Ch06

Enthalpy

Heat at constant pressure,
a measurable state function.

Enthalpy (H)

- Change of Enthalpy (ΔH)
  - A new property and why we need it.
  - What is enthalpy?
  - Another Reaction Type
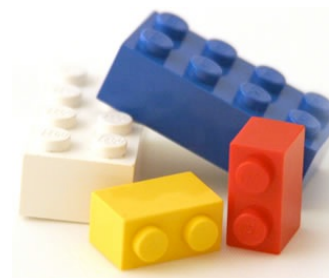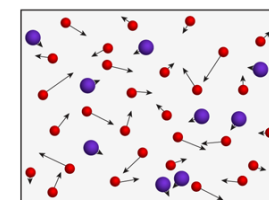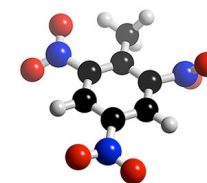   - Endothermic vs Exothermic
- Stoichiometry with Enthalpy
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    - ΔH$_{rxn}$ Depends on State
    - ΔH is Extensive
    - It's a new coefficient
  - Stoichiometry Problems
    - kJ → grams, mol → kJ, etc
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  - Constant Pressure Calorimetry
  - Experimentally Measuring Enthalpy Changes

- Hess's Law
  - "The path doesn't matter."
    - Heat & Algebra
    - Solving Hess's Law Problems
  - Tabulated ΔH's
    - of Fusion
    - of Fission
      - more in chapter 11
    - of Combustion
    - of Formation
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    - using heat of formation reactions makes using Hess's Law _really_ easy!

Why we need Enthalpy (H)

‣ We want to know the change in energy of chemical reactions. The difference in energy between what we start with and what's left after a chemical reaction.

‣ Example:

  ‣ How much energy we get out of burning a gallon of gasoline.

  ‣ How much energy we need to put into water to make hydrogen fuel cells.

‣ We can't use the total internal energy of the system because:

  ‣ It's hard to measure. We have to use a bomb calorimeter to prevent volume changes which is expensive and difficult to use.

  ‣ It's not a good representation of real conditions. It gives us the energy conditional on there being no change in volume of the system — which isn't the conditions under which we live and interact with most chemical reactions.

  ‣ We can't just add q and w.

    ‣ PV work is difficult to account for and interconverts with heat. Since q and w are not state properties how those variables change over time is complex.

	Energy Change (ΔE) Heat (q) & Work (w)		Internal Energy (E)	
Easy to measure	✔	✘	✘	✔
A state property (Δ is easy to calculate)	✘	✘	✔	✔
Includes changes in thermal energy.	✔	✘	✔	✔
Includes energy needed to change volume of substance.	✘	✔	✘	✔

$$(q \rightleftarrows w)$$

‣ We need a new chemical property.

  ‣ Something that we can easily measure.

  ‣ It needs to be a state function.

  ‣ It needs to reflect real world conditions — including the PV work done when a substance expands or contracts.

‣ The solution is to make up a new property.

‣ The new property is called Enthalpy (H).

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Enthalpy (H)

We define H = int energy + the volume
of the substance x it's pressure.

$$H = E + PV$$

E, P, & V are state functions, so H is too.

Enthalpy Change (ΔH) is q *at constant Pressure*

We define H = int energy + the volume of the substance x it's pressure.

$$H = E + PV$$

E, P, & V are state functions, so H is too.

When enthalpy changes over time, energy and volume may change.

$$\Delta(H) = \Delta(E + PV)$$

But if we assume constant pressure: then P doesn't change with time.

$$\Delta H = \Delta E + P \, \Delta V \qquad \Delta E = q + w$$

$$\Delta H = (q_P + w) + (-w) \qquad w = -P \, \Delta V$$

PV work falls out for enthalpy changes.

$$\Delta H = q_P$$

This means, if P is constant, we can measure changes in the state function ΔH simply by measuring heat flow q_p ✔

That means ΔH is both easy to measure and consistent regardless of how the material is produced or where it comes from. It is a property of the substance. ✔

Most reactions we do are open to the atmosphere, so have a constant pressure. A very acceptable limitation.

We have found our useful property:

ΔH (Enthalpy Change)

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Enthalpy (H)

- **Change of Enthalpy (ΔH)**
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Endothermic Processes

Surroundings

System

Heat →

$\Delta H > 0$
(Endothermic)

Surroundings

System

Heat →

$\Delta H < 0$
(Exothermic)

$$\Delta H = q_P$$

- A process is endothermic when ΔH is positive (heat absorbed)

Exothermic Processes

Surroundings

System
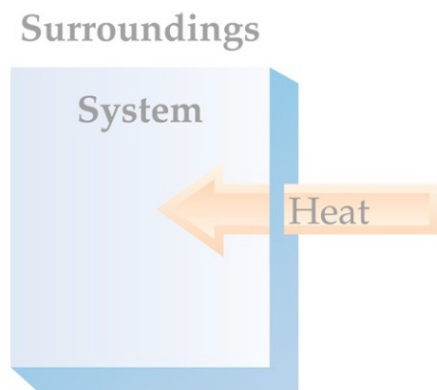
Heat

$\Delta H > 0$
(Endothermic)

$$\Delta H = q_P$$

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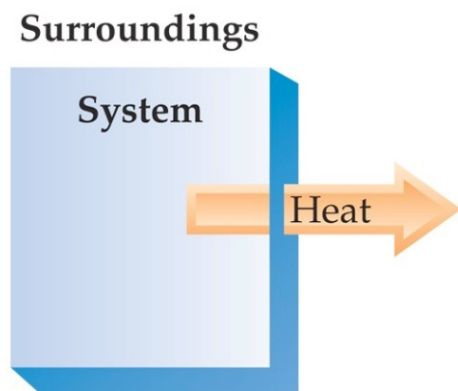
Heat

$\Delta H < 0$
(Exothermic)

- A process is endothermic when ΔH is positive. (heat absorbed)

- A process is exothermic when ΔH is negative. (heat released)

Endothermic vs Exothermic

Tips:

- Don't think about the **temperature (T)** (how hot or cold it is).
- Think about the **heat (q)** (thermal energy going in or out).
- Endothermic/Exothermic describes the <u>direction</u> of the heat.
- It describes action, what is being ***done***.

Ice Melting

Endothermic

Wood Burning

Exothermic

Breath Freezing

Exothermic

Water Boiling

Endothermic

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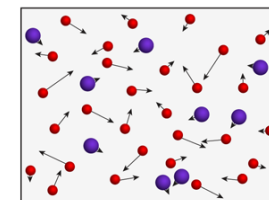 - "The path doesn't matter."
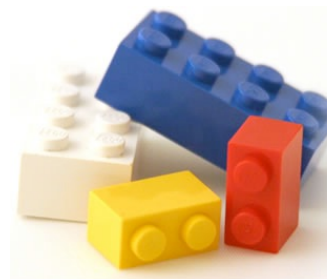   - Heat & Algebra
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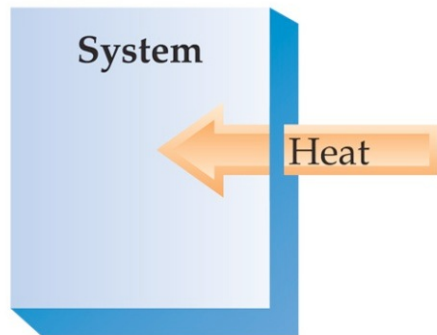   - more in chapter 11
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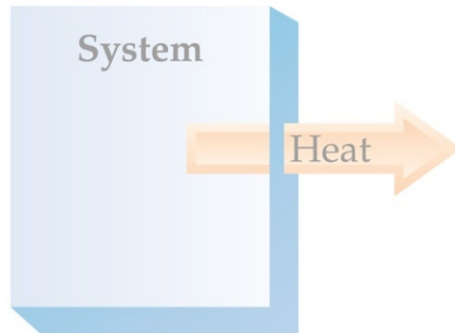   - using heat of formation reactions makes using Hess's Law _really_ easy!

Defining Heat of Reaction (ΔH_{rxn})

The amount of enthalpy absorbed or released in a balanced chemical equation is the enthalpy of reaction, also called the heat of reaction.

$$\Delta X = X_{final} - X_{initial}$$

Exothermic reaction release energy and have a negative heat of reaction.

Endothermic absorb release energy and have a positive heat of reaction.

