

# THERMOCHEMISTRY

## Lecture 14



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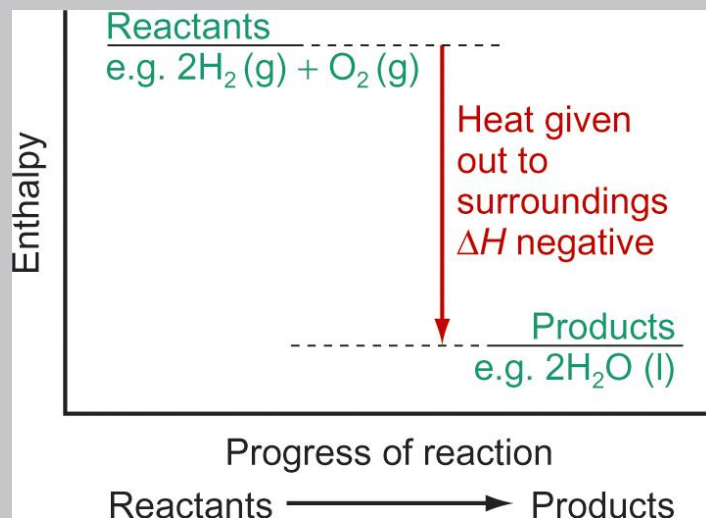
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# HEAT OF REACTION - $\Delta H$

thermochemistry – studies heat changes that occur during reactions

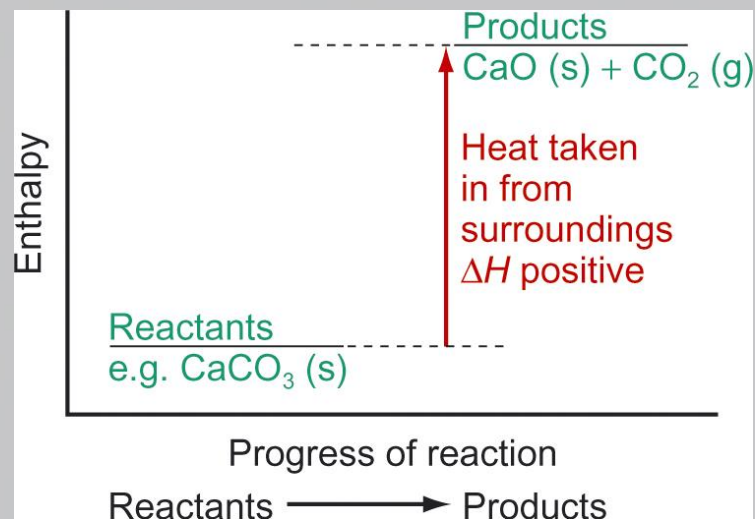
heat (q) – energy that is transferred as a result of temperature differences

enthalpy change,  $\Delta H$  or  $\Delta_{\text{rxn}}H$  - heat transferred at constant pressure by a chemical reaction or process



Reaction can **give off heat** and warm the 'outside'

$\Delta_{\text{rxn}}H$  becomes **negative**  
**EXOTHERMIC** reaction (e.g. combustion)



Reaction can 'give off cold' and cool down the 'outside' (**absorbs heat**)

$\Delta_{\text{rxn}}H$  becomes **positive**  
**ENDOTHERMIC** reaction (e.g. cold pack)



unit of heat: Joule,  $1 \text{ J} = 1 \text{ Nm} = 1 (\text{kgms}^{-1})\text{m} = 1 \text{ kgm}^2\text{s}^{-2}$

# $\Delta H$ – MOLAR QUANTITY



endothermic

1 mole of  $\text{CaCO}_3 (\text{s})$  reacts  
1 mole of  $\text{CaO} (\text{s})$  produced  
1 mole of  $\text{CO}_2 (\text{g})$  produced

needs 178 kJ  
needs 178 kJ  
needs 178 kJ

**BUT:**



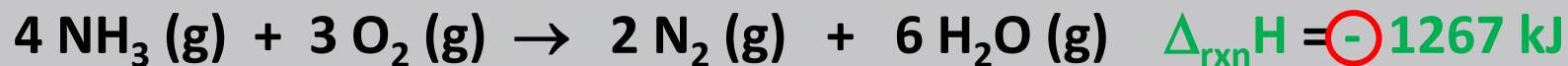
$$\Delta_{\text{rxn}} H = 2 \times 178 \text{ kJ} = 356 \text{ kJ}$$

2 moles of  $\text{CaCO}_3 (\text{s})$  react  
2 moles of  $\text{CaO} (\text{s})$  produced  
2 moles of  $\text{CO}_2 (\text{g})$  produced

needs 356 kJ  
needs 356 kJ  
needs 356 kJ



# $\Delta H$ – MOLAR QUANTITY



exothermic

|                                          |                     |                   |
|------------------------------------------|---------------------|-------------------|
| 4 moles of $\text{NH}_3$ (g) react       | -1267 kJ            | gives off 1267 kJ |
| 1 mole of $\text{NH}_3$ (g) reacts       | $-1267/4 = -317$ kJ | gives off 317 kJ  |
| 3 moles of $\text{O}_2$ (g) react        | -1267 kJ            | gives off 1267 kJ |
| 1 mole of $\text{O}_2$ (g) reacts        | $-1267/3 = -422$ kJ | gives off 422 kJ  |
| 2 moles of $\text{N}_2$ (g) form         | -1267 kJ            | gives off 1267 kJ |
| 1 mole of $\text{N}_2$ (g) forms         | $-1267/2 = -633$ kJ | gives off 633 kJ  |
| 6 moles of $\text{H}_2\text{O}$ (g) form | -1267 kJ            | gives off 1267 kJ |
| 1 mole of $\text{H}_2\text{O}$ (g) forms | $-1267/6 = -211$ kJ | gives off 211 kJ  |



# SAMPLE PROBLEM

A portable cap stove burns propane fuel according to equation:



How much heat will be released when 500g of propane combusts completely in oxygen?

*When 1 mol of  $\text{C}_3\text{H}_8$  reacts with oxygen, 2200 kJ of energy is released.*

*How many moles of  $\text{C}_3\text{H}_8$  in 500 g? molar mass = 44.1 g/mol*

Heat supplied by burning 500 g  $\text{C}_3\text{H}_8$

$$500 \text{ g C}_3\text{H}_8 \times \frac{1 \text{ mol}}{44.1 \text{ g}} = 11.3 \text{ mol C}_3\text{H}_8$$

$$2220 \frac{\text{kJ}}{\text{mol}} \times 11.3 \text{ mol} = \mathbf{25200 \text{ kJ}}$$

ALTERNATIVELY use **proportions**:

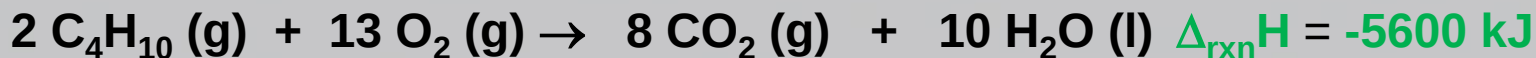
$$\frac{500 \text{ g}}{44.1 \text{ g}} = \frac{\text{heat released}}{2220 \text{ kJ}}$$

$$\text{heat released} = \frac{500 \text{ g} \times 2220 \text{ kJ}}{44.1 \text{ g}} = \mathbf{25200 \text{ kJ}}$$



# SAMPLE PROBLEM

How much heat will be released when 2.9 g of butane (molar mass 58.0 g/mol) combusts completely in oxygen according to:



2 moles of C<sub>4</sub>H<sub>10</sub> (2 × 58.0 = 116 g) can release 5600 kJ of heat

$$2.9 \text{ g} \times \frac{2 \text{ mol}}{116 \text{ g}} \times \frac{5600 \text{ kJ}}{2 \text{ mol}} = \frac{2.9 \text{ g} \times 5600 \text{ kJ}}{116 \text{ g}} = \mathbf{140 \text{ kJ of released heat}}$$

Proportions:

$$\frac{2.9 \text{ g}}{116 \text{ g}} = \frac{\text{heat released}}{5600 \text{ kJ}}$$

$$\text{heat released} = \frac{2.9 \text{ g} \times 5600 \text{ kJ}}{116 \text{ g}} = \mathbf{140 \text{ kJ of released heat}}$$



# PRACTICE PROBLEMS

PROBLEM 1: Although the process also requires water, a simplified equation for rusting (with rust shown as  $\text{Fe}_2\text{O}_3$ ) is:  $4\text{Fe(s)} + 3\text{O}_2\text{(g)} \Rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$   $\Delta_{\text{rxn}}H = -1.65 \times 10^3 \text{ kJ}$   
How much rust forms when  $4.93 \times 10^3 \text{ kJ}$  of heat is released?

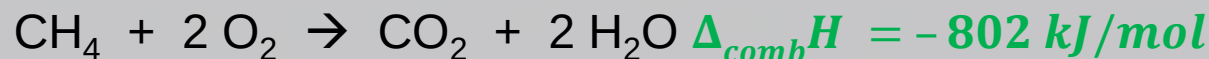
- $1.57 \times 10^6 \text{ g}$
- 238 g
- 477 g
- 954 g
- 107 g

$$\text{Fe}_2\text{O}_3 = 159.7 \text{ g/mol}$$

$$(4.03 \times 10^3 \text{ kJ}) \times \frac{2 \text{ mol Fe}_2\text{O}_3}{-1.65 \times 10^3 \text{ kJ}} \times \frac{159 \text{ g}}{1 \text{ mol Fe}_2\text{O}_3} = 954 \text{ g}$$

PROBLEM 2: The combustion of 1.00 mole of methane,  $\text{CH}_4$ , produces carbon dioxide and water and releases 802 kJ/mol. When 3.00 mol of oxygen react with a stoichiometric quantity of methane, what is the heat change for the reaction?

- $-8.02 \times 10^2 \text{ kJ}$
- $-2.41 \times 10^3 \text{ kJ}$
- $8.02 \times 10^2 \text{ kJ}$
- $1.20 \times 10^3 \text{ kJ}$
- $-1.20 \times 10^3 \text{ kJ}$



$$3 \text{ mol O}_2 \times \frac{1 \text{ mol CH}_4}{2 \text{ mol O}_2} \times \frac{(-802 \text{ kJ})}{1 \text{ mol CH}_4} = -1.20 \times 10^3 \text{ kJ}$$



# STANDARD CONDITIONS

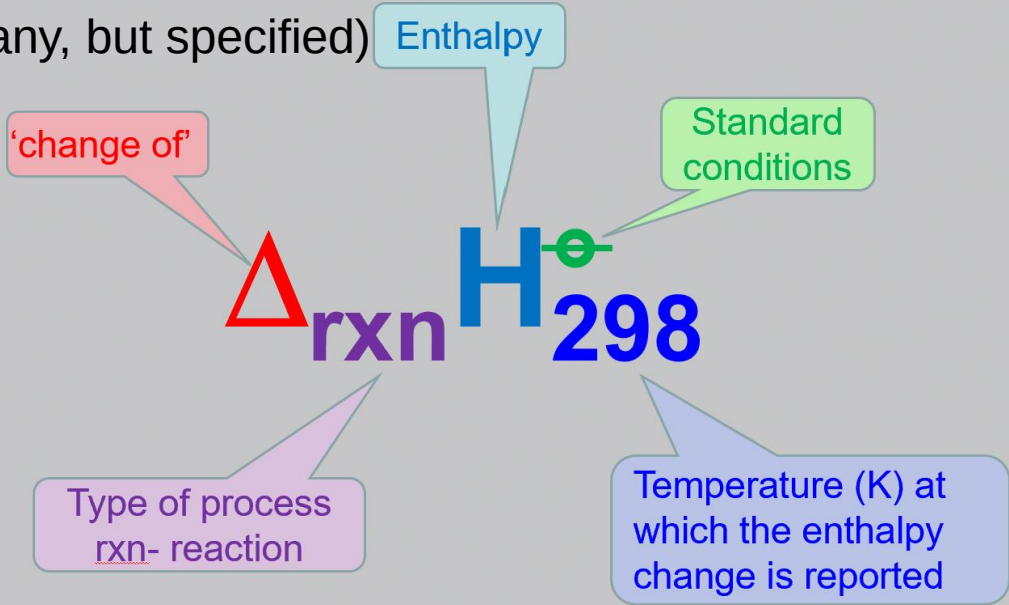
Any chemical equation that describes a reaction has a value of  $\Delta H$  ( $\Delta_{\text{rxn}}H$ )

