2. Tip: You will need an equation plus conversions.

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WANTED: q in **kJ**

The equation that relates q and ΔH is $\boxed{\Delta H = q}$ at constant pressure.

For conversions, list the DATA as equalities and single units.

DATA: -284 kJ = 1 mol H_2 (2 equivalent amounts)

             2.016 g H_2 = 1 mol H_2 (grams prompt)

             0.12 g H_2 (the single-unit *given*).

SOLVE: ? kJ = 0.12 g H_2 • $\dfrac{1 \text{ mol } H_2}{2.016 \text{ g } H_2}$ • $\dfrac{-284 \text{ kJ}}{1 \text{ mol } H_2}$ = $-$ **17 kJ** = ***q***

* * * * *

Lesson 22B: Exo- and Endothermic Reactions

Timing: Begin this lesson when you are assigned ΔH calculations.

* * * * *

The Energy Stored in Substances

Energy is stored in a substance during its formation. The amount of energy stored in a substance is dependent on (1) its atoms and bonds, and how they are arranged, and (2) the physical state of the substance: whether it is a gas, liquid, solid, or in solution.

Energy can be stored in the bonds of a substance. Some types of bonds have relatively large amounts of stored energy compared to others. For example, the C—H bond stores more energy than an O—H or a C—O bond.

Petroleum products have considerable commercial value in large part because they contain high-energy C—H bonds that release their energy when burned to form O—H and C—O bonds. That energy can be used to supply heat or to do work.

Enthalpy and ΔH Terminology

1. In general terms, the property **enthalpy** (***H***) is often described as the "heat content" of a substance: a measure of the energy that can be extracted from a substance.

    The absolute enthalpy (*H*) of a system is not possible to measure, but the absolute enthalpy (*H*) of a particle can be assigned a value relative to an arbitrary zero enthalpy. In enthalpy measurements, an arbitrary zero enthalpy is assigned to elements in their standard state, and the absolute enthalpy of other particles compared to those zero values by measuring the ΔH for chemical reactions and processes.

2. ΔH is the symbol for *change* in enthalpy during a reaction or process. ΔH is defined as:

ΔH = (enthalpy stored in products) minus (enthalpy stored in reactants)

$$\Delta H = H_{final} - H_{initial} = H_{products} - H_{reactants}$$

During most chemical processes, the change in enthalpy (ΔH) of a system is a measure of the heat flow (q) into or out of the system.

3. The SI *units* of ΔH are *joules*. In equations that include energy terms, the coefficients are understood to be moles.

If a chemical equation has *one* mole of *one* substance as a product, the units of ΔH can be written either as joules (J) *or* as joules/mol (J/mol). In energy equations, the energy term will often be expressed in kilojoules (kJ).

4. Energy and enthalpy changes in chemical processes can be classified as either **exothermic** or **endothermic**.

    a. *Exo*thermic reactions are those in which heat is released to the environment (*exo-* is a prefix from ancient Greek meaning "out of"). Heat flows *out* of the chemical *particles* in exothermic reactions.

    b. *Endo*thermic reactions are those in which heat is required. Heat must flow *endo,* "to the inside," into the chemical particles.

ΔH Notation

The energy change in a reaction can be expressed in two ways: *either* as a reactant or product *inside* the reaction equation, *or* written in ΔH **notation** *after* the equation.

Exothermic Reactions

The explosive burning of hydrogen gas is exothermic. The reaction can be written as

$H_2(gas)$ + $1/2\ O_2(g)$ → $H_2O(g)$ + **242 kilojoules** (Equation 1)
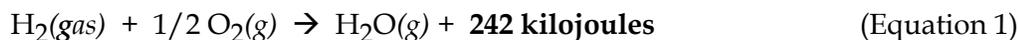
This equation indicates that heat is a *product* of the reaction: energy is released to the environment. When energy is a term in a reaction equation, the coefficients are understood to be in *moles*. An omitted coefficient is assumed to represent one mole.

Though the energy term can be written inside the equation as in equation (1), more often the energy factor is represented using ΔH notation. The above reaction is written as

$H_2(gas)$ + $1/2\ O_2(g)$ → $H_2O(g)$ ΔH = **− 242 kJ** (Equation 2)

When equations include ΔH notation, the units of ΔH are always *energy* units (such as joules or calories), and the coefficients of the reaction equation are read in *moles*.

In the above reaction, ΔH has a negative sign. For *exo*thermic reactions, ΔH is *defined* as *negative*. The minus sign indicates the chemical *particles* have *lost* stored energy in the reaction. Some of the energy stored in the reactant particles is released into the environment as the products are formed.
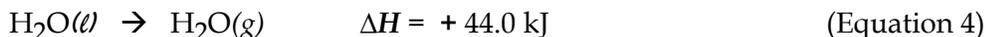
Endothermic Reactions

When the products of a reaction have a higher stored energy than the reactants, energy must be added to the chemical particles for the reaction to take place. Cooking food, melting ice, and boiling water are examples of chemical process that require energy to be added. For these reactions, ΔH will have a *positive* sign, because the chemical *particles gain* stored energy.

For example, the process of boiling water can be represented as either

$$1 \text{ mol } H_2O_{(liquid)} + 44.0 \text{ kJ} \rightarrow 1 \text{ mol } H_2O_{(gas)} \qquad \text{(Equation 3)}$$

OR as

$$H_2O(\ell) \rightarrow H_2O(g) \qquad \Delta H = +44.0 \text{ kJ} \qquad \text{(Equation 4)}$$

For *endo*thermic reactions, the ΔH value is always *positive*.

This reaction is an example of why, when representing the energy involved in a chemical process, the *phase* of each particle must be shown: *(s)*, *(1)*, *(g)*, or *(aq)*. The solid, liquid, gas, and aqueous phases of a substance have different amounts of stored energy.

Writing Energy Terms Inside Reactions

The explosion of hydrogen gas in reaction (1) above was written as

$$H_2(gas) + 1/2 \, O_2(g) \rightarrow H_2O(g) + 242 \text{ kilojoules}$$
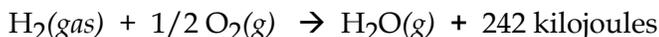
By the rules of algebra, we could also write the above reaction as

$$H_2(g) + 1/2 \, O_2(g) - 242 \text{ kilojoules} \rightarrow H_2O(g)$$
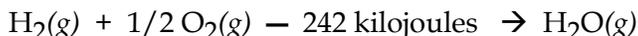
However, by the conventions of chemistry, we do *not* write negative signs in front of energy terms that are written *inside* reaction equations. An energy term written *inside* a reaction equation is always assigned a *positive* sign: written on the right side (as a product) for exothermic reactions, and on the left (as something which needs to be added) for endothermic reactions.

Energy terms are always positive *inside* equations, but may be positive or negative as ΔH.

Summary

To solve problems involving energy equations, first commit the following rules to memory.

Rules for Representing Energy Changes in Chemical Processes

When an energy term is included in a chemical equation:

1. The coefficients are in *moles*.

2. The *phase* of each particle must be shown: *(s)*, *(1)*, *(g)*, or *(aq)*.

3. In *exo*thermic reactions, energy is released into the environment. The energy term is shown

   • EITHER with a *positive* sign on the *products* side;

   • OR (preferred) with a *negative* ΔH value written after the reaction.

---

4. In *endo*thermic reactions, energy must be added as the reaction proceeds. The energy term is shown

   • EITHER with a *positive* sign on the *reactants* side of the equation,

   • OR with a *positive* ΔH value written *after* the reaction.

5. The SI *units* of ΔH are *joules.* In equations that include energy terms, the coefficients are understood to be moles. If a chemical equation has *one* mole of *one* substance as a product, the units of ΔH can be written either as joules (J) *or* as joules/mol (J/mol).

After you learn the rules, complete the problems below to cement your knowledge.

Practice A: Answers are at the end of this lesson. Check your answer after each part.

1. Re-write these equations so that the heat term appears as a product or a reactant inside the equation.

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

   b. $1/2\,N_2\,(g) + 1/2\,O_2(g) \rightarrow NO(g)$ $\Delta H = +90.3$ kJ

2. Label each reaction in (1) above as either exothermic or endothermic.

3. Re-write these equations using ΔH notation.

   a. $H_2O_2(\ell) + 187.6$ kJ $\rightarrow H_2(g) + O_2(g)$

   b. $C(s) + 1/2\,O_2(g) \rightarrow CO(g) + 110.5$ kJ

4. After each reaction in problem (3) above, add a label identifying the side that has more energy stored in its particles: the *reactants* or the *products*.

Reversing Equations That Include Heat Terms

In theory, any chemical reaction can go backwards. In practice, many do.

Any reaction with a heat term inside will be true if written in the reverse direction.

   <u>Example</u>: Since, from equation (3) above, $H_2O_{(liquid)} + 44.0$ kJ $\rightarrow H_2O_{(gas)}$

   This will also be true: $H_2O_{(gas)} \rightarrow H_2O_{(liquid)} + 44.0$ kJ

Given a reaction in which a ΔH value represents an energy change, the reaction can be written in the *reverse* direction if you change the sign of ΔH.

   <u>Example</u>: Since, from equation 4 above, $H_2O(\ell) \rightarrow H_2O(g)$ $\Delta H = +44.0$ kJ

   This equation is also true: $H_2O(g) \rightarrow H_2O(\ell)$ $\Delta H = -44.0$kJ

If an amount of energy must be added to change reactants to products, this same amount will be released when products are changed back to reactants. In chemical and physical processes, energy must be *conserved*.

Multiplying Equations That Include Heat Terms

Given a known balanced equation that includes an energy term, the *coefficients* representing the moles of the reactants and products may *all* be multiplied or divided by the same factor, provided you do the same to the *energy* term.

Examples

a. Since $H_2(gas) + 1/2\,O_2(g) \rightarrow H_2O(g) + 242$ kJ   is true,

Then   **2** $H_2(gas) + $ **1** $O_2(g) \rightarrow $ **2** $H_2O(g) + $ **484** kJ   (all doubled) is also true.

b. Since $H_2(g) + 1/2\,O_2(g) \rightarrow H_2O(g)$ $\Delta H = -242$ kJ   is true,

Then $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$ $\Delta H = -$ **484 kJ** (all doubled) is also true.