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

$$\Delta H_{rxn} = H_{products} - H_{reactants} = -483.6\ kJ$$

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g) \quad \Delta H_{rxn} = -483.6\ kJ$$

Reversing Heats of Reaction

▸ Heat of reaction is equal in magnitude
  but opposite in direction to the reverse reaction.
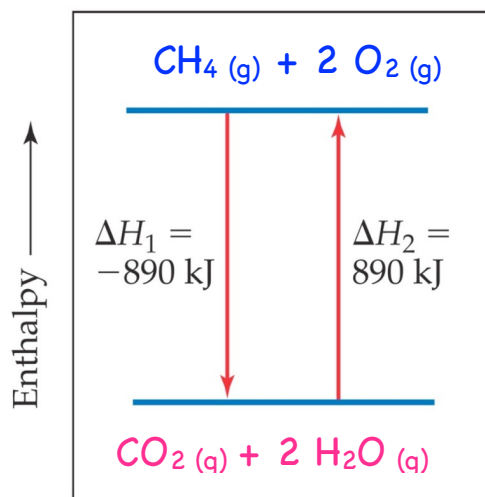
$$\Delta H_1 = H_{products} - H_{reactants}$$

$$\Delta H_2 = H_{products} - H_{reactants} = -\Delta H_1$$

$CH_{4\,(g)} + 2\ O_{2\,(g)}$

$\Delta H_1 = -890\ kJ$

$\Delta H_2 = 890\ kJ$

$CO_{2\,(g)} + 2\ H_2O_{(g)}$

Enthalpy

$CH_{4\,(g)} + 2\ O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2\ H_2O_{(g)} \quad \Delta H_{rxn} = -890\ kJ$

$CO_{2\,(g)} + 2\ H_2O_{(g)} \rightarrow CH_{4\,(g)} + 2\ O_{2\,(g)} \quad \Delta H_{rxn} = +890\ kJ$
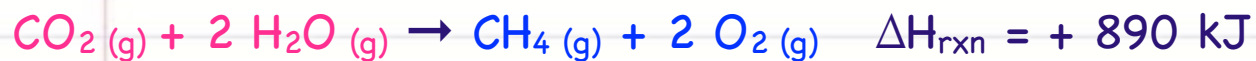
Heats of Reaction Depend on State

▸ Enthalpy change depends on state(s) of reactants and products.

▸ Gases contain more energy than liquids, than solids.

▸ We assume all material is at 25°C unless otherwise specified.

▸ If you don't see a state symbol use the state the matter would be at 25°C.

▸ Exception: combustion reactions usually produce gases.

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

$CH_{4\ (g)} + 2\ O_{2\ (g)} \rightarrow CO_{2\ (g)} + 2\ H_2O_{\ (l)}$ $\Delta H_{rxn} = -890\ kJ$

$CH_{4\ (g)} + 2\ O_{2\ (g)} \rightarrow CO_{2\ (g)} + 2\ H_2O_{\ (g)}$ $\Delta H_{rxn} = -802\ kJ$

Enthalpy Change is Extensive

▸ Enthalpy is an extensive property. It depends on quantity of materials.

▸ The reported heat of reaction is part of the balanced equation.

▸ Think of it as a new coefficient.

▸ It's a ratio per mole(s) in the balanced equation.

  ▸ If you burn 1 mol $O_{2(g)}$ you release 483.6 kJ

  ▸ If you burn 2 mol $H_{2(g)}$ you release 483.6 kJ

  ▸ If you burn 4 mol $H_{2(g)}$ you release 967.2 kJ (2x 483.6 kJ)

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g) \quad \Delta H_{rxn} = -\ 483.6\ kJ$$

$$4\ H_2\ (g) + 2\ O_2\ (g) \rightarrow 4\ H_2O\ (g) \quad \Delta H = -\ 967.2\ kJ$$

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Heat of Reaction Stoichiometry

grams

Molar Weight

Molarity

L (sol'n) ⟷ mol ⟷ mol ⟷ L (sol'n)

Mole Ratio

molar scale

Avogadro's number
1 mol = 6.022 x 10^{23}

molecules

grams

molecules

Heat of Reaction Stoichiometry

grams

kJ

grams

Important:
The conversion factor comes from the balanced equation just like the mole ratio does.

Heat can be calculated from moles of any substance in the balanced equation.

Molar Weight

Heat of Reaction

Molarity

L (sol'n)

mol

mol

L (sol'n)

Mole Ratio

molar scale

· ·

Avogadro's number
1 mol = 6.022 x 10^{23}

molecules

molecules

Problem: g → kJ

How much heat is released when 3.95 grams of $KClO_3$ decomposes to oxygen and potassium chloride? ΔH_{RXN} = -89.4 kJ

$$2\ KClO_{3\ (s)} \rightarrow 3\ O_{2\ (g)} + 2\ KCl_{(s)}\ \ \Delta H = -89.4\ kJ$$

$$g\ KClO_3 \xrightarrow{\ \textcircled{1}\ } mol\ KClO_3 \xrightarrow{\ \textcircled{2}\ } kJ$$

① $122.55g = 1mol$

$$
\begin{array}{ll}
1\ (K) & 39.0983 \\
1\ (Cl) & 35.453 \\
3\ (O) & 47.9982 \\
\hline
& 122.5495
\end{array}
$$

② $2\ KClO_3 = -89.4\ kJ$

$$3.95g\ KClO_3 \cdot \frac{1\ mol}{122.550g} \cdot \frac{-89.4\ kJ}{2\ KClO_3} = -1.44\ kJ$$

$$\Delta H = -1.44\ kJ$$
or
$1.44\ kJ$ released.

Problem: kJ → g

If 2.19 kJ were released, how much $KClO_3$ decomposed to oxygen and potassium chloride? ΔH_{RXN} = -89.4 kJ

$$2\ KClO_{3\ (s)} \longrightarrow 3\ O_{2\ (g)} + 2\ KCl_{(s)} \quad \Delta H = -89.4\ kJ$$

$$kJ \xrightarrow{②} mol\ KClO_3 \xrightarrow{①} g\ KClO_3$$
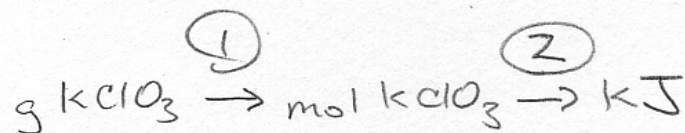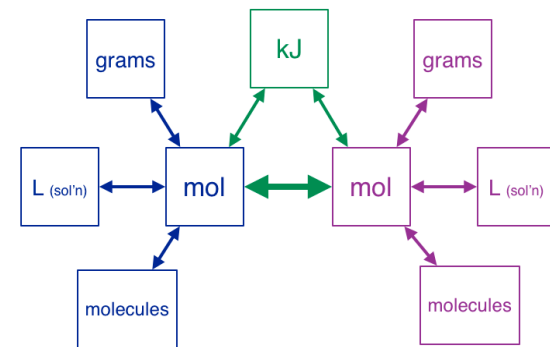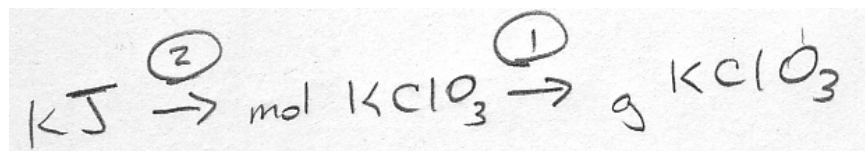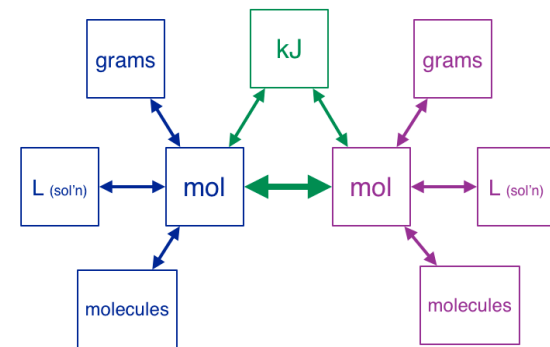
① $122.55 g = 1 mol$

$1 (K) \quad 39.0983$
$1 (Cl) \quad 35.453$
$3 (O) \quad + 47.9982$
$\overline{\quad 122.5495}$

② $2\ KClO_3 = -89.4\ kJ$

$$-2.19\ kJ \cdot \frac{2\ KClO_3}{-89.4\ kJ} \cdot \frac{122.55 g}{1\ mol} = \boxed{6.00 g\ KClO_3}$$