$\Delta_{\text{rxn}}H$  depends on  $T$ ,  $P$  and the physical state of the components ( $H_2O$ : liquid or steam)

Standard conditions – allow comparison between values:

- Solids and liquids must be **pure** solids and liquids
- Solutions at **1 mol/L**
- Gases at the pressure of **1 bar**
- Temperature usually **298 K** (can be any, but specified)
- Always have a **sign**

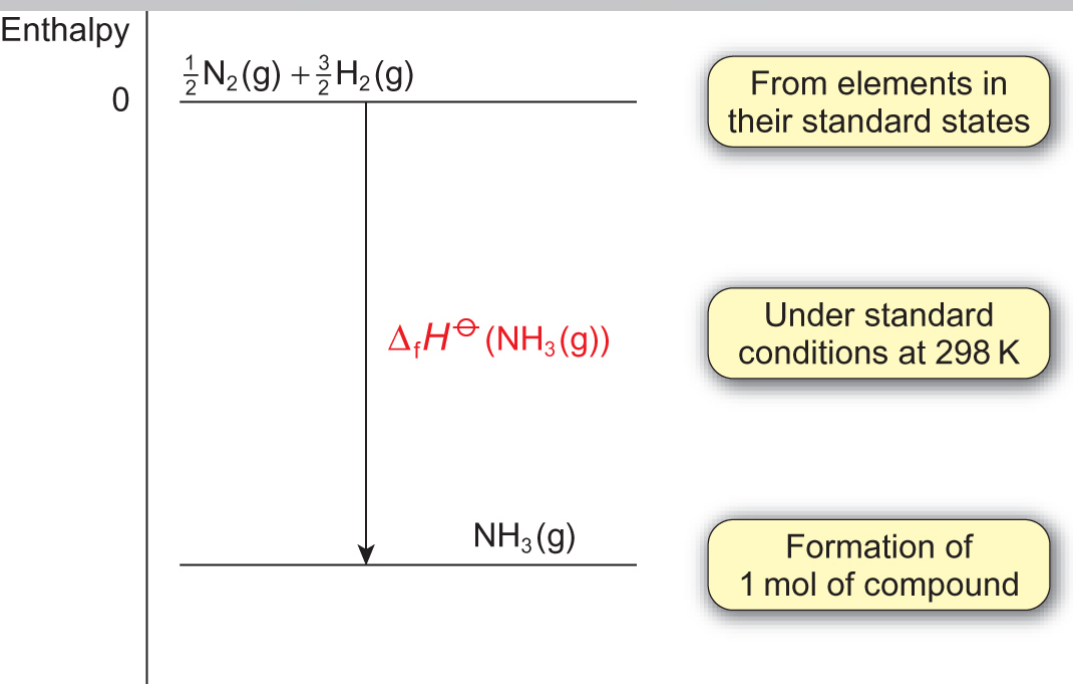
NOT STP or SATP !



# STANDARD HEAT OF FORMATION - $\Delta_f H^\circ$ (X)

standard enthalpy change of the formation  $\Delta_f H^\circ$  (X) = **heat of formation** - heat released or absorbed when 1 mole of pure substance X is formed from its elements at standard conditions (**kJ/mol**)

enthalpy of formation for an element in its standard state is **ZERO**



$$\Delta_f H^\circ_{298} (\text{N}_2 (\text{g})) = 0 \text{ kJ/mol}$$

$$\Delta_f H^\circ_{298} (\text{H}_2 (\text{g})) = 0 \text{ kJ/mol}$$

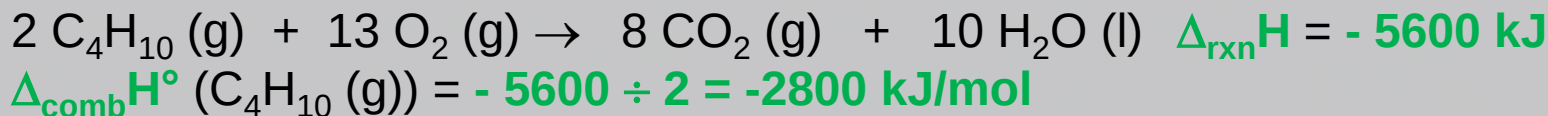
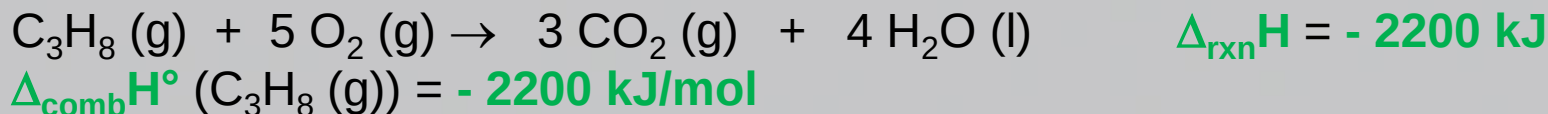
$\text{H}_2 (\text{g})$ ,  $\text{N}_2 (\text{g})$ ,  $\text{O}_2 (\text{g})$   
 $\text{F}_2 (\text{g})$ ,  $\text{Cl}_2 (\text{g})$ ,  $\text{Br}_2 (\text{l})$ ,  $\text{I}_2 (\text{s})$   
Noble gases (g)  
 $\text{P}_4 (\text{s})$ ,  $\text{As}_4 (\text{s})$ ,  $\text{S}_8 (\text{s})$ , C (s, graphite)  
Metals (s) except Hg (l), [Cs and Ga]



# STANDARD HEAT OF COMBUSTION - $\Delta_{\text{comb}}H^\circ$

standard enthalpy change of combustion  $\Delta_{\text{comb}}H^\circ$  (X) – **heat of combustion**- released when **1 mole** of substance X burns completely in oxygen gas at **1 bar** pressure (**kJ/mol**)

always negative – always exothermic - -  $\Delta_{\text{comb}}H^\circ$ (X)



Thermochemical equation can have fractional coefficients



# OTHER STANDARD HEATS

$\Delta_{\text{fus}}H^\circ$  (X)      heat of fusion of X,       $X(s) \rightarrow X(l)$       **always ENDO**

$\Delta_{\text{vap}}H^\circ$  (X)      heat of vaporisation of X,       $X(l) \rightarrow X(g)$       **always ENDO**

$\Delta_{\text{sub}}H^\circ$  (X)      heat of sublimation of X,       $X(s) \rightarrow X(g)$       **always ENDO**

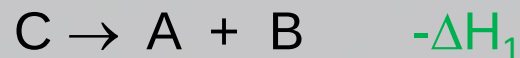
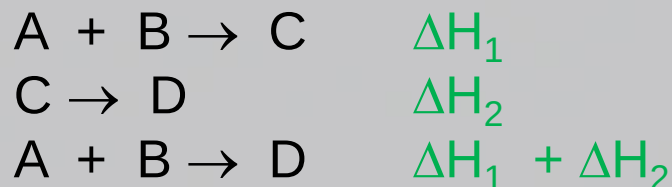
**per 1 mole of substance !!!**



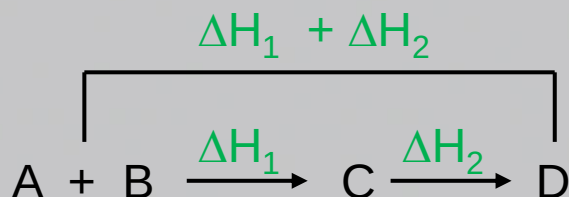
# HESS'S LAW

The total enthalpy change for a chemical reaction is independent of the path by which the reaction occurs, provided the starting and finishing states are the same for each reaction path

$\Delta H$  – state function – change independent of path,  
change is reversible



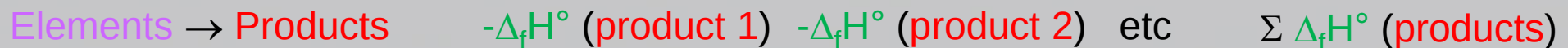
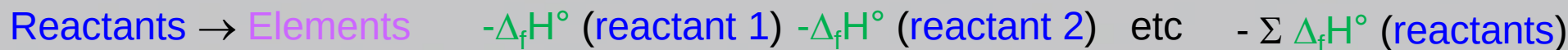
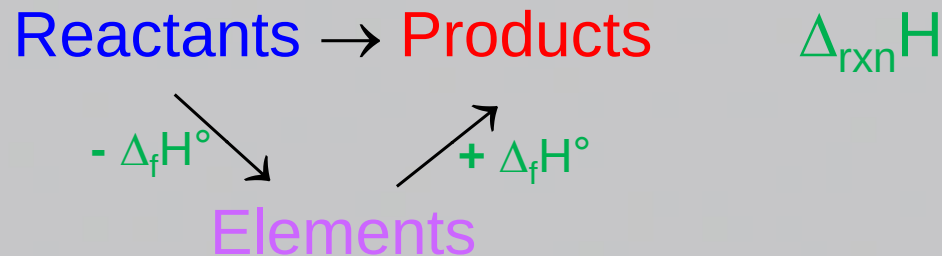
$$\Delta_{\text{rxn}} H \text{ (forward reaction)} = -\Delta_{\text{rxn}} H \text{ (backward reaction)}$$



The overall reaction enthalpy is the sum of the reaction enthalpies of the steps into which the reaction can be divided



# HESS'S LAW, cnt.



$$\Delta_{\text{rxn}}H = -\sum \Delta_f H^\circ (\text{reactants}) + \sum \Delta_f H^\circ (\text{products})$$

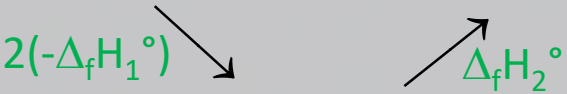
$$\Delta_{\text{rxn}}H = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$$



# SAMPLE PROBLEMS

PROBLEM 1(5): What is the value of  $\Delta_r H^\circ$  in kJ for:  $2 \text{ HgCl}_2(\text{s}) \rightarrow \text{Hg}_2\text{Cl}_2(\text{s}) + \text{Cl}_2(\text{g})$  given the  $\Delta_f H^\circ$  values (in kJ/mol) for  $\text{HgCl}_2 = -230$  and  $\text{Hg}_2\text{Cl}_2 = -265$ ?

