

# 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

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

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

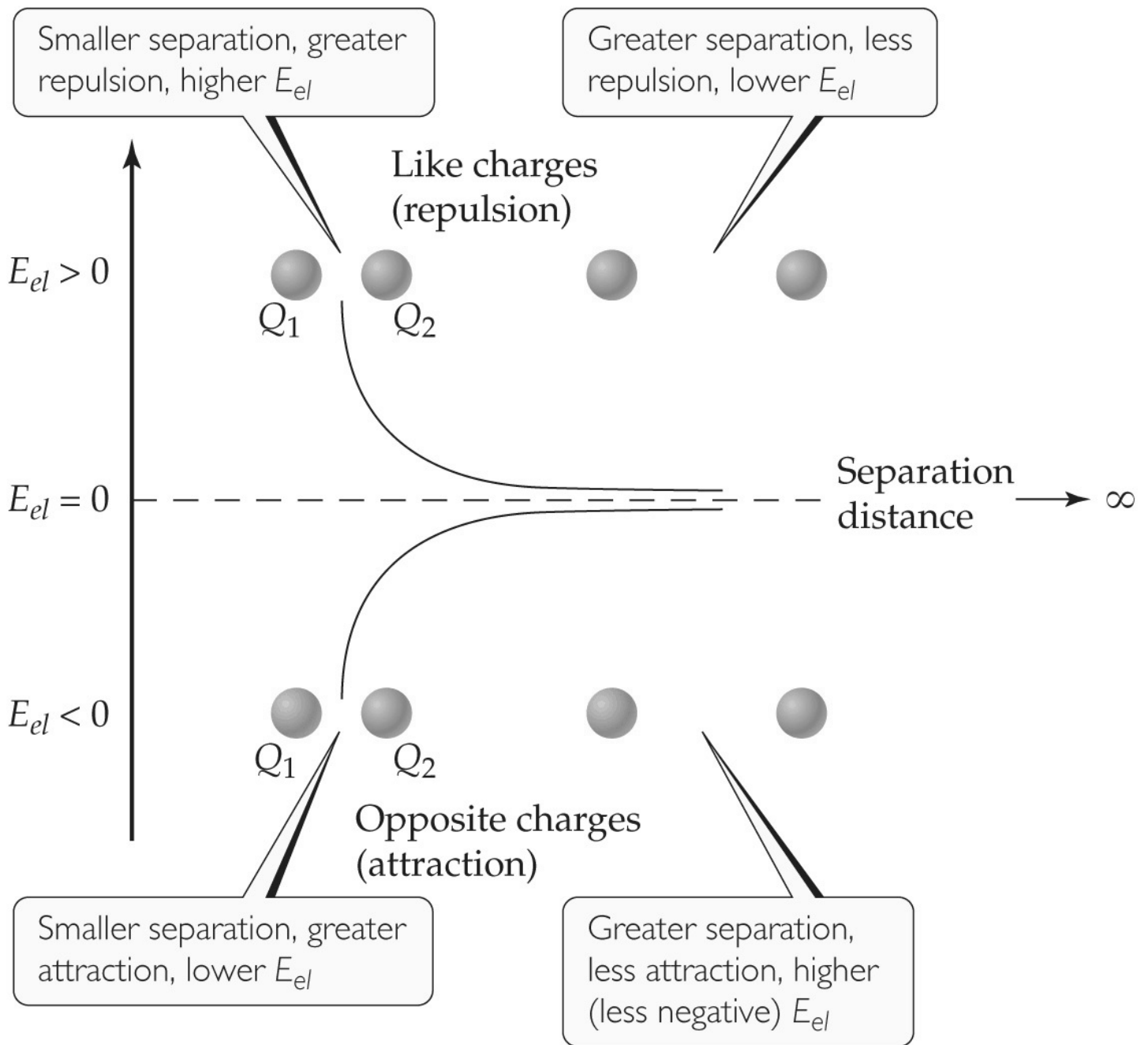
### Electrostatic P.E.

