Unit 7
Thermodynamics II
Enthalpy

Enthalpy (*H*)

- *H* is a state function incorporating *PV*-work, defined as:

$$H \equiv U + PV$$

- Enthalpy has units of Joules (J) or kilojoules (kJ).
- The change in enthalpy between two states, 1 and 2, is

$$\Delta H = H_2 - H_1 = \Delta U + \Delta(PV)$$

Constant Pressure Process

- If a process is carried out with <u>constant pressure</u> then $P = P_1 = P_2 = P_{ext}$, so that using the First Law gives

$$\Delta U = q_p + w = q_p - P\Delta V$$

where the subscript on q reminds us P is constant, and we have assumed only PV-work is acting, then

$$q_p = \Delta U + P\Delta V = \Delta H$$

ΔH is the heat gained or released during a constant pressure process, including a chemical reaction.

Heat and matter – Phase changes

- During phase changes:
- heat is required to overcome IMFs, or
- heat is released upon the formation of IMFs

This heat is called 'latent heat'

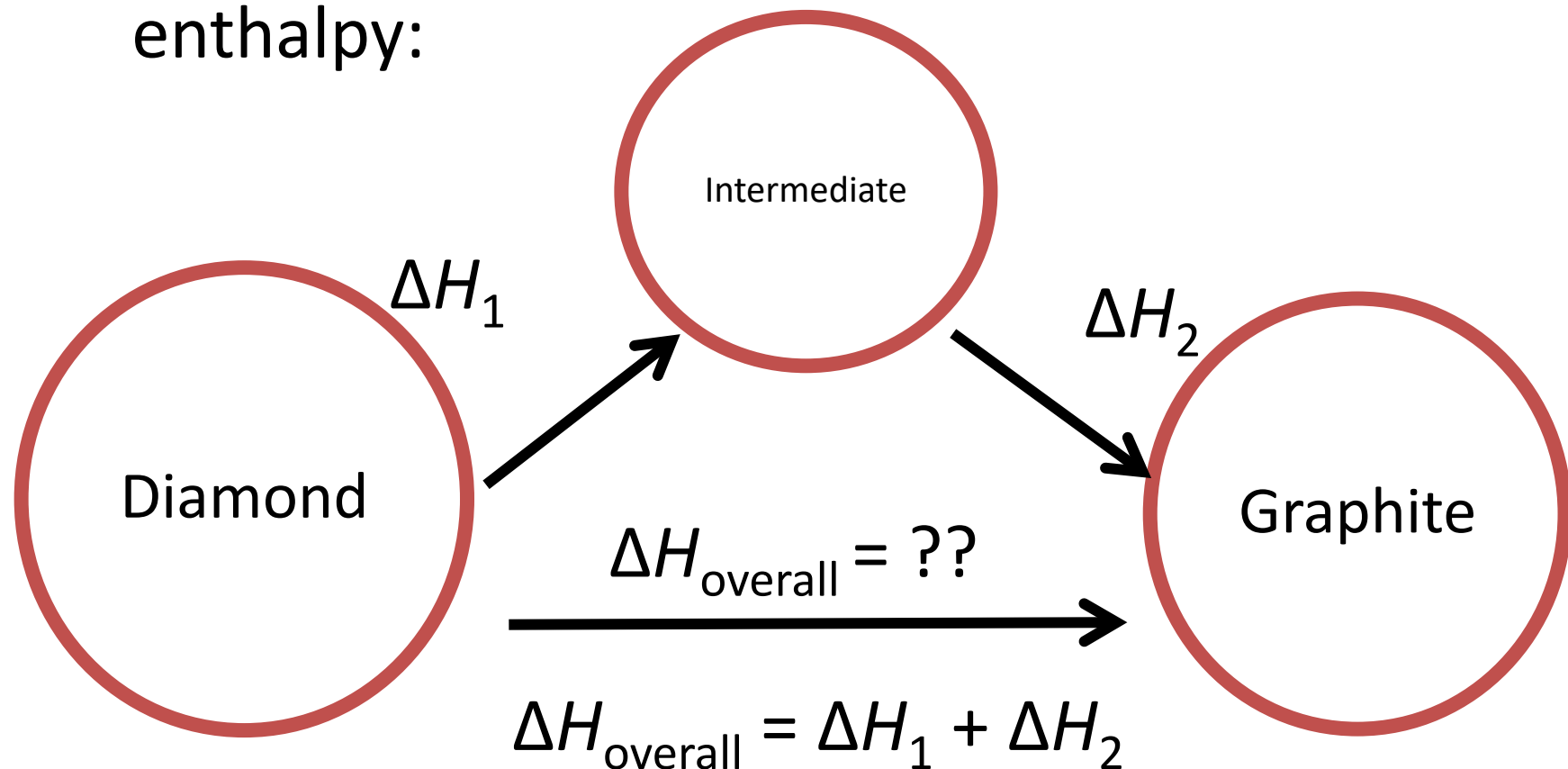$$\Delta H = n \cdot \Delta H_{\text{phase change}}$$

n = number of moles of substance

$\Delta H_{\text{phase change}}$ = molar enthalpy of phase change

REMINDER: ΔH is an EXTENSIVE property. Therefore it scales with size/quantity/extent.