- 195
  - 495
  - 35
  - +195
  - 725**
- Reactants:**  $\Delta_f H^\circ \text{ HgCl}_2 = -230 \text{ kJ/mol}$  is for reaction  $\text{Hg} + \text{Cl}_2 \rightarrow 1 \text{ mol HgCl}_2$
- Products:**  $\Delta_f H^\circ \text{ Hg}_2\text{Cl}_2 = -265 \text{ kJ/mol}$  is for reaction  $2 \text{ Hg} + 2 \text{ Cl}_2 \rightarrow 1 \text{ mol Hg}_2\text{Cl}_2 + \text{Cl}_2$



$2(-\Delta_f H_1^\circ) = 2 \times (-(-230)) = +460 \text{ kJ}$

$2 \text{ Hg} + 2 \text{ Cl}_2$

$\Delta_f H_2^\circ = -265 - 0 = -265 \text{ kJ}$

$\Delta_{\text{rxn}} H = \Sigma \Delta_f H^\circ (\text{products}) - \Sigma \Delta_f H^\circ (\text{reactants})$

$\Delta_{\text{rxn}} H = (-265) - 460 = - 725 \text{ kJ}$



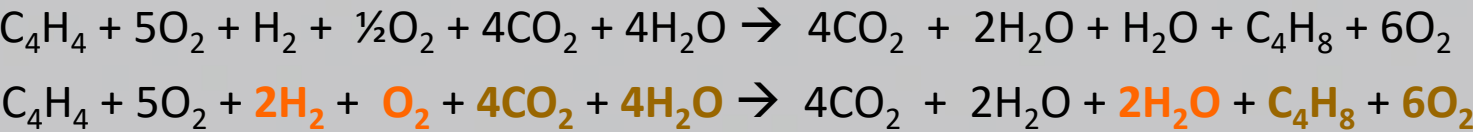
# SAMPLE PROBLEMS

**PROBLEM 2:** Calculate  $\Delta_r H$  for the reaction  $C_4H_4(g) + 2H_2(g) \Rightarrow C_4H_8(g)$ , using the following information:

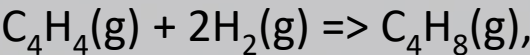
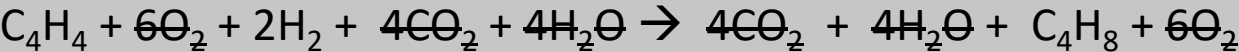
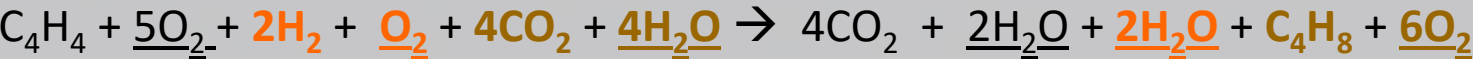
|                                                                       |                                           |          |
|-----------------------------------------------------------------------|-------------------------------------------|----------|
| $\Delta_{\text{combustion}} H$ for $C_4H_4(g) = -2341 \text{ kJ/mol}$ | <b>combustion reactions</b>               |          |
| $\Delta_{\text{combustion}} H$ for $H_2(g) = -286 \text{ kJ/mol}$     | $C_4H_4 + 5O_2 \rightarrow 4CO_2 + 2H_2O$ | as is    |
| $\Delta_{\text{combustion}} H$ for $C_4H_8(g) = -2755 \text{ kJ/mol}$ | $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$  | x 2      |
|                                                                       | $C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$ | reversed |

- 700 kJ
- 128 kJ
- 158 kJ
- 316 kJ
- 4810 kJ

Combine these combustion reactions:



Group/cancel  $H_2O$ ,  $CO_2$



$$\Delta_{\text{rxn}} H = (-2341 + 2(-286)) + 2755 = (-2913) + 2755 = -158 \text{ kJ}$$



# PRACTICE PROBLEMS

PROBLEM 1: Given the thermochemical equation:  $2 \text{NO(g)} + \text{O}_2\text{(g)} \Rightarrow 2 \text{NO}_2\text{(g)}$ .  
 $\Delta H = 1140 \text{ kJ}$  Calculate  $\Delta H$  for the reaction  $\text{NO}_2\text{(g)} \Rightarrow \text{NO(g)} + 1/2 \text{O}_2\text{(g)}$

-114 kJ

+114.0 kJ

-570 kJ

+570 kJ

+128 kJ

Reaction 2 is the reversed reaction 1 divided by 2

$$\Delta H (2) = \frac{1}{2} (- \Delta H (1)) = -570 \text{ kJ}$$

PROBLEM 2: What is the standard enthalpy of formation of propane,  $\text{C}_3\text{H}_6$ , in kJ/mol, if its standard enthalpy of combustion is  $-2059 \text{ kJ/mol}$ ?

The heats of formation of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are  $-286 \text{ kJ/mol}$  and  $-394 \text{ kJ/mol}$ , respectively.

-1379

-19

-2059

-699

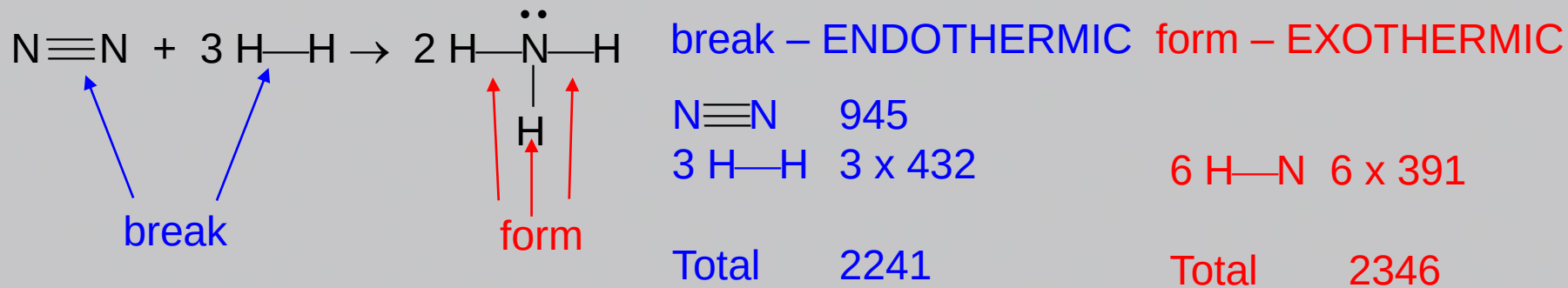
19



# BOND ENTHALPY

Bond dissociation enthalpy,  $D(A-B)$ , is the enthalpy change per mole when a particular chemical bond,  $A-B$ , is broken under standard conditions in the gas phase

|             |   |            |                                                      |
|-------------|---|------------|------------------------------------------------------|
| Reactants   | → | Products   | The overall result is an approximation of $\Delta H$ |
| break bonds | → | form bonds |                                                      |
| ENDOTHERMIC | → | EXOTHERMIC |                                                      |



$N \equiv N$  945 kJ/mol  
 $H-H$  432 kJ/mol  
 $H-N$  391 kJ/mol

$$\Delta_{rxn}H = 2241 - 2346$$

$$\Delta_{rxn}H = -105 \text{ kJ}$$



# SAMPLE PROBLEMS:

PROBLEM 1(2): Estimate the  $\Delta H$  in kJ, for the following reaction from the bond energies given.

$H_2 + I_2 \Rightarrow 2 HI$  Bond energy (kJ/mol); H-H = 436; H-I = 297; I-I = 151.

884

-7

-290

+7

+290

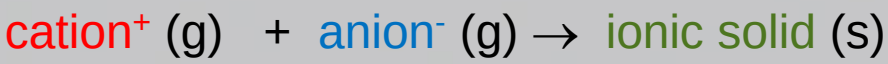
PROBLEM 2(1): Which of the following statements concerning estimating  $\Delta H$  from bond energies is incorrect?

- a) The sum of the bond energies of the reactants is subtracted from the sum of the bond energies of the products.
- b) Bond breaking is endothermic (pos).
- c) Bond making is exothermic (neg).
- d) Bond energies must be multiplied by the number of each bond and the number of moles of the species in the balanced equation.
- e) Bond energies are average values.



# LATTICE ENERGY

reflects 'strength' of ionic bond



$\Delta_{\text{latt}}H^\circ$  kJ/mol  
lattice energy

**EXOTHERMIC !!!**

## QUALITATIVE TRENDS:

a) Charge

Charge increases,  
 $\Delta_{\text{latt}}H^\circ$  increases (more negative)

| compound          | $\Delta_{\text{latt}}H^\circ$ kJ/mol |
|-------------------|--------------------------------------|
| NaCl              | -787                                 |
| MgCl <sub>2</sub> | -2524                                |
| AlCl <sub>3</sub> | -5492                                |
| NaO <sub>2</sub>  | -2695                                |
| MgO               | -3791                                |

b) Size

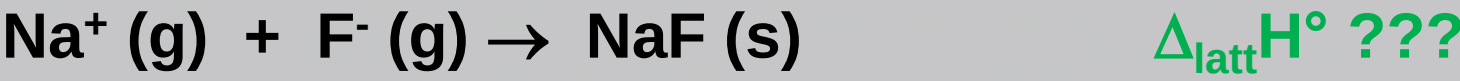
Size increases,  
 $\Delta_{\text{latt}}H^\circ$  decreases (less negative)

| compound | $\Delta_{\text{latt}}H^\circ$ kJ/mol |
|----------|--------------------------------------|
| LiCl     | -853                                 |
| NaCl     | -787                                 |
| KCl      | -715                                 |
| LiBr     | -807                                 |
| NaBr     | -747                                 |
| KBr      | -682                                 |



# HESS'S LAW

Lattice energy cannot be measured directly !!! Can be calculated using Hess's law