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 : H<sub>2</sub>O 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

$\Delta E$ , change in energy, can  
be determined

$\Delta$  = final state - initial state

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

Sign of  $\Delta E$  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 $\Delta E$ 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

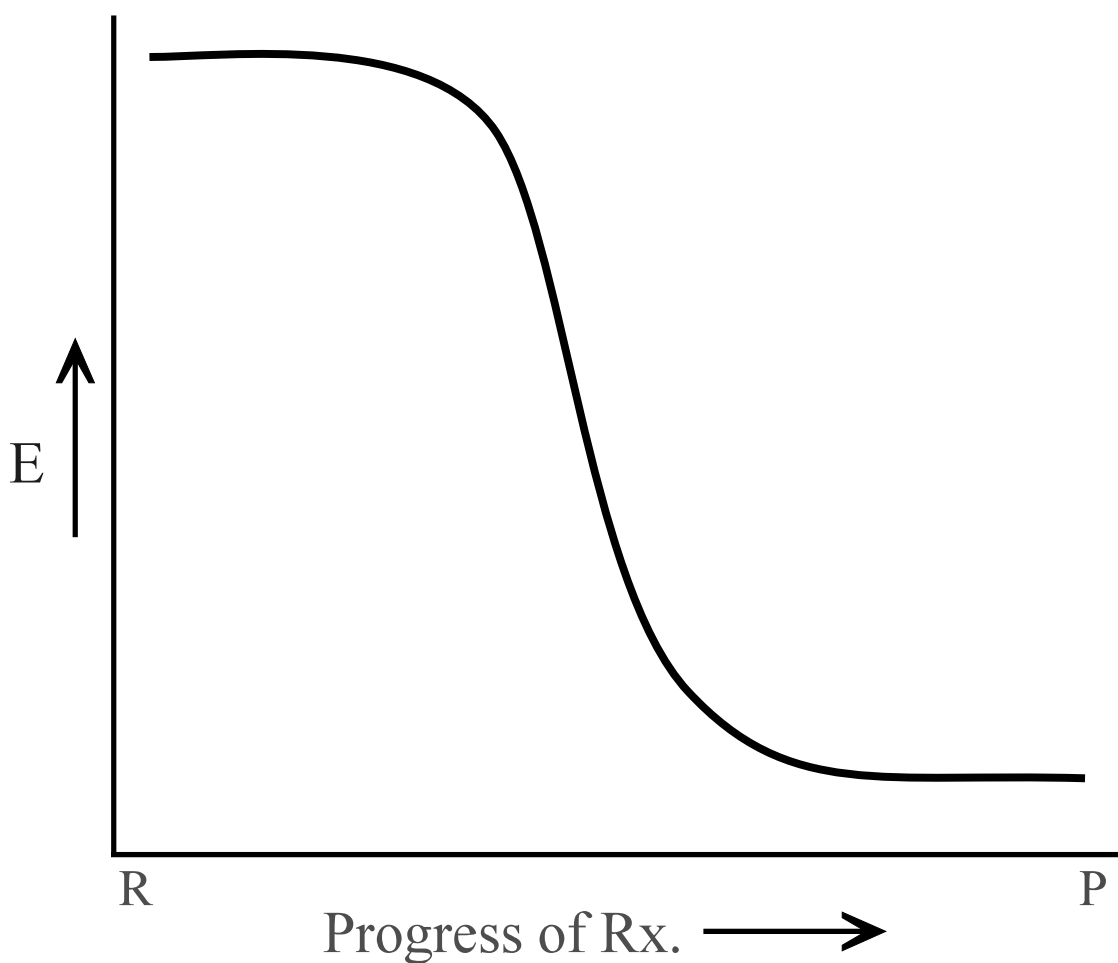
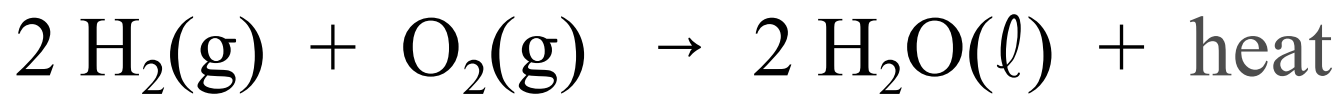
- w : work done by the system

