy

1) Kinetic Energy

$$\boxed{KE = \tfrac{1}{2} m v^2}$$

Energy due to motion

SI units:

$\text{Energy} = \text{kg}\ (\text{m/s})^2 = \text{J}$

2) Potential Energy

Energy stored in an object by virtue of its position or composition

Chemical energy is due to composition of substances

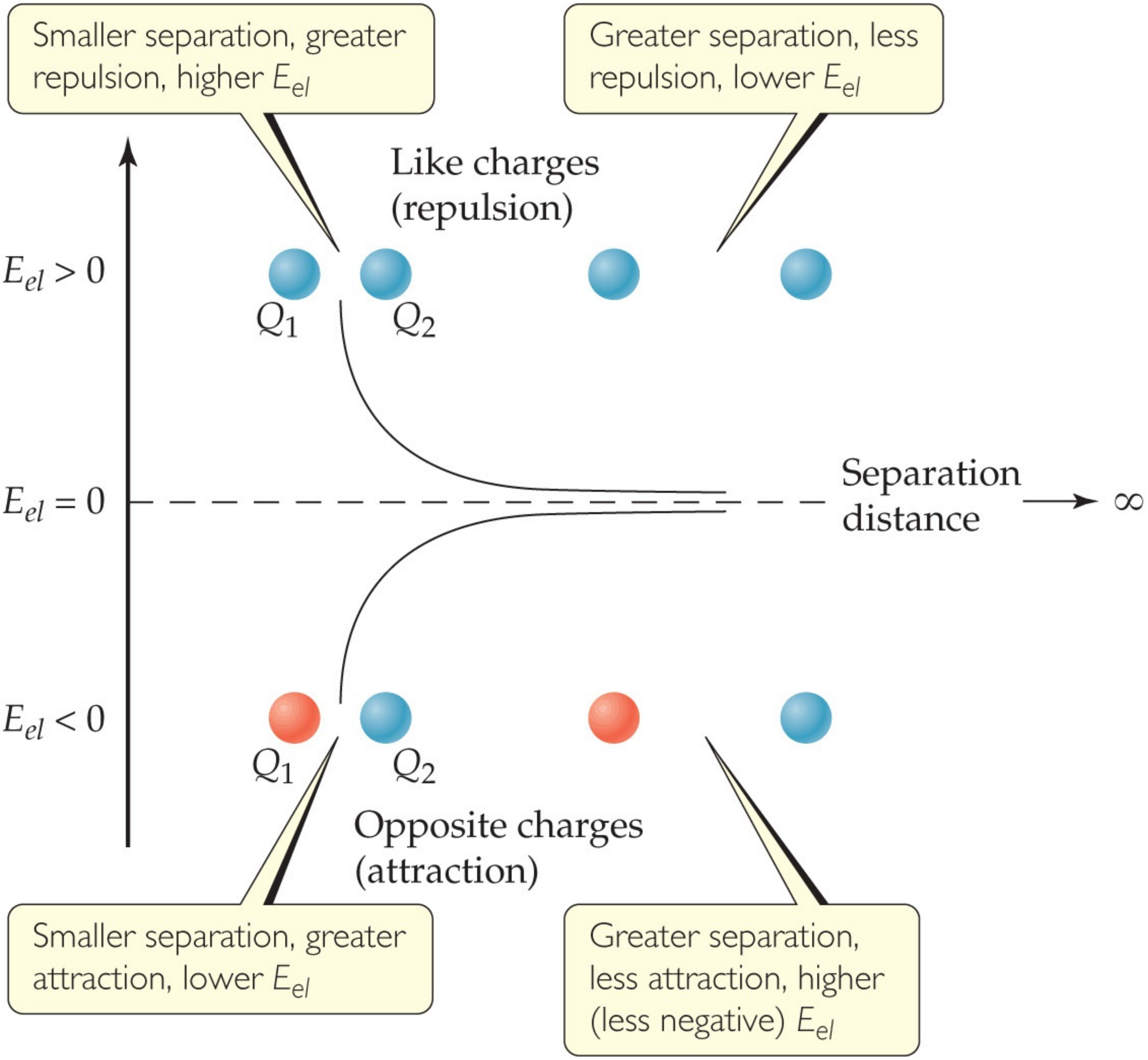
Electrostatic P.E.

Interaction between charged particles

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

Q = charge

d = distance between particles


Smaller separation, greater repulsion, higher E_{el}
Greater separation, less repulsion, lower E_{el}
Like charges (repulsion)
$E_{el} > 0$
Q_1
Q_2
$E_{el} = 0$
Separation distance
∞
$E_{el} < 0$
Q_1
Q_2
Opposite charges (attraction)
Smaller separation, greater attraction, lower E_{el}
Greater separation, less attraction, higher (less negative) E_{el}

C) System and Surroundings

System = portion we single out for study

- focus attention on changes which occur w/in definite boundaries

Surroundings = everything else

System : Contents of rx. flask

Surround. : Flask & everything outside it

Agueous soln. rx :

System : dissolved ions & molecules
Surround : H_2O that forms the soln.

II) First Law of Thermodynamics

Law of Conservation of Energy :

Energy can be neither created nor destroyed but may be converted from one form to another.

Energy lost = Energy gained
by system by surroundings

A) Internal Energy, E

E = total energy of the system

Actual value of E
cannot be determined

ΔE, change in energy, can
be determined

Δ = final state − initial state

$$\Delta E \equiv E_f - E_i$$

Sign of ΔE is important

$E_f > E_i$, $\Delta E > 0$ system gained energy

$E_f < E_i$, $\Delta E < 0$ system lost energy

Systems tend to go to lower energy state

- more stable products

i.e. rx's in which $\Delta E < 0$

B) Thermodynamic State & State Functions

Thermodynamic State of a System

defined by completely specifying
ALL properites of the system

- P, V, T, composition, physical st.

1) State Function

prop. of a system determined
by specifying its state.

depends only on its present
conditions & NOT how it got there

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

independent of path taken
to carry out the change

- Also is an extensive prop.