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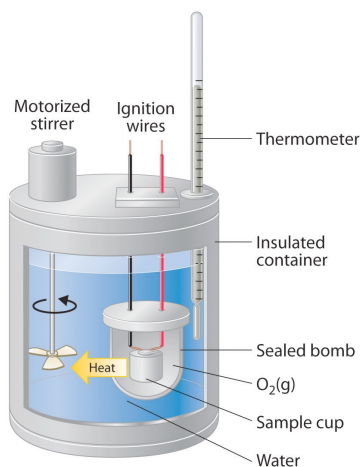
Bomb Calorimeter
(Constant Volume Calorimetry)

- – Expensive
- – Complicated
- – Hard to Use
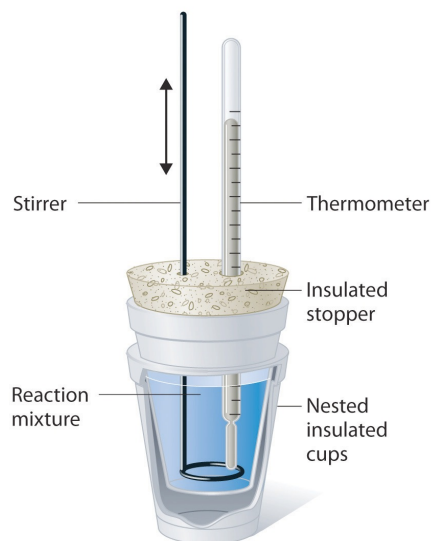
Coffee Cup Calorimeter
(Constant Pressure Calorimetry)

- – It's just a couple coffee cups!

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

$$q = C \cdot \Delta T \qquad \Delta H = q_p$$

Measuring enthalpy change is easier than measuring internal energy change, because we removed any pressure-volume work.

We don't need a bomb calorimeter to force pressure-volume work to not happen, we can ignore it because enthalpy doesn't involve pressure-volume work.

We just need an isolated system — we need to keep matter and energy from escaping or entering.

A set of nested coffee cups with a cap creates an isolated system around a test reaction — so we can find the enthalpy change for that reaction (ΔH).

We need to determine the heat capacity (C) of the calorimeter, but once we have it we can find the heat of reaction (ΔH) simply by measuring the temperature change (ΔT) and solving for q.

Because ΔH_{rxn} is equal to q, *as long as we're at constant pressure*.

Finding Heat of Reaction

$$H_2SO_{4\,(aq)} + NaOH_{(aq)} \rightarrow H_2O_{(l)} + Na_2SO_4 \qquad \Delta H_{rxn} = ?$$
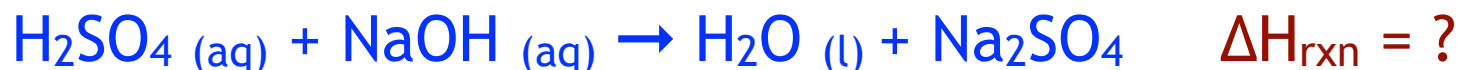
Calibrate your device (find it's heat capacity C_{cup}):

‣ Mix hot and cold water in a calorimeter.

‣ Since it's an isolated system all the heat has to cancel out.

$$q_{hot} = \text{-1 x } (q_{cold} + q_{cup})$$

$$[\, mass_{hot} \text{ x } Cs_{water} \text{ x } \Delta T_{hot} \,] = \text{- } [\, mass_{cold} \text{ x } Cs_{water} \text{ x } \Delta T_{cold} \,] \text{ - } [\, C_{cup} \text{ x } \Delta T_{cup} \,]$$

solve for C_{cup}

‣ The specific heat of water is known (4.18 J/g˚C). If you measure the mass of hot and cold water and measure the temperature change you can find the heat capacity of the calorimeter.

Finding the heat of reaction (ΔH_{rxn}):

‣ Do a reaction in the cup and measure the change in temperature.

$$\Delta H = \text{-1 x } (q_{solution} + q_{cup})$$

$$\Delta H = \text{- } [\, mass_{solution} \text{ x } Cs_{solution} \text{ x } \Delta T_{solution} \,] \text{ - } [\, C_{cup} \text{ x } \Delta T_{cup} \,]$$

$$\Delta H_{rxn} = \Delta H \text{ / moles used}$$

Stirrer — Thermometer
Insulated stopper
Reaction mixture — Nested insulated cups

Coffee Cup Calorimeter
(Constant Pressure Calorimetry)

– It's just a couple coffee cups!

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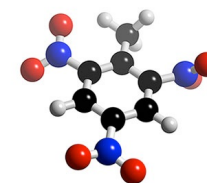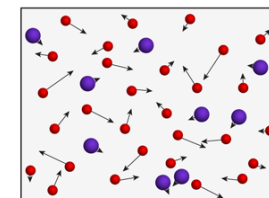 - Tabulated ΔH's
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Hess's Law
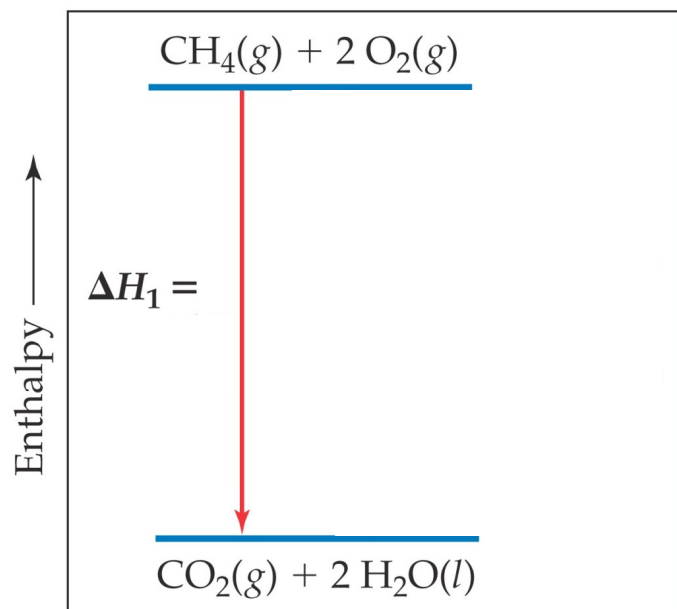
Hess's law states that:

"If a reaction is carried out in a series of steps, ΔH for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps."

(The path doesn't matter — so if one path won't work, just use one that does.)

$CH_4 (g) + 2 O_2 (g) \rightarrow CO_2 (g) + 2 H_2O (l)$ $\Delta H_1 = ?$

$CH_4 (g) + 2 O_2 (g) \rightarrow CO (g) + 2 H_2O + \frac{1}{2} O_2$ $\Delta H_2 = -607$ kJ

$CO (g) + 2 H_2O + \frac{1}{2} O_2 \rightarrow CO_2 (g) + 2 H_2O (l)$ $\Delta H_3 = -283$ kJ

$CH_4 (g) + 2 O_2 (g) \rightarrow CO (g) + 2 H_2O + \frac{1}{2} O_2 \rightarrow CO_2 (g) + 2 H_2O (l)$ $\Delta H_1 = \Delta H_2 + \Delta H_3$

$CH_4 (g) + 2 O_2 (g) \rightarrow CO_2 (g) + 2 H_2O (l)$ $\Delta H_1 = \Delta H_2 + \Delta H_3 = -607$kJ $+ (-283$ kJ$) = -890$ kJ
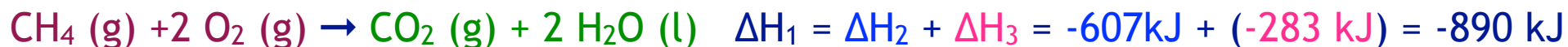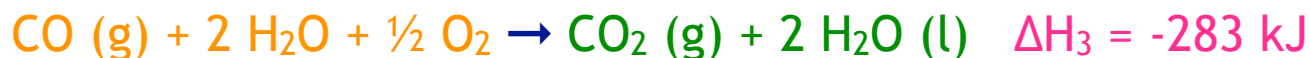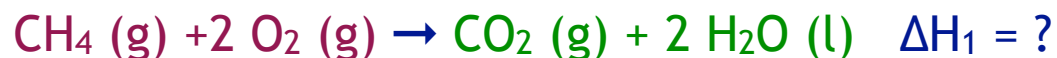
Algebra with ΔH_{rxn}

‣ You're going to use component reactions, like building blocks, to make an alternative path from the initial state of the main reaction to the final state.

