Thermochemistry 3:
Applications of the First Law

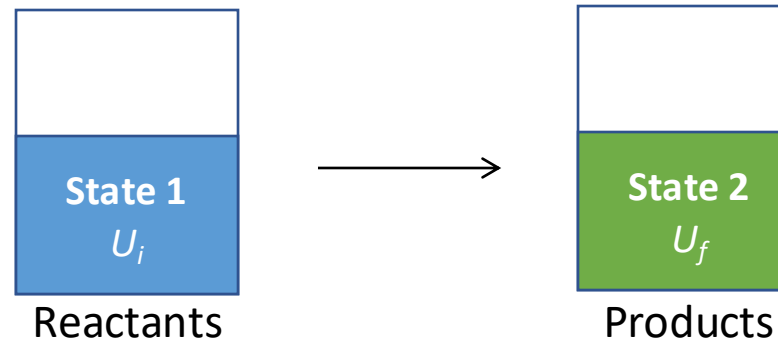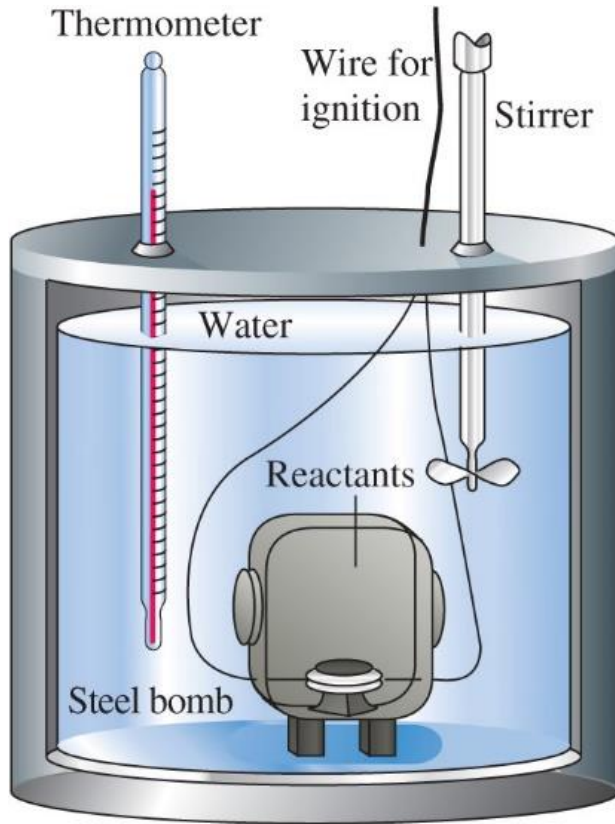| Learning Objective	Openstax 2e Chapter
Enthalpy (H)	5.3
Hess's Law	5.3

Suggested Practice Problems

Chapter 5 Exercises – Questions: 49, 53*, 59, 63, 65, 67

Answers can be found in the Chapter 5 Answer Key

*Use Appendix E for the heat capacity of water

Application of the First Law to Chemical and Physical Changes (Constant Volume)

$$\Delta U = U_f - U_i$$
$$\Delta U = q + w$$

Reaction at <u>constant volume</u> in a bomb calorimeter, $w = 0$.
Thus,

$$\Delta U = q_{rxn} + 0 = q_{rxn} = q_V$$

Heat measured at constant volume gives internal energy change ΔU.
So, heat transferred in a constant volume process appears to be a state function!

Application of the First Law to Chemical and Physical Changes (Constant Pressure)

Most reactions we see occur at <u>constant ambient pressure</u>!
- in a beaker in a lab
- cooking and baking
- burning wood/candles
- yeast making bread
- yeast fermenting beer
- biological processes
- etc.

We know that $w = -P_{ext}\Delta V$ at <u>constant pressure</u>:

$$\Delta U = q_P - P_{ext}\Delta V$$

$$U_f - U_i = q_P - (P_{ext}V_f - P_{ext}V_i)$$

$$U_f - U_i = q_P - P_{ext}V_f + P_{ext}V_i$$

$$(U_f + P_{ext}V_f) - (U_i + P_{ext}V_i) = q_P$$

Since P_{ext} is constant and $P_i = P_f = P_{ext}$, we get,

$$(U_f + P_f V_f) - (U_i + P_i V_i) = q_P$$

Enthalpy H and q_P

At constant P: $$(U_f + P_fV_f) - (U_i + P_iV_i) = q_P$$

The state of n moles of an ideal gas is defined by P, V, and T and $PV = nRT$.