C) Relating ΔE to Heat & Work

2 types of energy exchanges occur between system & surroundings

Heat & Work

+ q : heat absorbed, endothermic

– q : heat evolved, exothermic

+ w : work done on the system

– w : work done by the system

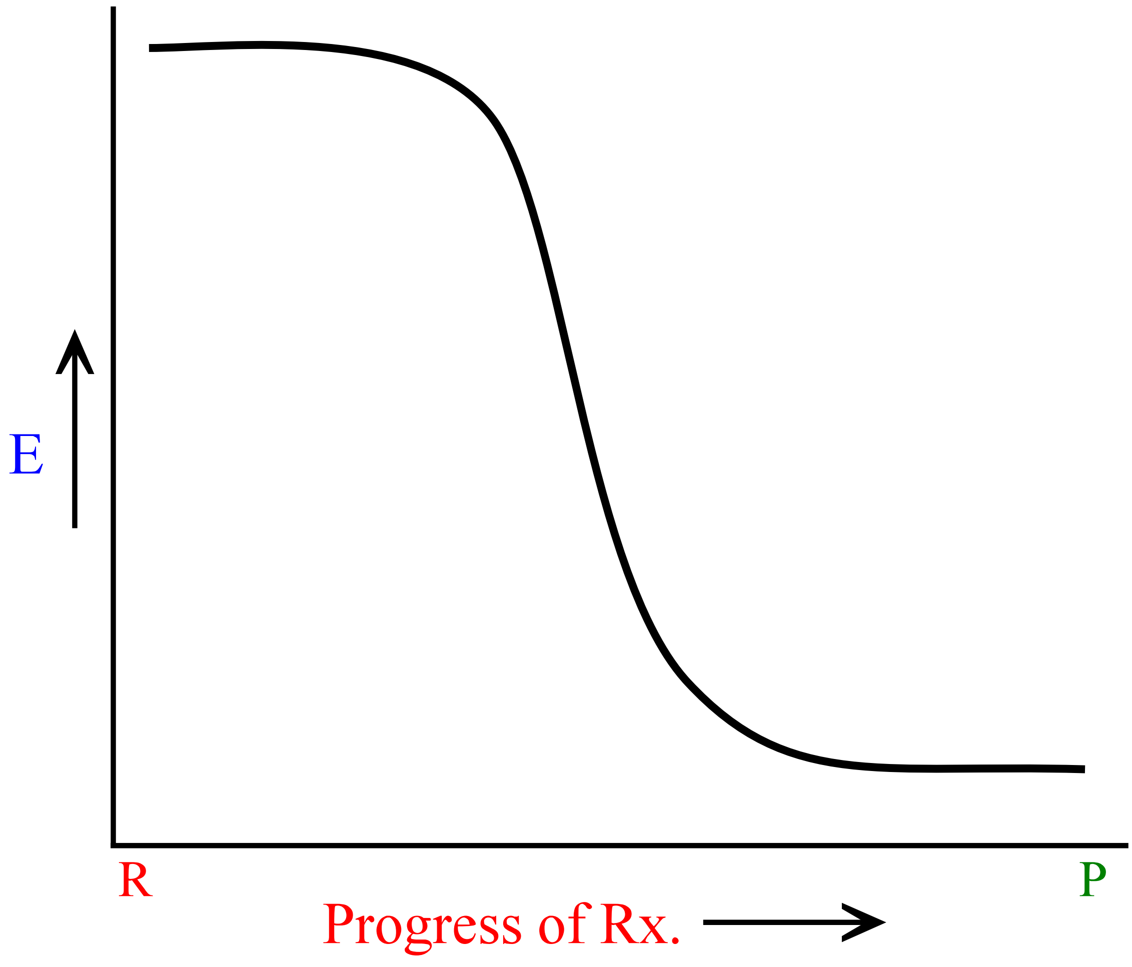
1) First Law

$$\boxed{\Delta E = q + w}$$

1) Exothermic Reactions

heat is released

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(\ell) + \text{heat}$$

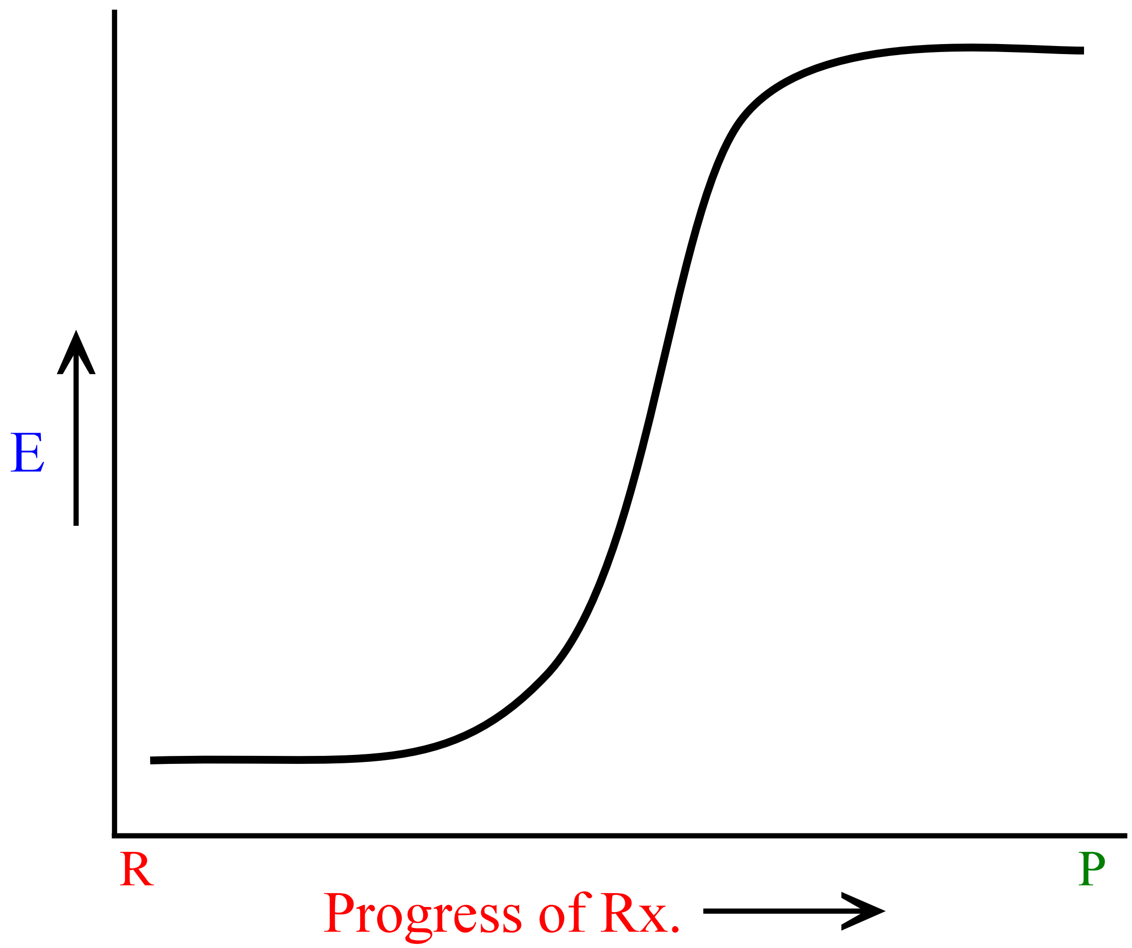


2) Endothermic Reactions

heat is absorbed

- reaction requires input of energy

$$2\,H_2O(\ell) + \text{heat} \rightarrow 2\,H_2(g) + O_2(g)$$



III) Enthalpy

In ordinary chem. rx., work generally arises as a result of pressure-volume changes