Summary

Memorize these additional rules for energy terms in equations.

> 6. Reactions that include energy terms can be *reversed* (written backwards). If ΔH notation is used, *change the sign* of ΔH.
>
> 7. All coefficients and energy terms in a balanced equation can be multiplied or divided by a factor. If ΔH notation is used, do the *same* to the ΔH.

Once you have the above seven rules firmly in memory, try the problems below.
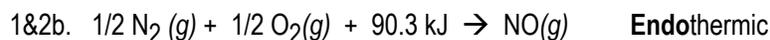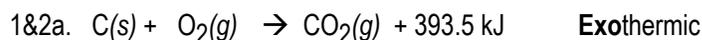

Practice B: Do every other problem. Save the rest for your next practice session.

1. Write these reactions in the reverse direction.   Express the energy term as a ΔH value.

a. $UF_6(\ell) \rightarrow UF_6(g)$ $\Delta H = +30.1$ kJ

b. $C(s) + 2\,H_2(g) \rightarrow CH_4(g)$ $\Delta H = -74.9$ kJ

2 Use these 4 "known" reactions to fill in the blanks below.

$$H_2(g) + 1/2\,O_2(g) \rightarrow H_2O(g) \qquad \Delta H = -241.8 \text{ kJ} \qquad (1)$$

$$H_2(g) + 1/2\,O_2(g) \rightarrow H_2O(\ell) \qquad \Delta H = -285.8 \text{ kJ} \qquad (2)$$

$$1/2\,N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H = +33.8 \text{ kJ} \qquad (3)$$

$$H_2(g) + 1/8\,S_8(s) + 2\,O_2(g) \rightarrow H_2SO_4(\ell) \quad \Delta H = -812 \text{ kJ} \qquad (4)$$

a. $2\,NO_2(g) \rightarrow N_2(g) + 2\,O_2(g)$ $\Delta H = $ _____

b. $4\,H_2(g) + 2\,O_2(g) \rightarrow 4\,H_2O(\ell)$ $\Delta H = $ _____

c. $8\,H_2SO_4(\ell) \rightarrow 8\,H_2(g) + S_8(s) + 16\,O_2(g)$ $\Delta H = $ _____

ANSWERS

Practice A

1&2a. $C(s) + O_2(g) \rightarrow CO_2(g) + 393.5$ kJ   **Exo**thermic

1&2b. $1/2$ N_2 $(g) + 1/2$ $O_2(g) + 90.3$ kJ $\rightarrow$ $NO(g)$ **Endo**thermic

3&4a. $H_2O_2(\ell) \rightarrow H_2(g) + O_2(g)$ ΔH = **+**187.6 kJ   (**Products** have more PE)

3&4b. $C(s) + 1/2$ $O_2(g) \rightarrow CO(g)$ ΔH = **−** 110.5 kJ   (**Reactants** have more PE)

Practice B

1a. $UF_6(g) \rightarrow UF_6(\ell)$ ΔH **= − 30.1 kJ**   1b. $CH_4(g) \rightarrow C(s) + 2$ $H_2(g)$ ΔH **= + 74.9 kJ**

2a. 2 NO_2 $(g) \rightarrow$ N_2 $(g) + 2$ O_2 (g) ΔH **= − 67.6 kJ**
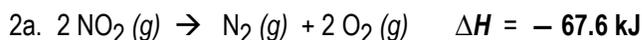
This reaction is table reaction # 3 doubled and written backwards: double and change sign of ΔH.

2b. 4 H_2 $(g) + 2$ $O_2(g) \rightarrow 4$ $H_2O(\ell)$ ΔH **= − 1,143.2 kJ**

This reaction is table reaction **#2** quadrupled – be careful to distinguish the gas/liquid/solid *states*.

Significant figures: Multiplying by an exact number does not change the *place* with doubt.

2c. 8 $H_2SO_4(\ell) \rightarrow 8$ H_2 $(g) + S_8(s) + 16$ O_2 (g) ΔH **= + 6,496 kJ**
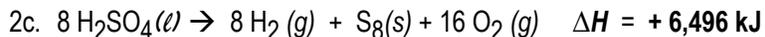
This is table reaction #4 multiplied by 8: multiply ΔH by 8. Since this reaction is also written backwards from reaction #4; change the sign of ΔH.

* * * * *

Lesson 22C: Adding Δ**H** Equations (Hess's Law)

Timing: Do this lesson when you are assigned problems that require finding a ΔH by adding equations with ΔH values attached.

* * * * *

Hess's Law

Hess's law of heat summation states that the enthalpy change in an overall chemical process can be calculated by adding its individual steps.

This means that for reactions where the heat of reaction (ΔH) is *not* known, ΔH can be calculated by adding reactions for which ΔH *is* known.

Rules For Adding Equations With Δ*H* Terms

All reaction equations with energy terms can be *added*.

- Multiple equations can be added to produce one net equation.

- Like particles on *opposite sides* of the *arrows* in the added reactions can *cancel*.

- *Like particles* on the same side of the *arrows* of added equations can add.

- All particles to the left of the arrows add to become the reactants in the final equation.

- All particles to the right of the arrows add to become the products of the final reaction.

- The final ΔH will be the added ΔH values of the reactions being added.

The meaning of these rules is best explained with an example. Apply the above rules to the following problem, and then check the answer below.

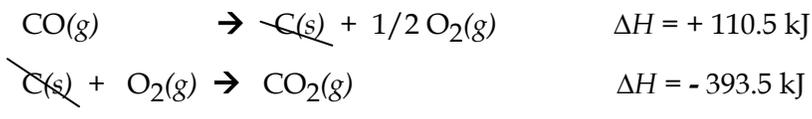**Q.** Find the heat of reaction for the burning of carbon monoxide

$$CO(g) + 1/2\,O_2(g) \rightarrow CO_2(g) \qquad \Delta H = ???$$

by *adding* these two reactions.

$$CO(g) \rightarrow C(s) + 1/2\,O_2(g) \qquad \Delta H = +\,110.5\text{ kJ}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -\,393.5\text{ kJ}$$


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Answer

When adding, first cancel *like* terms on *opposite* sides of the arrows in the equations being added. Writing your equations with the arrows lined up one above the other will help keep the two *sides* separated.
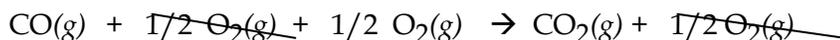
$$CO(g) \qquad \rightarrow \quad \cancel{C(s)} \; + \; 1/2\,O_2(g) \qquad \qquad \Delta H = +\;110.5 \text{ kJ}$$

$$\cancel{C(s)} \; + \; O_2(g) \rightarrow \; CO_2(g) \qquad \qquad \Delta H = \text{-}\;393.5 \text{ kJ}$$

If we add the reactions at this point, the result is:

$$CO(g) \; + \; \mathbf{1\;O_2}(g) \; \rightarrow \; CO_2(g) \; + \; \mathbf{1/2\;O_2}(g)$$

However, another cancellation can be made. The **1** O_2 on the left can be *split* into

$$CO(g) \; + \; \mathbf{1/2}\;O_2(g) \; + \; \mathbf{1/2}\;O_2(g) \; \rightarrow \; CO_2(g) + 1/2\,O_2(g)$$
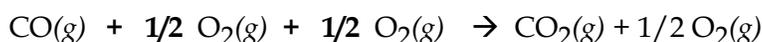
The $1/2\,O_2$ on the right now cancels a $1/2\,O_2$ on the left, leaving $1/2\,O_2$ on the left.

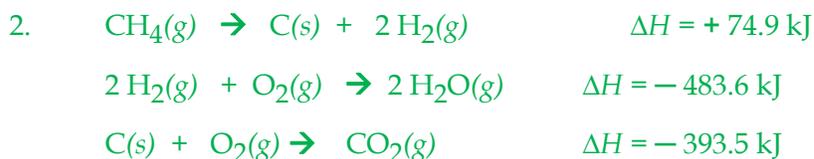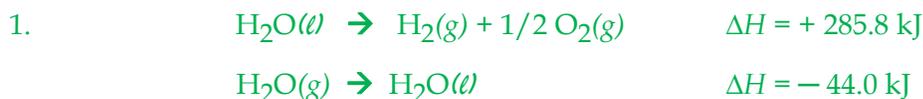$$CO(g) \; + \; \cancel{1/2\;O_2(g)} + \; 1/2\;O_2(g) \; \rightarrow \; CO_2(g) + \; \cancel{1/2\;O_2(g)}$$

After cancellation, the result is the *reaction* that was WANTED.

When reactions add to give the reaction wanted, add the ΔH's to find the ΔH wanted.

$$CO(g) \qquad \rightarrow \quad \cancel{C(s)} \; + \; \cancel{1/2\,O_2(g)} \qquad \qquad \mathbf{\Delta H = +\;110.5 \text{ kJ}}$$

$$\cancel{C(s)} \; + \; ^{\mathbf{1/2}}\cancel{1}\,O_2(g) \; \rightarrow \; CO_2(g) \qquad \qquad \mathbf{\Delta H = -\;393.5 \text{ kJ}}$$

$$CO(g) \; + \; 1/2\,O_2(g) \; \rightarrow \; CO_2(g) \qquad \qquad \mathbf{\Delta H = -\;283.0 \text{ kJ}}$$
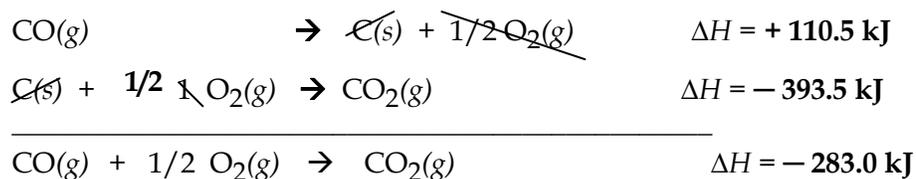
This process of adding equations will become easier with practice.

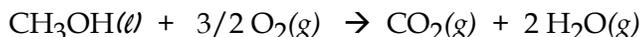## Practice A: Add these equations and their ΔH values. Check answers as you go.