Hess' Law

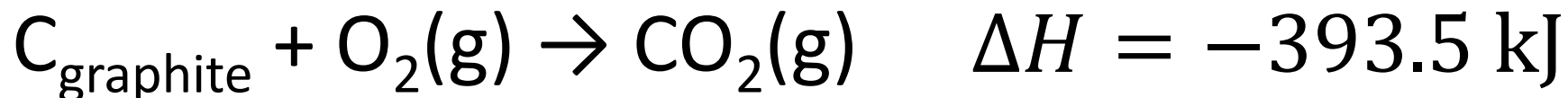- Sum of ΔH for all steps gives overall reaction enthalpy:

Intermediate

ΔH_1

ΔH_2

Diamond

Graphite

$\Delta H_{\text{overall}} = ??$

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

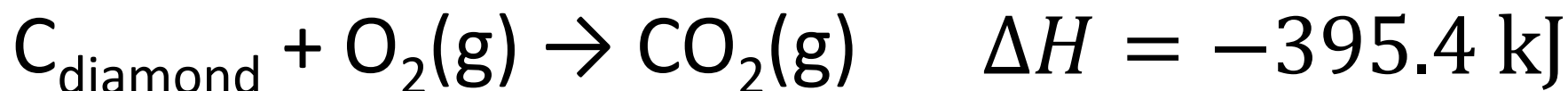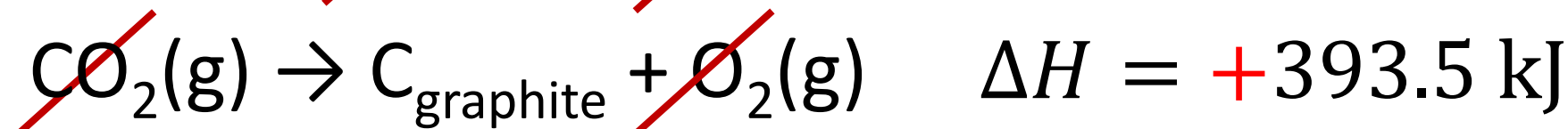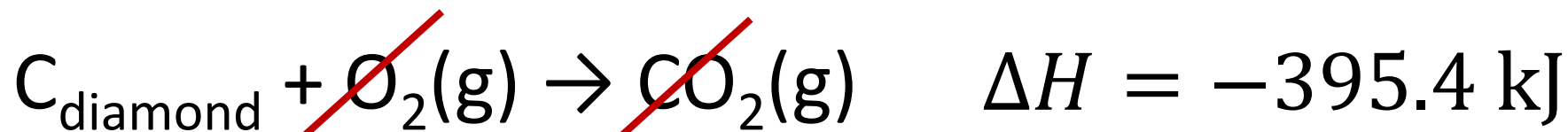**REMINDER: ΔH is an state function
(it is path independent)**

Enthalpy Changes in Chemical Reactions

How can we measure the enthalpy of reactions that are very slow? (or don't happen at all?)

Example:

$$\text{C(diamond)} \rightarrow \text{C(graphite)} \qquad \Delta H = \text{???}$$

$$\text{C}_{\text{diamond}} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \qquad \Delta H = -395.4 \text{ kJ}$$
$$\text{C}_{\text{graphite}} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \qquad \Delta H = -393.5 \text{ kJ}$$

Diamond to graphite…

$C(\text{diamond}) \rightarrow C(\text{graphite})$ ΔH = ???

$C_{\text{diamond}} + \cancel{O_2(g)} \rightarrow \cancel{C}O_2(g)$ $\Delta H = -395.4 \text{ kJ}$

$\cancel{C}O_2(g) \rightarrow C_{\text{graphite}} + \cancel{O_2(g)}$ $\Delta H = +393.5 \text{ kJ}$

$C_{\text{diamond}} \rightarrow C_{\text{graphite}}$ $\Delta H = -1.9 \text{ kJ}$

1. Reversing reaction inverts sign of ΔH.

$$C_{diamond} + O_2(g) \rightarrow CO_2(g)$$

(reverse reaction)
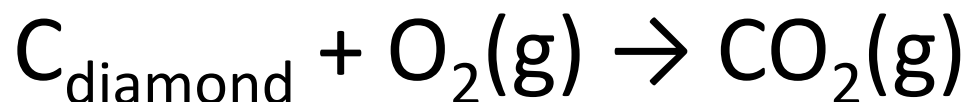
$$CO_2(g) \rightarrow C_{diamond} + O_2(g)$$
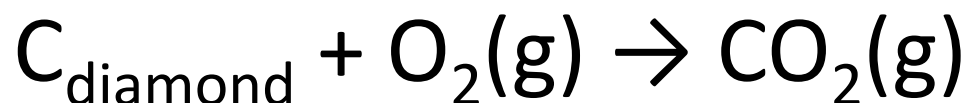
$\Delta H = -395.4 \text{ kJ}$