### 1) First Law

$$\Delta E = q + w$$

# 1) Exothermic Reactions

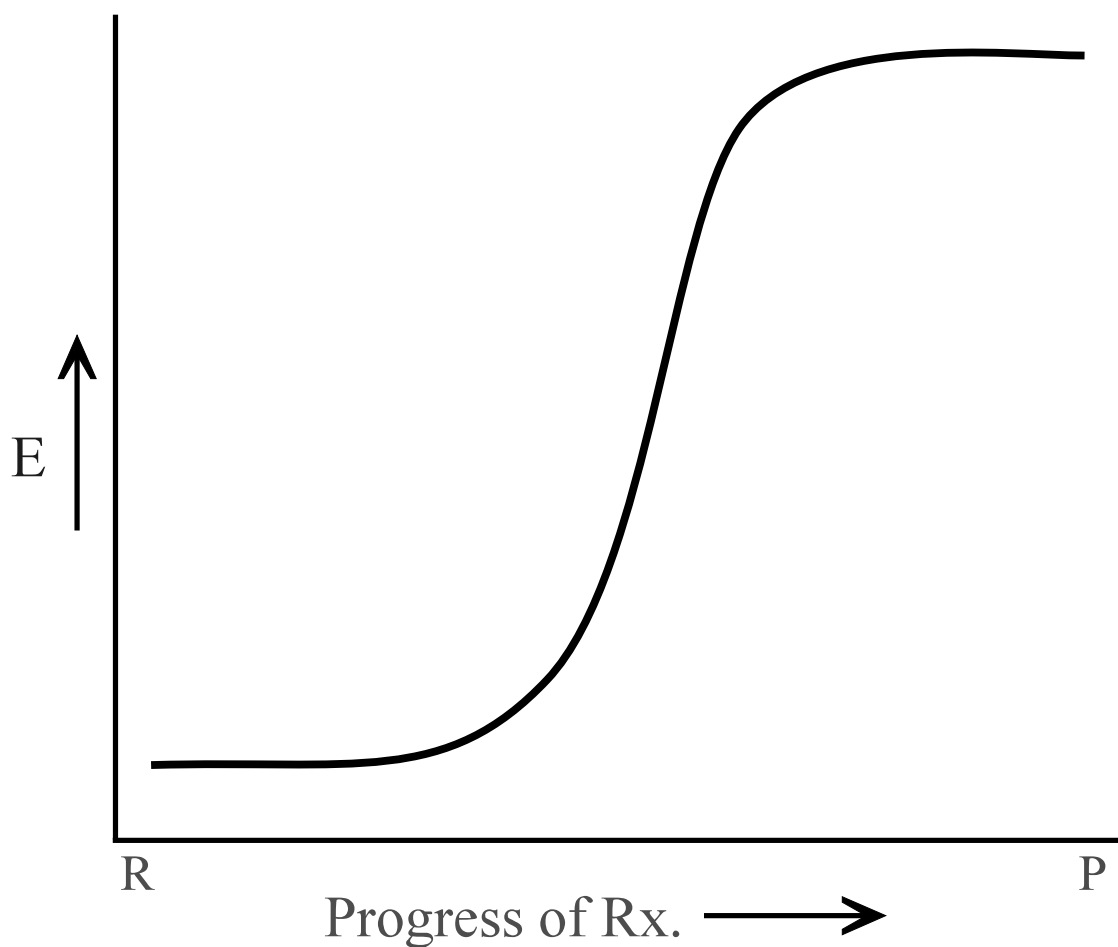
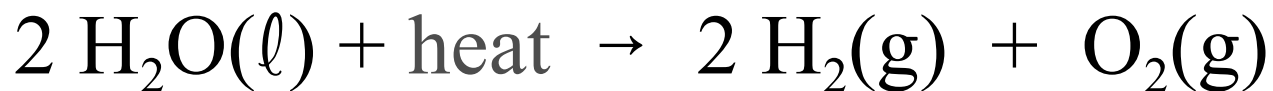
heat is released



