

Chapter 5 - Thermochemistry

Study of **energy changes** that accompany **chemical rx's**.

I) Nature of Energy

Energy \equiv 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

$$\begin{aligned}w &= F \times d \\&= (m \times a) \times d \\&= (\text{kg} \times \text{m/s}^2) \times \text{m} \\&\quad \downarrow \\&= (\text{kg} \cdot \text{m}^2) / \text{s}^2 = \text{N} \times \text{m} \\&= \text{joule, J (SI unit)}\end{aligned}$$

calorie (cal)

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

$$1 \text{ cal} = 4.184 \text{ J}$$

Cal - nutritional calorie

$$1 \text{ kcal}$$

B) Kinetic & Potential Energy

1) Kinetic Energy

$$KE = \frac{1}{2} m v^2$$

Energy due to motion

SI units:

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

2) Potential Energy

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

Chemical energy is due to composition of substances

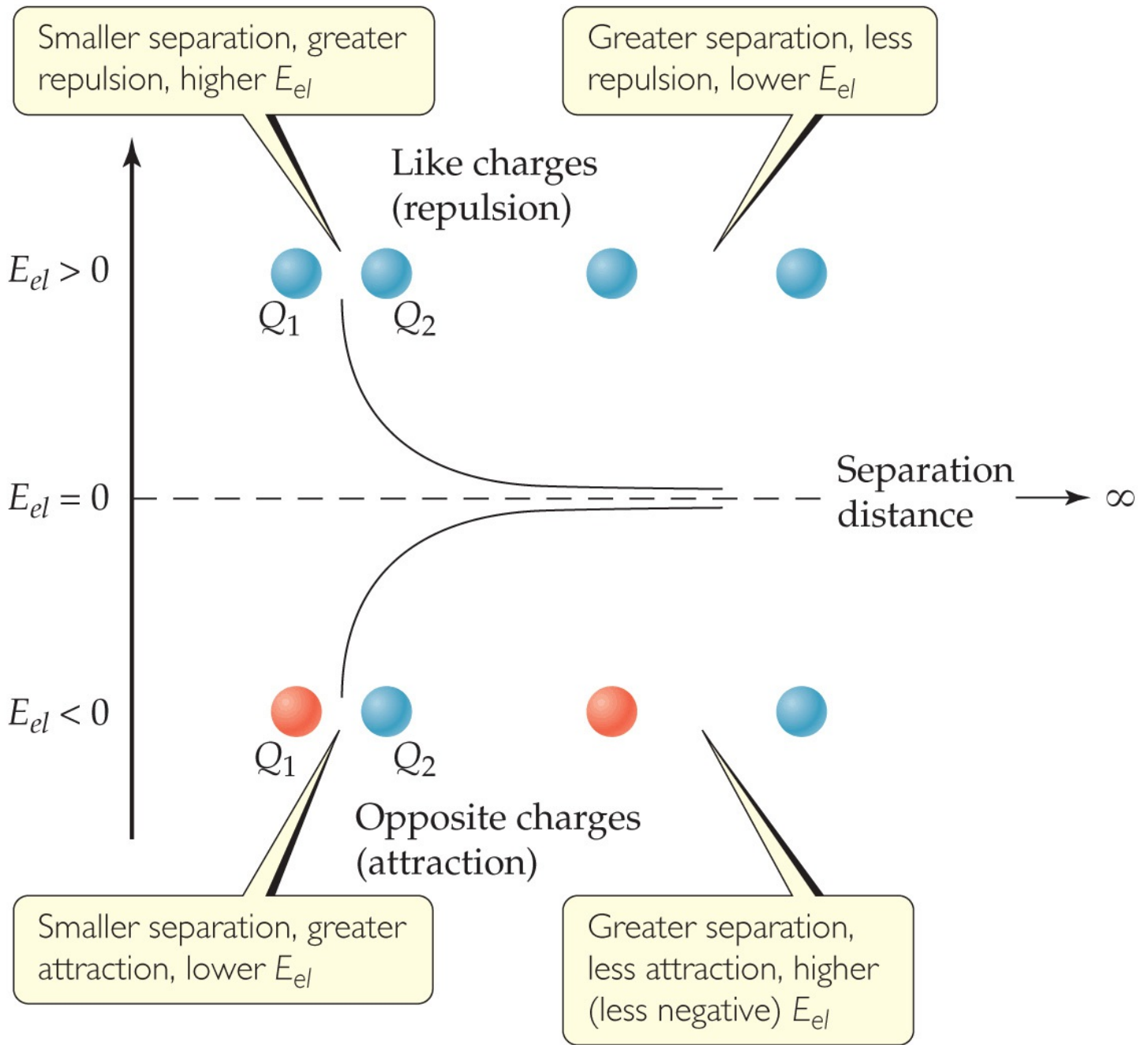
Electrostatic P.E.