1. $\qquad\qquad$ $H_2O(\ell) \; \rightarrow \; H_2(g) + 1/2\,O_2(g) \qquad \Delta H = +\;285.8 \text{ kJ}$

   $\qquad\qquad$ $H_2O(g) \rightarrow H_2O(\ell) \qquad\qquad\qquad \Delta H = -\;44.0 \text{ kJ}$

2. $\quad$ $CH_4(g) \; \rightarrow \; C(s) \; + \; 2\,H_2(g) \qquad\qquad \Delta H = +\;74.9 \text{ kJ}$

   $\quad$ $2\,H_2(g) \; + \; O_2(g) \; \rightarrow \; 2\,H_2O(g) \qquad \Delta H = -\;483.6 \text{ kJ}$

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

Finding An Unknown Δ*H* By Adding Equations

When Δ*H* for an equation is not known, it can be found by adding equations for which Δ*H* **is** known. The key is to arrange the known equations so that they *add* to result in the equation with the unknown Δ*H*.

The following problem will illustrate a *system* for deciding *which* known equations to add, as well as when to multiply and reverse them.

Q. Find the Δ*H* for the burning of methyl alcohol,

$$CH_3OH(l) + 3/2 \, O_2(g) \rightarrow CO_2(g) + 2 \, H_2O(g)$$

using these three equations for which Δ*H* values are supplied.

|		
$C(s) + 2 \, H_2(g) + 1/2 \, O_2(g) \rightarrow CH_3OH(l)$	Δ*H* = − 238.6 kJ	(1)
$H_2(g) + 1/2 \, O_2(g) \rightarrow H_2O(g)$	Δ*H* = − 241.8 kJ	(2)
$C(s) + O_2(g) \rightarrow CO_2(g)$	Δ*H* = − 393.5 kJ	(3)

Complete the following steps in your notebook.

1. Write the WANTED equation, and then draw a dotted line beneath it.

2. Re-write the *first* term in the WANTED equation, *with* its coefficient, *below* the dotted line.

   (Putting a WANTED reactant on the side where it must be in the final added equation will help to arrange the rest of the added equations).

   ★ ★ ★ ★ ★

   At this point, your paper should look like this:

   WANTED: **$CH_3OH(l)$ + 3/2 $O_2(g)$ → $CO_2(g)$ + 2 $H_2O(g)$ Δ*H* = ???**

   -
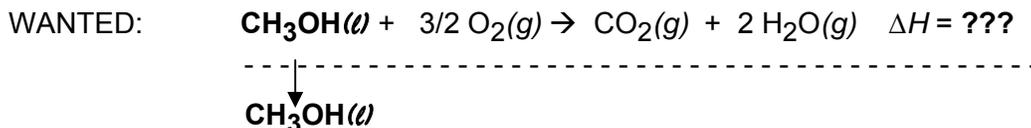
   $CH_3OH(l)$

3. Find an equation that both *includes* the *dropped* particle *and* has a known Δ*H*.

   ★ ★ ★ ★ ★

   CH_3OH is part of equation (1) in the problem, which includes a Δ*H*.
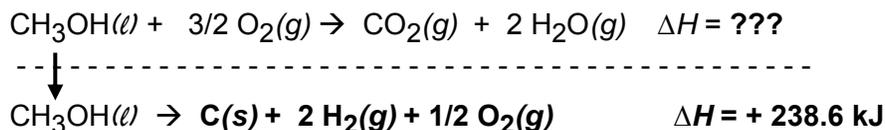
   Your goal is to write a known equation, *reversed* and/or *multiplied* if needed, so that the *dropped* particle is on the side it is dropped on and has the same coefficient as the particle dropped.

   If needed, reverse the direction of the *known* equation so that the term dropped below the line is on the *side* of the arrow, left or right, where it was dropped. If needed, multiply the coefficients of the *known* equation so that the coefficient of the dropped particle is the coefficient WANTED. *Modify* and write the Δ*H value* after the equation.

   Try that step, then check your answer below.

   ★ ★ ★ ★ ★

In this problem, 1 CH_3OH is needed on the *left* side of the arrow, so write known equation (1) *backwards*.

$CH_3OH(\ell)$ + 3/2 $O_2(g)$ → $CO_2(g)$ + 2 $H_2O(g)$ ΔH = **???**

$CH_3OH(\ell)$ → **C(s)** + **2 $H_2(g)$** + **1/2 $O_2(g)$**   ΔH = **+ 238.6 kJ**
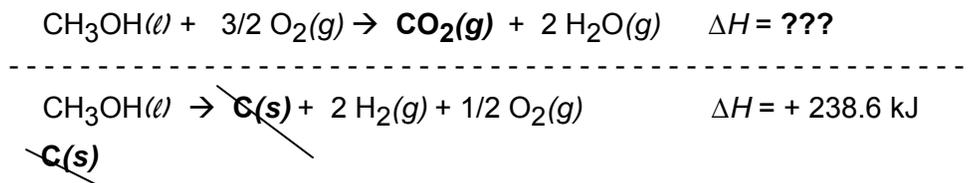
Because the known equation must be reversed, reverse the *sign* of its ΔH.

4. A TIP that works often in problems involving *burning* or *combustion* (both mean reacting with O_2 gas) is "don't worry about **O_2** until the end." If the equations have been chosen properly, when you add the terms at the end, O_2 should have the coefficient WANTED. This will be a check that you have selected the reactions properly.

5. Now compare the first particle on the *right* side of the arrow *below* the dotted line to the particles WANTED on the right *above* the dotted line.

If what you **have** *below* the dotted line does not exactly match what is WANTED *above* the dotted line, get rid of the UNwanted particle. Start a new equation on the line *below* by writing the unwanted particle, with its coefficient, on the side where it will *cancel* the same term in the first equation.

Try that step, then check your answer below.

★ ★ ★ ★ ★

In this problem, after the arrow and below the dotted line, is **C(s)**. What is WANTED on the right that contains carbon is CO_2. , so we need to get rid of C(s). Write C(s) at the start of a **new** equation below, on the **side** where it will cancel when the equations are added:

$CH_3OH(\ell)$ + 3/2 $O_2(g)$ → **$CO_2(g)$** + 2 $H_2O(g)$ ΔH = **???**

$CH_3OH(\ell)$ → ~~C(s)~~ + 2 $H_2(g)$ + 1/2 $O_2(g)$ ΔH = + 238.6 kJ
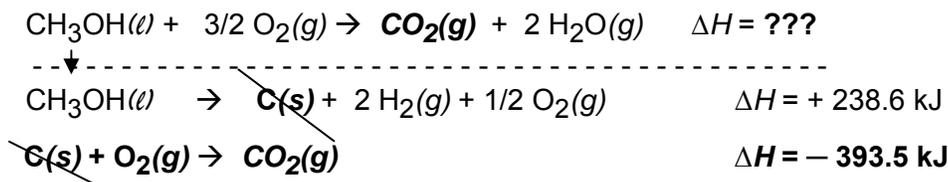
~~C(s)~~

Then find an equation with a known ΔH that both *includes* the particle in the bottom equation that you set up to cancel, and places its atoms in a compound WANTED *above* the dotted line.

Try that step, then check your answer below.

★ ★ ★ ★ ★

The equation that converts the C(s) you need to get rid of on the left to the CO_2 you WANT on the right is equation (3) supplied in the problem.

$CH_3OH(\ell)$ + 3/2 $O_2(g)$ → **$CO_2(g)$** + 2 $H_2O(g)$ ΔH = **???**

$CH_3OH(\ell)$ →   ~~C(s)~~ + 2 $H_2(g)$ + 1/2 $O_2(g)$ ΔH = + 238.6 kJ

~~C(s)~~ + $O_2(g)$ → **$CO_2(g)$**   ΔH = − 393.5 kJ

5. Ignoring O_2, *compare* the particles *below* the dotted line to what is WANTED above the dotted line.   If there is *any* particle and coefficient below the dotted line that does not match exactly what is WANTED above the line, put the coefficient and particle that is *not* WANTED where it will *cancel*.   Then find an equation that will convert the unwanted particle to a WANTED particle.
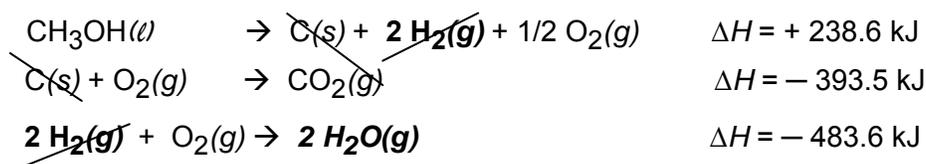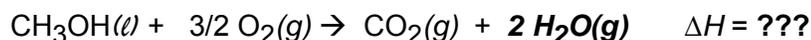
    Take a look: what coefficient and particle below the dotted line do you *not* want?
    ★ ★ ★ ★ ★

    Ignoring O_2, it is   **2 H$_2$**(g) . Try step 5, and then check the answer below.
    ★ ★ ★ ★ ★

    After the arrow and below the dotted line, is $2 H_2$. What is WANTED that contains hydrogen is $2 H_2O$. So, write $2 H_2$ below in a new equation where it will cancel, and find an equation that converts H_2 to the H_2O WANTED.

    CH_3OH(ℓ) +   3/2 O_2(g) → CO_2(g) + **2 H$_2$O(g)**   ΔH = **???**

    -

    CH_3OH(ℓ)   → C̶(̶s̶)̶ + **2 H̶$_2$(̶g̶)̶** + 1/2 O_2(g)   ΔH = + 238.6 kJ

    C̶(̶s̶)̶ + O_2(g)   → CO_2(̶g̶)̶   ΔH = − 393.5 kJ

    2 H̶$_2$(̶g̶)̶ + O_2(g) → 2 H$_2$O(g)   ΔH = − 483.6 kJ
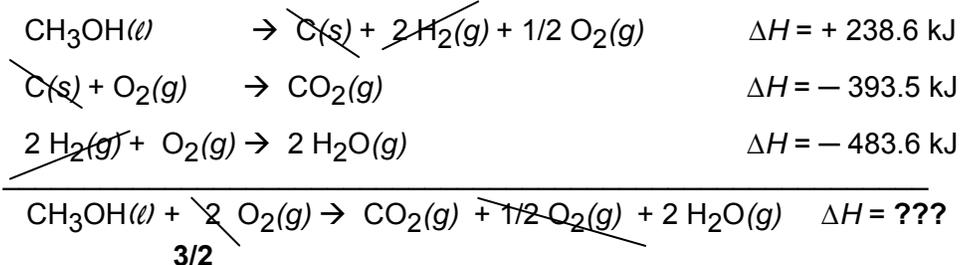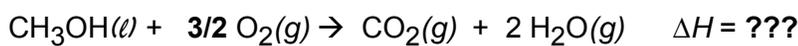
    Equation (2) supplied in the problem, *and* its ΔH, is doubled.