## 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

$P \cdot V$  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)  $\Delta E$  at Constant Volume

$$\Delta E = q_v$$

B)  $\Delta E$  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

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

Heat is evolved



### Thermochemical eqn.

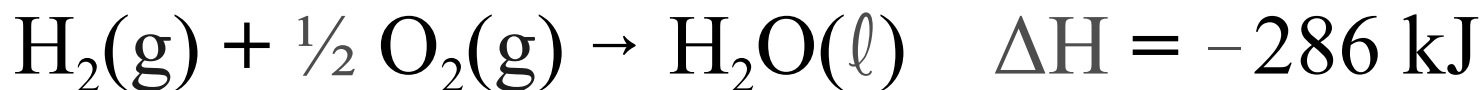
Physical states are given and energy associated w. rx. written to right

- MUST give physical states

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



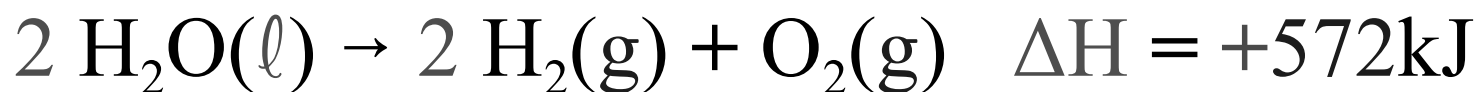
$\Delta H$  corresponds to molar quantities  
given in eqn. as written



## B) Endothermic Rx's

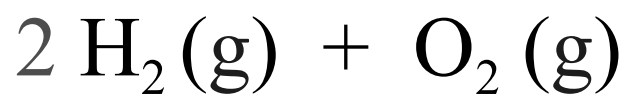


Heat is absorbed



Reverse of previous rx.

# Enthalpy Diagram



+572 kJ

-572 kJ



## C) Guidelines

### 1) Enthalpy is extensive

Multiply a rxn by some factor the  $\Delta H$  is multiplied by that factor

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

### 3) Enthalpy is a state function

$\Delta H$  depends on the states of reactants and products.

## D) Determining $\Delta H$ 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  $\text{Fe}_2\text{O}_3$  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  $\Delta H$  &  $\Delta E$