Interaction between charged particles

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

Q = charge

d = distance between particles



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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

Aqueous soln. rx :

System : dissolved ions & molecules

Surround : H₂O 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** properties 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

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

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

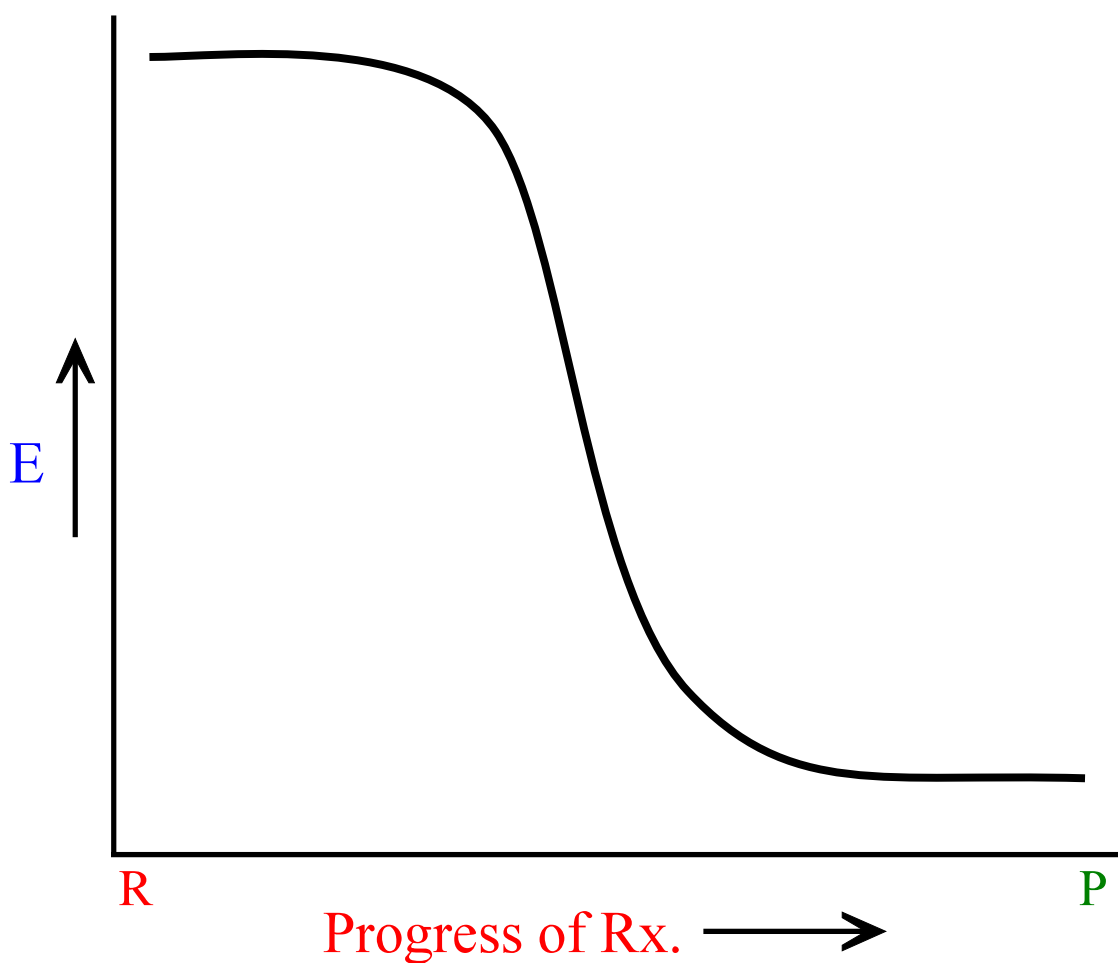
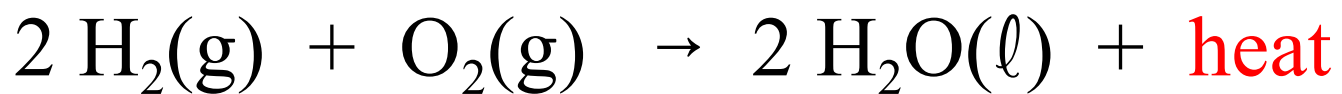
- w : work done by the system