6. *Compare* what is WANTED above the dotted line to what is written below the line.

    If what is below adds to give what is above, *add* the equations *below* the dotted line. Then add the ΔH values to get the WANTED ΔH.
    ★ ★ ★ ★ ★

    Your paper should look like this:

    CH_3OH(ℓ) +   **3/2** O_2(g) → CO_2(g) + 2 H_2O(g)   ΔH = **???**

    -

    CH_3OH(ℓ)   → C̶(̶s̶)̶ + 2̶ H̶$_2$(̶g̶)̶ + 1/2 O_2(g)   ΔH = + 238.6 kJ

    C̶(̶s̶)̶ + O_2(g)   → CO_2(g)   ΔH = − 393.5 kJ

    2 H̶$_2$(̶g̶)̶ + O_2(g) → 2 H_2O(g)   ΔH = − 483.6 kJ

    _____

    CH_3OH(ℓ) + 2̶ O_2(g) → CO_2(g) + 1̶/̶2̶ Q̶$_2$(̶g̶)̶ + 2 H_2O(g)   ΔH = **???**
           3/2

    Note that the O_2 coefficient, after cancellation, matches what is WANTED. That's an indication that you have probably added the proper equations.

    Once the *equations* below the dotted line add to give the equation WANTED, add the modified ΔH values.
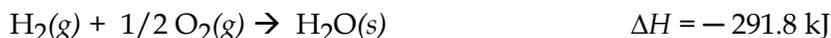   ★ ★ ★ ★ ★

$\Delta H = +238.6 - 393.5 - 483.6 = -\textbf{638.5 kJ}$ **Done!**

Summary: To find an unknown ΔH for a reaction equation,

- *write* the equation WANTED; write a dotted line below it.

- *Drop* the *first* coefficient and particle below the dotted line.

- *Including* that first coefficient and particle, write an equation with a known ΔH.

- *Add* other equations with *known ΔH* values that cancel particles you don't want, form particles you want, and add to give the equation WANTED.

- *Add* the ΔH values.

Practice B: Use the method above on these. If you get stuck, check a part of the answer and try again. More practice can be found in the next lesson.

1. Use the first two equations to find ΔH for the third: the heat required to melt ice.

    $H_2(g) + 1/2\,O_2(g) \rightarrow H_2O(\ell)$ $\Delta H = -285.8$ kJ

    $H_2(g) + 1/2\,O_2(g) \rightarrow H_2O(s)$ $\Delta H = -291.8$ kJ

    $H_2O(s) \rightarrow H_2O(\ell)$ $\Delta H = ?$

2. The gas ethane (C_2H_6) is one of the constituents of natural gas, a major component of the world energy economy. The equation for the burning of ethane is
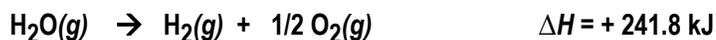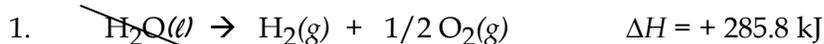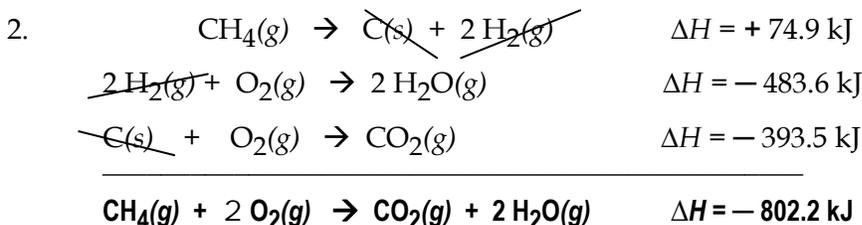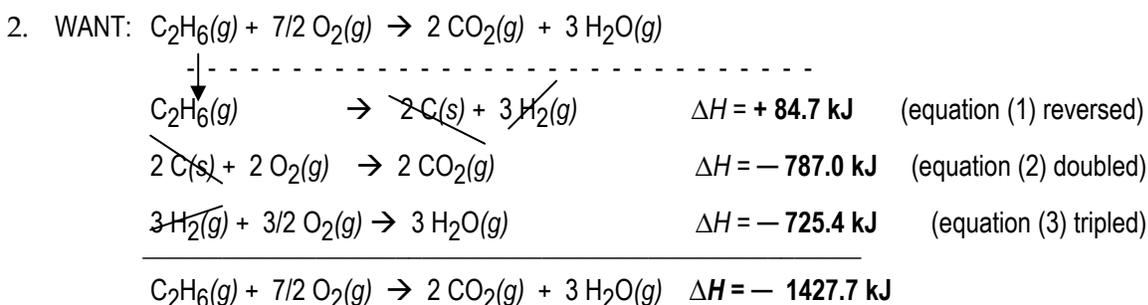
    $C_2H_6(g) + 7/2\,O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(g)$

    Use the formation equations below to find ΔH for the burning of ethane.

    $2\,C(s) + 3\,H_2(g) \rightarrow C_2H_6(g)$ $\Delta H = -84.7$ kJ   (1)

    $H_2(g) + 1/2\,O_2(g) \rightarrow H_2O(g)$ $\Delta H = -241.8$ kJ   (2)

    $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ   (3)

ANSWERS

Practice A

1. $\cancel{H_2O(\ell)} \rightarrow H_2(g) + 1/2\,O_2(g)$ $\Delta H = +285.8$ kJ

       $H_2O(g) \rightarrow \cancel{H_2O(\ell)}$ $\Delta H = -44.0$ kJ

       ————————————————————————————

       $H_2O(g) \rightarrow H_2(g) + 1/2\,O_2(g)$ $\Delta H = +\textbf{241.8 kJ}$

2. $\quad\quad\quad$ CH$_4$(g) $\rightarrow$ ~~C(s)~~ + 2 ~~H$_2$(g)~~ $\quad\quad\quad$ ΔH = **+** 74.9 kJ

$\quad$ ~~2 H$_2$(g)~~ + O$_2$(g) $\rightarrow$ 2 H$_2$O(g) $\quad\quad\quad$ ΔH = **−** 483.6 kJ

$\quad$ ~~C(s)~~ + O$_2$(g) $\rightarrow$ CO$_2$(g) $\quad\quad\quad$ ΔH = **−** 393.5 kJ

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$\quad$ **CH$_4$(g) + 2 O$_2$(g) $\rightarrow$ CO$_2$(g) + 2 H$_2$O(g)** $\quad\quad$ **ΔH = − 802.2 kJ**

Practice B

1. WANTED: $\quad$ H$_2$O(s) $\rightarrow$ H$_2$O(ℓ) $\quad\quad\quad\quad\quad$ ΔH = **?**

$\quad\quad$ - - - ┆ -

$\quad\quad\quad\quad$ H$_2$O(s) $\quad\quad\quad$ $\rightarrow$ ~~H$_2$(g) + 1/2 O$_2$(g)~~ $\quad\quad$ ΔH = **+** 291.8 kJ

$\quad\quad\quad$ ~~H$_2$(g) + 1/2 O$_2$(g)~~ $\rightarrow$ H$_2$O(ℓ) $\quad\quad\quad\quad$ ΔH = **−** 285.8 kJ

─────────────────────────────────────

$\quad\quad\quad\quad$ H$_2$O(s) $\quad\quad\quad$ $\rightarrow$ $\quad$ H$_2$O(ℓ) $\quad\quad\quad\quad$ ΔH = **+** 6.0 kJ

2. WANT: $\quad$ C$_2$H$_6$(g) + 7/2 O$_2$(g) $\rightarrow$ 2 CO$_2$(g) + 3 H$_2$O(g)

$\quad\quad$ - ┆ -

$\quad\quad$ C$_2$H$_6$(g) $\quad\quad\quad$ $\rightarrow$ ~~2 C(s)~~ + ~~3 H$_2$(g)~~ $\quad\quad$ ΔH = **+ 84.7 kJ** $\quad$ (equation (1) reversed)

$\quad\quad$ ~~2 C(s)~~ + 2 O$_2$(g) $\rightarrow$ 2 CO$_2$(g) $\quad\quad\quad\quad$ ΔH = **− 787.0 kJ** $\quad$ (equation (2) doubled)

$\quad\quad$ ~~3 H$_2$(g)~~ + 3/2 O$_2$(g) $\rightarrow$ 3 H$_2$O(g) $\quad\quad\quad$ ΔH = **− 725.4 kJ** $\quad$ (equation (3) tripled)

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$\quad\quad$ C$_2$H$_6$(g) + 7/2 O$_2$(g) $\rightarrow$ 2 CO$_2$(g) + 3 H$_2$O(g) $\quad$ **ΔH = − 1427.7 kJ**

* * * * *

Lesson 22D: Heats of Formation and Element Formulas

Timing: Complete this lesson when you are asked to solve problems using heats of *formation*.

* * * * *

Gas Versus Thermodynamic Standard Conditions

The history of chemistry has given us multiple definitions for *standard* conditions.

- For *gas law* calculations, standard temperature and pressure (STP) is defined as **0°C** and 1 atmosphere pressure.

- For *thermodynamic* measurements, for substances to be in their **standard state,**

  - *elements* must be at **25°C** and 1 atm pressure and (in most cases) in the phase and/or solid structure that is most stable.

  - *Compounds* that are *gases* must be at *one atmosphere* pressure.