Inc. vol. & system does work against pressure of the atmosphere

$P \cdot V$ has dimensions of work :

$$P \cdot V = (F/A)V = (kg \cdot m/\,s^2 \cdot m^2)\,m^3 = (kg \cdot m^2)/(s^2) = J$$

Constant Pressure

$$w = -P\,\Delta V$$

Negative because work done by system

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

A) ΔE at Constant Volume

$$\boxed{\Delta E = q_v}$$

B) ΔE at Constant Pressure :

$$\Delta E = q_p - P\,\Delta V$$

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

C) Enthalpy, H

$$H = E + PV$$

Change in enthalpy at constant P is:

$$\boxed{\Delta H = \Delta E + P\,\Delta V}$$

&

$$\boxed{\Delta H = q_p}$$

Can think of as heat content

state fnc. & is extensive

IV) Enthalpies of Reaction

$$\Delta H_{rxn} = H_{products} - H_{reactants}$$

A) Exothermic Rx's

$H_p < H_r$, $\Delta H_{rxn} < 0$, exothermic

Heat is evolved

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(\ell) \quad \Delta H = -572\ \text{kJ}$$

Thermochemical eqn.

Physical states are given and energy associated w. rx. written to right

- MUST give physical states

If product is $H_2O(g)$, $\Delta H = -484\text{kJ}$

ΔH corresponds to molar quantities given in eqn. as written

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell) \quad \Delta H = -286 \text{ kJ}$

B) Endothermic Rx's

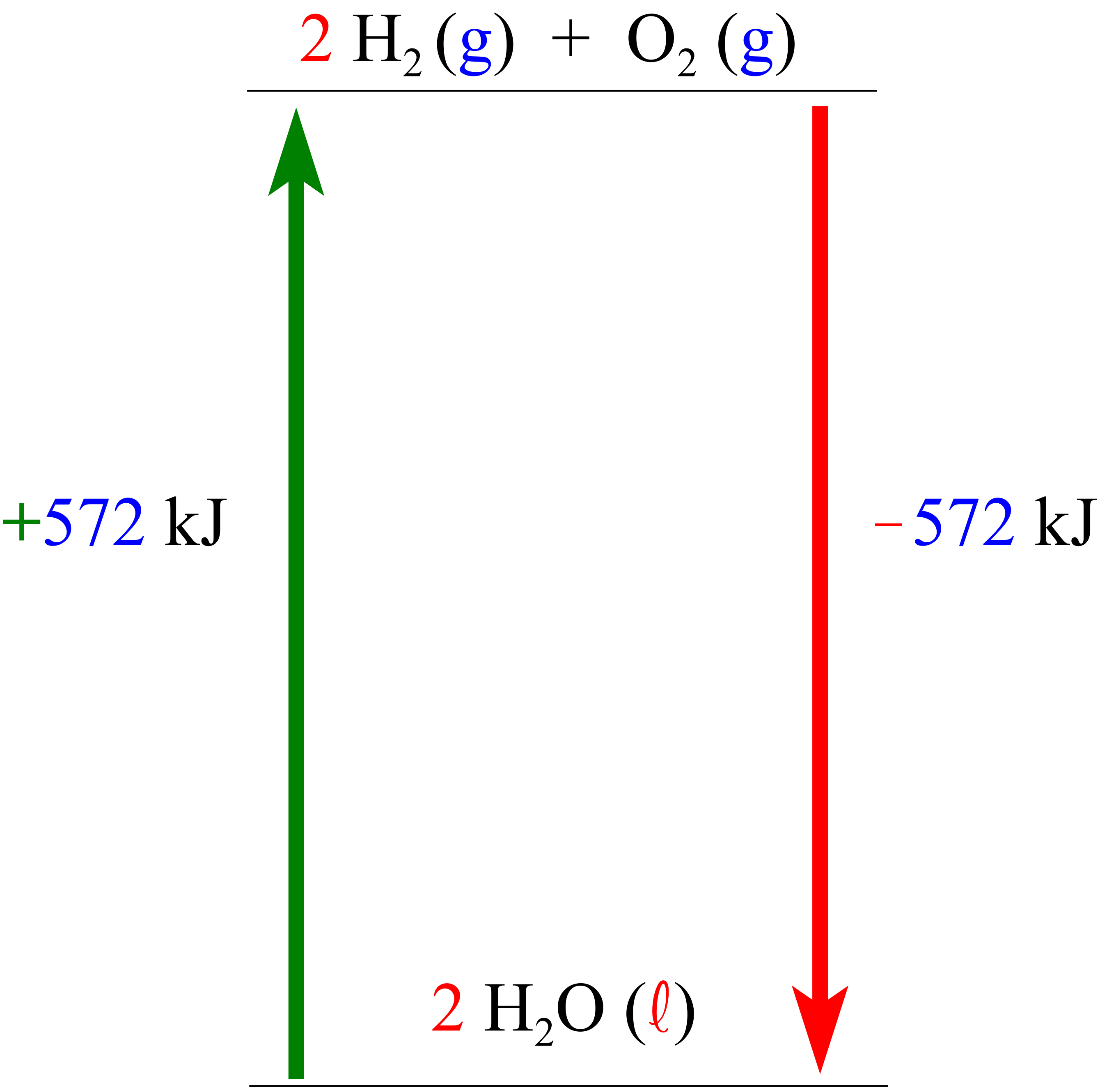
$H_p > H_r$, $\Delta H_{rxn} > O$, endothermic

Heat is absorbed

$2\, H_2O(\ell) \rightarrow 2\, H_2(g) + O_2(g) \quad \Delta H = +572 \text{kJ}$

Reverse of previous rx.

Enthalpy Diagram



$2\ H_2(g) + O_2(g)$

+572 kJ

−572 kJ

$2\ H_2O(\ell)$

C) Guidelines

1) Enthalpy is extensive

Multiply a rxn by some factor the ΔH is multiplied by that factor

2) $\Delta H_{\textbf{reverse}} = - \Delta H_{\textbf{forward}}$

3) Enthalpy is a state function

ΔH depends on the states of reactants and products.

D) Determining ΔH for a Rx.