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  $1^{\circ}\text{C}$

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

$C_m$  - molar heat capacity

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

$C_s$  - specific heat

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

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

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

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

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

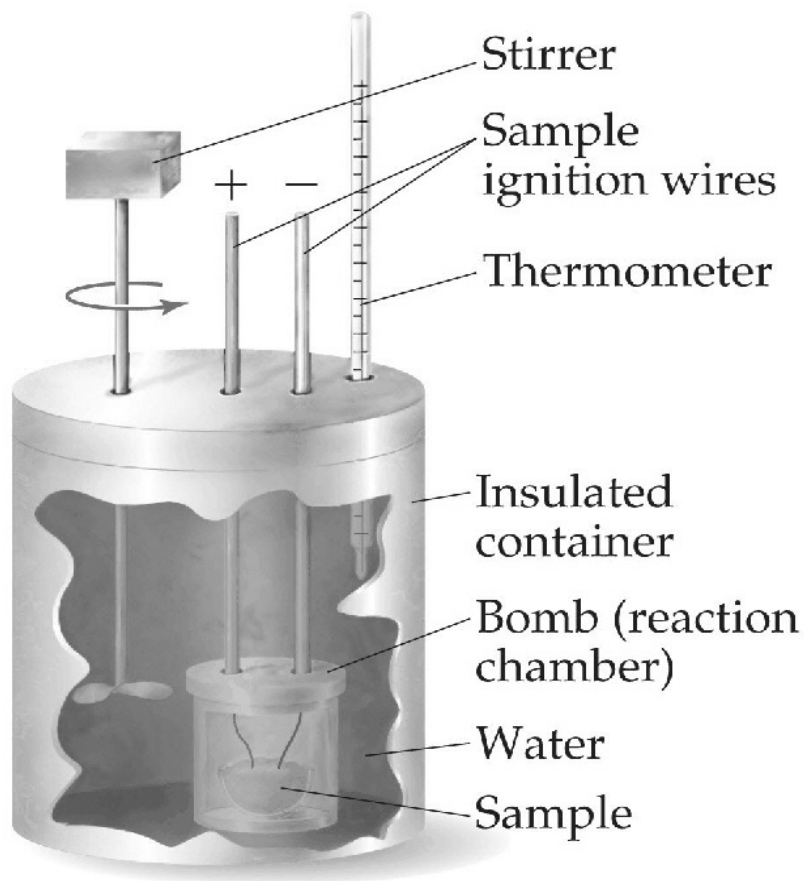
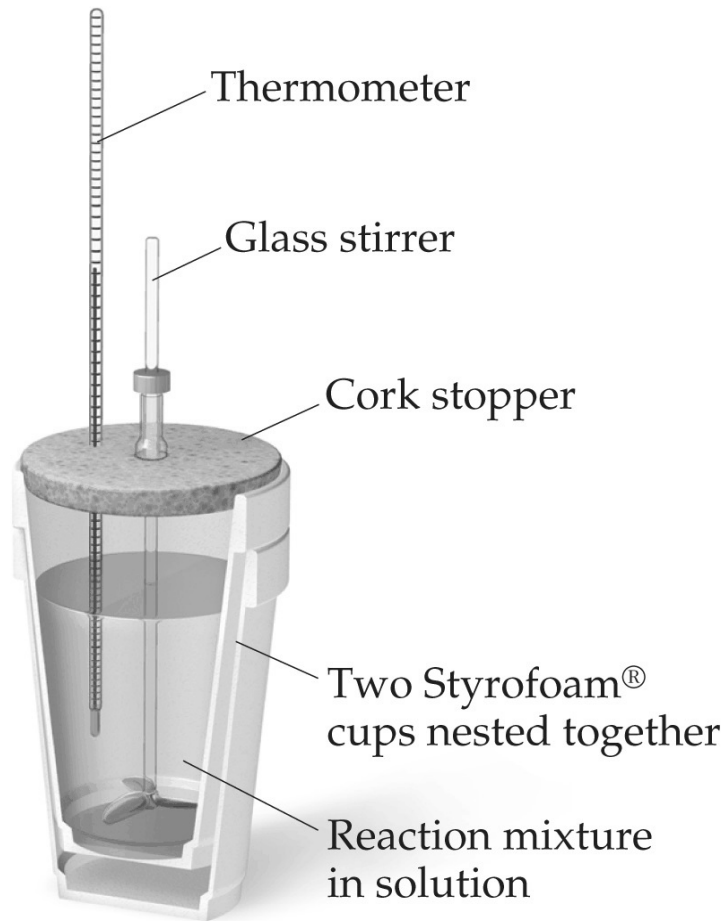
$$q_{\text{gained}} = - q_{\text{lost}}$$

Calorimeter

$\Delta H$  ( $q_p$ )

Bomb Calorimeter

$\Delta E$  ( $q_v$ )



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?

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

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

↓

$$4.51 \text{ }^\circ\text{C}$$

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

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



B) Ex 2: A 0.562 g sample of graphite is placed in a bomb calorimeter & ignited in the presence of excess O<sub>2</sub> 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,

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

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

since no change in moles of gas

$$\Delta H = \Delta E$$

## VI) Hess's Law

$\Delta H$  is a state fnc.

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

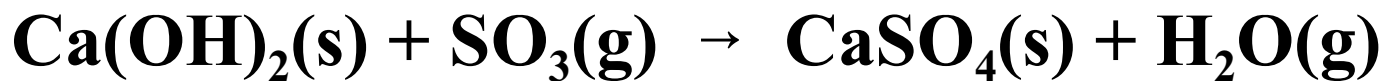
The  $\Delta H_{\text{rxn}}$  is the sum of the  $\Delta H$ 's for the individual steps.

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

\* 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  $\Delta H$  for



We know the following:

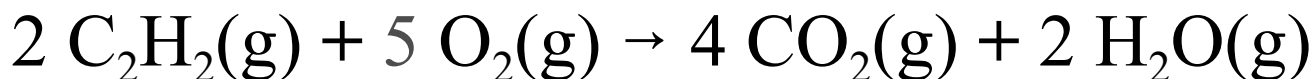


$$\Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_2$$

B) Ex 2 : Want  $\Delta H$  for rxn.