P, V, and T are all **state variables** that specify the state of an ideal gas. They are state variables for other systems as well. Since P and V are state variables and U is a state function, $U_f + P_fV_f$ is a state function.
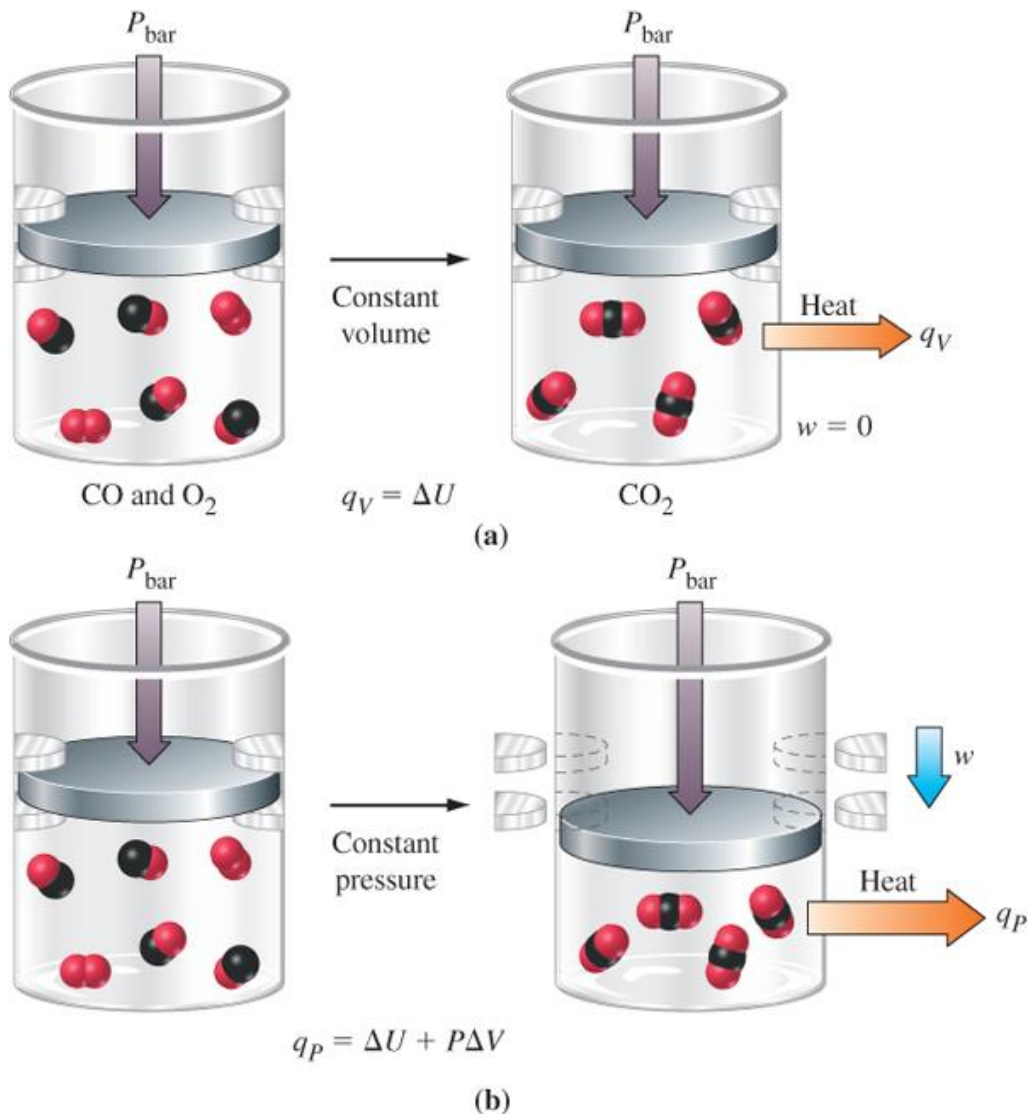
We define a new state function enthalpy:

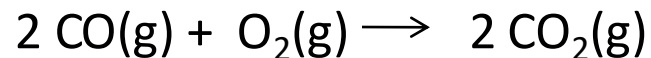$$H = U + PV$$

At constant P: $$\Delta H = H_f - H_i = q_P$$

Therefore, ΔH can be determined by measuring the heat released or absorbed during a constant-P process or reaction!

Comparison of q_v and q_p

P_{bar}

Constant volume

Heat → q_V

$w = 0$

CO and O_2 $q_V = \Delta U$ CO_2

(a)

P_{bar}

Constant pressure

Heat → q_P

w

$q_P = \Delta U + P\Delta V$

(b)

3 moles reactants   2 moles products

$$2\ CO(g) + O_2(g) \longrightarrow 2\ CO_2(g) \qquad q_v = \Delta U = -563.5\ kJ/mol$$

How does q_p relate to q_v?