Convenient sample sizes are reacted & conv. factors are used to obtain the heat energy

1) Ex 1: When 36.0g of Al reacts w. excess Fe_2O_3 how much heat is released?

$$2\,Al(s) + Fe_2O_3(s) \longrightarrow 2\,Fe(s) + Al_2O_3(s)$$

$$\Delta H_{rxn} = -847\text{ kJ}$$

$$?\text{ kJ} = 36.0\text{ g Al} \times \frac{1\text{ mol Al}}{26.98\text{ g Al}} \times \frac{847\text{ kJ}}{2\text{ mol Al}} = 56\underline{5}.08\text{ kJ} = 565\text{ kJ}$$

VII) Calorimetry

Exp. method of obtaining ΔH & ΔE

Heat evolved or absorbed by system will be reflected in the surroundings.

Need surr. Heat Capacity, C

$$\boxed{C = \frac{q}{\Delta T}}$$

Quantity of heat required to raise the temp. of an object by 1 °C

Unit: (J/°C) or (J/K)

C_m - molar heat capacity

heat capacity per mole, J/mol•°C

C_s - specific heat

heat capacity per gram, J/g•°C

C_s of H_2O = 4.184 J/g•°C

$$q = C \times \Delta T$$

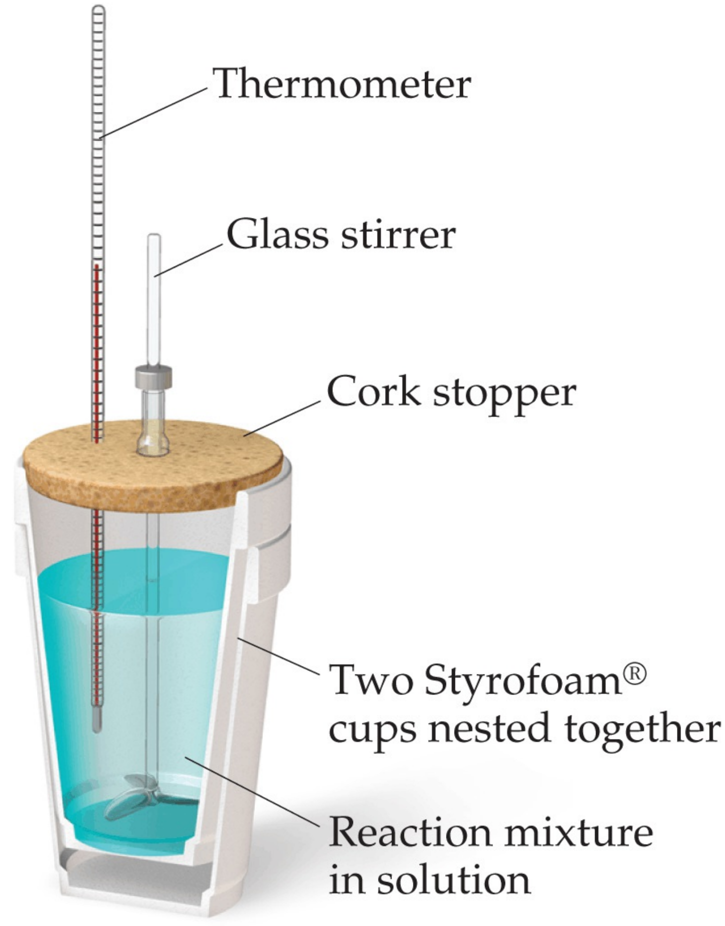
$$q = n \times C_m \times \Delta T$$

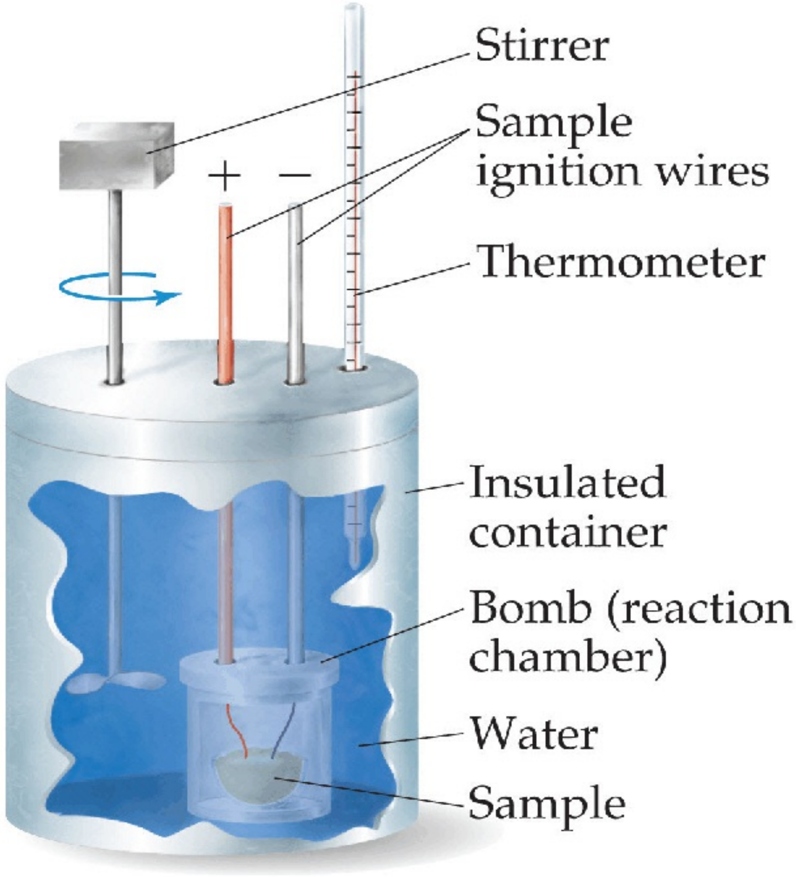
$$q = m \times C_s \times \Delta T$$

$$q_{gained} = -q_{lost}$$

Calorimeter ΔH (q_p)

Bomb Calorimeter ΔE (q_v)


Thermometer
Glass stirrer
Cork stopper
Two Styrofoam® cups nested together
Reaction mixture in solution


Stirrer
+
−
Sample ignition wires
Thermometer
Insulated container
Bomb (reaction chamber)
Water
Sample

A) Ex 1: What amt. of heat has been absorbed by 1.000 kg of water if its temp. inc. from 18.22 °C to 22.73 °C?

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

$$= (1.000 \times 10^3 g)(4.184\ J/g \bullet {}^\circ C)\underbrace{(22.73 - 18.22)}_{\downarrow\ 4.51\ {}^\circ C}$$

= 18,869.84 J

= 18.9 kJ (3 s.f.)

B) Ex 2: A 0.562 g sample of graphite is placed in a bomb calorimeter & ignited in the presence of excess O_2 at 25.00 °C & 1 atm. The temp. of the calorimeter rises to 25.89 °C. The heat capacity of the calorimeter & contents is 20.7 kJ/°C. What is ΔH at 25.00 °C and 1 atm?