Have:



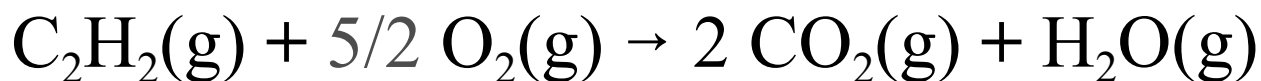
$$\Delta H_{1a} = -2512 \text{ kJ}$$



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  $\Delta H$ )



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

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,  $\Delta H$  is multiplied by the same factor.
- 2) If an eqn. is reversed, sign of  $\Delta H$  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

$$\Delta H_f$$

### A) Standard enthalpy change

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

$$\Delta H^\circ$$



## 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

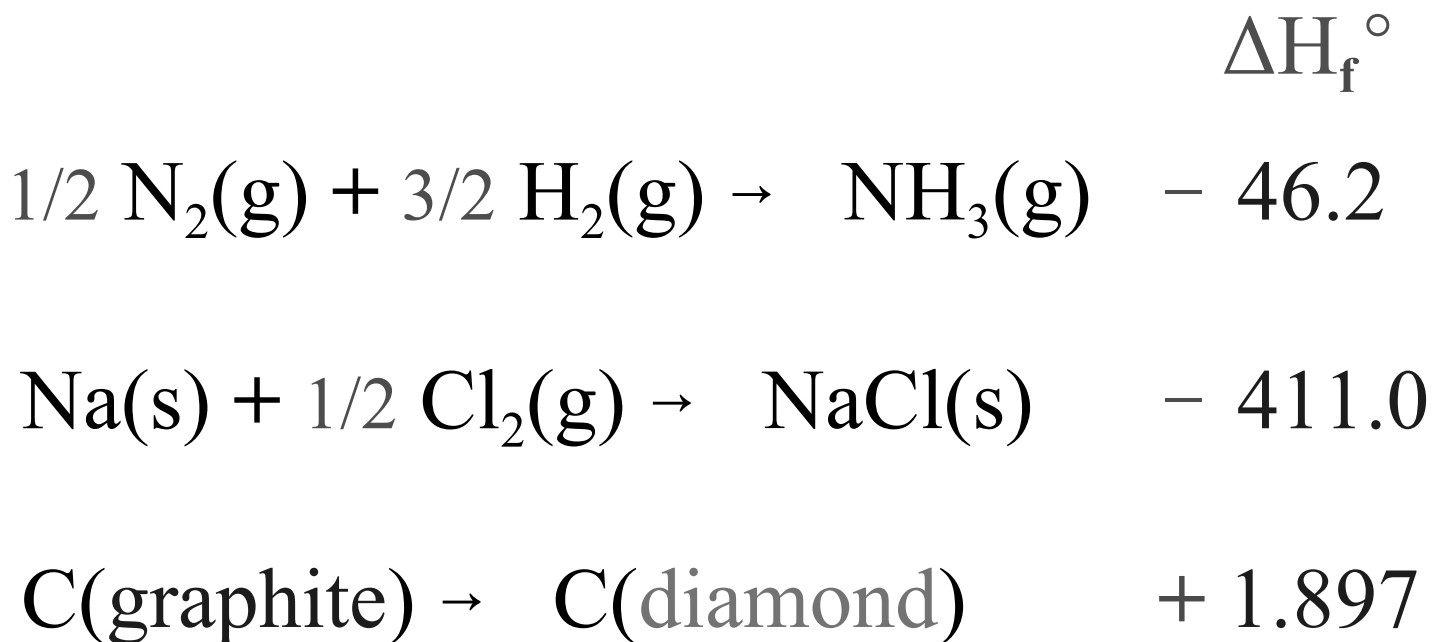
Conc. of 1 M

## B) Standard Enthalpy of Formation

$\Delta H$  for the rxn in which 1 mole of a compd. 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	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (j/mol-K)
<b>Aluminum</b>			
Al(s)	0	0	28.32
AlCl <sub>3</sub> (s)	-705.6	-630.0	109.3
Al <sub>2</sub> O <sub>3</sub> (s)	-1669.8	-1576.5	51.00
<b>Barium</b>			
Ba(s)	0	0	63.2
BaCO <sub>3</sub> (s)	-1216.3	-1137.6	112.1
BaO(s)	-553.5	-525.1	70.42
<b>Beryllium</b>			
Be(s)	0	0	9.44
BeO(s)	-608.4	-579.1	13.77
Be(OH) <sub>2</sub> (s)	-905.8	-817.9	50.21
<b>Bromine</b>			
Br(g)	111.8	82.38	174.9
Br <sup>-</sup> (aq)	-120.9	-102.8	80.71
Br <sub>2</sub> (g)	30.71	3.14	245.3
Br <sub>2</sub> (l)	0	0	152.3
HBr(g)	-36.23	-53.22	198.49