Remember: $q_v = \Delta U$, $q_p = \Delta H$, and $\Delta H = \Delta U + \Delta(PV)$

$$q_p = q_v + \Delta(PV)$$

If the reaction is done at <u>constant P and T</u> (25 °C), what is q_p?

$$q_p = q_v + \Delta(PV) = q_v + \Delta(nRT) = \Delta U + \Delta n \cdot RT$$

For the above reaction, $\Delta n = -1$

$$q_p = -563.5\ kJ/mol + \frac{(-1) \times 8.314\ J/(mol\ K) \times 298.15\ K}{1000\ J/kJ}$$

$$= -566.0\ kJ/mol$$

Thus, $\Delta H = q_p = -566\ kJ/mol$

Here, work is done on the system by the surroundings.

Note: Often, $\Delta(PV)$ *is quite small compared to ΔU and $\Delta U \approx \Delta H$*

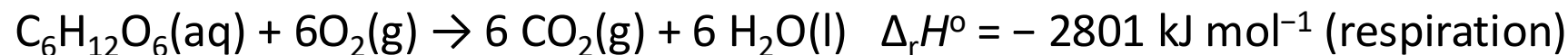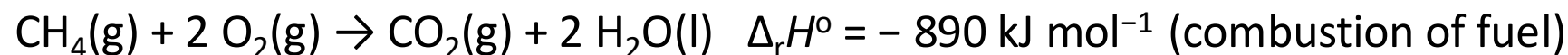# Standard States and Standard Enthalpy of Reaction

- The **standard state** is the state of a material at a defined set of conditions

  - pure gas at exactly 100 kPa pressure

  - pure solid or liquid in its most stable form at exactly 100 kPa pressure and temperature of interest (usually 25°C)

  - substance in a solution with concentration 1 M

- The **standard reaction enthalpy, $\Delta_r H^o$,** is the enthalpy change of a reaction when all reactants and products are in their standard states
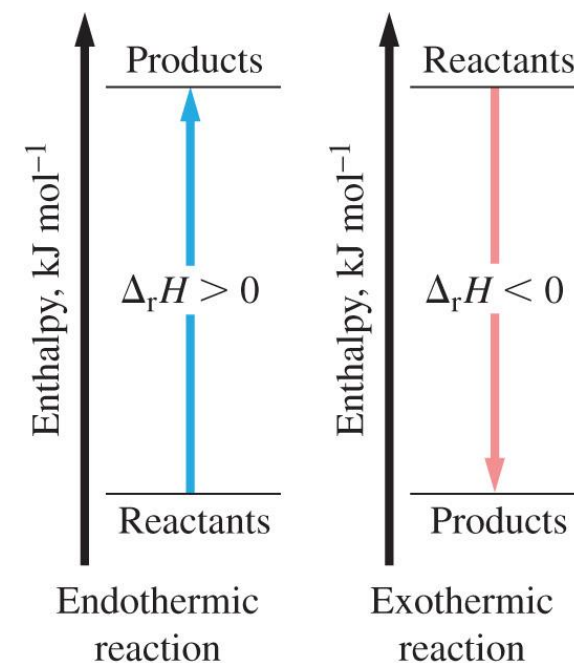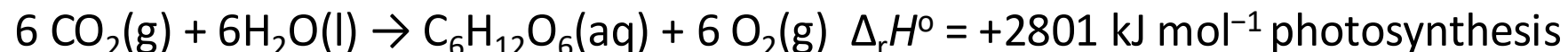
Endothermic and Exothermic Reactions

When $\Delta H < 0$, heat is being released by the system

- Reactions that release heat are called **exothermic reactions**

  $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ $\Delta_r H^o = -890$ kJ mol^{-1} (combustion of fuel)

  $C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$ $\Delta_r H^o = -2801$ kJ mol^{-1} (respiration)

When $\Delta H > 0$, heat is being absorbed by the system

- Reactions that absorb heat are called **endothermic reactions**

  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $\Delta_r H^o = +178$ kJ mol^{-1} decomposition

  $6\ CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6\ O_2(g)$ $\Delta_r H^o = +2801$ kJ mol^{-1} photosynthesis
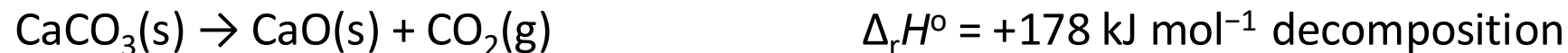
Example 1: The combustion of methane, CH_4, the main component of natural gas, has a $\Delta_r H° = -890.3$ kJ/mol. What quantity of heat, in kJ, is released in the complete combustion of 1400 L methane (at 18.6°C and 102 kPa)? This is approximately the average daily household consumption during Fall in Canada.