(reverse sign)

$\Delta H = +395.4 \text{ kJ}$

Hess' Law (cont'd)

2. ΔH depends on quantity of the reaction.
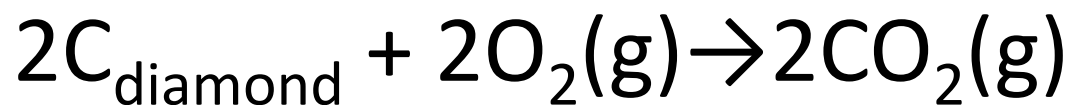
$$C_{diamond} + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -395.4 \text{ kJ}$$

<div style="text-align:center; color:red">X 2</div>

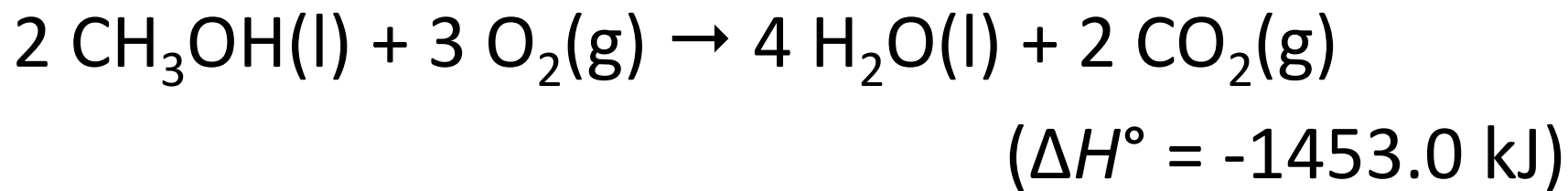$$2C_{diamond} + 2O_2(g) \rightarrow 2CO_2(g) \qquad \Delta H = -790.8 \text{ kJ}$$

REMINDER: ΔH is an EXTENSIVE property.
Therefore it scales with size/quantity/extent.
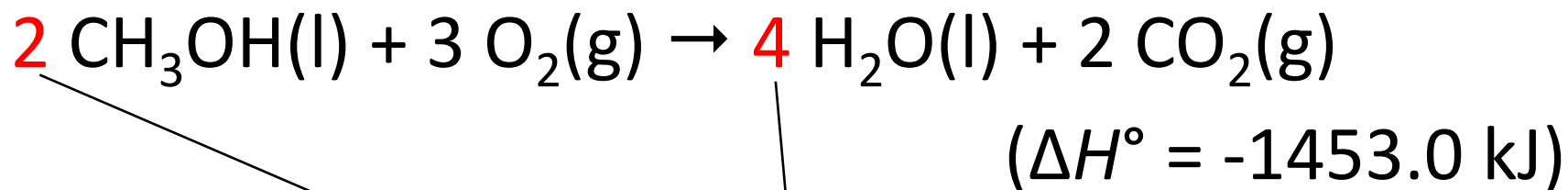
Consider the <u>combustion of methanol</u>:

2 $CH_3OH(l)$ + 3 $O_2(g)$ → 4 $H_2O(l)$ + 2 $CO_2(g)$

$$(\Delta H° = -1453.0 \text{ kJ})$$

What is the value of $\Delta H°$ under each of the following conditions:

a) 3 moles of methanol are oxidized:

b) The direction of the reaction is reversed:

c) Water vapor is produced during the reaction instead of liquid water: ($\Delta H°_{vap}$ = 44.0 kJ mol^{-1})

$2 \, CH_3OH(l) + 3 \, O_2(g) \rightarrow 4 \, H_2O(l) + 2 \, CO_2(g)$

$$(\Delta H° = -1453.0 \, kJ)$$

a) 3 moles of methanol are oxidized:

$\Delta H° = (-1453.0 \, kJ \, /2) \times 3 = -2179.5 \, kJ$

a) The direction of the reaction is reversed:

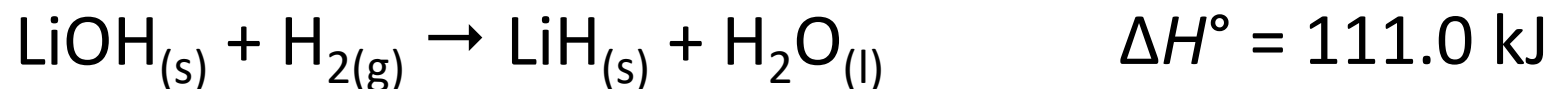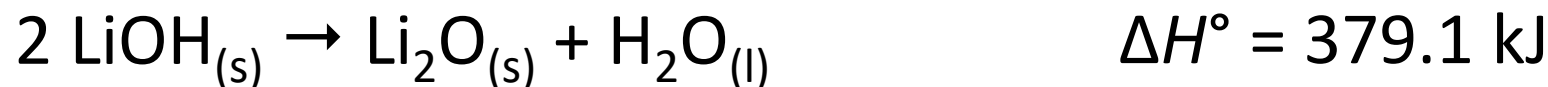$\Delta H° = 1453.0 \, kJ$

a) Water vapor is produced during the reaction instead of liquid water: $(\Delta H°_{vap} = 44.0 \, kJ \, mol^{-1})$

$\Delta H° = -1453.0 \, kJ + (44) \times 4 = -1277 \, (kJ)$

Use the following reactions:

$2\ LiOH_{(s)} \rightarrow Li_2O_{(s)} + H_2O_{(l)}$ $\Delta H° = 379.1\ kJ$

$LiOH_{(s)} + H_{2(g)} \rightarrow LiH_{(s)} + H_2O_{(l)}$ $\Delta H° = 111.0\ kJ$

$2\ H_2O_{(l)} \rightarrow 2\ H_{2(g)} + O_{2(g)}$ $\Delta H° = 285.9\ kJ$

To determine $\Delta H°$ for the reaction:

$2\ LiH_{(s)} + O_{2(g)} \rightarrow Li_2O_{(s)} + H_2O_{(l)}$

Use the following reactions:

$$2 \, LiOH_{(s)} \rightarrow Li_2O_{(s)} + H_2O_{(l)} \qquad \Delta H_1° = 379.1 \text{ kJ}$$

$$LiOH_{(s)} + H_{2(g)} \rightarrow LiH_{(s)} + H_2O_{(l)} \qquad \Delta H_2° = 111.0 \text{ kJ}$$

$$2 \, H_2O_{(l)} \rightarrow 2 \, H_{2(g)} + O_{2(g)} \qquad \Delta H_3° = 285.9 \text{ kJ}$$

To determine $\Delta H°$ for the reaction:

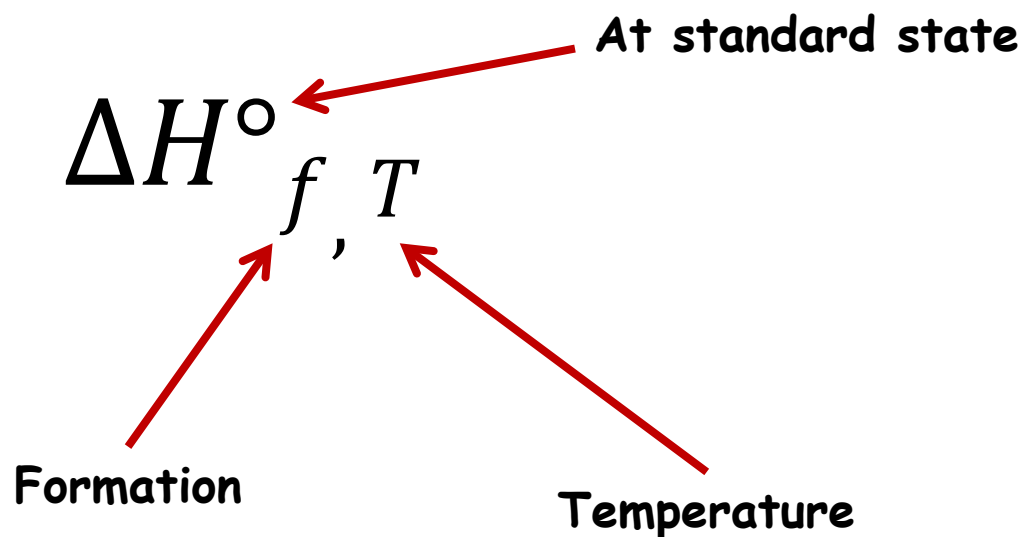$$2 \, LiH_{(s)} + O_{2(g)} \rightarrow Li_2O_{(s)} + H_2O_{(l)}$$
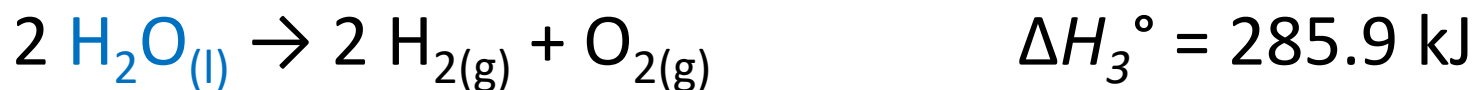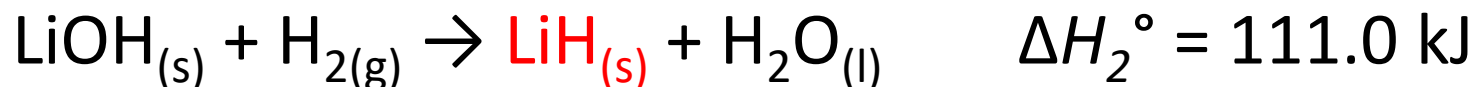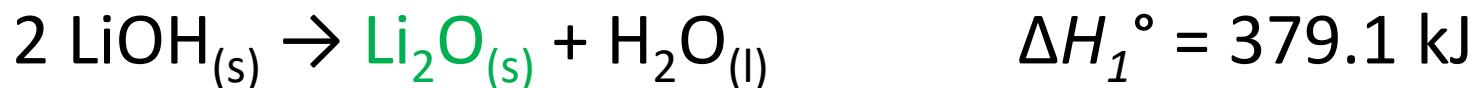
A) +125.2 kJ