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$$

$$q_{\textbf{(lost by rxn)}} = -\, q_{\textbf{(gained by calor. \& contents)}}$$

$$q_{\textbf{rxn}} = -\, C_{\textbf{cal}}\, \Delta T$$

$$= -\,(20.7\ \text{kJ/°C})(25.89\ \text{°C} - 25.00\ \text{°C})$$

$$= -\,1\underline{\mathbf{8}}.4\ \text{kJ}\ (q_v \text{ or } \Delta E \text{ for } 0.562\ \text{g})$$

Want kJ/mol,

$$? \frac{\text{kJ}}{\text{mol}} = \frac{-\ 1\underline{\mathbf{8}}.4\ \text{kJ}}{0.562\ \text{g C}} \text{ x } \frac{12.0\ \text{g C}}{1\ \text{mol C}}$$

$$= -\ 3.\underline{\mathbf{9}}3 \text{ x } 10^{2}\ \text{kJ/mol}$$

$$\Delta E = -\ 3.9 \text{ x } 10^{2}\ \text{kJ/mol}$$

since no change in moles of gas

$$\Delta H = \Delta E$$

VI) Hess's Law

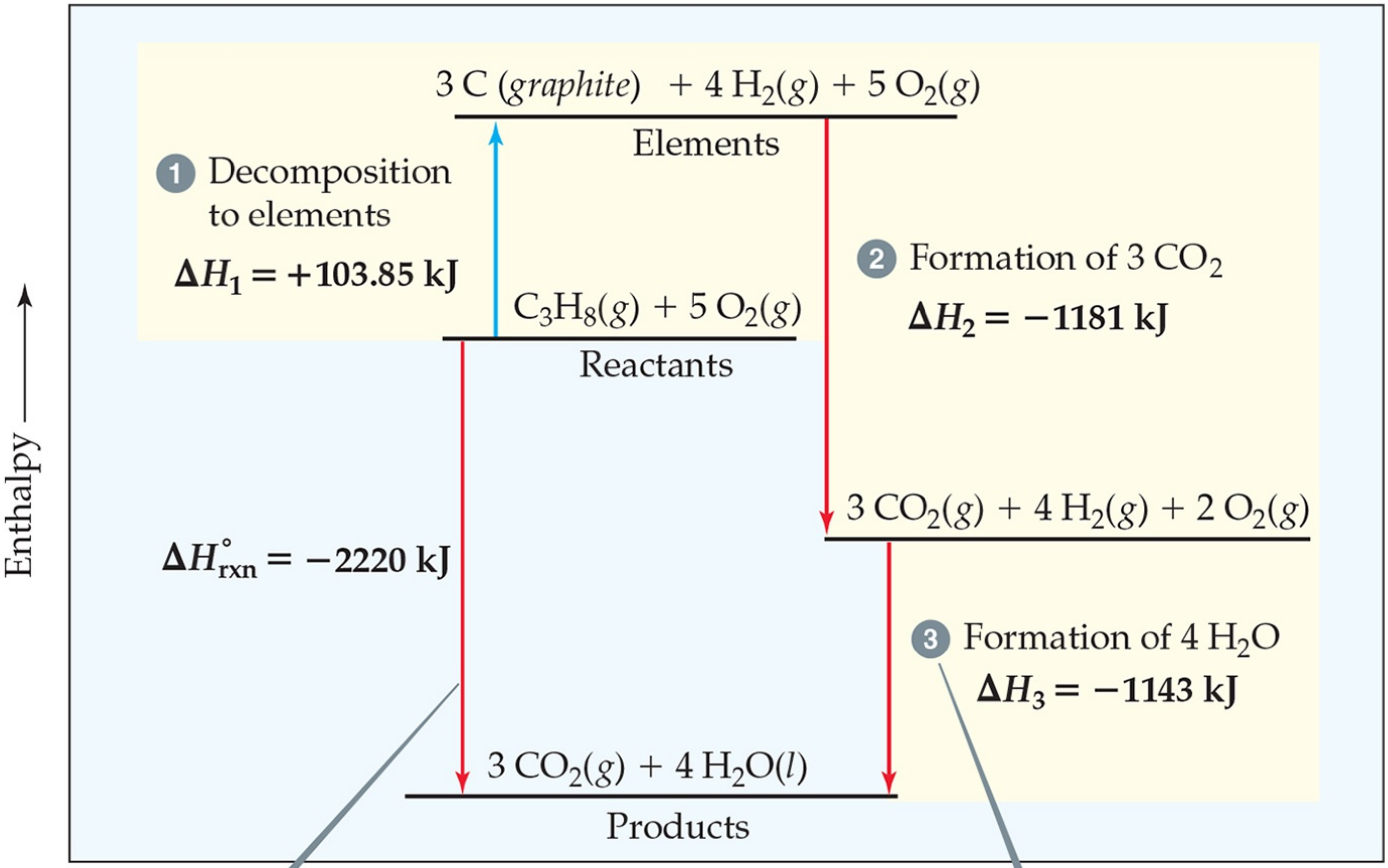
ΔH is a state fnc.

Same whether the process occurs as a single step or as a series of steps

The ΔH_{rxn} is the sum of the ΔH's for the individual steps.

$$\Delta H_{rx} = \sum_{\text{Steps}} \Delta H_{steps}$$

- * Add chem. eqn's for steps to get overall rxn.
- * Add $\Delta H_{steps} \Rightarrow \Delta H_{rxn}$



This red arrow shows one route to products $CO_2(g)$ and $H_2O(l)$.

Numbered steps with pale yellow background show multistep route to same products.

A) Ex 1 : What is ΔH for

$$\mathbf{Ca(OH)_2(s) + SO_3(g) \rightarrow CaSO_4(s) + H_2O(g)}$$

We know the following:

$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g)$ $\Delta H_1 = +109$ kJ

$CaO(s) + SO_3(g) \rightarrow CaSO_4(s)$ $\Delta H_2 = -401$ kJ

$Ca(OH)_2(s) + CaO(s) + SO_3(g) \rightarrow$ $\Delta H_{rxn} = -292$kJ

$CaSO_4(s) + CaO(s) + H_2O(g)$

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

B) Ex 2 :Want ΔH for rxn.

$C_2H_2(g) + 5N_2O(g) \rightarrow 2CO_2(g) + H_2O(g) + 5N_2(g)$

Have:

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

$\Delta H_{1a} = -2512$ kJ

$N_2(g) + \frac{1}{2}\ O_2(g) \rightarrow N_2O(g) \quad \Delta H_{2a} = +\ 81.6$ kJ

Adjust eqn's so they are in proper amt's and the correct directions so they add up to the desired eqn.

ALL substances NOT appearing in desired eqn. MUST cancel.