Known: $\Delta_r H° = -890.3$ kJ/mol., so we need number of moles for CH_4 in 1400 L

$P = 102$ kPa, $V = 1400$ L

$T = 18.6 + 273.15$ K $= 291.8$ K, $R = 8.3145$ kPa·L/mol·K

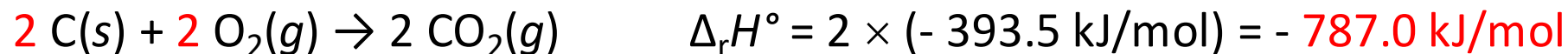$$n = \frac{PV}{RT} \longrightarrow n = \frac{102\ kPa \times 1400\ L}{8.3145\frac{kPa \cdot L}{mol \cdot K} \times 291.8\ K} = 58.87\ mol$$

$q_P = -890.3$ kJ/mol x 58.87 mol $= -5.2 \times 10^4$ kJ

(from 1400 L, we assume to have 2 sig figs)

Relationships Involving $\Delta_r H$ and Hess's Law

- $\Delta_r H^o$ depends upon the way the reaction is written

  When reaction is multiplied by a factor, $\Delta_r H^o$ is multiplied by that factor because $\Delta_r H^o$ is extensive
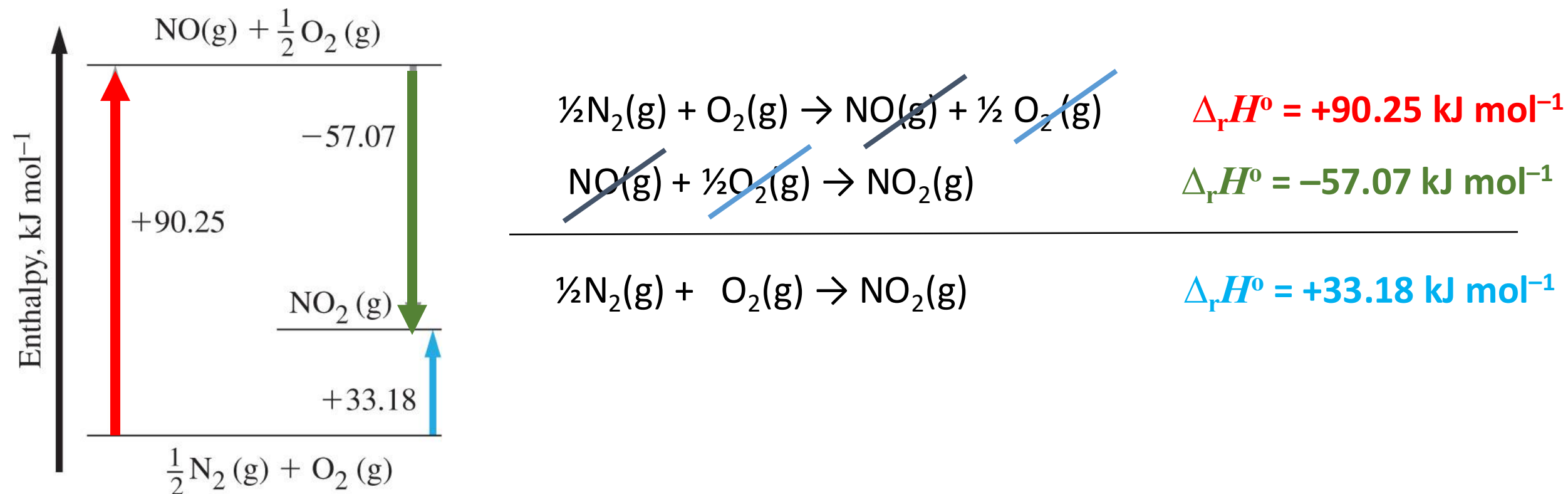
$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta_r H^o$ = - 393.5 KJ/mol
2 $C(s)$ + 2 $O_2(g) \rightarrow$ 2 $CO_2(g)$	$\Delta_r H°$ = 2 × (- 393.5 kJ/mol) = - 787.0 kJ/mol