B) -17.8 kJ

✓ C) -128.8 kJ ($\Delta H_1° - 2 \times \Delta H_2° - \Delta H_3°$)

D) -303.6 kJ

E) +128.8 kJ

- **Standard enthalpy of formation** is the enthalpy change in a reaction where <u>1 mole</u> of substance is formed from its <u>constituent elements</u> in their <u>standard states</u>.

$$\Delta H°_{f,\,T}$$

At standard state

Formation

Temperature

Standard Enthalpy of Formation

What is standard state?

Gases	1 bar pressure
Pure solids + liquids	Pure substance
Solutions	1 M solution

Note: has no specific temperature!

1. $\Delta H_f^\circ = 0$ for elements in standard state.

2. Need to select one allotrope of element as reference form.

   $C_{graphite}$ vs. $C_{diamond}$ vs. C_{60}

   $S_{rhombic}$ vs. $S_{monoclinic}$

3. ΔH_f^0 varies *slightly* with temperature… approximate as constant (usually at 298 K)

Standard State vs STP

- **Standard state** specifies a <u>pressure (1 bar)</u> for gases or a <u>concentration (1 mol/L)</u> for solutions but <u>NOT temperature</u>. Thus, $\Delta H_\mathrm{f}^{\circ}$ changes (for the same species) if T changes. This is why the temperature must be provided when standard state data is reported.

- **Standard temperature and pressure (STP)** denotes a common set of conditions under which experiments are performed. Since 1982, STP has been defined as <u>$T = 273.15$ K and $P = 1$ bar</u>.

Thermodynamics Experiment

Experiment 5 – Thermodynamics

- Each salt must be weighed out accurately ….
- Part I:
    - Dissolve a salt ($MgSO_4$) which is used to make a hot pack
    - Take measurements as temperature changes (increases) until the change is minimal for a few minutes

    -
- Part II:
    - Dissolve a salt (NH_4NO_3) which is used to make a cold pack
    - Take measurements as temperature changes (decreases) until the change is minimal for a few minutes

- Part III
    - Based on the data collected, design a hot/ cold pack with a pre-determined change in temperature.
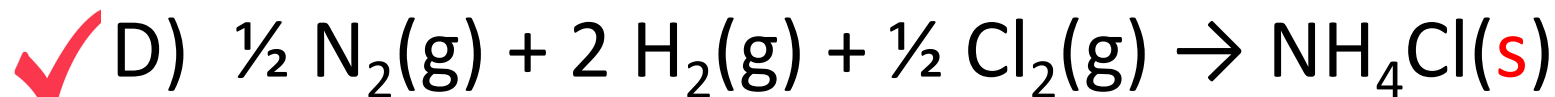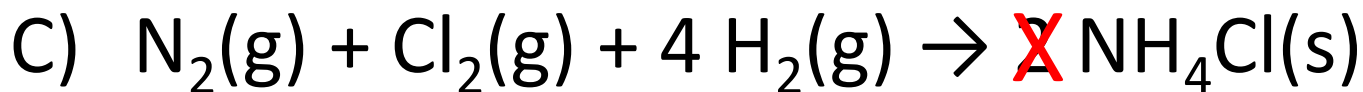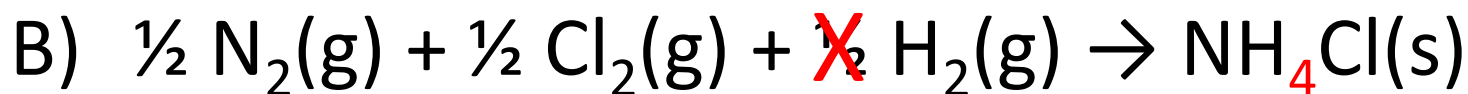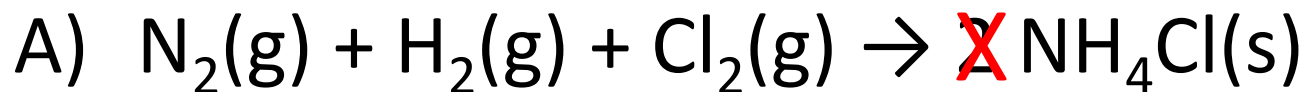
The <u>standard enthalpy of formation</u> of $NH_4Cl(s)$ is -315.4 kJ/mol. The equation that best describes the formation reaction for NH_4Cl is:

A) $N_2(g) + H_2(g) + Cl_2(g) \rightarrow 2\ NH_4Cl(s)$

B) $\frac{1}{2}\ N_2(g) + \frac{1}{2}\ Cl_2(g) + \frac{1}{2}\ H_2(g) \rightarrow NH_4Cl(s)$

C) $N_2(g) + Cl_2(g) + 4\ H_2(g) \rightarrow 2\ NH_4Cl(s)$

D) $\frac{1}{2}\ N_2(g) + 2\ H_2(g) + \frac{1}{2}\ Cl_2(g) \rightarrow NH_4Cl(s)$

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A) $N_2(g) + H_2(g) + Cl_2(g) \rightarrow$ ~~2~~ $NH_4Cl(s)$

B) $\frac{1}{2} N_2(g) + \frac{1}{2} Cl_2(g) +$ ~~½~~ $H_2(g) \rightarrow NH_4Cl(s)$

C) $N_2(g) + Cl_2(g) + 4 H_2(g) \rightarrow$ ~~2~~ $NH_4Cl(s)$

✔ D) $\frac{1}{2} N_2(g) + 2 H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow NH_4Cl(s)$

Worksheet Question #11 – Good Question

Use the following heat of combustion data to determine the <u>enthalpy of formation</u> of methanol (CH_3OH).

$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H° = -726.4$ kJ

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

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H° = -285.8$ kJ

Worksheet Question #11 – Good Question

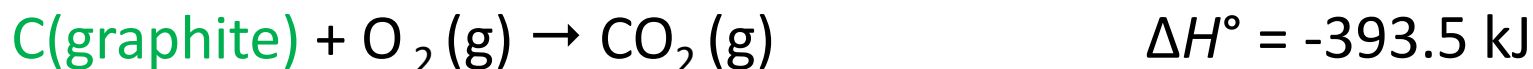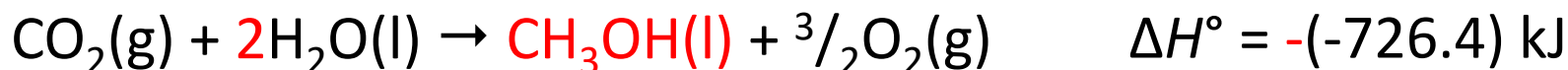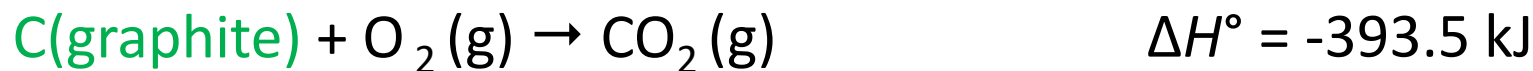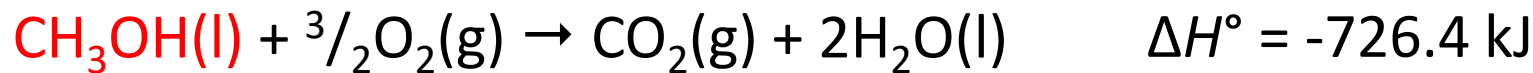$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H° = -726.4$ kJ

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

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H° = -285.8$ kJ

$CO_2(g) + 2H_2O(l) \rightarrow CH_3OH(l) + \frac{3}{2}O_2(g)$ $\Delta H° = -(-726.4)$ kJ

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

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\Delta H° = 2 \times (-285.8)$ kJ

$C(graphite) + \frac{1}{2}O_2(g) + 2H_2(g) \rightarrow CH_3OH(l)$
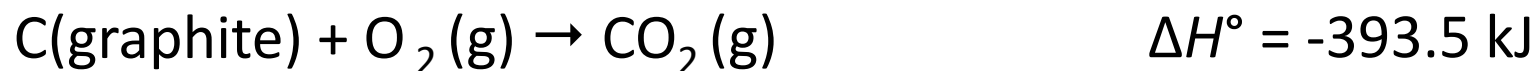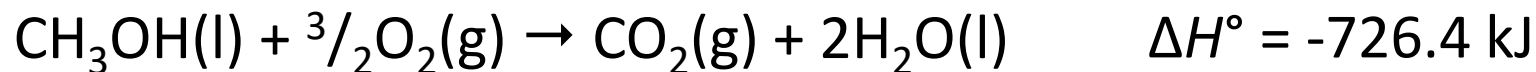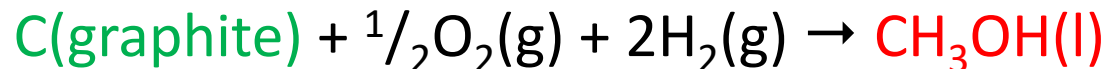
$\Delta H_f^0 = -\Delta H_1^0 + \Delta H_2^0 + 2\,\Delta H_3^0 = 726.4 - 393.5 - 571.6$