Divide eqn. 1a by 2 (also ΔH)

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

$\Delta H_{1b} = -\ 1256\ kJ$

Reverse eqn. 2a and multiply by 5

$5\ N_2O(g) \rightarrow 5\ N_2(g) + 5/2\ O_2(g)$

$\Delta H_{2b} = -\ 408\ kJ$

Add & Cancel

$C_2H_2(g) + 5N_2O(g) \rightarrow 2CO_2(g) + H_2O(g) + 5N_2(g)$

$$\Delta H_{rxn} = \Delta H_{1b} + \Delta H_{2b}$$

$$= -\ 1256\ kJ + -\ 408\ kJ$$

$$= -\ 1664\ kJ$$

C) Note:

In using Hess's Law:

1) If an eqn. is multiplied by a factor, ΔH is multiplied by the same factor.

2) If an eqn. is reversed, sign of ΔH changes

3) All substances NOT appearing in desired eqn. MUST cancel

VII) Enthalpy of Formation

Enthalpy change for the formation of a compound from its elements

ΔH_f

A) Standard enthalpy change

Enthalpy change when all reactants and and products are in their standard states

ΔH°

1) Standard State

Most stable state of a substance in its pure form under standard pressure (1 atm) & some specified temp. of interest (usually 25 °C)

2) Thermochemical Standard States

A) solid or liquid

Pure substance at 1 atm

b) gas

pressure of 1 atm

c) species in solution

Conc. of 1 M

B) Standard Enthalpy of Formation

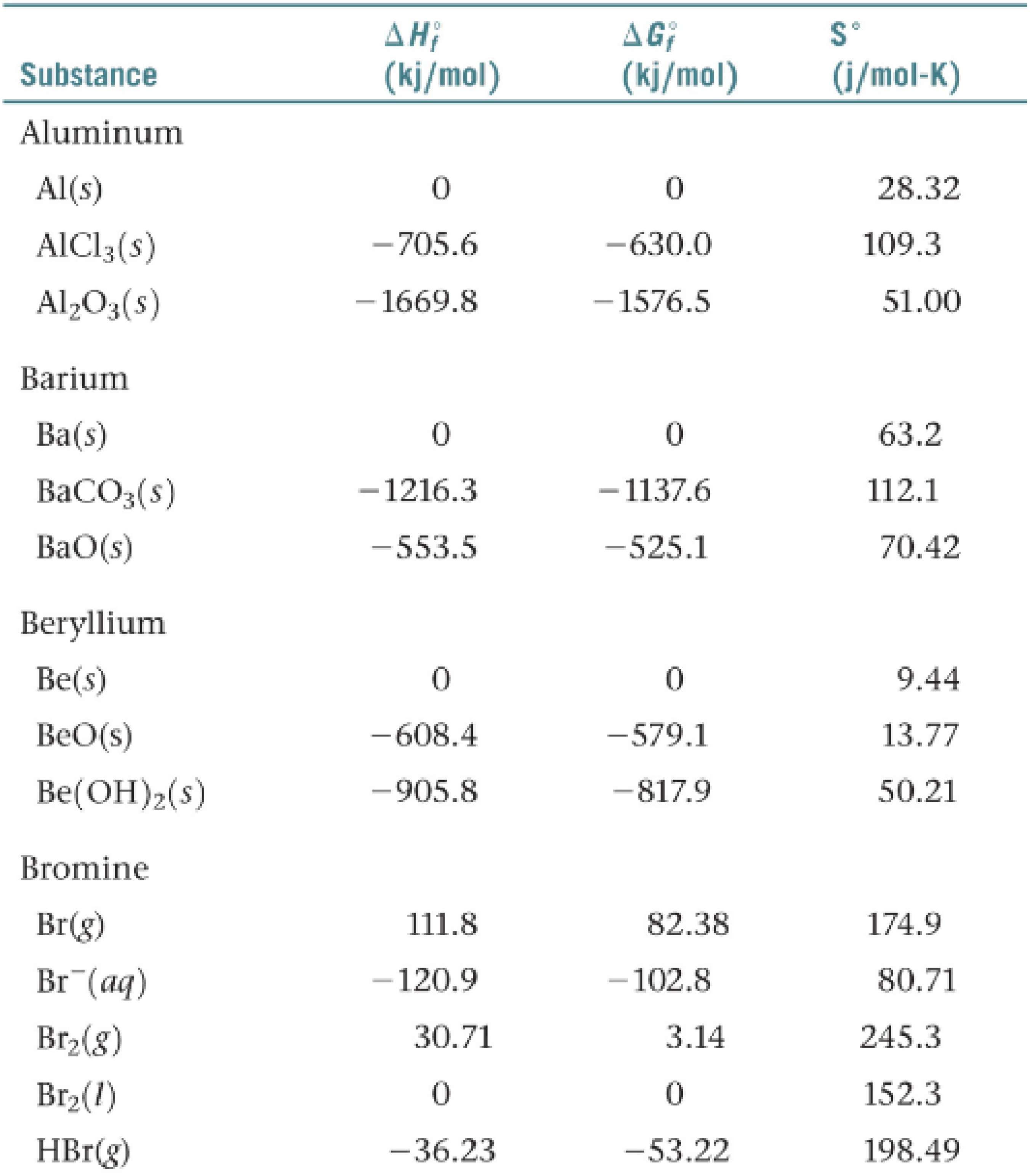
ΔH for the rxn in which 1 mole of a cmpd. is formed from its elements with ALL substances in their standard states (in kJ/mol)

ΔH_f°

Note: $\Delta H_f^\circ = \mathbf{0}$ for an element in its standard state

	ΔH_f°
$1/2\ N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g)$	− 46.2
$Na(s) + 1/2\ Cl_2(g) \rightarrow NaCl(s)$	− 411.0
C(graphite) → C(diamond)	+ 1.897

Thermodynamic Quantities at 298.15 K



Substance	ΔH_f° (kj/mol)	ΔG_f° (kj/mol)	S° (j/mol-K)
Aluminum			
$Al(s)$	0	0	28.32
$AlCl_3(s)$	−705.6	−630.0	109.3
$Al_2O_3(s)$	−1669.8	−1576.5	51.00
Barium			
$Ba(s)$	0	0	63.2
$BaCO_3(s)$	−1216.3	−1137.6	112.1
$BaO(s)$	−553.5	−525.1	70.42
Beryllium			
$Be(s)$	0	0	9.44
$BeO(s)$	−608.4	−579.1	13.77
$Be(OH)_2(s)$	−905.8	−817.9	50.21
Bromine			
$Br(g)$	111.8	82.38	174.9
$Br^-(aq)$	−120.9	−102.8	80.71
$Br_2(g)$	30.71	3.14	245.3
$Br_2(l)$	0	0	152.3
$HBr(g)$	−36.23	−53.22	198.49