‣ It might be necessary to manipulate those reactions to make them fit your problem.

‣ Remember the rules when manipulating component reactions:

  ‣ Anything you do to one coefficient you have to do to all of them — including the heat of reaction ΔH_{rxn}!

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g) \quad \Delta H_{rxn} = -\ 483.6\ kJ$$
$$4\ H_2\ (g) + 2\ O_2\ (g) \rightarrow 4\ H_2O\ (g) \quad \Delta H = -\ 967.2\ kJ$$
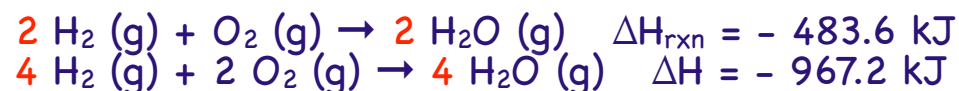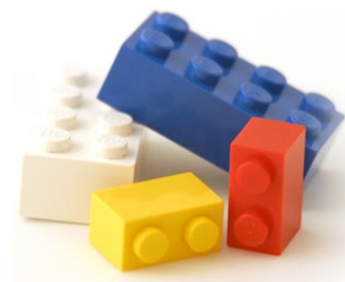
  ‣ You can reverse reactions to make them fit your problem, but if you do be sure to reverse the sign on ΔH_{rxn}!

$$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (g) \quad \Delta H_{rxn} = -\ 890\ kJ$$
$$CO_2\ (g) + 2\ H_2O\ (g) \rightarrow CH_4\ (g) + 2\ O_2\ (g) \quad \Delta H_{rxn} = +\ 890\ kJ$$
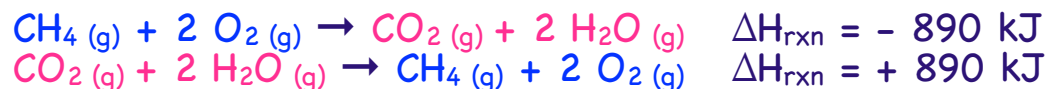
‣ And don't make these mistakes:

  ‣ You **<u>cannot</u>** change the substances in the reactions, that would create a different ΔH_{rxn}. So don't touch subscripts!

  ‣ You **<u>cannot</u>** change states, that would create a different ΔH_{rxn}. So watch the state (gas liquid, or solid) indicators carefully!

$$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l) \quad \Delta H_{rxn} = -\ 890\ kJ$$

$$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (g) \quad \Delta H_{rxn} = -\ 802\ kJ$$
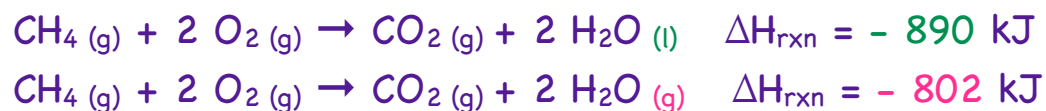
The enthalpy of reaction for combustion of C to CO_2 is -393.5 kJ/mol C, and the enthalpy for combustion of CO to CO_2 is -283.0 kJ/mol CO. What is the enthalpy for the combustion of C to CO?

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_1 = -393.5 \text{ kJ}$$

$$CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g) \quad \Delta H_2 = -283.0 \text{ kJ}$$

$$C(s) + \tfrac{1}{2} O_2(g) \rightarrow CO(g) \quad \Delta H_3 = ?$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_1 = -393.5 \text{ kJ}$$
$$+ \quad CO_2(g) \rightarrow CO(g) + \tfrac{1}{2} O_2(g) \quad \Delta H_2 = +283.0 \text{ kJ}$$
_____

$$C(s) + O_2(g) + CO_2(g) \rightarrow CO_2(g) + CO(g) + \tfrac{1}{2} O_2(g)$$

$$C(s) + \tfrac{1}{2} O_2(g) \rightarrow CO(g) \quad \Delta H_3 = -110.5 \text{ kJ}$$

Calculate ΔH for the reaction:
$$2\,C(s) + H_2(g) \rightarrow C_2H_2(g)$$
given:

$$C_2H_2(g) + \tfrac{5}{2}\,O_2(g) \rightarrow 2\,CO_2(g) + H_2O(L) \quad \Delta H = -1299.6\ kJ \quad .$$

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

$$H_2(g) + \tfrac{1}{2}\,O_2(g) \rightarrow H_2O(L) \quad \Delta H = -285.8\ kJ \quad .$$

$$2\,C(s) + 2\,O_2(g) \rightarrow 2\,CO_2(g) \quad \Delta H_1 = -787.0\ kJ$$

$$H_2(g) + \tfrac{1}{2}\,O_2(g) \rightarrow H_2O(L) \quad \Delta H_2 = -285.8\ kJ$$

$$+\quad 2\,CO_2(g) + H_2O(L) \rightarrow C_2H_2(g) + \tfrac{5}{2}\,O_2(g) \quad \Delta H_3 = +1299.6\ kJ$$

_____

$$2\,C(s) + 2\,O_2(g) + H_2(g) + \tfrac{1}{2}\,O_2(g) + 2\,CO_2(g) + H_2O(L)$$
$$\rightarrow$$
$$2\,CO_2(g) + H_2O(L) + C_2H_2(g) + \tfrac{5}{2}\,O_2(g)$$

$$2\,C(s) + H_2(g) \rightarrow C_2H_2(g)$$
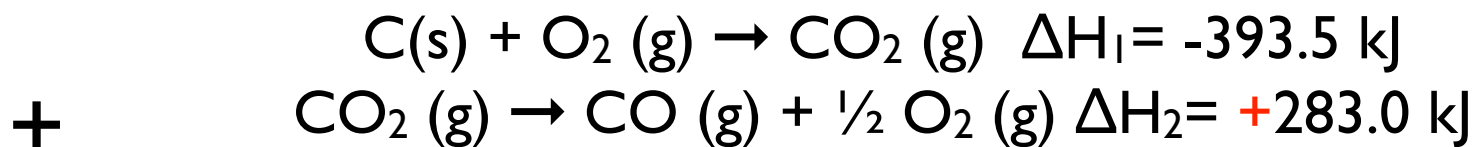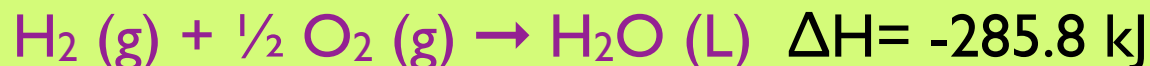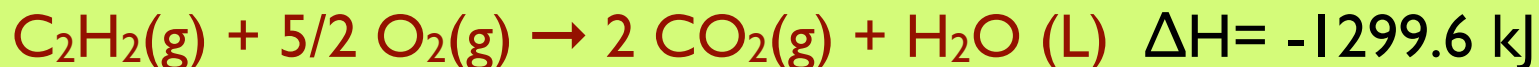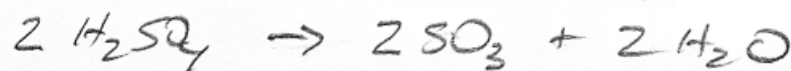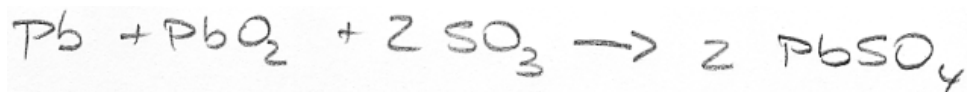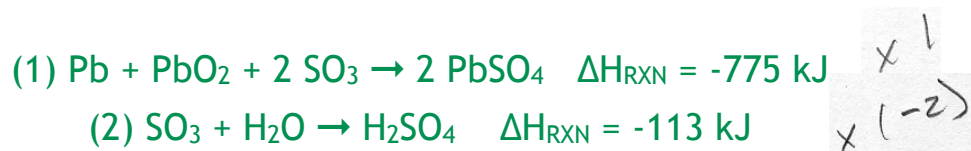
$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 = 226.8\ kJ$$