$= -238.7 \; kJ\,mol^{-1}$

Standard Enthalpy of Formation

$$\Delta H^0 = \sum v_p \cdot \Delta H_f^0(\text{products}) - \sum v_r \cdot \Delta H_f^0(\text{reactants})$$

ΔH_f^0 = Enthalpy of formation for each product / reactant

v = Stoichiometric coefficient from reaction equation

If we know ΔH_f^0 for products and reactants, we can use Hess' law to determine enthalpy change.

Use the enthalpy data to determine the standard internal energy change ($\Delta U°$) for the <u>combustion of 1 mol of glucose</u> ($C_6H_{12}O_6$) <u>under constant pressure</u> conditions and at <u>298 K</u>:

$$C_6H_{12}O_6 \text{ (s)} + 6\ O_2(g) \rightarrow 6\ CO_2 \text{ (aq)} + 6\ H_2O(l)$$

Species	$\Delta H°_f$ (kJ/mol)
$C_6H_{12}O_6$ (s)	-1273.3
CO_2 (aq)	-412.9
$H_2O(l)$	-285.8

$$C_6H_{12}O_6 \text{ (s)} + 6\ O_2(g) \rightarrow 6\ CO_2 \text{ (aq)} + 6\ H_2O(l)$$

Species	$\Delta H°_f$ (kJ/mol)
$C_6H_{12}O_6$ (s)	-1273.3
CO_2 (aq)	-412.9
$H_2O(l)$	-285.8

$\Delta H°$

$$= \left[6\ \textbf{mol} \times \left(-412.9\ kJ\,mol^{-1}\right) + 6\ \textbf{mol} \times \left(-285.8\ kJ\,mol^{-1}\right)\right]$$

$$- \left[1\ \textbf{mol} \times \left(-1273.3\ kJ\,mol^{-1}\right) + 6\ \textbf{mol} \times \left(0\ kJ\,mol^{-1}\right)\right] = -2918.9\ kJ$$

$$\Delta U° = \Delta H° - P\Delta V = \Delta H° - \Delta nRT$$

$$= -2918.9\ \text{kJ} - (-6\ \text{mol}) \times (8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}) \left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)(298\ \text{K})$$

$$= -2918.9\ \text{kJ} + 14.9\ \text{kJ} = -2904.0\ \text{kJ}$$

In its standard state, <u>elemental sulphur</u> (rhombic), with the help of a catalyst, <u>combusts</u> to produce <u>gaseous SO<u>3</u></u>. This reaction was performed with <u>excess sulphur</u> in a <u>closed container</u> with thin, flexible walls that was <u>submerged in 3.00 L of water</u> at <u>20.0 °C</u> with a <u>constant external pressure of 1.00 bar</u>. After the reaction, the temperature of the water <u>increased by 2.1 °C</u>, and from the change in water height, the <u>work</u> was calculated as <u>80.0 J</u>. Calculate:

i)   the mass of oxygen, in g, that reacted,

ii) ΔU, in kJ, for the reaction,

iii)   the standard enthalpy of formation for $SO_3(g)$, in kJ/mol. ($c_{p,water}$ = 4.184 J/(g ° C))

Bond energies/enthalpies

Enthalpy (Energy) required to break and form bonds over course of a reaction: ΔH

$$H_2(g) \rightarrow H(g) + H(g) \qquad \Delta H^0 = +436.4 \text{ kJ mol}^{-1}$$

Bond energies and standard enthalpies of formation are included in the Chemistry Data Sheet on the main CHEM 154 Canvas website.

Bond Enthalpies

$$\Delta H^0 = \sum E_{bond} \text{ (reactants)} - \sum E_{bond} \text{ (products)}$$

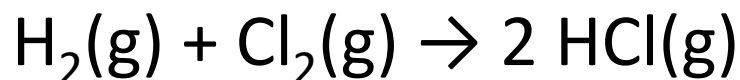Bonds Broken
(Energy input)

Bonds Formed
(Energy output)

Bond enthalpies can be used to get approximate values for enthalpies of reactions

Not ALL bond enthalpies are made equal – they are averaged over MANY compounds.

Consider the reaction of H_2 and Cl_2 gas to form gaseous HCl:

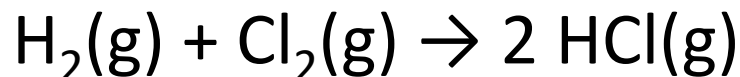$$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$$

The H-H and Cl-Cl bond enthalpies are determined to be 435 and 240 kJ mol^{-1} respectively. If the reaction as written releases 185 kJ of energy, determine the H-Cl bond enthalpy.