C) Determine ΔH°_{rxn} from ΔH_f°

$$\boxed{\Delta H^\circ_{rxn} = \sum_{\text{prod.}} n\,\Delta H_f^\circ - \sum_{\text{react.}} m\,\Delta H_f^\circ}$$

n = coef. in bal. eqn. for each **product**

m = coef. in bal. eqn. for each **reactant**

1) Ex1 : Find ΔH°_{rxn} for the following rx. using Hess's Law and ΔH_f°.

$$2\,H_2S(g) + 3\,O_2(g) \rightarrow 2\,H_2O(\ell) + 2\,SO_2(g)$$

	ΔH° (kJ/mol)
(a) $H_2(g) + S(s) \rightarrow H_2S(g)$	$-$ 20.2
(b) $H_2(g) + \frac{1}{2}\,O_2(g) \rightarrow H_2O(\ell)$	$-$ 285.8
(c) $S(s) + O_2(g) \rightarrow SO_2\,(g)$	$-$ 296.9

Need to:

Rev. eqn. (a) and × 2

Add eqn. (b) × 2

Add eqn. (c) × 2

$2H_2S(g) \rightarrow 2H_2(g) + 2S(s)$

$\Delta H_{rxn} = -2 \bullet (-20.2) = +\ 40.4\ \text{kJ}$

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

$\Delta H_{rxn} = 2(-285.8) = -\ 571.6\ \text{kJ}$

$2S(s) + 2O_2(g) \rightarrow 2SO_2(g)$

$\Delta H_{rxn} = 2(-296.9) = -\ 593.8\ \text{kJ}$

$2H_2S + 2H_2 + 2S + 3O_2 \rightarrow$
$2H_2 + 2S + 2H_2O + 2SO_2$

$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$

$\Delta H_{rx} = (+\ 40.4) + (-571.6) + (-593.8)$

$= -\ 1125\ \text{kJ}$

a) Use ΔH_f° instead

$$\Delta H^\circ_{rxn} = [\,2\,\Delta H_f^\circ\,(H_2O) + 2\,\Delta H_f^\circ\,(SO_2)]$$

$$-\,[\,2\,\Delta H_f^\circ\,(H_2S) + 3\,\Delta H_f^\circ\,(O_2)]$$

$$= [2\,(-285.8) + 2\,(-296.9)]$$

$$-\,[2\,(-20.2) + 3\,(0)]$$

$$= -\,1125\text{ kJ}$$

2) Ex 2: Useful when considering organic cmpds. for which $\Delta H_f°$ can not be determined directly.

What is $\Delta H_f°$ for benzene?

$6\ C(s) + 3\ H_2(g) \rightarrow C_6H_6(\ell) \qquad \Delta H_f° = ?$

This rx. does not happen.

Use of exp. heat of combustion

$$C_6H_6(\ell) + 15/2\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(\ell)$$

$$\Delta H°_{rxn} = -\ 3271\ \text{kJ}$$

$$\Delta H^\circ_{rxn} = [\,6\,\Delta H_f^\circ\,(CO_2) + 3\,\Delta H_f^\circ\,(H_2O)]$$

$$-\,[\,\Delta H_f^\circ\,(C_6H_6) + 15/2\,\Delta H_f^\circ\,(O_2)]$$

$$-3271\text{ kJ} = [\,6\,(-393.5) + 3\,(-285.8)\,]$$

$$-\,[\,\Delta H_f^\circ\,(C_6H_6) + 15/2\,(0)\,]$$

$$-3271\text{ kJ} = [-\,3218.4] - [\,\Delta H_f^\circ\,(C_6H_6)\,]$$

$$\Delta H_f^\circ\,(C_6H_6) = [-\,3218.4] - (-\,3271)$$

$$= +\,52.6\text{ kJ}$$

VIII) Bond Enthalpy

Energy changes in chem. rxns. are related to changes in forming & breaking bonds.

Assign an enthalpy to a specific bond - the bond dissociation energy (BDE) or bond enthalpy (BE).

Energy required to dissociate one mole of bonds in the gas phase (kJ/mol)

A) Homonuclear Molecules

$H_2(g) \rightarrow 2\,H(g)$ $\Delta H = D(H\text{-}H) = 436$

$Cl_2(g) \rightarrow 2\,Cl(g)$ $\Delta H = D(Cl\text{-}Cl) = 242$

H-H bond is stronger than Cl-Cl bond

$H_2(g)$ is more stable and less reactive

B) Polyatomic Molecules

Average BE values for a particular bond from several molecules

1) Atomization

$\text{H-O-H(g)} \rightarrow 2\,\text{H(g)} + \text{O(g)}$

$\Delta H = 926$ kJ/mol

Avg. for an O-H bond:

$D(\text{O-H}) = 926/2 = 463$ kJ/mol

2) Not same as individual ΔH's:

$$\text{H-O-H(g)} \rightarrow \text{H(g)} + \text{O-H(g)}$$

$$\Delta H = 501 \text{ kJ/mol}$$

$$\text{O-H(g)} \rightarrow \text{H(g)} + \text{O(g)}$$

$$\Delta H = 425 \text{ kJ/mol}$$

Due to H_2O and OH having diff. e^- config. (arrangement of e^-)