Applying Hess's Law

‣ During discharge of a lead-acid storage battery, the following chemical reaction takes place. Determine the enthalpy of reaction for the discharge reaction.
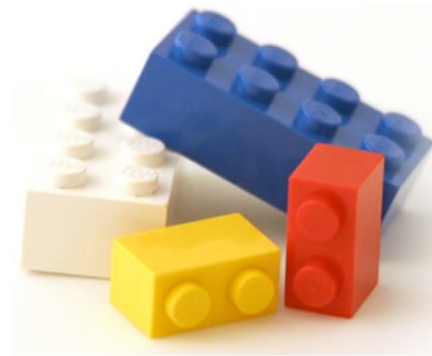
$$Pb + PbO_2 + 2\ H_2SO_4 \rightarrow 2\ PbSO_4 + 2\ H_2O \quad Find: \Delta H_{RXN}$$

(1) $Pb + PbO_2 + 2\ SO_3 \rightarrow 2\ PbSO_4$ $\quad \Delta H_{RXN} = -775$ kJ $\quad \times\ 1$

(2) $SO_3 + H_2O \rightarrow H_2SO_4$ $\quad \Delta H_{RXN} = -113$ kJ $\quad \times\ (-2)$

$$Pb + PbO_2 + 2\ SO_3 \rightarrow 2\ PbSO_4 \qquad \Delta H = -775\ kT$$

$$2\ H_2SO_4 \rightarrow 2\ SO_3 + 2\ H_2O \qquad \Delta H = -113\ kJ\ (\times\ -2)$$

$$= 226\ kJ$$

$$Pb + PbO_2 + 2\ \cancel{SO_3} + 2\ H_2SO_4 \rightarrow 2\ PbSO_4 + 2\ \cancel{SO_3} + 2\ H_2O$$

$$\Delta H = -775\ kJ + (-113\ kJ)$$
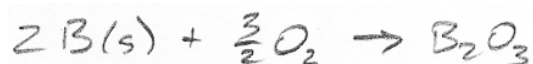
$$= \boxed{-888\ kJ}$$

Applying Hess's Law

▸ Calculate the standard enthalpy of reaction of gaseous diborane (B_2H_6) from elemental components using the following thermochemical information.
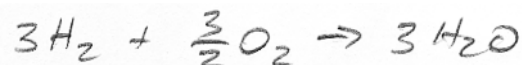
$$2\ B + 3\ H_2 \rightarrow B_2H_6 \quad \text{Find: } \Delta H_{RXN}$$

(a) $4\ B_{(s)} + 3\ O_{2\ (g)} \rightarrow 2\ B_2O_{3\ (s)}$ $\Delta H° = -2509.1\ kJ$ $\times \tfrac{1}{2}$

(b) $2\ H_{2\ (g)} + O_{2\ (g)} \rightarrow 2\ H_2O_{\ (l)}$ $\Delta H° = -571.7\ kJ$ $\times \tfrac{3}{2}$

(c) $B_2H_{6\ (g)} + 3\ O_{2\ (g)} \rightarrow B_2O_{3\ (s)} + 3\ H_2O_{\ (l)}$ $\Delta H° = -2147.5\ kJ$ $\times -1$

$$2\ B(s) + \tfrac{3}{2}O_2 \rightarrow B_2O_3$$

$$3\ H_2 + \tfrac{3}{2}O_2 \rightarrow 3\ H_2O$$

$$B_2O_3 + 3\ H_2O \rightarrow B_2H_6 + 3\ O_2$$

$\Delta H = -2509.1\ kJ \times \tfrac{1}{2}$
$= -1254.55\ kJ$

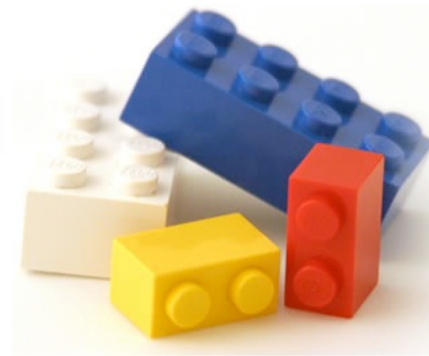$\Delta H = -571.7\ kJ \times \tfrac{3}{2}$
$= -857.55\ kJ$

$\Delta H = -2147.5\ kJ \times (-1)$
$= 2,147.5\ kJ$

$\Delta H = -1254.55$
$\quad\ -857.55$
$+\ \ +2,147.5$
$\overline{\qquad\qquad 35.4\ kJ}$

$$2B + \tfrac{3}{2}\cancel{O_2} + 3H_2 + \tfrac{3}{2}\cancel{O_2} + \cancel{B_2O_3} + 3\cancel{H_2O} \rightarrow \cancel{B_2O_3} + 3\cancel{H_2O} + B_2H_6 + 3\cancel{O_2}$$

$$\boxed{\Delta H = +35.4\ kJ}$$

Enthalpy (H)

- Change of Enthalpy (ΔH)
  - A new property and why we need it.
  - What is enthalpy?
  - Another Reaction Type
    - Endothermic vs Exothermic
- Stoichiometry with Enthalpy
  - Heat of Reaction (ΔH_{rxn})
    - Definition
    - Reversing Reactions/ΔH_{rxn}
    - ΔH_{rxn} Depends on State
    - ΔH is Extensive
    - It's a new coefficient
  - Stoichiometry Problems
    - kJ → grams, mol → kJ, etc
- Easier Calorimetry
  - Constant Pressure Calorimetry
  - Experimentally Measuring Enthalpy Changes

- Hess's Law
  - "The path doesn't matter."
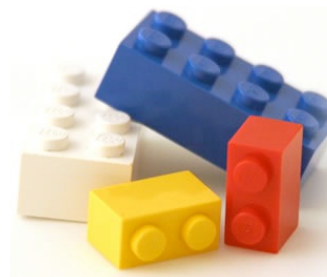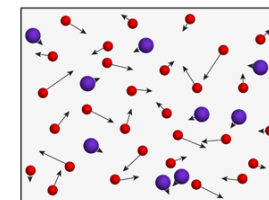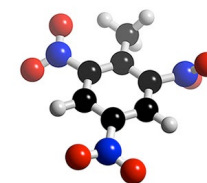   - Heat & Algebra
    - Solving Hess's Law Problems
  - Tabulated ΔH's
    - of Fusion
    - of Fission
   - more in chapter 11
    - of Combustion
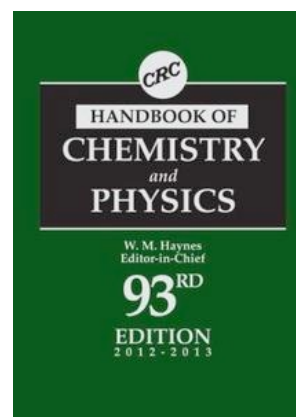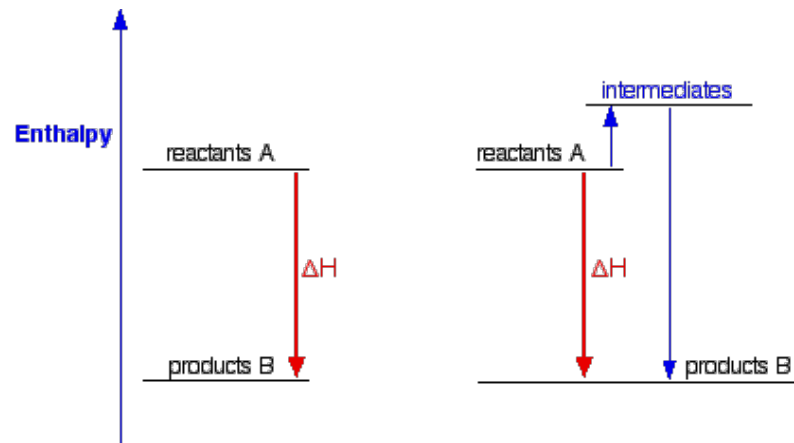   - of Formation
  - A Hess's Law shortcut
    - using heat of formation reactions makes using Hess's Law _really_ easy!

Tables of ΔH_{rxn}

▸ Because Enthalpy is a state function, the enthalpy change per mole for a reaction is fixed — it never changes.

▸ Chemists can use those known enthalpy changes with Hess's law to calculate the enthalpy changes of other reactions.

    ▸ We can even figure out the enthalpy of reaction for reactions that are too difficult or dangerous to ever try and measure directly.

        ▸ If we have enough pieces, to calculate it.

▸ So chemists compile tables of enthalpies of reaction.

▸ There are tabulated data for different types of reactions:

    ▸ Enthalpy of Vaporization (L → g)

    ▸ Enthalpy of Fusion (s → L)

    ▸ Enthalpy of Combustion (X + O_2 →)

    ▸ Enthalpy of Formation (elements → X)

        ▸ and many more…

▸ We can use any of these with Hess's law.