A) 245 kJ
B) 430 kJ
C) 490 kJ
D) 860 kJ

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The H-H and Cl-Cl bond enthalpies are determined to be 435 and 240 kJ mol^{-1} respectively. If the reaction as written releases 185 kJ of energy, determine the H-Cl bond enthalpy.

A) 245 kJ

✓ B) 430 kJ $435 + 240 = 2X - 185$

C) 490 kJ $\rightarrow X = 430$

D) 860 kJ

Blueprint question

Calorimetry

$\Delta H = mC\, \Delta T$

Sample of water with mass = m
Heat capacity = C
ΔT can be measured

Corn ethanol is burned to release energy and power engines – but how much energy is released by this combustion?

Measure mass of ethanol burned to produce the heat change of water

$\Delta H_{water} = \Delta H_{ethanol}$

(calculate molar enthalpy using mass of ethanol)

Blueprint question

Calorimetry
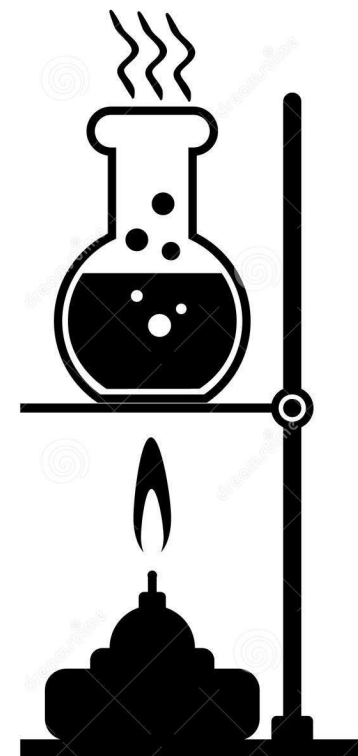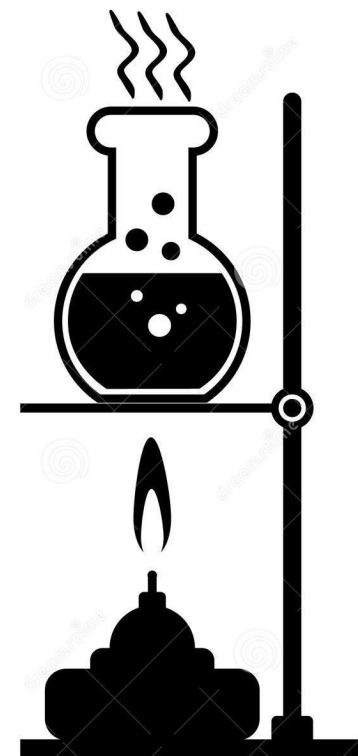
$\Delta H = mC \, \Delta T$

Sample of water with mass = m
Heat capacity = C
ΔT can be measured

Measure mass of ethanol
burned to produce the
heat change of water

$\Delta H_{water} = \Delta H_{ethanol}$

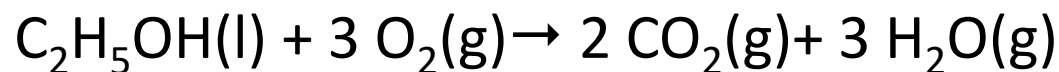(calculate molar enthalpy using mass of ethanol)

Corn ethanol is burned to release energy and power engines – but how much energy is released by this combustion?

Blueprint question

Hess' Law – Standard molar enthalpies

$$\Delta H^0 = \sum v_p \cdot \Delta H_f^0 (\text{products}) - \sum v_r \cdot \Delta H_f^0 (\text{reactants})$$

$$C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(g)$$

$\Delta H° = [(2 \times -393.5) + (3 \times -241.8)]$ kJ mol^{-1} - $[-277.6 + (3 \times 0)]$ kJ mol^{-1}

$\Delta H° = -1234.8$ kJ mol^{-1}

Compound	$\Delta H°_f$ (kJ mol^{-1})
$C_2H_5OH(l)$	- 277.6
$O_2(g)$	0
$CO_2(g)$	- 393.5
$H_2O(g)$	- 241.8

How much energy is -1234.8 kJ/mol?

What can you do with 1234 kJ?

- Heat approximately 3.5 L of water from 15 °C to 100 °C

- Light a 100W bulb for 3.4 hours

- Power your cell phone for approximately 2 months!!!

- Less than 1/3 the daily recommended calorie allowance

- Lift an elephant to a height of 31 metres

https://www.forbes.com/sites/christopherhelman/2013/09/07/how-much-energy-does-your-iphone-and-other-devices-use-and-what-to-do-about-it/#1acac522f702

https://www.betterhealth.vic.gov.au/health/healthyliving/kilojoules-and-calories

Brown, B. S. What does the kilojoule look like? *Biochemical Education,* **1979,** *7*, 4, 88-89.