1) First Law

$$\Delta E = q + w$$

1) Exothermic Reactions

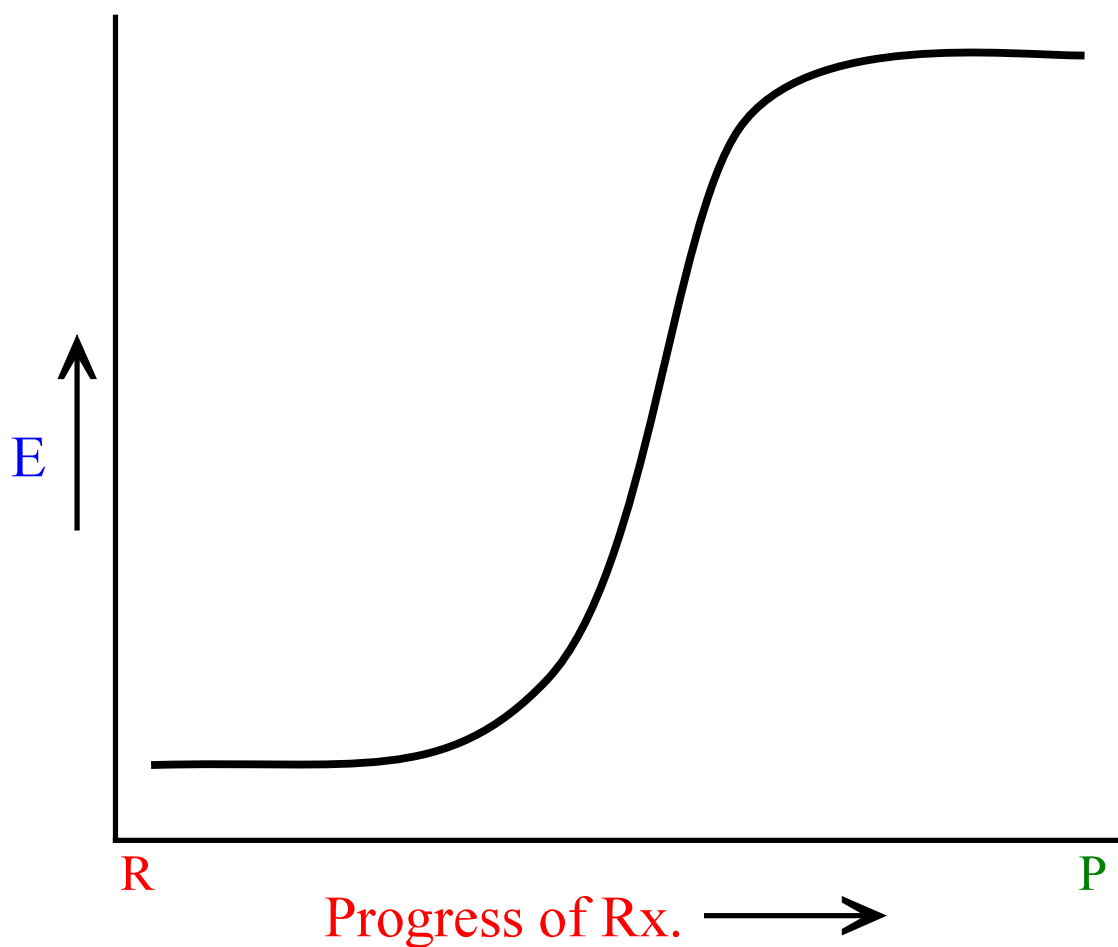
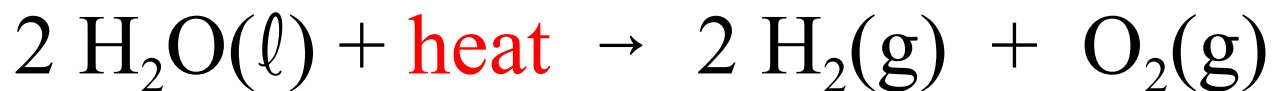
heat is released