▸ But what type of reactions would be our first choice?

Enthalpy of Formation

$$\Delta H^{0}_{f}$$

← means "from standard states"
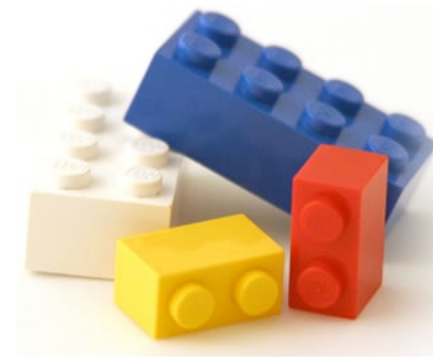
← means "of formation"
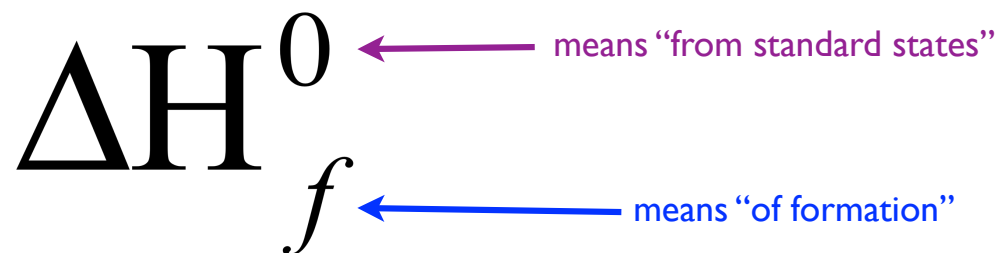
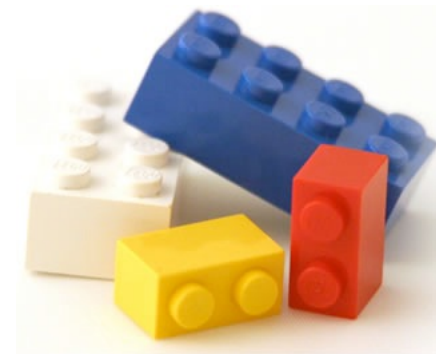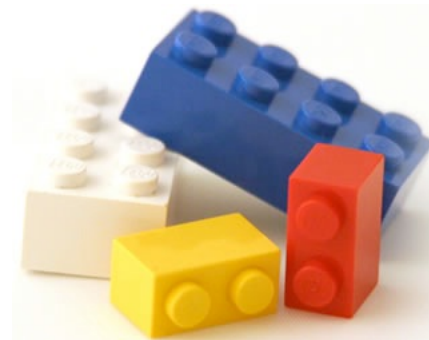component elements (in standard states) → compound (in standard state)

Standard State Means:

➡ at 1 atmosphere pressure (usually) ← the same as STP

➡ at 298 K (25 °C) (usually) ← **not** the same as STP (T in STP is 0°C)

➡ most common state at that T and P (L vs S vs G)

➡ most common form (O_2 vs O_3; $C_{(graphite)}$ vs $C_{(diamond)}$)

➡ Note: $\Delta H°_f$ for elements in standard state is zero.

Reading Standard Enthalpies of Formation

TABLE 5.3 ▪ Standard Enthalpies of Formation, ΔH_f°, at 298 K

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.80
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$	−1130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

$6\ C\ (graphite) + 3\ H_2(g) \rightarrow C_6H_6\ (L)$ $\Delta H_f^\circ = 49.0$ kJ/mol C_6H_6

$Ca\ (s) + C\ (graphite) + 3/2\ O_2\ (g) \rightarrow CaCO_3$ $\Delta H_f^\circ = -1207.1$ kJ/mol $CaCO_3$

Let's be clear on enthalpies of formation.

▸ For which of the following reactions at 25°C would the enthalpy change represent a standard enthalpy of formation? For each that does not, what changes are needed to make it an equation whose ΔH is an enthalpy of formation?
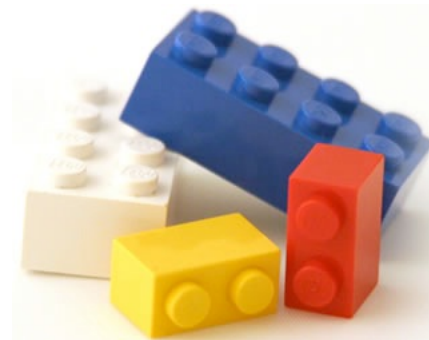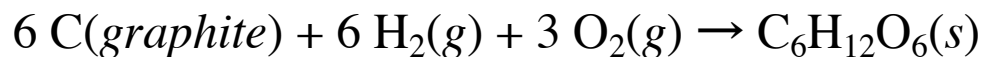
(a) $2\,Na(s) + \frac{1}{2}O_2(g) \longrightarrow Na_2O(s)$
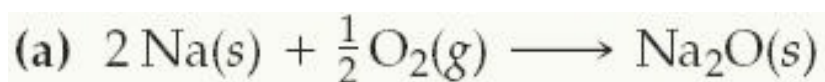
In this reaction 1 mol Na_2O is formed from the elements sodium and oxygen in their proper states, solid Na and O_2 gas, respectively. Therefore, the enthalpy change for the reaction corresponds to a standard enthalpy of formation.

(b) $2\,K(l) + Cl_2(g) \longrightarrow 2\,KCl(s)$
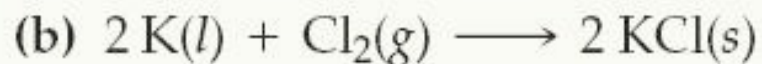
Reaction (b) potassium is given as a liquid. It must be changed to the solid form, its standard state at room temperature. Furthermore, two moles of product are formed, so the enthalpy change for the reaction as written is twice the standard enthalpy of formation of KCl(s). The equation for the formation reaction of 1 mol of KCl(s) is

$$K(s) + \frac{1}{2}Cl(g) \longrightarrow KCl(s)$$

(c) $C_6H_{12}O_6(s) \longrightarrow 6\,C(diamond) + 6\,H_2(g) + 3\,O_2(g)$
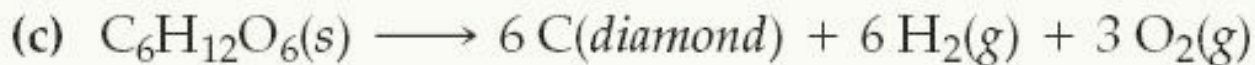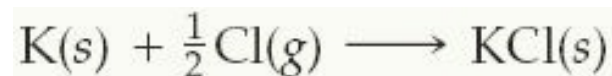
Reaction (c) does not form a substance from its elements. Instead, a substance decomposes to its elements, so this reaction must be reversed. Next, the element carbon is given as diamond, whereas graphite is the standard state of carbon at room temperature and 1 atm pressure. The equation that correctly represents the enthalpy of formation of glucose from its elements is:
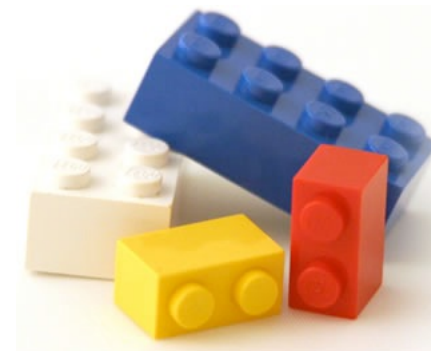
$$6\,C(graphite) + 6\,H_2(g) + 3\,O_2(g) \rightarrow C_6H_{12}O_6(s)$$

Enthalpy (H)

- Change of Enthalpy (ΔH)
  - A new property and why we need it.
  - What is enthalpy?
  - Another Reaction Type
    - Endothermic vs Exothermic

- Stoichiometry with Enthalpy
  - Heat of Reaction (ΔH_{rxn})
    - Definition
    - Reversing Reactions/ΔH_{rxn}
    - ΔH_{rxn} Depends on State
    - ΔH is Extensive
    - It's a new coefficient
  - Stoichiometry Problems
    - kJ → grams, mol → kJ, etc

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  - Constant Pressure Calorimetry
  - Experimentally Measuring Enthalpy Changes

- Hess's Law
  - "The path doesn't matter."
    - Heat & Algebra
    - Solving Hess's Law Problems
  - Tabulated ΔH's
    - of Fusion
    - of Fission
      - more in chapter 11
    - of Combustion
    - of Formation

- A Hess's Law shortcut
  - using heat of formation reactions makes using Hess's Law _really_ easy!