  - *Substances in solutions* must have a concentration of 1 mol/L.

  - *Solid and liquid compounds* are in their standard state under nearly all conditions if they are in the form that is most stable at **25°C** and 1 atm pressure.

You should be aware of the difference between *gas* and *thermodynamic* standard conditions, but in most problems it will be clear from the context which definition of "standard conditions" applies.

Writing the Standard State For Elements

To work with formation equations, you will need to be able to write the *standard state* of elements: both the molecular *formula* of the element and the *state* (gas, liquid, or solid) in which it is most stable at room temperature (25°C) and one atmosphere pressure. The following are rules for writing formulas and standard states for most of the elements you will encounter in first-year chemistry.

1. Only *two* elements are *liquids* at room temperature: mercury (Hg) and bromine (Br_2).

2. Over 75% of the elements are *metals*, and the formulas for all metals (except mercury) are written as *monatomic solids.*

    Examples of element formulas for metals: Na*(s)*, Al*(s)*, Ag*(s)*, Hg(liquid)

3. Eight elements are **diatomic**: The 5 halogens, plus the *gases* hydrogen, oxygen, and nitrogen:
    $$F_2(g), Cl_2(g), Br_2(\ell), I_2(s), At_2(s), H_2(g), O_2(g), N_2(g)$$

4. Except for hydrogen, all of the 11 elements that are *gases* at room temperature are toward the top and right of the periodic table. The gaseous elements are 5 of the diatomics: $H_2(g), O_2(g), N_2(g), F_2(g), Cl_2(g)$; plus all 6 of the monatomic noble gases.

5. Some periodic tables indicate the *state* of each element at 25°C by the color of the element symbol: often solids are black, the two liquids blue, and gases red.

6. If a table of heats of formation shows a particle with a value for its heat of formation ($\Delta H°_f$) of *zero*, the formula shown will be that of the *element* in its *standard state.*

    Example: In the table at the right, for the elements chlorine and hydrogen, the formulas in their standard state are the formulas with the **zero ΔH:** $Cl_2(g)$ and $H_2(g)$.

    The single-atom forms of each element can be formed at room temperature, but, as their higher enthalpy indicates, they are less stable than the molecules formed from *two* neutral atoms. They therefore tend to react readily with other particles.
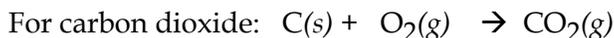
Formula	$\Delta H°_f$ in kJ/mole
Cl*(g)*	+ 121.0
$Cl_2(g)$	0
$H_2(g)$	0
H*(g)*	+ 218.0

7. Other frequently encountered non-metal elements are $S_8(s)$ and $P_4(s)$.

Writing Formation Equations

A **formation equation** is a balanced equation in which the reactants are *all elements*, the *product* is *one mole* of *one compound*, and the elements and the compound are all in their standard states.
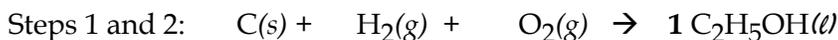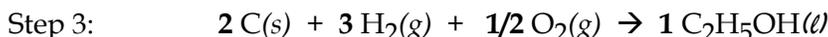
  Examples of formation equations are

    For carbon dioxide: $C(s) + O_2(g) \rightarrow CO_2(g)$

    For sulfuric acid: $H_2(g) + 1/8 \, S_8(s) + 2 \, O_2(g) \rightarrow H_2SO_4(\ell)$
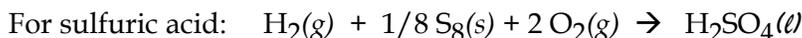
To write a formation equation for a compound,

1. To the right of an arrow, write the compound formula with a coefficient of 1.

2. On the left, for each of the *elements* that make up the compound, write the formula of the element in its *standard state* at 25°C and 1 atmosphere pressure.

3. Add element coefficients (that often include fractions) to *balance* the equation.

Try **Q.** Write the formation reaction for ethanol: $C_2H_5OH(\ell)$

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    Steps 1 and 2: $C(s) + \quad H_2(g) + \quad O_2(g) \rightarrow 1 \, C_2H_5OH(\ell)$

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    Step 3: $2 \, C(s) + 3 \, H_2(g) + 1/2 \, O_2(g) \rightarrow 1 \, C_2H_5OH(\ell)$

Practice A: Learn the rules above. Then, for each numbered problem, do every other letter. Check answers as you go. Save a few for your next practice session.

1. Which of these are not elements in their standard state?

    a. $H_2(g)$ b. $CO(g)$ c. $Co(s)$ d. $Hg(g)$ e. $N(g)$ f. $Cl_2(\ell)$

2. Write the formulas for these elements in their standard state at room temperature.

    a. Fluorine   b. Iron   c. Oxygen   d. Carbon   e. Nitrogen

3. Write balanced formation equations for these compounds.

    a. $NaCl(s)$ b. $HCl(g)$ c. $Al_2O_3(s)$ d. $C_2H_6(g)$ e. $NO_2(g)$

Defining Zero For ΔH

Every particle has a characteristic enthalpy that depends on its structural formula and its state. The absolute enthalpy of a substance cannot be measured, but we can work around this because in chemical processes, we are concerned with *changes* in enthalpy that occur (*ΔH*). To measure enthalpy changes, we can assign an *arbitrary* zero point to the enthalpy scale, and then measuring change relative to that zero value. For enthalpy, the zero point that has been chosen is: all *elements* in their standard state are *assigned* a heat of formation (**H°f**) of *zero* kJ/mol.

> For all elements in their standard state, $\Delta H°_f \equiv 0$ kJ/mol.

Heat of Formation

A particle in a given state has a *characteristic* **heat of formation** ($\Delta H°_f$) and this can be considered to be the value for its enthalpy. For elements in their standard state, this value is always 0 kJ/mol. For all other particles, $\Delta H°_f$ is the change in enthalpy that occurs in its formation reaction.

In the symbol for a heat of formation, $\Delta H°_f$, the subscript **f** means "formed from elements in their standard state." The superscript degree symbol ° means that the particle formed is also in its standard state.

Values for heats of formation are often provided in reference tables. The table at the right tells us that

Name	Formula	$\Delta H°_f$ in kJ/mol
Graphite	C(s)	**0**
Diamond	C(s)	+ 1.9
Carbon Dioxide	$CO_2(g)$	− 393.5
Methane	$CH_4(g)$	− 74.9
Steam	$H_2O(g)$	− 241.8

1. *Graphite* (used in "pencil lead") and *diamond* are composed of solid carbon.

2. Graphite and diamond are often represented by the same molecular formula: C(s).

 However, they have different structural formulas, and graphite has slightly lower enthalpy. Graphite is therefore the *more stable* of the two forms of pure carbon. The system with *lower* enthalpy is termed "more stable" because more energy must be added to change it.

The most stable form at at 25ºC is designated as the *standard state* of an element.

Heats of formation are the *ΔH* values for *formation equations*. Formation equations may be written with *ΔH* values labeled as either *ΔH*, *ΔH°* or *ΔH°*f .

Examples

For carbon dioxide: C(s) + $O_2(g)$ → $CO_2(g)$ $\Delta H°_f$ = − 393.5 kJ/mol

For sulfuric acid: $H_2(g)$ + 1/8 $S_8(s)$ + 2 $O_2(g)$ → $H_2SO_4(\ell)$ $\Delta H°_f$ = − 812 kJ/mol

A formation equation can be treated as any other equation with a *ΔH* attached: it can be multiplied, reversed, and added.

If you are given a $\Delta H°_f$ value for a compound in a problem or in a table, you can write a formation equation for the compound, attach the $\Delta H°_f$, and then reverse, multiply, or add that equation to find *ΔH* values for other reactions. Try this example.

 Q. Using a $\Delta H°_f$ in the table above, write the *ΔH* for

 2 $H_2O(g)$ → 2 $H_2(g)$ + $O_2(g)$ ΔH = _____

★ ★ ★ ★ ★

Starting from a $\Delta H°_f$ table value, to find ΔH for a related equation, first write the balanced formation *equation* and attach its $\Delta H°_f$.

$$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(g) \qquad\qquad \Delta H°_f = -241.8\ kJ/mol$$

Then reverse and/or multiply the formation reaction to get the WANTED reaction.

$$2\ H_2O(g) \rightarrow 2\ H_2(g) + O_2(g) \qquad \Delta H = -2(-241.8\ kJ) = +483.6\ kJ$$

Note that the unit converts from kJ/mol to kJ when the product is no longer one mole of one substance. Note also that if a formation equation is multiplied or reversed, the $\Delta H°_f$ becomes a ΔH because the equation is no longer a *formation* equation.

Practice B: Learn the rules above. Then, for each numbered problem, do every other letter. Check answers as you go. Save a few for your next practice session.

1. In your notebook, based on the table data at the right, write the formation equation for each compound and attach a ΔH value to each equation.

Formula	$\Delta H°_f$ in kJ/mol
$NH_3(g)$	− 45.9
$AgCl(s)$	− 127.0
$NO(g)$	+ 90.3
$H_2O(\ell)$	− 285.8

2. Using the table values from Problem 1, write ΔH values for these reactions.

   a. $AgCl(s) \rightarrow Ag(s) + 1/2\ Cl_2(g)$ $\Delta H =$ _____

   b. $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ $\Delta H =$ _____

   c. $3\ H_2O(\ell) \rightarrow 3\ H_2(g) + 3/2\ O_2(g)$ $\Delta H =$ _____
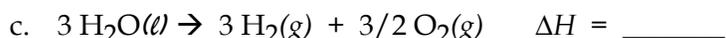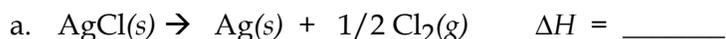
3. Which of the reactions in Problem 2 are endothermic?