2) Endothermic Reactions

heat is absorbed

- reaction requires input of energy



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·V has dimensions of **work** :

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

Constant Pressure

$$w = - P \Delta V$$

Negative because **work** done **by** system

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

A) ΔE at Constant Volume

$$\Delta E = q_v$$

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:

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

&

$$\Delta H = q_p$$

Can think of as heat content

state fnc. & is extensive

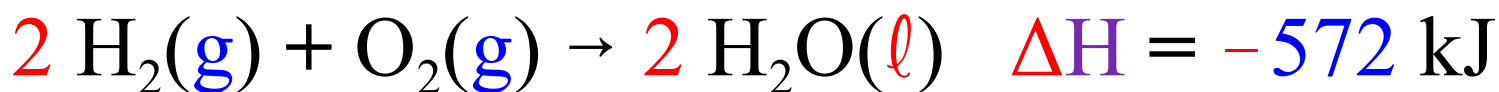
IV) Enthalpies of Reaction

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

A) Exothermic Rx's

$$H_{\text{p}} < H_{\text{r}}, \Delta H_{\text{rxn}} < 0, \text{ exothermic}$$

Heat is evolved



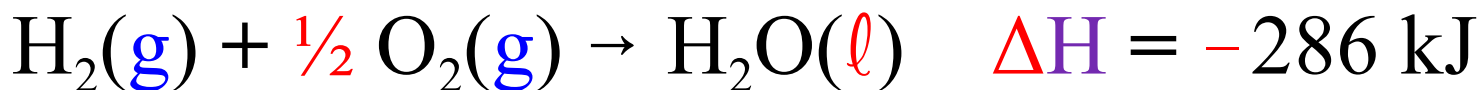
Thermochemical eqn.

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

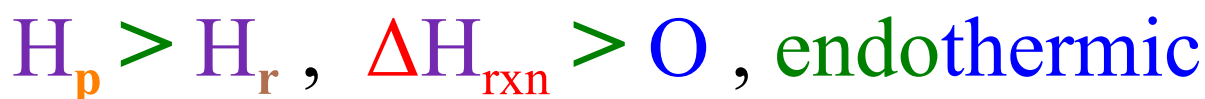
- **MUST** give physical states

If product is $\text{H}_2\text{O}(\text{g})$, $\Delta H = -484 \text{ kJ}$

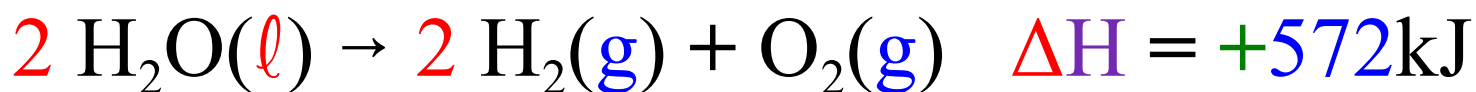
ΔH corresponds to **molar** quantities given in eqn. as written



B) Endothermic Rx's

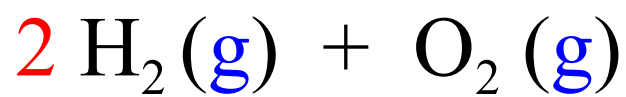


Heat is absorbed



Reverse of previous rx.