- 1  $\Delta_{\text{f}}\text{H}^\circ (\text{NaF})$

2  $\Delta_{\text{subl}}\text{H}^\circ (\text{Na})$

3 IE (Na)

4 EA (F)

5 Bond energy F-F
- $\text{Na} (\text{s}) + \frac{1}{2} \text{F}_2 (\text{g}) \rightarrow \text{NaF} (\text{s})$

$\text{Na} (\text{s}) \rightarrow \text{Na} (\text{g})$

$\text{Na} (\text{g}) \rightarrow \text{Na}^+ (\text{g}) + \text{e}$

$\text{F} (\text{g}) + \text{e} \rightarrow \text{F}^- (\text{g})$

$\text{F}_2 (\text{g}) \rightarrow 2 \text{F} (\text{g})$

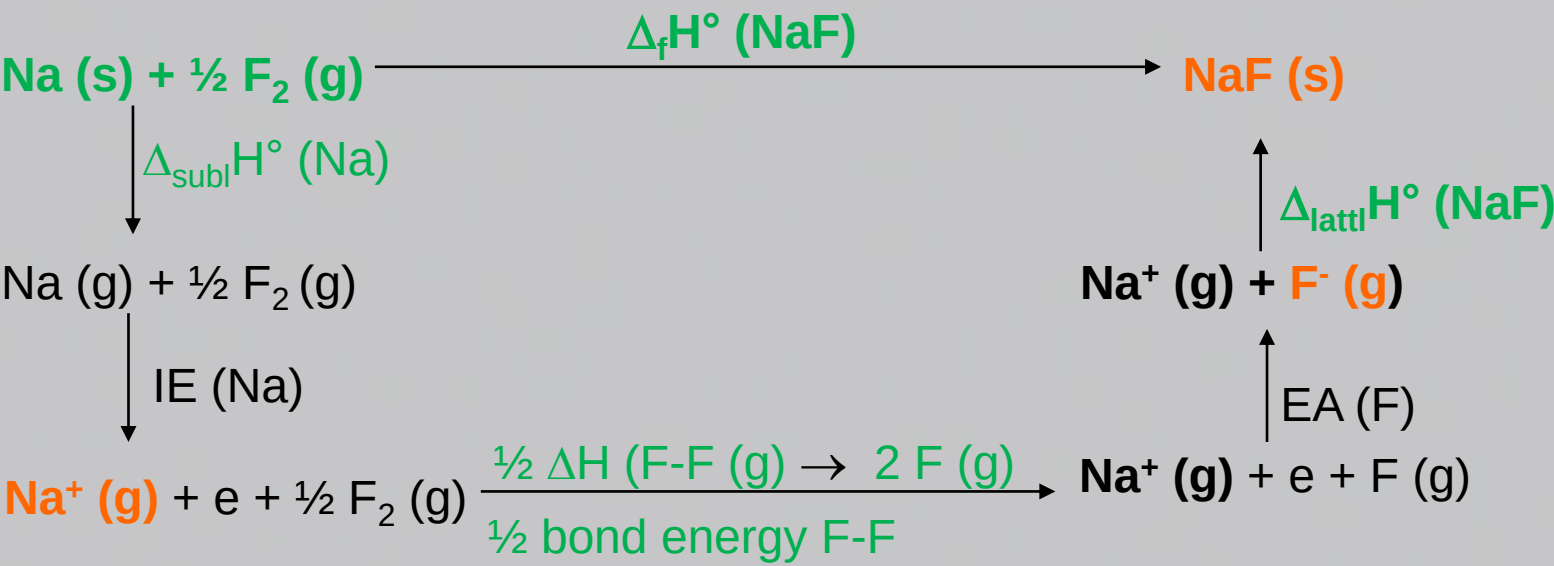
|   |                 |                                                            |                                                 |                                                    |
|---|-----------------|------------------------------------------------------------|-------------------------------------------------|----------------------------------------------------|
| 3 | Flip            | $\text{Na}^+ (\text{g}) + \text{e}$                        | $\rightarrow \text{Na} (\text{g})$              | - IE (Na)                                          |
| 2 | Flip            | $\text{Na} (\text{g})$                                     | $\rightarrow \text{Na} (\text{s})$              | - $\Delta_{\text{subl}}\text{H}^\circ (\text{Na})$ |
| 1 |                 | $\text{Na} (\text{s}) + \frac{1}{2} \text{F}_2 (\text{g})$ | $\rightarrow \text{NaF} (\text{s})$             | $\Delta_{\text{f}}\text{H}^\circ (\text{NaF})$     |
| 5 | Flip            | $\text{F} (\text{g})$                                      | $\rightarrow \frac{1}{2} \text{F}_2 (\text{g})$ | - $\frac{1}{2}$ Bond energy F-F                    |
|   | x $\frac{1}{2}$ |                                                            |                                                 |                                                    |
| 4 | Flip            | $\text{F}^- (\text{g})$                                    | $\rightarrow \text{F} (\text{g}) + \text{e}$    | - EA (F)                                           |



$$\Delta_{\text{latt}}\text{H}^\circ (\text{NaF}) = \Delta_{\text{f}}\text{H}^\circ (\text{NaF}) - \Delta_{\text{subl}}\text{H}^\circ (\text{Na}) - \text{IE} (\text{Na}) - \frac{1}{2} \text{Bond energy F-F} - \text{EA} (\text{F})$$



# BORN – HABER CYCLE



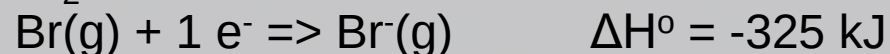
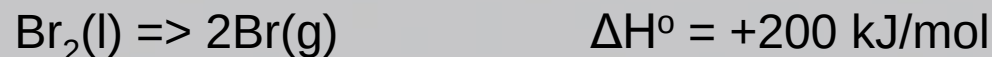
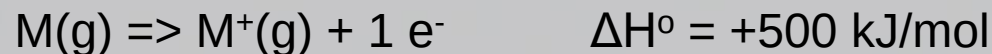
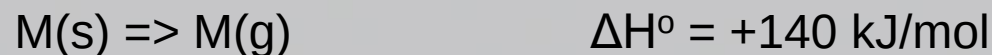
$$\Delta_f\text{H}^\circ (\text{NaF}) = \Delta_{\text{subl}}\text{H}^\circ (\text{Na}) + \text{IE} (\text{Na}) + \frac{1}{2} \text{ Bond energy F-F} + \text{EA} (\text{F}) + \Delta_{\text{latt}}\text{H}^\circ (\text{NaF})$$

$$\Delta_{\text{latt}}\text{H}^\circ (\text{NaF}) = \Delta_f\text{H}^\circ (\text{NaF}) - \Delta_{\text{subl}}\text{H}^\circ (\text{Na}) - \text{IE} (\text{Na}) - \frac{1}{2} \text{ Bond energy F-F} - \text{EA} (\text{F})$$



# SAMPLE PROBLEM

An ionic compound, MBr, has  $\Delta H^\circ_f = -500 \text{ kJ/mol}$ . Given the information below, calculate its lattice energy.



-515 kJ/mol

-1015 kJ/mol

-15 kJ/mol

+515 kJ/mol

-915 kJ/mol



# MACROSCOPIC HEAT

heating causes changes of temperature but different substances heated with the same amount of energy do not give the same temperature change

Substance

**specific heat (capacity),  $c_p$**

Amount of heat needed to raise the temperature of 1 g of the substance by 1 °C

$$c_p = \frac{q}{\text{mass} \times \Delta T} \quad [\text{J/g}^\circ\text{C}]$$

$$q = \text{mass} \times \Delta T \times c_p$$

## EXAMPLE

If it takes 28.0 J to raise the temperature of 8.0 g of a metal by 5.0 °C, calculate the specific heat of the metal.



$$28.0 \text{ J} = 8.0 \text{ g} \times 5.0^\circ\text{C} \times c_p$$

$$c_p = 0.70 \text{ J/g}^\circ\text{C}$$

Object

**heat capacity, HC**

Amount of heat needed to raise the temperature of an object by 1 °C

$$HC = \frac{q}{\Delta T} \quad [\text{J}^\circ\text{C}]$$

$$q = \Delta T \times HC$$

## EXAMPLE

An insulated coffee cup has a heat capacity of 12.0 J/°C. Calculate the amount of heat needed to raise the temperature of the coffee cup by 14.0 degC

$$q = 14.0^\circ\text{C} \times 12.0 \text{ J}^\circ\text{C}$$

$$q = 168 \text{ J}$$

# CALORIMETRY

*First law of thermodynamics:*

Energy cannot be created nor destroyed, just transferred

Assume heat and heat transfer

heat lost by one = heat gained by other

$$q(\text{system}) = -q(\text{surroundings})$$

## EXAMPLE

A 15.0 g piece of metal at 95 °C is dropped into 26.0 g of water at 25 °C. If the final temperature of the combination is 32 °C, calculate the specific heat of the metal. The specific heat of water is 4.184 J/g-°C.

$$\begin{aligned} q(\text{metal}) &= \text{mass} \times \Delta T \times C_p = \\ &= 15.0 \text{ g} \times (32 - 95) ^\circ\text{C} \times C_p \text{ metal} \\ &= -945 \times C_p \text{ metal J} \end{aligned}$$

$$\begin{aligned} q(\text{water}) &= \text{mass} \times \Delta T \times C_p = \\ &= 26.0 \text{ g} \times (32 - 25) ^\circ\text{C} \times 4.184 \text{ J/g-} ^\circ\text{C} = \\ &= 761 \text{ J} \end{aligned}$$

$$-945 \times C_p \text{ metal J} = -761 \text{ J}$$

$C_p \text{ metal} = 0.805 \text{ J/g-} ^\circ\text{C}$



# SAMPLE PROBLEM

50.0 g of hot water at 90 °C is added to 25.0 g of water at 22 °C that is contained in insulated cup that has a heat capacity of 75 J/ °C. Determin the final temperature. The specific heat of water is 4.184 J/g- °C.

$$\begin{array}{ccc} q \text{ (system)} = -q \text{ (surroundings)} & & \\ \downarrow & & \downarrow \\ \text{hot water} & & \text{cold water} + \text{cup} \end{array}$$

$$q \text{ (hot water)} = \text{mass} \times \Delta T \times C_p = 50.0 \text{ g} \times (T_f - 90) \text{ }^\circ\text{C} \times 4.184 \text{ J/g- }^\circ\text{C}$$

$$q \text{ (cold water)} = \text{mass} \times \Delta T \times C_p = 25.0 \text{ g} \times (T_f - 22) \text{ }^\circ\text{C} \times 4.184 \text{ J/g-}^\circ\text{C}$$

$$q \text{ (cup)} = \text{HC} \times \Delta T = 75 \text{ J/}^\circ\text{C} \times (T_f - 22) \text{ }^\circ\text{C}$$

$$q \text{ (hot water)} = - [q \text{ (cold water)} + q \text{ (cup)}]$$

$$209.2(T_f - 90) \text{ }^\circ\text{C} = - [104.6(T_f - 22) \text{ }^\circ\text{C} + 75(T_f - 22) \text{ }^\circ\text{C}]$$