A trick from using enthalpies of formation.

$$C_3H_{8\,(g)} + 5\ O_{2\,(g)} \rightarrow 3\ CO_{2\,(g)} + 4\ H_2O_{(l)}$$

3 C (graphite) + 4 H$_2$(g) + 5 O$_2$(g)

Elements

$\Delta H_1 = +103.85$ kJ   ① Decomposition   ② Formation of 3 CO$_2$

C$_3$H$_8$(g) + 5 O$_2$(g)

Reactants

$\Delta H_2 = -1181$ kJ

3 CO$_2$(g) + 4 H$_2$(g) + 2 O$_2$(g)

③ Formation of 4 H$_2$O

$\Delta H_3 = -1143$ kJ

$\Delta H_{rxn}^\circ = -2220$ kJ

3 CO$_2$(g) + 4 H$_2$O(l)

Products

Enthalpy

A trick from using enthalpies of formation.

$$C_3H_{8\ (g)} + 5\ O_{2\ (g)} \longrightarrow 3\ CO_{2\ (g)} + 4\ H_2O_{\ (l)}$$

▸ Imagine this occurring in three steps:

$$C_3H_{8\ (g)} \longrightarrow 3\ C_{\ (graphite)} + 4\ H_{2\ (g)}$$

Enthalpy →

3 C (graphite) + 4 H$_2$(g) + 5 O$_2$(g)

Elements

$\Delta H_1 =$ +103.85 kJ

① Decomposition ② Formation of 3 CO$_2$

C$_3$H$_8$(g) + 5 O$_2$(g)

Reactants

$\Delta H_2 = -1181$ kJ

$\Delta H^{\circ}_{rxn} = -2220$ kJ

3 CO$_2$(g) + 4 H$_2$(g) + 2 O$_2$(g)

③ Formation of 4 H$_2$O

$\Delta H_3 = -1143$ kJ

3 CO$_2$(g) + 4 H$_2$O(l)

Products

A trick from using enthalpies of formation.

$$C_3H_{8\,(g)} + 5\ O_{2\,(g)} \rightarrow 3\ CO_{2\,(g)} + 4\ H_2O_{\,(l)}$$

▸ Imagine this occurring in three steps:

$$C_3H_{8\,(g)} \rightarrow 3\ C_{\,(graphite)} + 4\ H_{2\,(g)}$$

$$3\ C_{\,(graphite)} + 3\ O_{2\,(g)} \rightarrow 3\ CO_{2\,(g)}$$

A trick from using enthalpies of formation.

$$C_3H_{8\,(g)} + 5\,O_{2\,(g)} \rightarrow 3\,CO_{2\,(g)} + 4\,H_2O_{(l)}$$

▸ Imagine this occurring in three steps:

$$C_3H_{8\,(g)} \rightarrow 3\,C_{(graphite)} + 4\,H_{2\,(g)}$$

$$3\,C_{(graphite)} + 3\,O_{2\,(g)} \rightarrow 3\,CO_{2\,(g)}$$

$$4\,H_{2\,(g)} + 2\,O_{2\,(g)} \rightarrow 4\,H_2O_{(l)}$$

Enthalpy →

3 C (graphite) + 4 H$_2$(g) + 5 O$_2$(g)
Elements

$\Delta H_1 = +103.85$ kJ ① Decomposition ② Formation of 3 CO$_2$

C$_3$H$_8$(g) + 5 O$_2$(g)
Reactants

$\Delta H_2 = -1181$ kJ

3 CO$_2$(g) + 4 H$_2$(g) + 2 O$_2$(g)

③ Formation of 4 H$_2$O

$\Delta H^\circ_{rxn} = -2220$ kJ

$\Delta H_3 = -1143$ kJ

3 CO$_2$(g) + 4 H$_2$O(l)
Products

A trick from using enthalpies of formation.

$$C_3H_{8\ (g)} + 5\ O_{2\ (g)} \rightarrow 3\ CO_{2\ (g)} + 4\ H_2O_{\ (l)}$$

▸ Imagine this occurring in three steps:

$$C_3H_{8\ (g)} \rightarrow 3\ C_{\ (graphite)} + 4\ H_{2\ (g)}$$

$$3\ C_{\ (graphite)} + 3\ O_{2\ (g)} \rightarrow 3\ CO_{2\ (g)}$$

$$4\ H_{2\ (g)} + 2\ O_{2\ (g)} \rightarrow 4\ H_2O_{\ (l)}$$

3 C (graphite) + 4 H$_2$(g) + 5 O$_2$(g)
Elements
$\Delta H_1 = +103.85$ kJ ① Decomposition ② Formation of 3 CO$_2$
C$_3$H$_8$(g) + 5 O$_2$(g)
Reactants
$\Delta H_2 = -1181$ kJ
Enthalpy
$\Delta H^\circ_{rxn} = -2220$ kJ
3 CO$_2$(g) + 4 H$_2$(g) + 2 O$_2$(g)
③ Formation of 4 H$_2$O
$\Delta H_3 = -1143$ kJ
3 CO$_2$(g) + 4 H$_2$O(l)
Products

$$C_3H_{8\ (g)} + 5\ O_{2\ (g)} \rightarrow 3\ CO_{2\ (g)} + 4\ H_2O_{\ (l)}$$

$\Delta H_{RXN} = -1 \cdot \Delta H_2 \quad\quad + 3 \cdot \Delta H_1 \quad\quad + 4 \cdot \Delta H_3 \quad = \quad$ **-2219.9 kJ**

$\Delta H_{RXN} = -1 \cdot \Delta H_{f\ (C3H8)} + 3 \cdot \Delta H_{f\ (CO2)} + 4 \cdot \Delta H_{f\ (H2O)} + \Delta H_{f\ (O2)}$
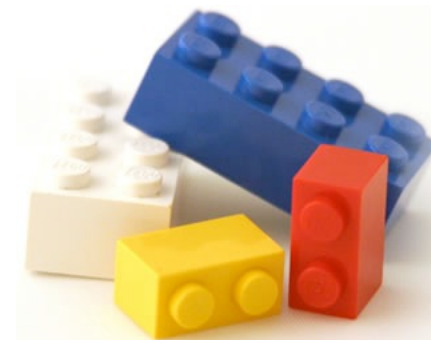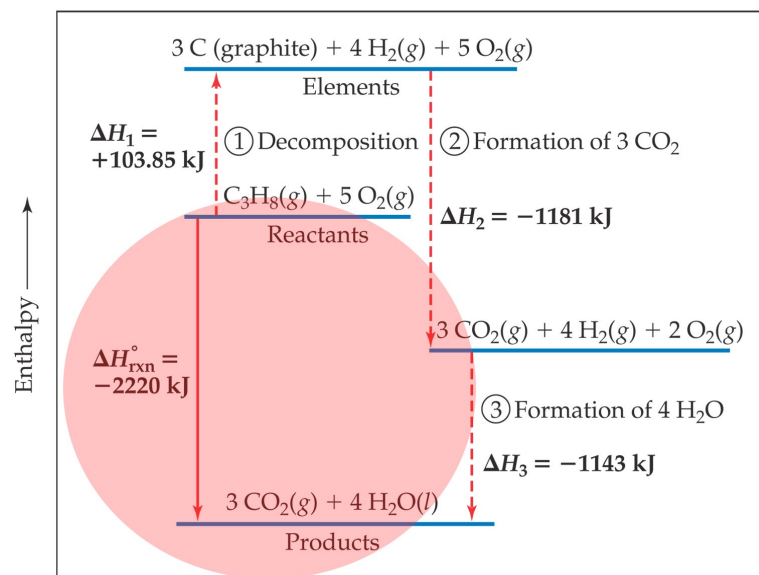
A Shortcut Using Enthalpies of Formation

$$A + B \rightarrow C + D$$

elements that form C $\rightarrow$ C $\quad \Delta H_{C}{}^{\circ}{}_{f}$

elements that form D $\rightarrow$ D $\quad \Delta H_{D}{}^{\circ}{}_{f}$

A $\rightarrow$ elements that form A $\quad -\Delta H_{A}{}^{\circ}{}_{f}$

B $\rightarrow$ elements that form B $\quad -\Delta H_{B}{}^{\circ}{}_{f}$

Since it's a balanced equation, these are equal and cancel out!