Enthalpy Diagram



+572 kJ



-572 kJ



C) Guidelines

1) Enthalpy is extensive

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

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

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?



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

$$? \text{ kJ} = 36.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{847 \text{ kJ}}{2 \text{ mol Al}} = 565.08 \text{ kJ} = 565 \text{ kJ}$$

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

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

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

Unit: $(\text{J}/^\circ\text{C})$ or (J/K)

C_m - molar heat capacity

heat capacity per mole, $J/mol \cdot ^\circ C$

C_s - specific heat

heat capacity per gram, $J/g \cdot ^\circ C$

$$C_s \text{ of H}_2\text{O} = 4.184 \text{ J/g} \cdot ^\circ C$$

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

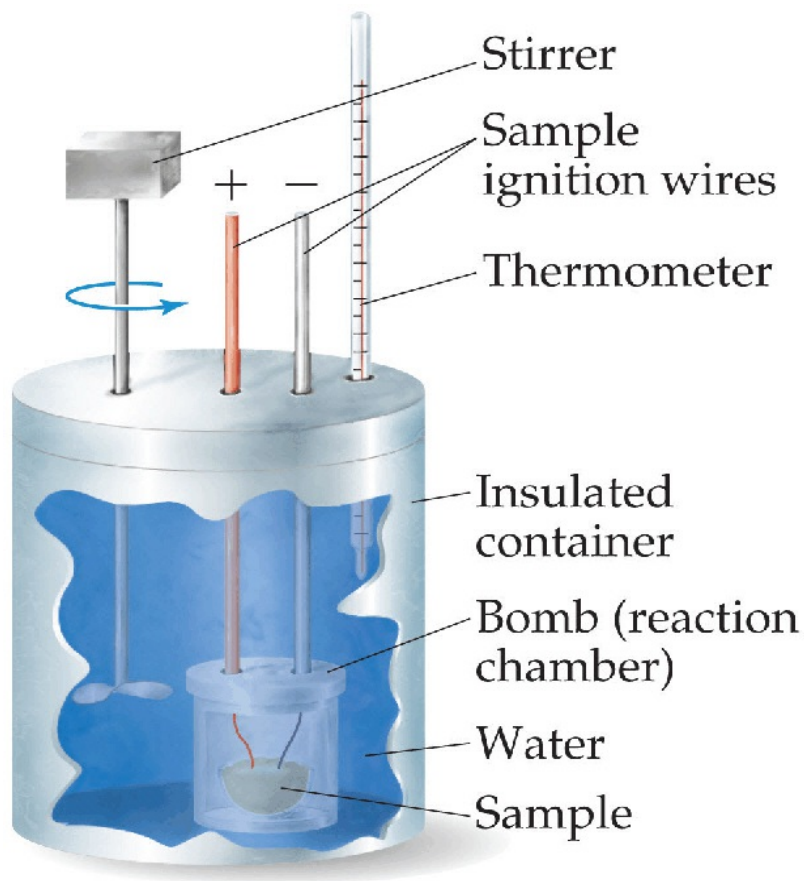
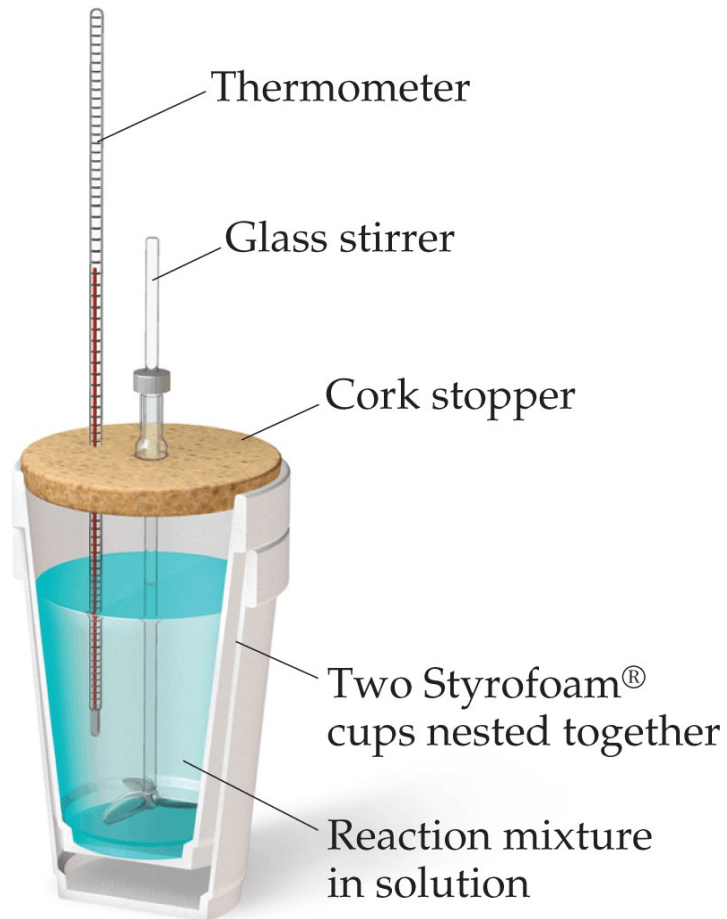
$$q = n \times C_m \times \Delta T$$