$$209.2T_f - 18828 = - 104.6T_f + 2301.2 - 75T_f + 1650$$

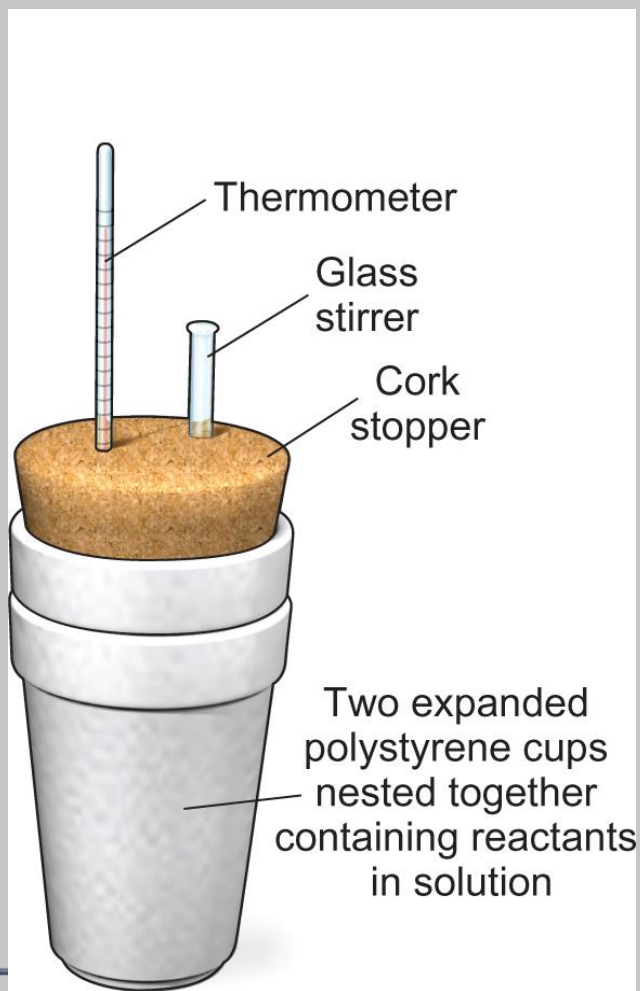
$$388.8 T_f = 22779.2$$

$$T_f = 58.6 \text{ }^\circ\text{C}$$

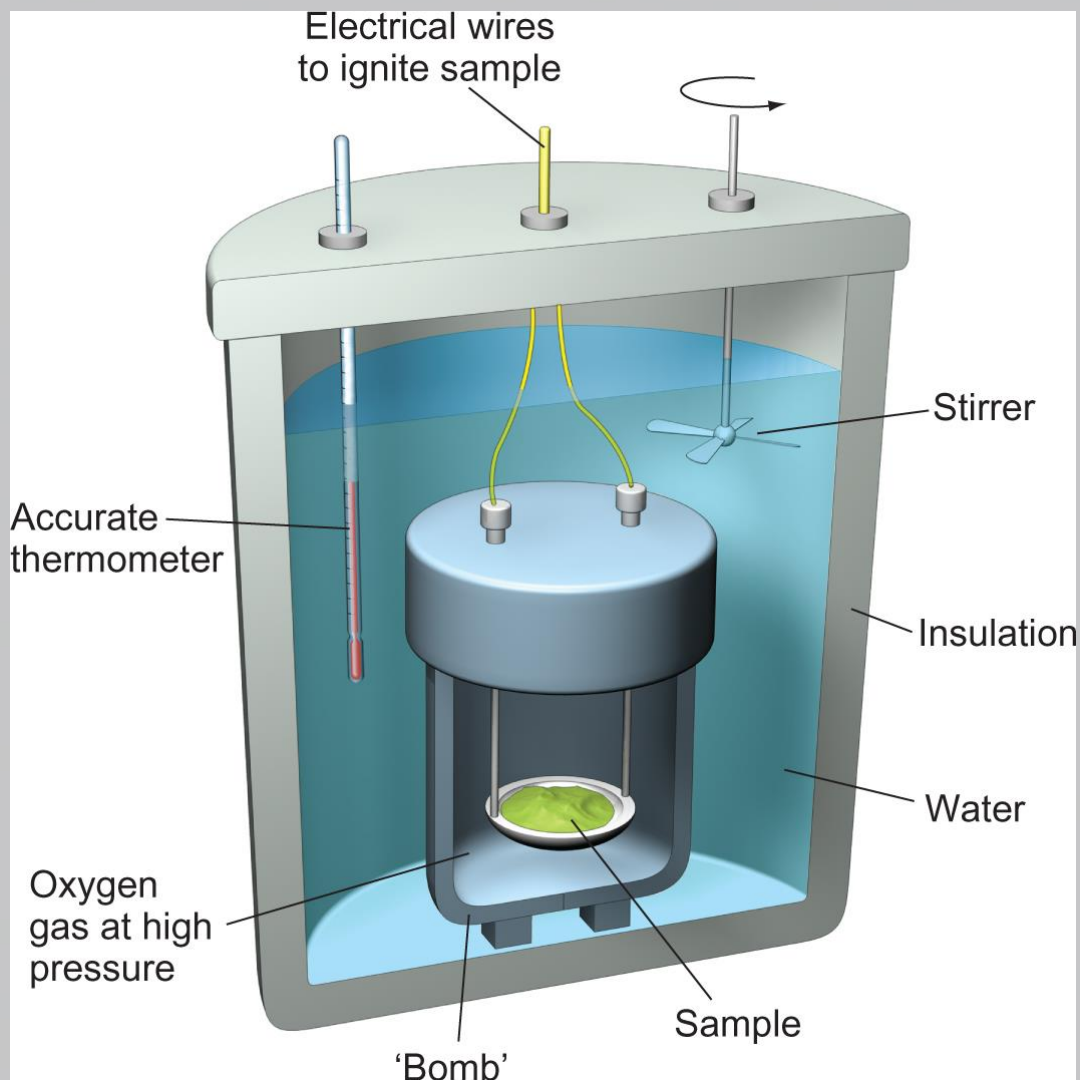


# CALORIMETERS

Solution Reaction  
Simple coffee cup



Combustion Reaction  
Bomb

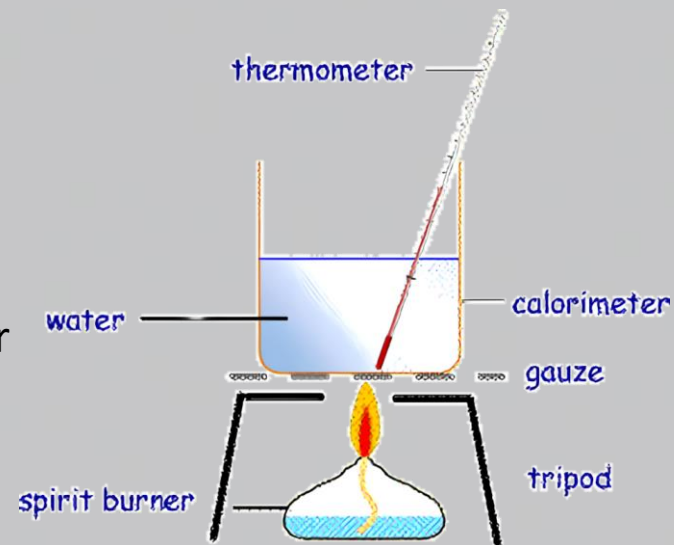


<https://youtu.be/ohyA9amFfsc>

# HEAT OF REACTION

$$q(\text{system}) = -q(\text{surroundings})$$

0.300 g of acetylene ( $\text{C}_2\text{H}_2$ ) is combusted in a calorimeter that contains 80.0 g of water at  $27^\circ\text{C}$ . The empty calorimeter has a heat capacity of  $82\text{ J}/^\circ\text{C}$ . If the final temperature of calorimeter is  $63.0^\circ\text{C}$ , calculate a) heat of combustion of the acetylene sample and b) the molar heat of combustion of cetylene. The specific heat of water is  $4.184\text{ J/g}\cdot^\circ\text{C}$



$$q(\text{system}) = q(\text{reaction}) - \text{cannot be measured directly !}$$

$$\text{surroundings} = \text{cold water} + \text{cup}$$

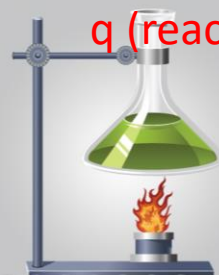
$$q(\text{water}) = \text{mass} \times \Delta T \times C_p = 80.0\text{ g} \times (63 - 27)^\circ\text{C} \times 4.184\text{ J/g}\cdot^\circ\text{C} = 12050\text{ J}$$

$$q(\text{cup}) = \text{HC} \times \Delta T = 82\text{ J}/^\circ\text{C} \times (63 - 27)^\circ\text{C} = 2952\text{ J}$$

$$q(\text{reaction}) = -[\text{water} + \text{calorimeter}]$$

$$q(\text{reaction}) = -[12050\text{ J} + 2952\text{ J}]$$

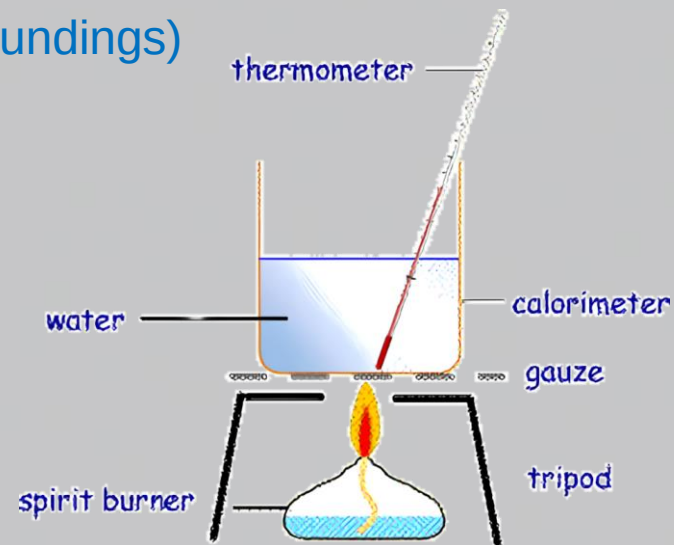
$$q(\text{reaction}) = -15,000\text{ J} = -15\text{ kJ}$$



# HEAT OF REACTION

$$q(\text{system}) = -q(\text{surroundings})$$

0.300 g of acetylene ( $\text{C}_2\text{H}_2$ ) is combusted in a calorimeter that contains 80.0 g of water at 27 degC. The empty calorimeter has a heat capacity of 82 J/degC. If the final temperature of calorimeter is 63.0 degC, calculate a) heat of combustion of the acetylene sample and b) the molar heat of combustion of acetylene. The specific heat of water is 4.184 J/g-degC



$$q(\text{reaction}) = -15,000 \text{ J} = -15 \text{ kJ}$$

This is the heat from 0.300 g of acetylene ( $\text{C}_2\text{H}_2$ ). Now we want MOLAR heat of combustion – heat from 1 mole

$$1 \text{ mole } \text{C}_2\text{H}_2 = 26 \text{ g}$$

$$\frac{26 \text{ g}}{0.300 \text{ g}} = \frac{\Delta_c H^\circ \text{ kJ}}{-15 \text{ kJ}}$$

$$\Delta_c H^\circ \text{ kJ} = \frac{(26 \text{ g} \times -15 \text{ kJ})}{0.300 \text{ g}}$$

$$\Delta_c H^\circ \text{ kJ} = -1300 \text{ kJ/mol}$$



# HEAT OF REACTION

$$q(\text{system}) = -q(\text{surroundings})$$

At 28 °C, 75.0 mL of 0.100 M KOH (aq) is mixed with 25 mL of 0.100 M HCl in a calorimeter that has a heat capacity of 65 J/°C. If the final temperature of the calorimeter is 37 °C, calculate a) heat of this reaction and b) the molar heat of neutralization. Assume that volumes are additive and that the specific heat of the solution is 4.184 J/g-°C, and that the density of all solutions is 1.0 g/mL.

$$q(\text{system}) = q(\text{reaction}) - \text{cannot be measured directly !}$$

$$\text{surroundings} = \text{macroscopic solution mixture} + \text{calorimeter}$$

$$q(\text{solution mixture}) = \text{mass} \times \Delta T \times C_p = 100 \text{ g} \times (37-28) ^\circ\text{C} \times 4.184 \text{ J/g-}^\circ\text{C} = 3766 \text{ J}$$

$$q(\text{cup}) = HC \times \Delta T = 65 \text{ J/}^\circ\text{C} \times (37-28) ^\circ\text{C} = 585 \text{ J}$$

$$q(\text{reaction}) = - [q(\text{solution mixture}) + q(\text{calorimeter})]$$

$$q(\text{reaction}) = - [3766 \text{ J} + 585 \text{ J}]$$

$$q(\text{reaction}) = - 4351 \text{ J} = - 4.35 \text{ kJ}$$



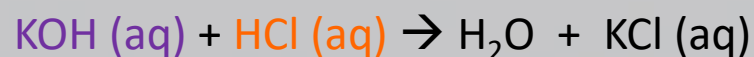
# HEAT OF REACTION

$$q(\text{system}) = -q(\text{surroundings})$$

At 28 degC, 75.0 mL of 0.100 M KOH (aq) is mixed with 25 mL of 0.100 M HCl in a calorimeter that has a heat capacity of 65 J/degC. If the final temperature of the calorimeter is 37 degC, calculate a) heat of this reaction and b) the molar heat of neutralization. Assume that volumes are additive and that the specific heat of the solution is 4.184 J/g-degC, and that the density of all solutions is 1.0 g/mL

$$q(\text{reaction}) = -4351 \text{ J} = -4.35 \text{ kJ}$$

This is the heat from the reaction that occurred



How much reaction occurred?