4. Circle the *compounds* involved in each of these reactions, then write the value for the heat of formation ($\Delta H°_f$) for each compound.

   a. $1/8\ S_8(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H = -296.8\ kJ$

   b. $3/8\ S_8(s) + 9/2\ O_2(g) \rightarrow 3\ SO_3(g)$ $\Delta H = -1,188\ kJ$

   c. $2\ NO(g) \rightarrow N_2(g) + O_2(g)$ $\Delta H = -180.6\ kJ$

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

5. Which equation(s) in Problem 4 are formation equations?

6. Use this table data to find ΔH values for the two reactions below, then add the two reactions and their ΔH values.

Formula	$\Delta H°_f$
$NO_2(g)$	+ 33.8 kJ/mol
$NO(g)$	+ 90.3 kJ/mol

$NO_2(g)$ → $1/2\ N_2(g)$ + $O_2(g)$ ΔH = _____

$1/2\ N_2(g)$ + $1/2\ O_2(g)$ → $NO(g)$ ΔH = _____

_____

7. Acetylene gas can be burned to produce the extremely hot flame used in a "cutting torch." The equation is

$C_2H_2(g)$ + $5/2\ O_2(g)$ → $2\ CO_2(g)$ + $H_2O(g)$ ΔH = − 1,255.8 kJ

Use the above equation plus the table values to find the heat of formation for acetylene.

Formula	$\Delta H°_f$ in kJ/mole
$H_2O(g)$	− 241.8
$CO_2(g)$	− 393.5

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ANSWERS

Practice A

1. **b, d, e,** and **f.**   b. CO*(g)* is a compound.   d. Hg*(g)* . Mercury is a liquid at room temperature.
   e. N*(g)* . Nitrogen as an element is N_2 .   f. $Cl_2(\ell)$. Chlorine is a gas at room temperature.

2. a. Fluorine **$F_2(g)$**   Fluorine is a halogen. All halogen elements are **di**atomic. Fluorine is at the top right of the periodic table, where several elements are gases at room temperature.

   b. Iron **Fe(s)**   Iron is a metal. All metal elements are monatomic solids (except mercury).

   c. Oxygen **$O_2(g)$**   Oxygen is a gas at room temperature. The fact that the formula for the element oxygen is O_2 must be memorized.

   d. Carbon **C(s)**   The elemental form of carbon is graphite ("pencil lead").

   e. Nitrogen **$N_2(g)$**   The air we breathe is about 80% nitrogen gas. The diatomic formula for elemental nitrogen gas is used frequently and must be memorized.

3. a. NaCl*(s)*   In formation equations, **elements** in their standard state are the reactants, **one** mole of the **compound** is the product, and coefficients must be **added** that **balance** the equation:
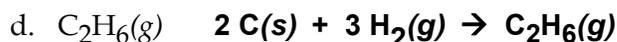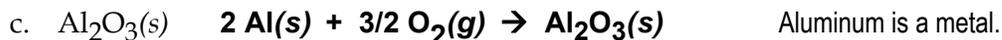
   Na(s) + 1/2 Cl$_2$(g) → NaCl(s)
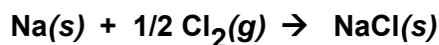
   Sodium is a metal. For metals, the formula is written as one atom; all are solids except Hg.

   Chlorine is a halogen: all halogen elements are diatomic. In the halogen column, the elements above bromine are gases, and below bromine are solids, at room temperature.
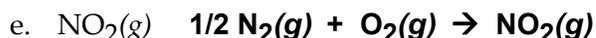
NaCl is a compound: it has more than one kind of atom. You must add coefficients that keep the same particle formulas, but make one mole of the compound in a balanced equation.

b. $HCl(g)$ **1/2 H$_2$(g) + 1/2 Cl$_2$(g) → HCl(g)**
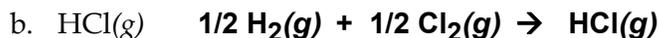
Hydrogen atoms are stable at room temperature as H$_2$ gas; this element formula should be memorized.

c. $Al_2O_3(s)$ **2 Al(s) + 3/2 O$_2$(g) → Al$_2$O$_3$(s)**   Aluminum is a metal.

d. $C_2H_6(g)$ **2 C(s) + 3 H$_2$(g) → C$_2$H$_6$(g)**

Some texts write **C(graphite)** to distinguish graphite, diamonds, buckyballs, and other forms of pure carbon. Graphite is the "standard state" form of carbon.

e. $NO_2(g)$ **1/2 N$_2$(g) + O$_2$(g) → NO$_2$(g)**

Practice B

1. a.   **1/2 N$_2$(g) + 3/2 H$_2$(g) → NH$_3$(g)   ΔH = − 45.9 kJ/mol**

When translating heats of formation into formation equations, elements are added as reactants, one mole of the compound is the product, and the heat of formation is the ΔH for the reaction.

b. **Ag(s) +   1/2 Cl$_2$(g) → AgCl(s)   ΔH = − 127.0 kJ/mol**

c. **1/2 N$_2$(g) + 1/2 O$_2$(g) → NO(g)   ΔH = + 90.3 kJ/mol**

d. **H$_2$(g) + 1/2 O$_2$(g) → H$_2$O(ℓ)   ΔH = − 285.8 kJ/mol**

When a reaction has one product and its coefficient is one, the units of ΔH may be written as either kJ/mol or as kJ. In equations with energy terms, coefficients are in moles.

2. a. $AgCl(s) →$ $Ag(s) +   1/2 Cl_2(g)$ **ΔH = + 127.0 kJ**
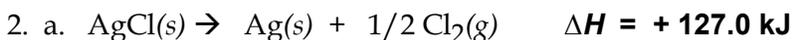
When starting from the table, first write out the formation reaction, as in answer 3b. Then, since this problem asks for the *reverse* of the formation reaction, change the *sign* of ΔH.

b. $N_2(g) + 3 H_2(g) → 2 NH_3(g)$ ΔH = − **91.8 kJ**

Starting from the table, first write the formation reaction, as in answer 3a. Then, since this problem doubles the formation reaction, double the ΔH.

c. $3 H_2O(ℓ) → 3 H_2(g) + 3/2 O_2(g)$ ΔH = **+ 857.4 kJ**
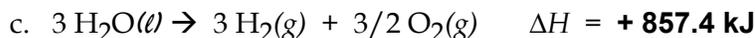
This problem is table equation 3d, tripled and reversed.

When a reaction does not have one particle as a product, the units of ΔH are kJ.

3. **2a** and **2c.** Endothermic reactions have a positive ΔH.

4. Compounds have more than one kind of atom.

   a. $1/8\ S_8(s)\ +\ O_2(g) \rightarrow SO_2(g)$　　　　　　　$\Delta H\ =\ -296.8$ kJ *or* kJ/mol

   Assuming that all of the formulas in the reactants are elements in their "standard state" (and they are), this is a formation reaction for one mole of $SO_2(g)$. The heat of this reaction (ΔH) is therefore the heat of formation of the compound: $\Delta H°_f$ for $SO_2(g)$ = **– 296.8 kJ/mol**

   b. $3/8\ S_8(s)\ +\ 9/2\ O_2(g)$　　$\rightarrow$　　$3\ SO_3(g)$　　　　　$\Delta H\ =-1188$ kJ

   In this reaction, the elements are on the left, the compound is on the right, and **3** moles of compound is formed. For a *formation reaction* involving heat, we must make **one** mole of the compound. To get the formation reaction, multiply all terms of the given reaction by 1/3.

   $\Delta H°_f\ = 1/3\ x\ (-1188$ kJ$) = -396.0$ **kJ .**

   c. $2\ NO(g) \rightarrow N_2(g)\ +\ O_2(g)$　　　　　　$\Delta H\ =\ -180.6$ kJ
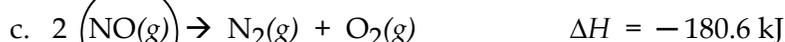
   In a formation reaction, elements must be on the left, so this reaction must be reversed.

   Reversing this reaction, the sign of ΔH is reversed. This is double a formation reaction, so the ΔH would be cut in half for the heat of formation. Heats for formation must be for *one* mole of compound.

   $\Delta H°_f$ for NO(g) = **1/2** x $(-180.6$ kJ$)$, reversed= **+ 90.3 kJ .**

   d. $4\ H_2O(g) \rightarrow 2\ H_2(g)\ +\ O_2(g)$　　　　　$\Delta H\ =\ +967.2$ kJ
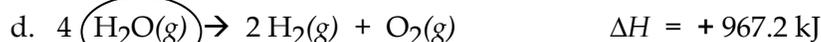
   This is the formation reaction for water vapor, quadruped and reversed. To find to the formation reaction, write the reaction backwards, changing the sign of ΔH. Then multiply the coefficients and ΔH by 1/4, to make **one** mole of water vapor.

   $\Delta H°_f$ for water vapor = **1/4** x (+ 967.2 kJ) **reversed**= **– 241.8 kJ**

5. Only **4a.** Formation equations must have elements in their standard state on the left and *one* mole of a *non*-element on the right.

6. $NO_2(g)\ \rightarrow\ 1/2\ N_2(g)\ +\ \dfrac{1}{2}\ O_2(g)$　　$\Delta H =-$ **33.8 kJ**　　　　　(reverse of formation)

   $1/2\ N_2(g)\ +\ 1/2\ O_2(g)\ \rightarrow\ NO(g)$　　　$\Delta H =\ +$ **90.3 kJ**　　(this is the formation equation)

   _____

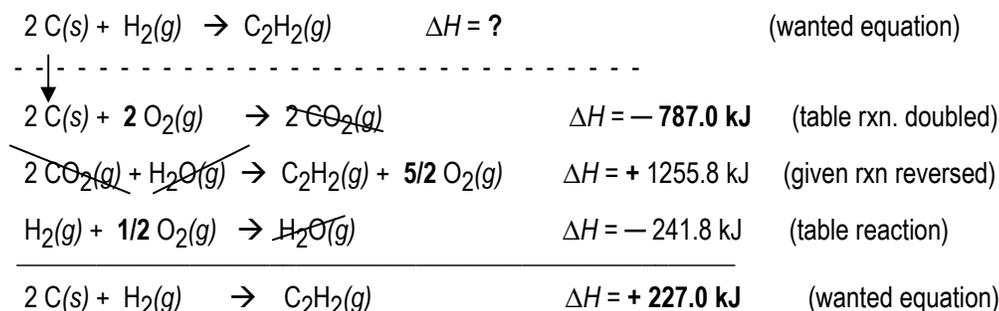   **$NO_2(g)\ \rightarrow\ NO(g)\ +\ \dfrac{1}{2}\ O_2(g)$**　　　　　$\Delta H =\ +$ **56.5 kJ**
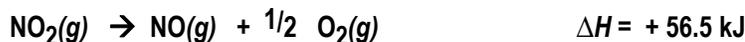
   When you add the equations, 1/2 O_2 cancels on both sides. When the equations are written so that the arrows do not line up in a column, be careful to cancel substances on *opposite* sides of the arrows.