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

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

Calorimeter ΔH (q_p)

Bomb Calorimeter ΔE (q_v)



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?

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

$$= (1.000 \times 10^3 \text{g}) (4.184 \text{ J/g}\cdot\text{°C})(22.73 - 18.22)$$

↓

$$4.51 \text{ °C}$$

$$= 18,869.84 \text{ J}$$

$$= 18.9 \text{ kJ (3 s.f.)}$$

B) Ex 2: A 0.562 g sample of graphite is placed in a bomb calorimeter & ignited in the presence of excess O₂ 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?



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

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

$$= - (20.7 \text{ kJ/}^\circ\text{C})(25.89 \text{ }^\circ\text{C} - 25.00 \text{ }^\circ\text{C})$$

$$= - \underline{18.4} \text{ kJ } (q_v \text{ or } \Delta E \text{ for } 0.562 \text{ g})$$

Want kJ/mol,

$$\begin{aligned} ? \frac{\text{kJ}}{\text{mol}} &= \frac{- \underline{18.4} \text{ kJ}}{0.562 \text{ g C}} \times \frac{12.0 \text{ g C}}{1 \text{ mol C}} \\ &= - \underline{3.93} \times 10^2 \text{ kJ/mol} \end{aligned}$$

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

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

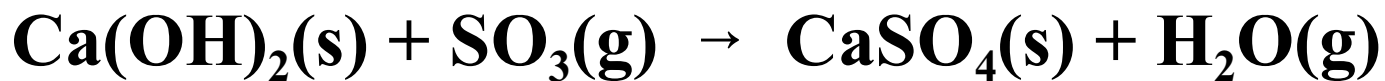
The ΔH_{rxn} is the sum of the ΔH 's for the individual steps.

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

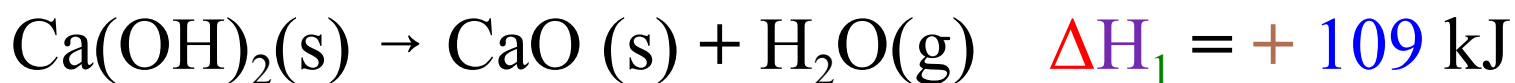
* Add chem. eqn's for steps to get overall rxn.

* Add $\Delta H_{\text{steps}} \Rightarrow \Delta H_{\text{rxn}}$

A) Ex 1 : What is ΔH for



We know the following:

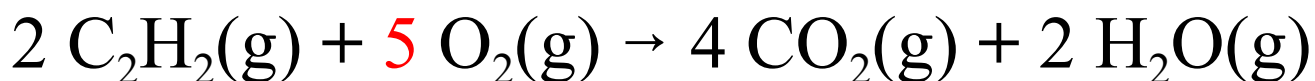


$$\Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_2$$

B) Ex 2 : Want ΔH for rxn.