$$n(\text{KOH}) = 0.100 \text{ M} \times 0.075 \text{ L} = 0.0075 \text{ mol KOH}$$

$$n(\text{HCl}) = 0.100 \text{ M} \times 0.025 \text{ L} = 0.0025 \text{ mol HCl} \quad \text{Limiting reactant}$$

$$\frac{1 \text{ mol HCl}}{0.0025 \text{ mol HCl}} = \frac{\Delta H^\circ \text{ kJ}}{-4.35 \text{ kJ}}$$

$$\Delta H^\circ \text{ kJ} = -1740 \text{ kJ/mol}$$



# HEAT CAPACITIES

Heat required to raise the temperature of:

|                                                        |                                                   |          |       |
|--------------------------------------------------------|---------------------------------------------------|----------|-------|
| Heat capacity                                          | a substance by 1 °C                               | J/°C     | $C$   |
| Specific heat capacity                                 | 1 g of a substance by 1 °C                        | J/°C-g   | $C_s$ |
| Molar heat capacity                                    | 1 mol of a substance by 1 °C                      | J/°C-mol | $C_m$ |
| Molar heat capacity<br>@ constant pressure<br>ISOBARIC | 1 mol of a substance by 1 °C<br>CONSTANT PRESSURE | J/°C-mol | $C_p$ |
| Molar heat capacity<br>@ constant volume<br>ISOCHORIC  | 1 mol of a substance by 1 °C<br>CONSTANT VOLUME   | J/°C-mol | $C_v$ |



# HEAT CAPACITIES

| Substance                                   | Heat capacity                         |                                         |
|---------------------------------------------|---------------------------------------|-----------------------------------------|
|                                             | $C_s / \text{J K}^{-1} \text{g}^{-1}$ | $C_m / \text{J K}^{-1} \text{mol}^{-1}$ |
| Carbon (graphite)                           | 0.67                                  | 8.5                                     |
| Iron (Fe(s))                                | 0.45                                  | 25.1                                    |
| Copper (Cu(s))                              | 0.38                                  | 24.4                                    |
| Gold (Au(s))                                | 0.129                                 | 25.4                                    |
| Hydrogen (H <sub>2</sub> (g))               | 14.4                                  | 28.8                                    |
| Nitrogen (N <sub>2</sub> (g))               | 1.04                                  | 29.1                                    |
| Oxygen (O <sub>2</sub> (g))                 | 0.92                                  | 29.4                                    |
| Carbon monoxide (CO(g))                     | 1.04                                  | 29.1                                    |
| Carbon dioxide (CO <sub>2</sub> (g))        | 0.84                                  | 37.1                                    |
| Methane (CH <sub>4</sub> (g))               | 2.23                                  | 35.7                                    |
| Ethane (C <sub>2</sub> H <sub>6</sub> (g))  | 1.75                                  | 52.5                                    |
| Benzene (C <sub>6</sub> H <sub>6</sub> (g)) | 1.05                                  | 82.4                                    |
| Water (H <sub>2</sub> O(l))                 | 4.18                                  | 75.3                                    |
| Water vapour (H <sub>2</sub> O(g))          | 1.87                                  | 33.6                                    |

Important early molar mass concept:  
MM of metals  $\propto 1/(\text{gram})$  specific heat

Similar - diatomic

Increasing number of bonds

\* The values are measured at constant pressure.



# $\Delta H$ AND TEMPERATURE

Consider H                      Heat of 1 mol of substance at a given temperature at constant pressure

Heat substance                      H increases                       $\Delta H_{T_2}(\text{rxn}) - \Delta H_{T_1}(\text{rxn}) = (2 \times H_{T_2}(\text{B}) - H_{T_2}(\text{A})) - (2 \times H_{T_1}(\text{B}) - H_{T_1}(\text{A}))$

Change in H =                       $C_p \times \Delta T$                        $\Delta H_{T_2}(\text{rxn}) - \Delta H_{T_1}(\text{rxn}) = (2 \times H_{T_2}(\text{B}) - 2 \times H_{T_1}(\text{B})) - (H_{T_2}(\text{A}) - H_{T_1}(\text{A}))$

$H_{T_2} - H_{T_1} = C_p \Delta T$                        $\Delta H_{T_2}(\text{rxn}) - \Delta H_{T_1}(\text{rxn}) = 2 \times (H_{T_2}(\text{B}) - H_{T_1}(\text{B})) - (H_{T_2}(\text{A}) - H_{T_1}(\text{A}))$

Imagine reaction,  $A \rightarrow 2B$                        $\Delta H_{T_2}(\text{rxn}) - \Delta H_{T_1}(\text{rxn}) = 2 \times (H_{T_2}(\text{B}) - H_{T_1}(\text{B})) - (H_{T_2}(\text{A}) - H_{T_1}(\text{A}))$

$\Delta H(\text{rxn}) = \Sigma H(\text{prod}) - \Sigma H(\text{react})$                        $\Delta H_{T_2}(\text{rxn}) - \Delta H_{T_1}(\text{rxn}) = 2 \times C_p(\text{B})\Delta T - C_p(\text{A})\Delta T$

$\Delta H(\text{rxn}) = 2 \times H(\text{B}) - H(\text{A})$                        $\Delta H_{T_2}(\text{rxn}) - \Delta H_{T_1}(\text{rxn}) = (2 \times C_p(\text{B}) - C_p(\text{A}))\Delta T$

At  $T_1$ :  $\Delta H_{T_2}(\text{rxn}) =$   
 $2 \times H_{T_1}(\text{B}) - H_{T_1}(\text{A})$

At  $T_2$ :  $\Delta H_{T_1}(\text{rxn}) =$   
 $2 \times H_{T_2}(\text{B}) - H_{T_2}(\text{A})$

$\Delta C_p = \Sigma \text{coefficients} \times C_p(\text{products}) - \Sigma \text{coefficients} \times C_p(\text{reactants})$

$\Delta H_{T_2}(\text{rxn}) = \Delta H_{T_1}(\text{rxn}) + \Delta C_p \Delta T$

Kirchhoff's Equation



# $\Delta H$ AND TEMPERATURE

$$\Delta H_{T_2}(\text{rxn}) = \Delta H_{T_1}(\text{rxn}) + \Delta C_p \Delta T \qquad \Delta C_p = \sum \text{coefficients} \times C_p (\text{products}) - \sum \text{coefficients} \times C_p (\text{reactants})$$

At 300K,  $\Delta H$  is -92.4 kJ for the reaction  $\text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g}) \rightarrow 2 \text{NH}_3 (\text{g})$ . Given that the molar specific heats for  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  are 29.1, 28.8 and 35.1 J/K-mol, respectively, calculate the value of  $\Delta H$  at 800K

$$\Delta C_p = \sum \text{coefficients} \times C_p (\text{products}) - \sum \text{coefficients} \times C_p (\text{reactants})$$

$$\Delta C_p = 2 \sum \text{coefficients} \times C_p (\text{products}) - \sum \text{coefficients} \times C_p (\text{reactants})$$

$$\Delta C_p = [2 \times C_p (\text{NH}_3)] - [C_p (\text{N}_2) + 3 \times C_p (\text{H}_2)]$$

$$\Delta C_p = [2 \times 35.1] - [29.1 + 3 \times 28.8]$$

$$\Delta C_p = -45.3 \text{ J/K}$$

$$\Delta H_{T_2}(\text{rxn}) = \Delta H_{T_1}(\text{rxn}) + \Delta C_p \Delta T$$

$$\Delta H_{T_2}(\text{rxn}) = -92.4 \text{ kJ} + (-45.3 \text{ J/K}) (800 \text{ K} - 300 \text{ K})$$

$$\Delta H_{T_2}(\text{rxn}) = -92.4 \text{ kJ} + (-0.0453 \text{ kJ/K}) (800 \text{ K} - 300 \text{ K})$$

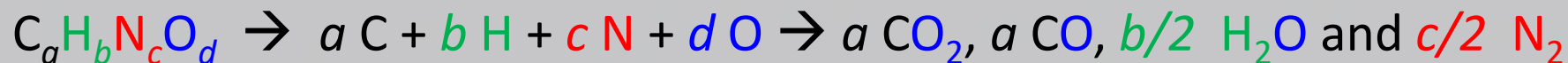
$$\Delta H_{T_2}(\text{rxn}) = -115.1 \text{ kJ}$$

UNITS



# THERMOCHEMISTRY OF EXPLOSIVES

when an explosive reaction takes place, the explosive molecule



- breaks apart into its constituent atoms
- followed by a rearrangement of the atoms into a series of small, stable molecules of gases, such as  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{N}_2$
- $\text{H}_2$ ,  $\text{C}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SO}_2$ , etc can be also formed
- the nature of the products depends upon the amount of oxygen available for the reaction
- this supply of oxygen depends on the quantity of oxidizing atoms in the explosive molecule.



# OXYGEN BALANCE

the amount of oxygen expressed as wt% needed or produced to ensure the complete oxidation of all the carbon, hydrogen, or other elements to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , (and  $\text{SO}_2$ ,  $\text{Al}_2\text{O}_3$ , *etc.*)

used to indicate the degree to which an explosive can be oxidized

for an explosive with the general formula  $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$  and molecular weight **MW**:

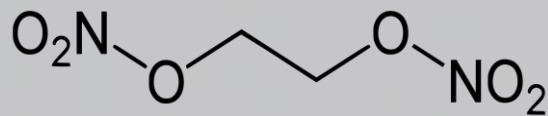
$$\Omega = \frac{16}{MW} \times \left[ d - (2a) - \left(\frac{b}{2}\right) \right] \times 100\% \quad \text{oxygen balance}$$

The **sensitivity**, **strength** and **brisance** of an explosive depend upon oxygen balance and tend to approach their maxima as oxygen balance approaches zero.



# OXYGEN BALANCE

## EXAMPLE 1:



ethylene glycol dinitrate  
(nitroglycol)

As a result of detonation, the explosive molecule EGDN ( $C_2H_4N_2O_6$ , MW = 152) is fully oxidized to form gaseous products,  $CO_2$ ,  $H_2O$  and  $N_2$ . Calculate the oxygen balance for EGDN.