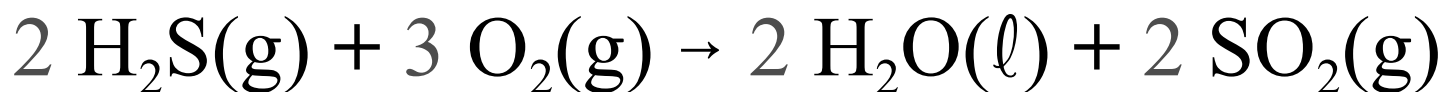
C) Determine  $\Delta H_{\text{rxn}}^{\circ}$  from  $\Delta H_{\text{f}}^{\circ}$

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

**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  $\Delta H_f^{\circ}$ .



	$\Delta H^{\circ}$ (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:

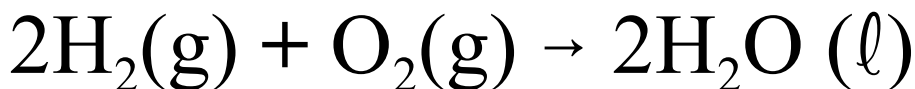
Rev. eqn. (a) and  $\times 2$

Add eqn. (b)  $\times 2$

Add eqn. (c)  $\times 2$



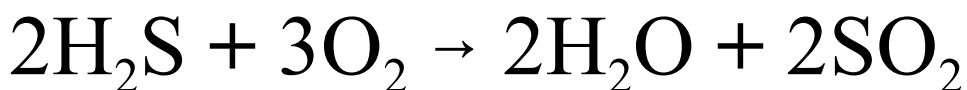
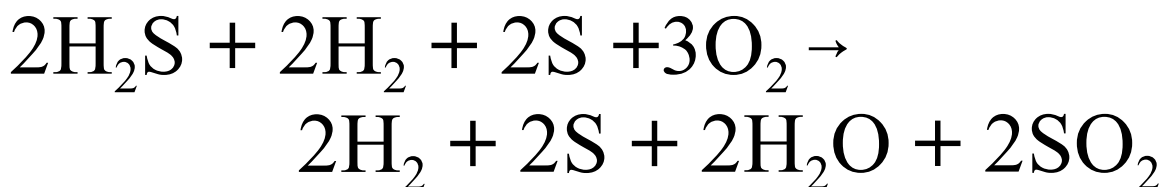
$$\Delta H_{\text{rxn}} = -2 \cdot (-20.2) = +40.4 \text{ kJ}$$



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



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



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

a) Use  $\Delta H_f^\circ$  instead

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

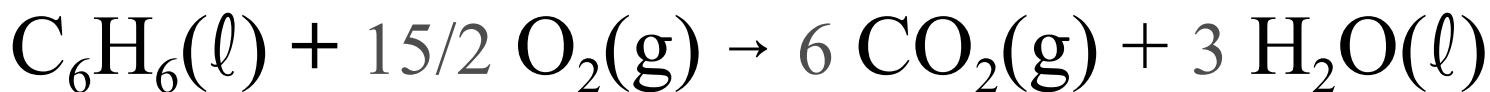
2) Ex 2: Useful when considering organic cmpds. for which  $\Delta H_f^\circ$  can not be determined directly.

What is  $\Delta H_f^\circ$  for benzene?



This rx. does not happen.

Use of exp. heat of combustion



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



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

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

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

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