Not same in all molecules w. OH bond

- variation is slight and get BE by taking an average from several molecules

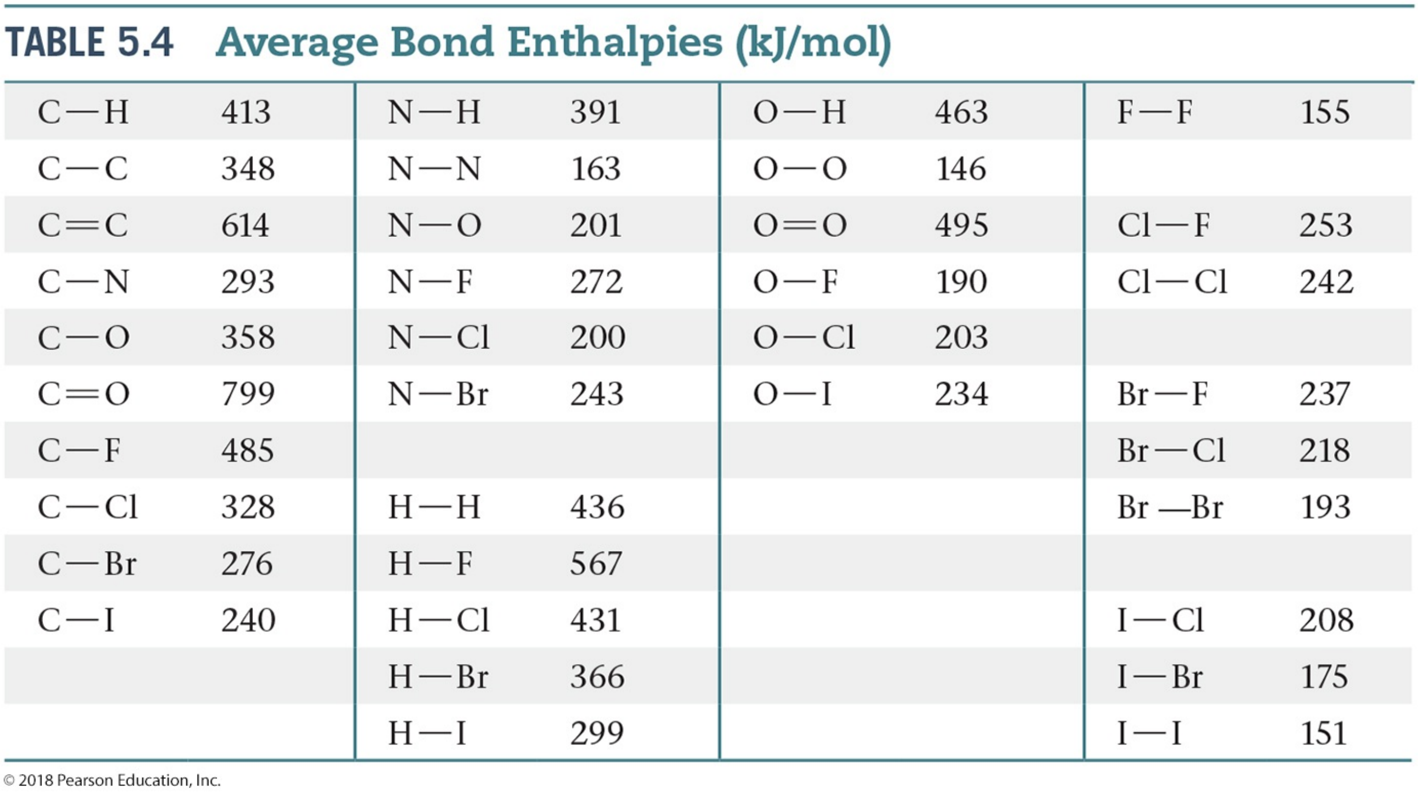


TABLE 5.4 Average Bond Enthalpies (kJ/mol)

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C═C	614	N—O	201	O═O	495	Cl—F	253
C—N	293	N—F	272	O—F	190	Cl—Cl	242
C—O	358	N—Cl	200	O—Cl	203		
C═O	799	N—Br	243	O—I	234	Br—F	237
C—F	485					Br—Cl	218
C—Cl	328	H—H	436			Br—Br	193
C—Br	276	H—F	567				
C—I	240	H—Cl	431			I—Cl	208
		H—Br	366			I—Br	175
		H—I	299			I—I	151

NOTE:

$$D(O=O) \neq 2\,D(O-O)$$

C) Estimating ΔH_{rxn} from BE

ΔH_{rxn} = Σ BE(bonds broken) −

Σ BE(bonds formed)

1) Ex: Determine ΔH_{rxn}

$$2\ NH_3(g) + 3\ Cl_2(g) \rightarrow N_2(g) + 6\ HCl(g)$$

D(N-H) = 391 kJ/mol
D(Cl-Cl) = 242 kJ/mol
D(N≡N) = 941 kJ/mol
D(H-Cl) = 431 kJ/mol

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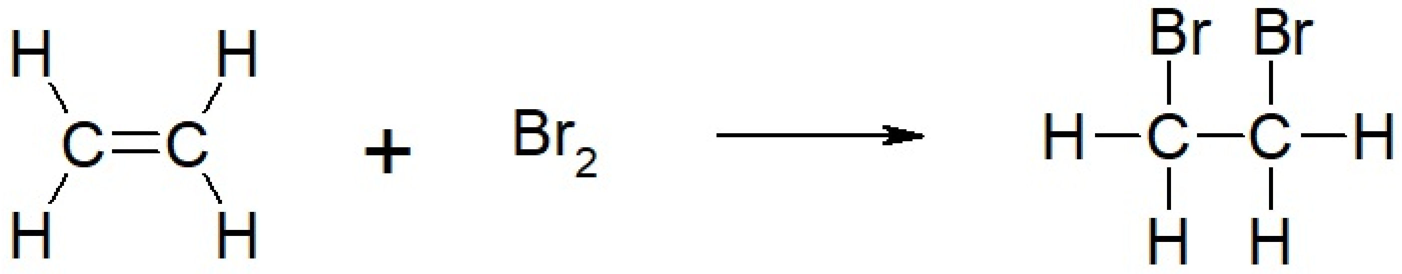
2) Ex: Determine ΔH_{rxn}

Can consider only the bonds broken and formed



$$D(C=C) = 614 \text{ kJ/mol}$$
$$D(Br-Br) = 193 \text{ kJ/mol}$$
$$D(C-C) = 348 \text{ kJ/mol}$$
$$D(C-Br) = 276 \text{ kJ/mol}$$

$$\Delta H = \{D(C=C) + D(Br-Br)\} - \{D(C-C) + 2\,D(C-Br)\}$$

$$= \{614 + 193\} - \{348 + 2(276)\}$$

$$= -\ 93 \text{ kJ}$$

IX) Foods and Fuels

A) Fuel Values of Foods

Carbohydrate:	4 kcal/g	(17 kJ/g)
Fat:	9 kcal/g	(38 kJ/g)
Protein:	4 kcal/g	(17 kJ/g)

Represents heat released in a combustion rxn but reported as positive numbers.

Excess energy stored as Fats:

1) insoluble in H_2O - helps with storage in the body.

2) produce more energy per gram

3) Ex: 28 g of a cereal with 120 mL of skim milk provides 8 g of protein, 26 g of carbohydrates and 2 g of fat. Estimate the fuel value (caloric content).

B) Fuels

1) Fossil fuels

Hydrocarbons (C_xH_y) with a few other elements: O, N, S

Natural Gas:	CH_4, C_2H_6, C_3H_8, C_4H_{10}
Fuel Value:	49 kJ/g
Petroleum:	mostly C_xH_y with some O, N, S
Fuel Value:	45 kJ/g (oil) 48 kJ/g (gasoline)
Coal:	mostly C_xH_y with some O, N, S
Fuel Value:	32 kJ/g

Combustion Reactions

C_xH_y + O_2(g) → CO_2(g) + H_2O (g)

(Unbalanced)

$C_xH_yS_z$ get SO_2 (H_2SO_3)
and SO_3 (H_2SO_4)

$C_xH_yN_z$ get nitrogen oxides
(HNO_3)

Acid Rain