Have:



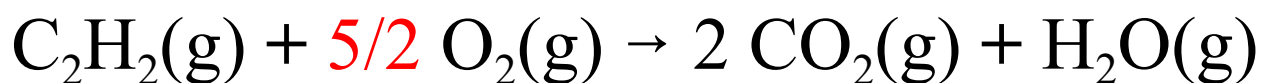
$$\Delta H_{1a} = -2512 \text{ kJ}$$



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)



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

Reverse eqn. 2a and multiply by 5



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

Add & Cancel



$$\begin{aligned} \Delta H_{\text{rxn}} &= \Delta H_{1b} + \Delta H_{2b} \\ &= - 1256 \text{ kJ} + - 408 \text{ kJ} \\ &= - 1664 \text{ kJ} \end{aligned}$$

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



A) Standard enthalpy change

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



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**

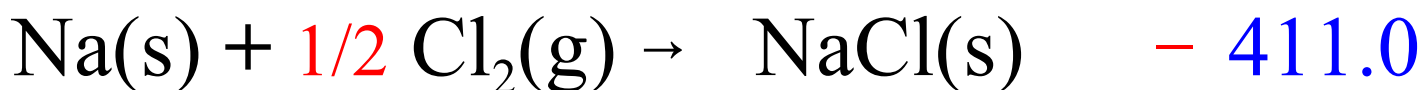
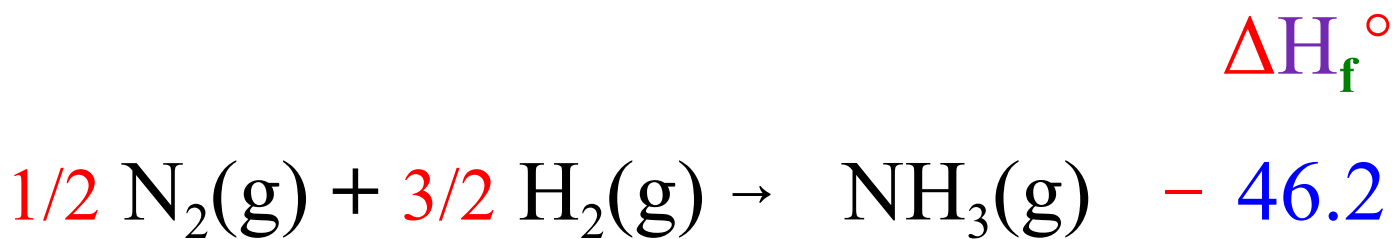
Conc. of 1 M

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**)

$$\Delta H_f^\circ$$

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



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 ₂ O 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

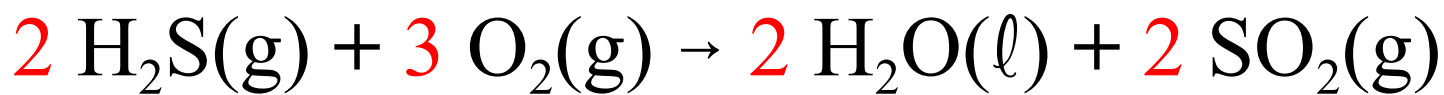
C) Determine $\Delta H_{\text{rxn}}^{\circ}$ from $\Delta H_{\text{f}}^{\circ}$

$$\Delta H_{\text{rxn}}^{\circ} = \sum_{\text{prod.}} n \Delta H_{\text{f}}^{\circ} - \sum_{\text{react.}} m \Delta H_{\text{f}}^{\circ}$$

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

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

1) Ex1 : Find $\Delta H_{\text{rxn}}^{\circ}$ for the following rx. using Hess's Law and $\Delta H_{\text{f}}^{\circ}$.