$a = 2$   
 $b = 4$   
 $d = 6$

just enough oxygen in EGDN to oxidize reactants fully to  $CO_2$  and  $H_2O$

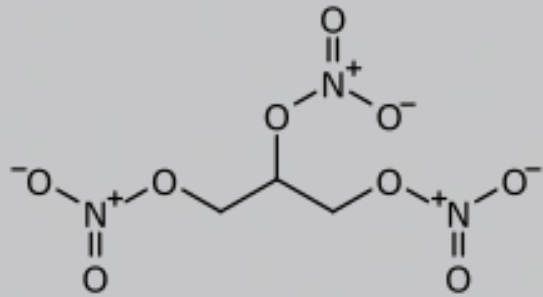
$$\Omega = \frac{16}{MW} \times \left[ d - (2a) - \left( \frac{b}{2} \right) \right] \times 100\% =$$
$$= \frac{16}{152} \times \left[ 6 - (2 \times 2) - \left( \frac{4}{2} \right) \right] = 0$$

zero oxygen balance



# OXYGEN BALANCE, cnt

## EXAMPLE 2:



As a result of detonation, nitroglycerin ( $\text{C}_3\text{H}_5\text{N}_3\text{O}_9$ , MW = 227) is fully oxidized to form gaseous products,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$ . Calculate the oxygen balance for TNT.



$$a = 3$$

$$b = 5$$

$$d = 9$$

excess of oxygen in NG to oxidize reactants fully to  $\text{CO}_2$  and  $\text{H}_2\text{O}$

$$\Omega = \frac{16}{\text{MW}} \times \left[ d - (2a) - \left( \frac{b}{2} \right) \right] 100\% =$$

$$= \frac{16}{227} \times \left[ 9 - (2 \times 3) - \left( \frac{5}{2} \right) \right] 100\% = +3.5\%$$

*amount of oxygen liberated*

$$\text{wt}\% \text{ O} = \frac{8 \times 100\%}{227} = +3.5\%$$

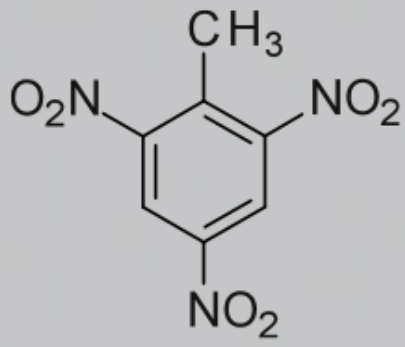
wt% of O as the total MW of O atoms in the product ( $\frac{1}{2} \times 16 = 8$ ) divided by the MW of nitroglycerin

**positive oxygen balance**

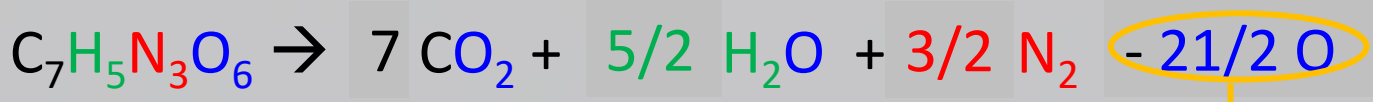


# OXYGEN BALANCE, cnt

## EXAMPLE 3:



As a result of detonation, the explosive molecule TNT ( $C_7H_5N_3O_6$ , MW = 227) is fully oxidized to form gaseous products,  $CO_2$ ,  $H_2O$  and  $N_2$ . Calculate the oxygen balance for TNT.



a = 7  
b = 5  
d = 6

insufficient oxygen in TNT to oxidize reactants fully to  $CO_2$  and  $H_2O$

$$\Omega = \frac{16}{MW} \times \left[ d - (2a) - \left( \frac{b}{2} \right) \right] 100\% =$$
$$= \frac{16}{227} \times \left[ 6 - (2 \times 7) - \left( \frac{5}{2} \right) \right] 100\% =$$
$$= -74\%$$

*amount of oxygen taken in*

$$wt\% O = \frac{-168 \times 100\%}{227} = -74\%$$

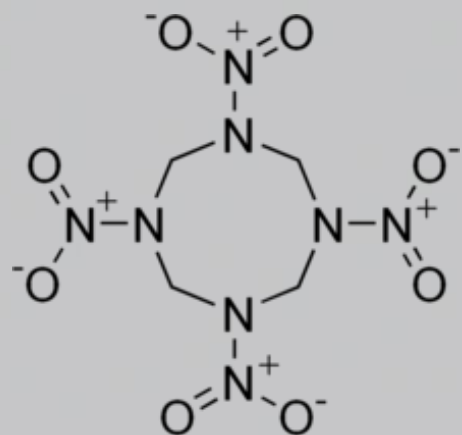
wt% of O as the total MW of O atoms in the product ( $10\frac{1}{2} \times 16 = 168$ ) divided by the MW of TNT

negative oxygen balance

incomplete combustion; a large amount of toxic gases like CO produced



# DECOMPOSITION REACTIONS

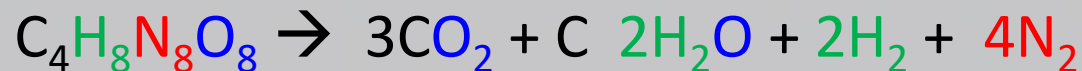
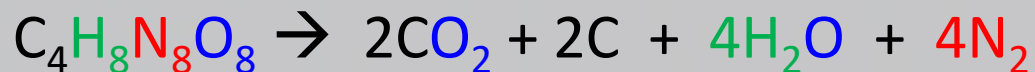


HMX (octogen)

$a = 4$ ,  $b = 8$ ,  $d = 8$

$$\Omega = \frac{16}{\text{MW}} \times \left[ d - (2a) - \left( \frac{b}{2} \right) \right] \times 100\% =$$
$$= \frac{16}{296} \times \left[ 8 - (2 \times 4) - \left( \frac{8}{2} \right) \right] \times 100\% = -21.6\%$$

detonation of explosive results in the formation of decomposition products



# KISTIAKOWSKY-WILSON RULES

for moderately oxygen-deficient explosives with  $\Omega > -40.0$  (HMX,  $\text{C}_4\text{H}_8\text{N}_8\text{O}_8$ )

| Rule | Conditions                                      | Products                                        |
|------|-------------------------------------------------|-------------------------------------------------|
| 1    | C atoms converted to CO                         | $4 \text{ C} \rightarrow 4 \text{ CO}$          |
| 2    | Remaining O oxidizes H to $\text{H}_2\text{O}$  | $4 \text{ O} \rightarrow 4 \text{ H}_2\text{O}$ |
| 3    | Still remaining O, oxidizes CO to $\text{CO}_2$ | No more O left                                  |
| 4    | All N converted to $\text{N}_2$                 | $8 \text{ N} \rightarrow 4 \text{ N}_2$         |

overall reaction for decomposition of HMX:



# MODIFIED KISTIAKOWSKY-WILSON RULES

for explosives with  $\Omega > -40.0$  (TNT,  $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$ )

| Rule | Conditions                                      | Products                                                     |
|------|-------------------------------------------------|--------------------------------------------------------------|
| 1    | H atoms converted to $\text{H}_2\text{O}$       | $5 \text{ H} \rightarrow 2\frac{1}{2} \text{ H}_2\text{O}$   |
| 2    | Remaining O oxidizes C to CO                    | $3\frac{1}{2} \text{ O} \rightarrow 3\frac{1}{2} \text{ CO}$ |
| 3    | Still remaining O, oxidizes CO to $\text{CO}_2$ | No more O left                                               |
| 4    | All N converted to $\text{N}_2$                 | $3 \text{ N} \rightarrow 1\frac{1}{2} \text{ N}_2$           |

overall reaction for decomposition of TNT:



# SPRINGALL ROBERTS RULES

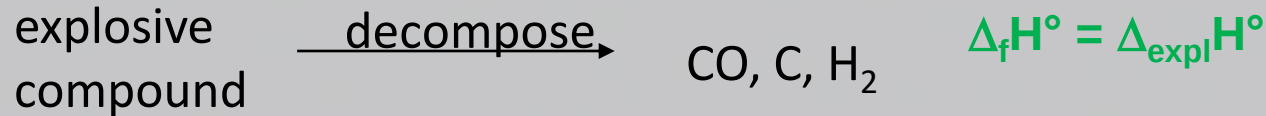
unmodified Kistiakowsky-Wilson rules PLUS two more conditions (TNT,  $C_7H_5N_3O_6$ )

| Rule | Conditions                                                                                                                      | Products                                                           |
|------|---------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|
| 1    | C atoms converted to CO                                                                                                         | $6\text{ C} \rightarrow 6\text{ CO}$                               |
| 2    | Remaining O oxidizes H to $H_2O$                                                                                                | No more O left                                                     |
| 3    | Still remaining O, oxidizes CO to $CO_2$                                                                                        | No more O left                                                     |
| 4    | All N converted to $N_2$                                                                                                        | $3\text{ N} \rightarrow 1\frac{1}{2}\text{ N}_2$                   |
|      | This results in equation: $C_7H_5N_3O_6 \rightarrow 6\text{ CO} + \text{C} + 2\frac{1}{2}\text{ H}_2 + 1\frac{1}{2}\text{ N}_2$ |                                                                    |
| 5    | 1/3 of CO converts to $CO_2$                                                                                                    | $2\text{ CO} \rightarrow \text{C} + \text{CO}_2$                   |
| 6    | 1/6 of original CO converts to C and $H_2O$                                                                                     | $\text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O}$ |

Overall reaction for decomposition of TNT:



# HEATS OF FORMATION



the energy liberated during the formation of decomposition products is known as the '**heat of explosion**'

$$\Delta_{\text{comb}} H^\circ > \Delta_{\text{expl}} H^\circ \text{ when } \Omega < 0$$

$$\Delta_{\text{comb}} H^\circ = \Delta_{\text{expl}} H^\circ \text{ when } \Omega > 0$$

The key difference between combustion and explosion is that:  
**combustion is a chemical reaction that produces heat and gases slowly for a certain time period,**  
**whereas explosion is a chemical reaction that produces heat and gases rapidly in an instant.**

Detonation is a **supersonic explosions created by high explosives are known as detonations** and travel through shock waves.



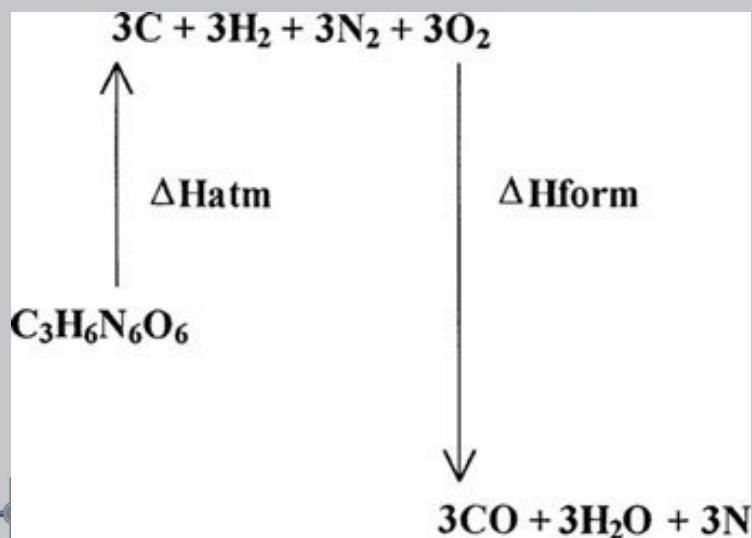
# HESS'S LAW - EXAMPLE

## Decomposition of RDX:

energy required to break the interatomic bonds of the explosive into its constituent elements (the 'heats of atomization' )



elements quickly form new bonds and release a greater quantity of energy



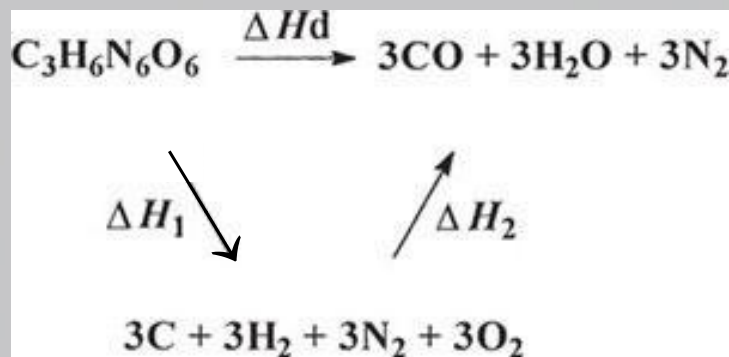
the energy evolved - state function (depends only on the initial and final states)

the net heat evolved is the same as if the reactant molecules were first dissociated into their atoms, and then reacted directly to form the final products