A + B + [elements that form C & D] $\rightarrow$

C + D + [elements that form A & B]

$$A + B \rightarrow C + D$$

$$\Delta H_{rxn} = -\Delta H_{A}{}^{\circ}{}_{f} + -\Delta H_{B}{}^{\circ}{}_{f} + \Delta H_{C}{}^{\circ}{}_{f} + \Delta H_{D}{}^{\circ}{}_{f}$$

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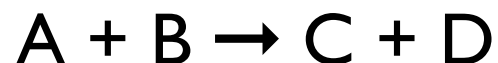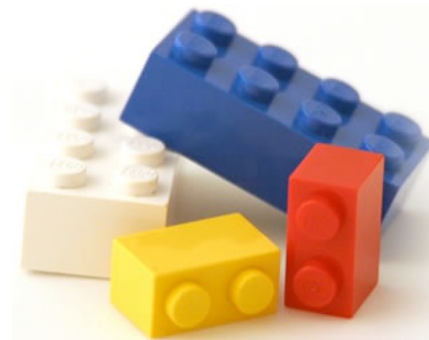
Using Enthalpy's of Formation

$$A + B \rightarrow C + D$$

$$\Delta H_{rxn} = -\Delta H_{A}{}^{\circ}{}_{f} + -\Delta H_{B}{}^{\circ}{}_{f} + \Delta H_{C}{}^{\circ}{}_{f} + \Delta H_{D}{}^{\circ}{}_{f}$$

$$C_3H_8\ (g) + 5\ O_2\ (g) \rightarrow 3\ CO_2\ (g) + 4\ H_2O\ (L)$$
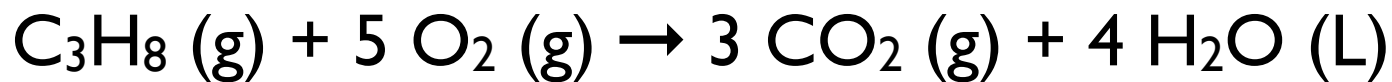
$$\Delta H_{rxn} = -(-103.85\ kJ) + -5\ (0\ kJ) + 3\ (-393.5\ kJ) + 4\ (-285.8\ kJ)$$

$$\Delta H_{rxn} = -2{,}219.9\ kJ$$

TABLE 5.3 ■ Standard Enthalpies of Formation, ΔH_f°, at 298 K

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.80
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$	−1130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

A trick from using enthalpies of formation.

$$C_3H_{8\ (g)} + 5\ O_{2\ (g)} \rightarrow 3\ CO_{2\ (g)} + 4\ H_2O_{\ (l)}$$
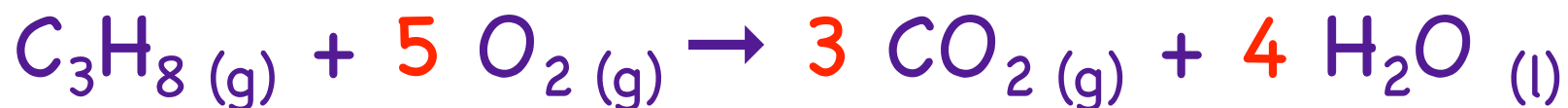
- We can use Hess's law in this way:

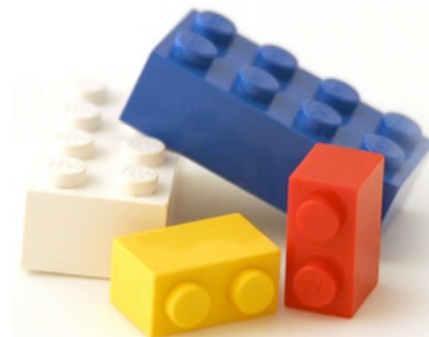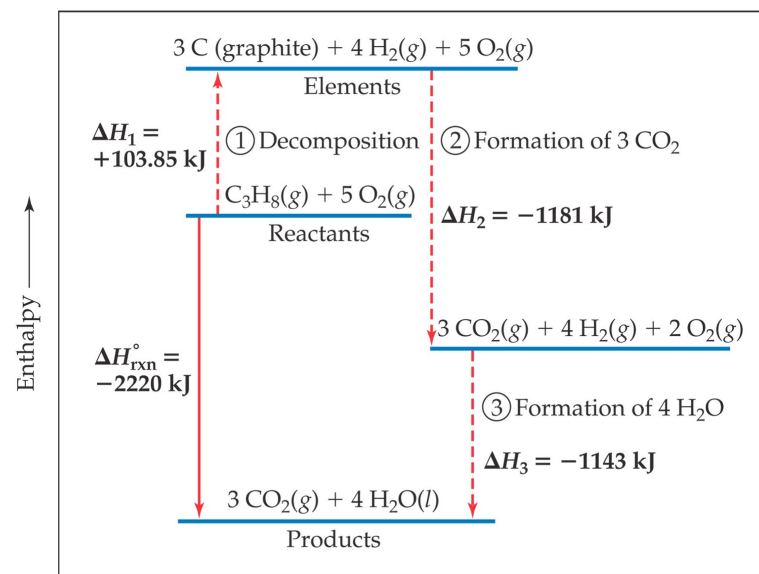 $$\Delta H = \Sigma\ n\ \Delta H_f^\circ\ \text{products} - \Sigma\ m\ \Delta H_f^\circ\ \text{reactants}$$

- where n and m are the stoichiometric coefficients.

Enthalpy diagram:

3 C (graphite) + 4 H$_2$(g) + 5 O$_2$(g) — Elements

$\Delta H_1 = +103.85$ kJ — ① Decomposition | ② Formation of 3 CO$_2$

C$_3$H$_8$(g) + 5 O$_2$(g) — Reactants

$\Delta H_2 = -1181$ kJ

$\Delta H_{rxn}^\circ = -2220$ kJ

3 CO$_2$(g) + 4 H$_2$(g) + 2 O$_2$(g)

③ Formation of 4 H$_2$O

$\Delta H_3 = -1143$ kJ

3 CO$_2$(g) + 4 H$_2$O(l) — Products

$$C_3H_{8\ (g)} + 5\ O_{2\ (g)} \rightarrow 3\ CO_{2\ (g)} + 4\ H_2O_{\ (l)}$$

$$\Delta H = [3 \cdot \Delta H_{f\ (CO2)} + 4 \cdot \Delta H_{f\ (H2O)}] - [1 \cdot \Delta H_{f\ (C3H8)} + 5\ \Delta H_{f\ (O2)}]$$

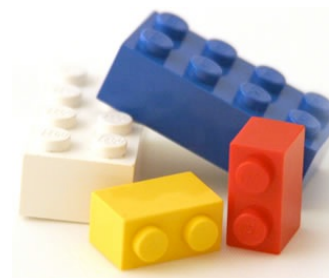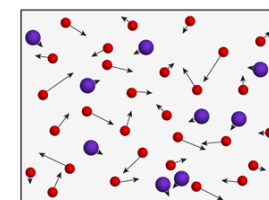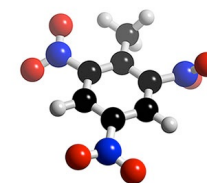$$\Delta H = [3(-393.5\ \text{kJ}) + 4(-285.8\ \text{kJ})] - [1(-103.85\ \text{kJ}) + 5(0\ \text{kJ})]$$

$$= -2219.9\ \text{kJ}$$

Enthalpy (H)

- Change of Enthalpy (ΔH)
  - A new property and why we need it.
  - What is enthalpy?
  - Another Reaction Type
    - Endothermic vs Exothermic

- Stoichiometry with Enthalpy
  - Heat of Reaction (ΔH_{rxn})
    - Definition
    - Reversing Reactions/ΔH_{rxn}
    - ΔH_{rxn} Depends on State
    - ΔH is Extensive
    - It's a new coefficient
  - Stoichiometry Problems
    - kJ → grams, mol → kJ, etc

- Easier Calorimetry
  - Constant Pressure Calorimetry
  - Experimentally Measuring Enthalpy Changes

- Hess's Law
  - "The path doesn't matter."
    - Heat & Algebra
    - Solving Hess's Law Problems
  - Tabulated ΔH's
    - of Fusion
    - of Fission
      - more in chapter 11
    - of Combustion
    - of Formation
  - A Hess's Law shortcut
    - using heat of formation reactions makes using Hess's Law _really_ easy!

Questions?