7. The heat of *formation* of acetylene is WANTED. That equation would be:

   $2\ C(s)\ +\ H_2(g)\ \rightarrow\ C_2H_2(g)$　　　　$\Delta H =\ ?$

★　★　★　★　★
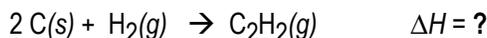
   Arrange the given equations to add and cancel to result in the equation wanted. The equations may be added in any order. In burning (combustion) reactions, the O_2 coefficients should add correctly if the equations to be added are correct. Here, the 5/2 O_2 on both sides will cancel.

$2\ C(s) + H_2(g) \rightarrow C_2H_2(g)$　　　　$\Delta H = ?$　　　　　　　(wanted equation)

- - -|- -

$2\ C(s) + \mathbf{2}\ O_2(g) \rightarrow 2\ CO_2(g)$　　　　　$\Delta H = -\ \mathbf{787.0\ kJ}$　(table rxn. doubled)

$2\ CO_2(g) + H_2O(g) \rightarrow C_2H_2(g) + \mathbf{5/2}\ O_2(g)$　　$\Delta H = +\ 1255.8\ kJ$　(given rxn reversed)

$H_2(g) + \mathbf{1/2}\ O_2(g) \rightarrow H_2O(g)$　　　　　　$\Delta H = -\ 241.8\ kJ$　(table reaction)

_____

$2\ C(s) + H_2(g) \rightarrow C_2H_2(g)$　　　　$\Delta H = +\ \mathbf{227.0\ kJ}$　　(wanted equation)

* * * * *

Lesson 22E: Using Summation To Find *ΔH*

Enthalpy is a state function: the change in enthalpy in a process (Δ*H*) is simply the *difference* between the total enthalpy of the particles at the end (the products) and at the beginning (the reactants). This means that one way to measure the enthalpy change of a reaction is to add up the enthalpy values of all of the products, then subtract the enthalpy values of all of the reactants.

$$\Delta H_{reaction} = \text{sum of } \Delta H°_f \text{ for } \textit{final} \text{ particles} - \text{sum of } \Delta H°_f \text{ for initial particles}$$

Δ*H*°$_f$ values measure the enthalpy in one mole of a particle. Two moles of the particles will have double that value for their total enthalpy.

Apply the logic of the above to this

Q. If we needed to find Δ*H* for the reaction in problem 7 above

$$C_2H_2(g) + 5/2\ O_2(g) \rightarrow 2\ CO_2(g) + H_2O(g) \qquad \Delta H = ?$$

and we know the Δ*H*°$_f$ for each of the particles in the equation, as given in the table at the right,

a. calculate the total Δ*H*°$_f$ of the *products* of the above reaction, based on the table and reaction coefficients.

Formula	ΔH°$_f$
$H_2O(g)$	$-\ 241.8$ kJ/mol
$CO_2(g)$	$-\ 393.5$ kJ/mol
$C_2H_2(g)$	$+\ 227.0$ kJ/mol

★ ★ ★ ★ ★

Total **Δ*H*°$_f$** of the *products* **=** **2** (Δ*H*°$_f$ of $CO_2(g)$) + **1** (Δ*H*°$_f$ of $H_2O(g)$) =

= **2** ($-$ 393.5 kJ)　　+ **1** ($-$ 241.8 kJ) = **$-$1,028.8 kJ**

b. Find the total Δ*H*°$_f$ of the *reactants*.

★ ★ ★ ★ ★

Sum of Δ*H*°$_f$ of the *reactants* = **1** (Δ*H*°$_f$ of $C_2H_2(g)$ + **5/2** (Δ*H*°$_f$ of $O_2(g)$) =

= **1** (+ 227.0 kJ)　　+　**5/2** (0 kJ)　 = **+ 227.0 kJ**

$O_2(g)$ is an element, and the Δ*H*°$_f$ of all elements is 0 kJ.

c. Using the equation above with sums, find ΔH for the reaction.

★ ★ ★ ★ ★

$\Delta H_{reaction}$ = sum of $\Delta H°_f$ of products $-$ sum of $\Delta H°_f$ of reactants

$=$ $-1{,}028.8$ kJ $-$ (+ 227.0 kJ) $=$ $\mathbf{-1{,}255.8}$ **kJ**

Compare this answer to the ΔH supplied after the reaction in problem 7 above.

What is the difference between the above Question Part c and problem 7?

- In this question, we knew all of the heats of **formation** for the particles in the reaction.

- In problem 7, we WANTED one of the heats of formation, and had data for a reaction that was not a formation reaction, but could be used to find the $\Delta H°_f$.

To find a reaction ΔH, if the $\Delta H°_f$ values for all of the compounds in an equation are known, this summation method is likely to be quicker than writing out formation equations and adding using Hess's law. However, in problems with data that *mix* formation and non-formation reactions, such as problem 7, the summation method does not work, but writing out the formation reactions then adding both types of reactions using Hess's law does work.

Hess's law is slower, but it will solve using heats of formation equations, non-formation equations, or a mixture of the two.

To find $\Delta H_{reaction}$, a suggested strategy that may speed your work is

- use the summation method *if* you know *all* of the needed $\Delta H°_f$ values.

- If not, write out the formation equations and add equations using Hess's Law.

Let's summarize:

To find $\Delta H_{reaction}$:

1. *If* standard enthalpy of formation ($\Delta H°_f$) values are known for *all* of the particles in a chemical reaction, the **ΔH** of the reaction can be calculated by substituting those values into the state function equation that defines **ΔH**:

$\Delta H_{reaction}$ = ΔH_{final} $-\Delta H_{initial}$

$=$ sum of $\Delta H°_f$ of products $-$ sum of $\Delta H°_f$ of reactants

= [**sum** of (coefficient x $\Delta H°_f$) of *products*] $-$ [**sum** of (coefficient x $\Delta H°_f$) of *reactants*]

Abbreviated in symbols, we will call this the heat of formation **summation equation**.

$$\boxed{\Delta H_{reaction} \ = \ \sum c\, \Delta H°_f \text{ of products} - \sum c\, \Delta H°_f \text{ of reactants}}$$

2. If *not all* of the needed $\Delta H°_f$ values are known, write out the formation equations and other supplied equations, adding the equations using Hess's Law.

Try **Q.** Use the table and the summation equation to find ΔH for this reaction.

$$2\,SO_2(g) + O_2(g) \rightarrow 2\,SO_3(g)$$
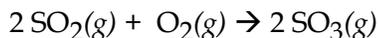
Formula	$\Delta H°_f$ in kJ/mole
$SO_2(g)$	− 296.8
$SO_3(g)$	− 396.0

★ ★ ★ ★ ★

ΔH = [sum of (coefficient x $\Delta H°_f$) of *products*] − [sum of (coefficient x $\Delta H°_f$) of *reactants*]

= [2 (− 396.0 kJ)] − [2 (− 296.8 kJ) + **0** kJ] = **− 198.4 kJ**

Practice. On these, use the summation equation and table values to find ΔH.

1. Steam can be added to hot coal (which is primarily carbon) to produce a burnable mixture. Find ΔH for the reaction.
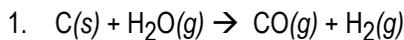
$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \qquad \Delta H = ?$$

Formula	$\Delta H°_f$ in kJ/mol
$CO(g)$	− 110.5
$H_2O(g)$	− 241.8

2. For the burning of ethane, a component of natural gas, balance the equation, then find ΔH.

$$C_2H_6(g) + \quad O_2(g) \rightarrow \quad CO_2(g) + \quad H_2O(g)$$

Formula	$\Delta H°_f$ in kJ/mol
$C_2H_6(g)$	− 84.7
$CO_2(g)$	− 393.5
$H_2O(g)$	− 241.8

ANSWERS

Practice

1. $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

    $\Delta H_{reaction}$ = (sum of $\Delta H°_f$ values of *products*) — (sum of $\Delta H°_f$ values of *reactants*)

    $= (-110.5 + 0) - (0 + -241.8) = 241.8 - 110.5 = $ **+ 131.3 kJ**

2. $C_2H_6(g) + $ **7/2** $O_2(g) \rightarrow $ **2** $CO_2(g) + $ **3** $H_2O(g)$
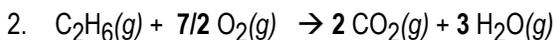
    | $\Delta H_{reaction} = \sum c \, \Delta H°_f$ of products — $\sum c \, \Delta H°_f$ of reactants |

    $= [2(-393.5 \text{ kJ}) + 3(-241.8)] - [1(-84.7 + 7/2 (0)] = $ **—1427.7 kJ**

* * * * *

SUMMARY: Heats of Reaction (*ΔH*)

A summary for initial thermodynamic and PV work equations is given at the end of Lesson 22A. The summary below covers calculations that involve ΔH.

If you have not already done so, you may want to organize this summary into charts, numbered lists, and flashcards that help with long-term memory.

1. Energy (E), heat (*q*), and work (*w*) in the SI system are measured in joules (J).

2. If the external pressure on a system is held constant and work is limited to "PV work" , then the heat flow in our out of a system of particles equals its change in enthalpy.

    | $\Delta H = q$ | at constant P and PV work.

3. In equations that include energy terms, the coefficients are in *moles*.

4. In energy equations, the *phase* of each particle must be shown: *(s)*, (1), *(g)*, or *(aq)*.

5. In **exo**thermic reactions, energy is *released* into the environment, and the energy term is shown

    * EITHER with a *positive* sign on the *products* side;

    * OR (preferred) with a *negative ΔH* value written *after* the equation.