# ENTHALPY OF DETONATION

detonation – supersonic explosion (travels through shock waves)



$$\Delta_f H^\circ (\text{RDX}) = +70.3 \text{ kJ/mol}$$

$$\Delta_f H^\circ (\text{CO}) = -110.5 \text{ kJ/mol}$$

$$\Delta_f H^\circ (\text{H}_2\text{O}_{(g)}) = -241.8 \text{ kJ/mol}$$

$$\Delta_f H^\circ (\text{C}), (\text{H}_2), (\text{O}_2), (\text{N}_2) = 0 \text{ kJ/mol}$$

$$\Delta_{\text{exp}} H = \Delta_{\text{detonation}} H = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$$

$$\Delta H_1 = \Delta_{\text{atom}} H = -\Delta_f H^\circ = (\sum \Delta_f H^\circ (\text{C}), (\text{H}_2), (\text{O}_2), (\text{N}_2)) - \Delta_f H^\circ (\text{RDX}) = 0 - (-70.3) = 70.3 \text{ kJ/mol}$$

$$\begin{aligned} \Delta H_2 = \Delta_f H^\circ &= [3 \times \Delta_f H^\circ (\text{CO}) + 3 \times \Delta_f H^\circ (\text{H}_2\text{O}_{(g)}) + 3 \times \Delta_f H^\circ (\text{N}_2)] - [\sum \Delta_f H^\circ (\text{C}), (\text{H}_2), (\text{O}_2), (\text{N}_2)] = \\ &= [3 \times (-110.5) + 3 \times (-241.8) + 3 \times 0] - 0 = -1057.1 - 0 = -1057.1 \text{ kJ/mol} \end{aligned}$$

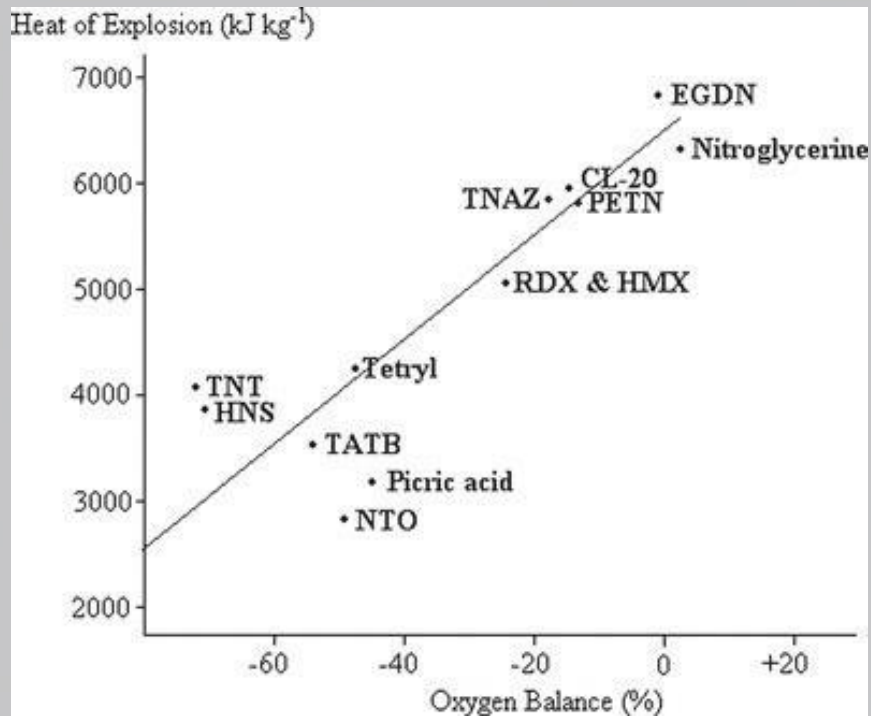
$$\Delta_{\text{detonation}} H = \Delta H_2 - \Delta H_1 = -1057.1 - 70.3 = -1127.4 \text{ kJ/mol}$$

the heat of detonation can be converted to the heat of explosion  $Q$

$$Q_{\text{exp}} = \frac{\Delta_{\text{detonation}} H^\circ \times 1000}{MM} = \frac{(-1127.4 \text{ kJ/mol} \times 1000)}{222.1 \text{ g/mol}} = -5075.5 \text{ kJ/kg}$$



# EFFECT OF OXYGEN BALANCE ON THE HEAT OF EXPLOSION



highest heat of explosion when oxygen balance is zero (all C and H stoichiometrically oxidized to CO<sub>2</sub> and H<sub>2</sub>O)

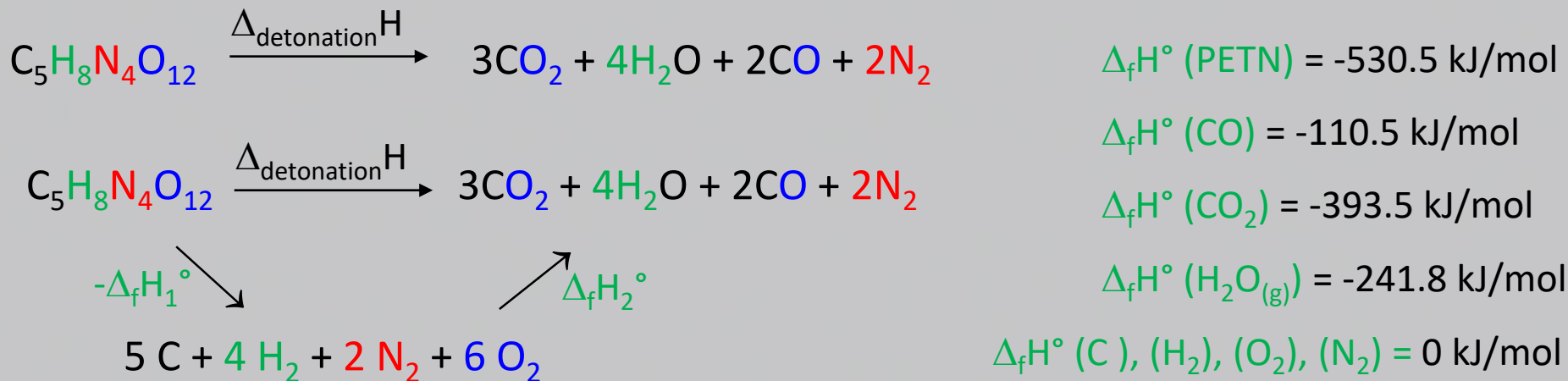
oxygen balance can be used to optimize the composition of the explosive to give an oxygen balance as close to zero as possible

**Example:** TNT has an oxygen balance of -74% (very deficient in oxygen) and by mixing it with 79% NH<sub>4</sub>NO<sub>3</sub> which has an oxygen balance of +20% the oxygen balance is reduced to zero resulting in a high value for the heat of explosion.



# PRACTICE PROBLEM

Calculate the heat of explosion (detonation) of PETN ( $C_5H_8N_4O_{12}$ , MM 316.3 g/mol), given the following products and heats of formation:



$$\Delta_{detonation}H = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$$

$$-\Delta_f H_1^\circ = \Delta_{atom}H = -(\sum \Delta_f H^\circ (C), (H_2), (O_2), (N_2)) - \Delta_f H^\circ (\text{PETN}) = -(0 - (-530.5)) = -530.5 \text{ kJ/mol}$$

$$\Delta_f H_2^\circ = [3 \times \Delta_f H^\circ (\text{CO}_2) + 4 \times \Delta_f H^\circ (\text{H}_2\text{O}_{(g)}) + 2 \times \Delta_f H^\circ (\text{CO}) + 2 \times \Delta_f H^\circ (\text{N}_2)] - [\sum \Delta_f H^\circ (C), (H_2), (O_2), (N_2)] = [3 \times (-393.5) + 4 \times (-241.8) + 2 \times (-110.5) + 3 \times 0] - 0 = -2368.7 - 0 = -2368.7 \text{ kJ/mol}$$

$$\Delta_{detonation}H = \Delta H_2 - \Delta H_1 = -2368.7 - (-530.5) = -1838.2 \text{ kJ/mol}$$

$$Q_{exp} = \frac{\Delta_{detonation}H^\circ \times 1000}{MM} = \frac{(-1838.2 \text{ kJ/mol} \times 1000)}{316.3 \text{ g/mol}} = -5811.6 \text{ kJ/kg}$$



# VOLUME OF GASEOUS PRODUCTS OF EXPLOSION

- **IMPORTANT** because the volume of gas produced during an explosion provides information on the amount of work done by the explosive.
- **STP** (**0 °C** or **273K**, **1 atm**)
  - volume of gas varies with temperature at which the measurement is taken.
  - enable comparisons between one explosive and another.
  - one mole of gas occupies **22.4 dm<sup>3</sup>** (molar gas volume)
- volume of gas **V** liberated from an explosive during detonation can be calculated from its equation of decomposition
- $\text{C}_3\text{H}_6\text{N}_6\text{O}_6 \rightarrow 3 \text{CO (g)} + 3 \text{H}_2\text{O (g)} + 3 \text{N}_2 \text{(g)}$ 
  - **9 moles** of gas are produced from **1 mole** of RDX (MM = 222.1 g/mol)
  - at **STP 9 moles** of gas will occupy (9 moles x 22.4 dm<sup>3</sup>/mol) **201.6 dm<sup>3</sup>**
  - **1 g** of RDX will produce 201.6 dm<sup>3</sup> / 222.1 g) **0.908 dm<sup>3</sup>/g** (**908 cm<sup>3</sup>/g**)



# PRACTICE PROBLEM

The chemical equation for an explosion of TNT ( $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$ ) was derived using the modified K-W rules and is shown below.



Calculate the **volume** of all gas products liberated upon detonation of **one mole** of TNT.

What **volume** of gases is produced from **1 g** of TNT?

*One mole of TNT produces  $7\frac{1}{2}$  moles of gas which will occupy  $168 \text{ dm}^3$  and 1 g of TNT will produce  $0.740 \text{ dm}^3/\text{g}$  ( $740 \text{ cm}^3/\text{g}$ ) of gas at 'STP' as shown in Equation*

*$7\frac{1}{2} \text{ mol of gas will occupy } 22.4 \times 7\frac{1}{2} = 168 \text{ dm}^3$*

*Therefore, 1 mol of TNT produces  $168 \text{ dm}^3$  of gas*

*1 g TNT produces  $168/227 = 0.740 \text{ dm}^3/\text{g}$  where the molecular mass of TNT is 227*



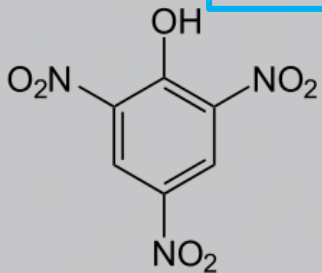
# EXPLOSIVE POWER, POWER INDEX and TNT EQUIVALENCE

- in an explosive reaction, the amount of heat and gases liberated ( $Q_{\text{explosion}}$  and  $V_{\text{gas}}$ , calculated independently) combine to give the value for the **explosive power**

$$\text{explosive power} = Q_{\text{explosion}} \times V_{\text{gas}}$$

- power index** in relation to standard explosive, picric acid

$$\text{power index} = \frac{Q_{\text{explosion}} \times V_{\text{gas}}}{Q_{\text{explosion}}(\text{PA}) \times V_{\text{gas}}(\text{PA})} \times 100\%$$



picric acid  
 $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$   
229 g/mol

$Q_{\text{explosion}}$  3301.02 kJ/kg and  $V_{\text{gas}}$  831.06 dm<sup>3</sup>/kg

- “TNT equivalence”** - a normalization technique for equating properties of an explosive to TNT, the standard compares the explosive power to the explosive power of TNT

$$\text{TNT equivalence} = \frac{Q_{\text{explosion}} \times V_{\text{gas}}}{Q_{\text{explosion}}(\text{TNT}) \times V_{\text{gas}}(\text{TNT})}$$



power index and TNT equivalence of secondary explosives are much higher than the values for primary explosives.