	ΔH° (kJ/mol)
(a) $\text{H}_2(\text{g}) + \text{S}(\text{s}) \rightarrow \text{H}_2\text{S}(\text{g})$	- 20.2
(b) $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\ell)$	- 285.8
(c) $\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$	- 296.9

Need to:

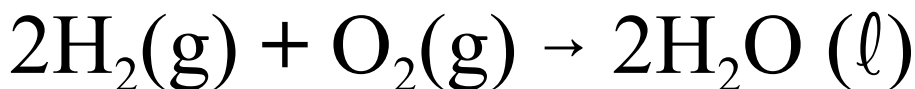
Rev. eqn. (a) and $\times 2$

Add eqn. (b) $\times 2$

Add eqn. (c) $\times 2$



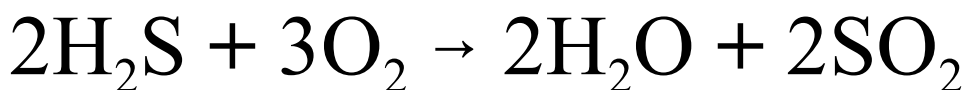
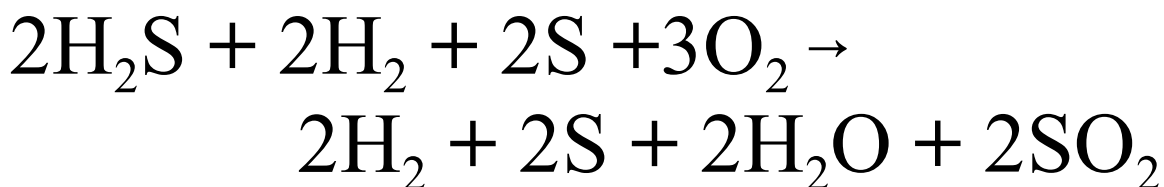
$$\Delta H_{\text{rxn}} = -2 \cdot (-20.2) = +40.4 \text{ kJ}$$



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



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



$$\Delta H_{\text{rx}} = (+40.4) + (-571.6) + (-593.8)$$
$$= -1125 \text{ kJ}$$

a) Use ΔH_f° instead

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= [2 \Delta H_f^\circ (\text{H}_2\text{O}) + 2 \Delta H_f^\circ (\text{SO}_2)] \\ &\quad - [2 \Delta H_f^\circ (\text{H}_2\text{S}) + 3 \Delta H_f^\circ (\text{O}_2)] \\ &= [2 (-285.8) + 2 (-296.9)] \\ &\quad - [2 (-20.2) + 3 (0)] \\ &= -1125 \text{ kJ}\end{aligned}$$

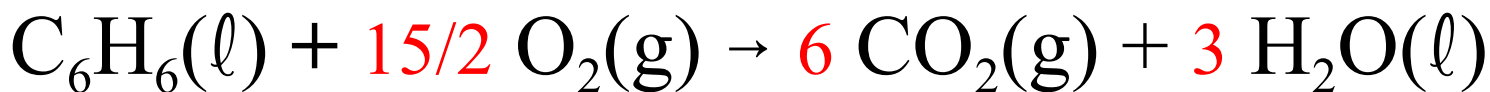
2) Ex 2: Useful when considering organic cmpds. for which ΔH_f° can not be determined directly.

What is ΔH_f° for benzene?



This rx. does **not** happen.

Use of **exp. heat of combustion**



$$\Delta H_{\text{rxn}}^\circ = - 3271 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^{\circ} = [6 \Delta H_{\text{f}}^{\circ} (\text{CO}_2) + 3 \Delta H_{\text{f}}^{\circ} (\text{H}_2\text{O})] \\ - [\Delta H_{\text{f}}^{\circ} (\text{C}_6\text{H}_6) + 15/2 \Delta H_{\text{f}}^{\circ} (\text{O}_2)]$$

$$-3271 \text{ kJ} = [6 (-393.5) + 3 (-285.8)] \\ - [\Delta H_{\text{f}}^{\circ} (\text{C}_6\text{H}_6) + 15/2 (0)]$$

$$-3271 \text{ kJ} = [- 3218.4] - [\Delta H_{\text{f}}^{\circ} (\text{C}_6\text{H}_6)]$$

$$\Delta H_{\text{f}}^{\circ} (\text{C}_6\text{H}_6) = [- 3218.4] - (- 3271) \\ = + 52.6 \text{ kJ}$$