6. In **endo**thermic reactions, energy must be *added*, and the energy term is shown

    * EITHER with a *positive* sign on the *reactants* side of the equation,

    * OR with a *positive ΔH* written *after* the reaction.

7. Reactions involving energy or heat can be *reversed* (the equation can be written backwards). If a ΔH is attached to the equation, *change the sign* of ΔH.

8. All reaction coefficients and energy terms can be multiplied or divided by a number. If ΔH notation is used, do the same to the value of ΔH.

9. Equations with energy terms can be added to produce a new equation.

    *   Like particles on the same side in different equations can add, and on opposite sides can cancel.

    *   When equations are added, *ΔH* values add according to their signs.

10. **Hess's Law.** When *ΔH* for an equation is not known, it can be found by adding together equations for which *ΔH* is known.

    *   Write the reaction equation WANTED, then a dotted line below it.

    *   Write the first coefficient and substance formula below the dotted line.

    *   Find an equation with a known *ΔH* that includes that first formula. Adjust the direction and coefficients of the known equation to put the dropped particle and its coefficient on the side where it is WANTED. Modify and include a *ΔH*.

    *   Arrange other equations and their known *ΔH* to cancel particles not wanted, and add to result in the equation WANTED.

11. In a *formation* equation, the reactants are all *elements* in their *standard state* at 25°C and 1 atm pressure, and the product is *one mole* of a compound or other particle that is not an element.

12. The *heat* of formation ($\Delta H°_f$) of a compound is the amount of heat required or released when one mole of the compound is formed from its elements in their standard state.

13. All elements in their standard state are assigned a heat of formation of *zero* kJ/mole.

14. The standard enthalpy value for a compound ($\Delta H°$) is its $\Delta H°_f$.

15. *If* heats of formation are known for all of the substances in a reaction, the *ΔH* of the reaction can be found by substituting $\Delta H°_f$ values into:

    $\Delta H = \Delta H_{final} - \Delta H_{initial}$

    ΔH = [sum of (coefficient x $\Delta H°$) of *products*] $-$ [sum of (coefficient x $\Delta H°$) of *reactants*]

    or $\boxed{\Delta H_{reaction} \; = \; \sum c \, \Delta H°_f \text{ of products} - \sum c \, \Delta H°_f \text{ of reactants}}$

16. To find a $\Delta H_{reaction}$, Hess's law is slower, but it will solve using heats of formation equations, non-formation equations, or a mixture of both.

# # # # #

# Module 22 — Heats of Reaction ($\triangle H$)

613

Practice A: Chart and learn the rules above, *then* answer these questions from memory.

1. From the perspective of the particles in a chemical system,
    a. if heat is added to the particles, is the sign of q positive *or* negative ?
    b. If a gas expands by pushing a piston that is under pressure, is the sign of
        w positive *or* negative ?

2. If a substance burns, but no work is done,
    a. is the sign of q positive *or* negative ?
    b. Is the sign of ΔE positive *or* negative ?
    c. Is the reaction exothermic *or* endothermic?

3. If a gas is compressed by a piston, but no heat is added to the gas,
    a. is the sign of w positive *or* negative ?
    b. is the sign of q positive *or* negative ?
    c. Is the sign of ΔE is   positive *or* negative ?

4. If 30.0 joules of heat … (Finish this problem in your notebook)

621

Practice A: Answers are at the end of this lesson. Check your answer after each part.

1. Re-write these equations so that the heat term appears as a product or a reactant inside
    the equation.
    a. $C(s) +\ O_2(g)\ \rightarrow CO_2(g)$ $\Delta H\ =\ -393.5$ kJ

    b. $1/2\ N_2\ (g) +\ 1/2\ O_2(g)\ \rightarrow NO(g)$ $\Delta H\ =\ +\ 90.3$ kJ

2. Label each reaction in (1) above as either exothermic or endothermic.

3. Re-write these equations using ΔH notation.
    a. $H_2O_2(\ell)\ +187.6$ kJ $\rightarrow H_2(g) +\ O_2(g)$

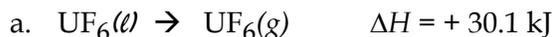b. $C(s) + 1/2\,O_2(g) \rightarrow CO(g) + 110.5$ kJ
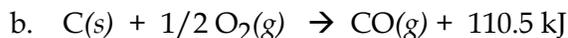
4.   After each reaction in problem (3) above, add a label identifying the side that has more energy stored in its particles: the *reactants* or the *products*.

622

Practice B: Do every other problem. Save the rest for your next practice session.

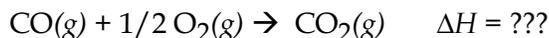1.   Write these reactions in the reverse direction.   Express the energy term as a Δ***H*** value.

a. $UF_6(\ell) \rightarrow UF_6(g)$ $\Delta H = + 30.1$ kJ

b. $C(s) + 2\,H_2(g) \rightarrow CH_4(g)$ $\Delta H = - 74.9$ kJ

2   Use these 4 "known" reactions to fill in the blanks below.

$$H_2(g) + 1/2\,O_2(g) \rightarrow H_2O(g) \qquad \Delta H = - 241.8 \text{ kJ} \qquad (1)$$
$$H_2(g) + 1/2\,O_2(g) \rightarrow H_2O(\ell) \qquad \Delta H = - 285.8 \text{ kJ} \qquad (2)$$
$$1/2\,N_2\ (g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H = + 33.8 \text{ kJ} \qquad (3)$$
$$H_2(g) + 1/8\,S_8(s) + 2\,O_2(g) \rightarrow H_2SO_4(\ell) \quad \Delta H = - 812 \text{ kJ} \qquad (4)$$

a. $2\,NO_2(g) \rightarrow N_2(g) + 2\,O_2(g)$ $\Delta \boldsymbol{H} =$ _____

b. $4\,H_2(g) + 2\,O_2(g) \rightarrow 4\,H_2O(\ell)$ $\Delta \boldsymbol{H} =$ _____

c. $8\,H_2SO_4(\ell) \rightarrow 8\,H_2(g) + S_8(s) + 16\,O_2(g)$ $\Delta \boldsymbol{H} =$ _____

624

Q. Find the heat of reaction for the burning of carbon monoxide

$CO(g) + 1/2\,O_2(g) \rightarrow CO_2(g)$ $\Delta H = ???$

by *adding* these two reactions.

$CO(g) \rightarrow C(s) + 1/2\,O_2(g)$ $\Delta H = + 110.5$ kJ

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

_____

625

Practice A: Add these equations and their ΔH values.

1.
$$H_2O(\ell) \rightarrow H_2(g) + 1/2\, O_2(g) \qquad \Delta H = +\,285.8 \text{ kJ}$$

$$H_2O(g) \rightarrow H_2O(\ell) \qquad \Delta H = -\,44.0 \text{ kJ}$$

2.
$$CH_4(g) \rightarrow C(s) + 2\,H_2(g) \qquad \Delta H = +\,74.9 \text{ kJ}$$

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \qquad \Delta H = -\,483.6 \text{ kJ}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -\,393.5 \text{ kJ}$$
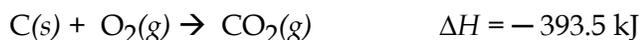
632

Practice A: Learn the rules above. Then, for each numbered problem, do every other letter. Check answers as you go. Save a few for your next practice session.
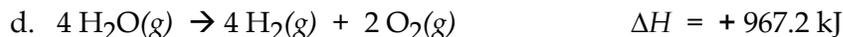
1. Which of these are not elements in their standard state?

   a. $H_2(g)$ b. $CO(g)$ c. $Co(s)$ d. $Hg(g)$ e. $N(g)$ f. $Cl_2(\ell)$

2. Write the formulas for these elements in their standard state at room temperature.

   a. Fluorine   b. Iron   c. Oxygen

   d. Carbon   e. Nitrogen

3. (Finish the Practice in your notebook)

633

Q. Using a $\Delta H°_f$ in the table above, write the ΔH for

$$2\,H_2O(g) \rightarrow 2\,H_2(g) + O_2(g) \qquad \Delta H = \underline{\quad\quad}$$

634

4. Circle the *compounds* involved in each of these reactions, then write the value for the heat of formation ($\Delta H°_f$) for each compound.

   a. $1/8\,S_8(s) + O_2(g) \rightarrow SO_2(g)$ $\qquad \Delta H = -\,296.8 \text{ kJ}$

   b. $3/8\,S_8(s) + 9/2\,O_2(g) \rightarrow 3\,SO_3(g)$ $\qquad \Delta H = -\,1{,}188 \text{ kJ}$

c. $2\,NO(g)$ → $N_2(g)$ + $O_2(g)$ ΔH = − 180.6 kJ

d. $4\,H_2O(g)$ → $4\,H_2(g)$ + $2\,O_2(g)$ ΔH = + 967.2 kJ
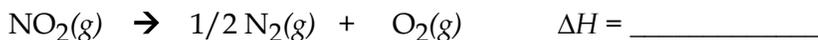
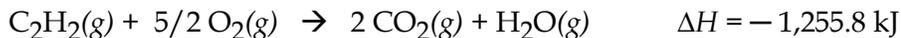5. Which equation(s) in Problem 4 are formation equations?

635

6. Use this table data to find ΔH values for the two reactions below, then add the two reactions and their ΔH values.

Formula	$\Delta H°_f$
$NO_2(g)$	+ 33.8 kJ/mol
$NO(g)$	+ 90.3 kJ/mol

$NO_2(g)$ → $1/2\,N_2(g)$ + $O_2(g)$ ΔH = _____

$1/2\,N_2(g)$ + $1/2\,O_2(g)$ → $NO(g)$ ΔH = _____

_____

7. Acetylene gas can be burned to produce the extremely hot flame used in a "cutting torch."   The equation is

$C_2H_2(g)$ + $5/2\,O_2(g)$ → $2\,CO_2(g)$ + $H_2O(g)$ ΔH = − 1,255.8 kJ

Use the above equation plus the table values to find the heat of formation for acetylene.

Formula	$\Delta H°_f$ in kJ/mole
$H_2O(g)$	− 241.8
$CO_2(g)$	− 393.5