$N_2(g) + O_2(g) \rightarrow$ 2 $NO(g)$	$\Delta_r H^o$ = + 180.50 kJ mol^{-1}
½$N_2(g)$ + ½$O_2(g) \rightarrow NO(g)$	$\Delta_r H^o$ = + 90.25 kJ mol^{-1}

- $\Delta_r H^o$ changes sign when the process is reversed

$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta_r H^o$ = - 393.5 KJ/mol
$CO_2(g) \rightarrow C(s) + O_2(g)$	$\Delta_r H^o$ = + 393.5 kJ/mol

Hess's Law: If a reaction can be expressed as a series of steps, then the $\Delta_r H$ for the overall reaction is the sum of the $\Delta_r H$ values for each step.
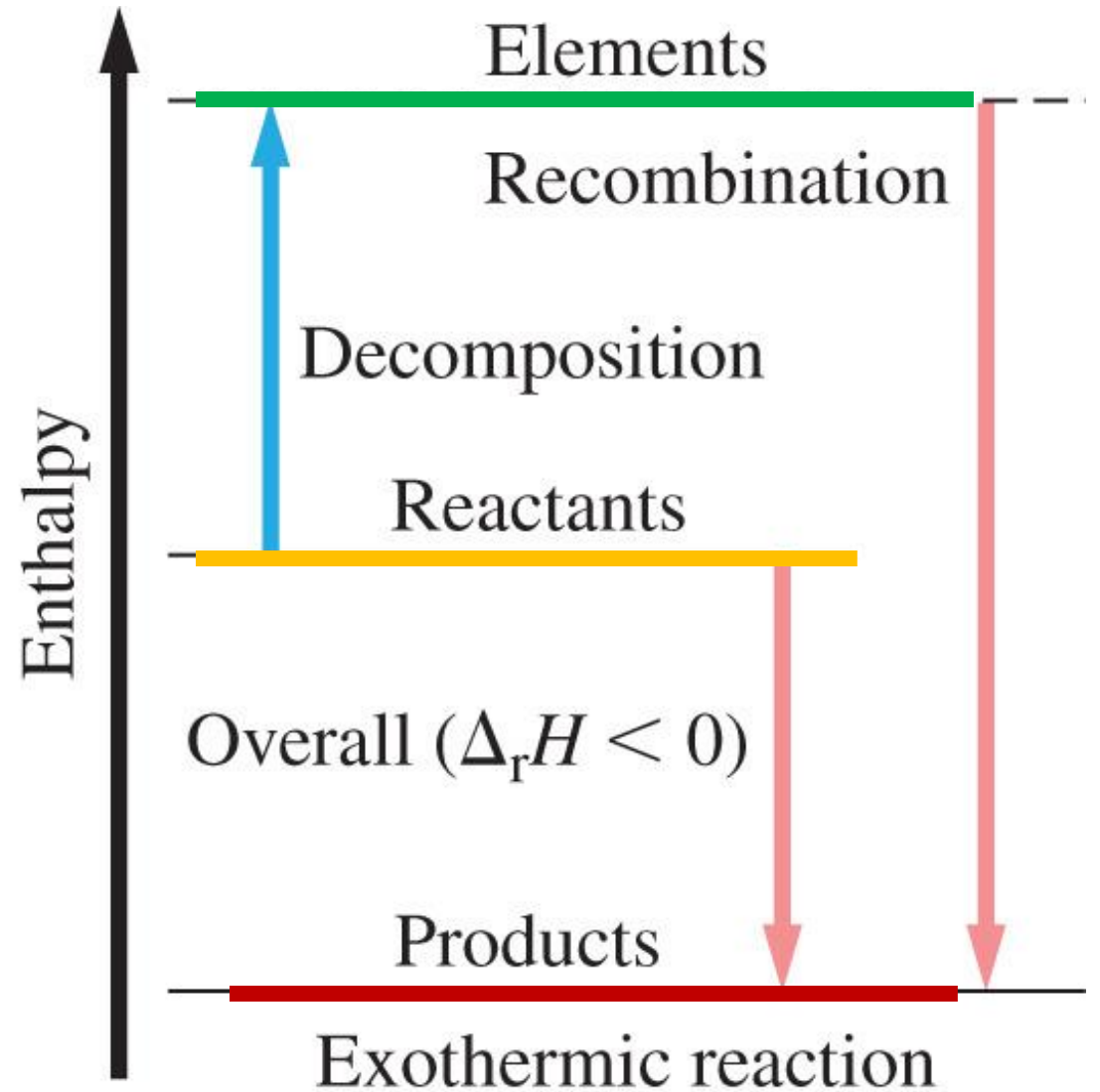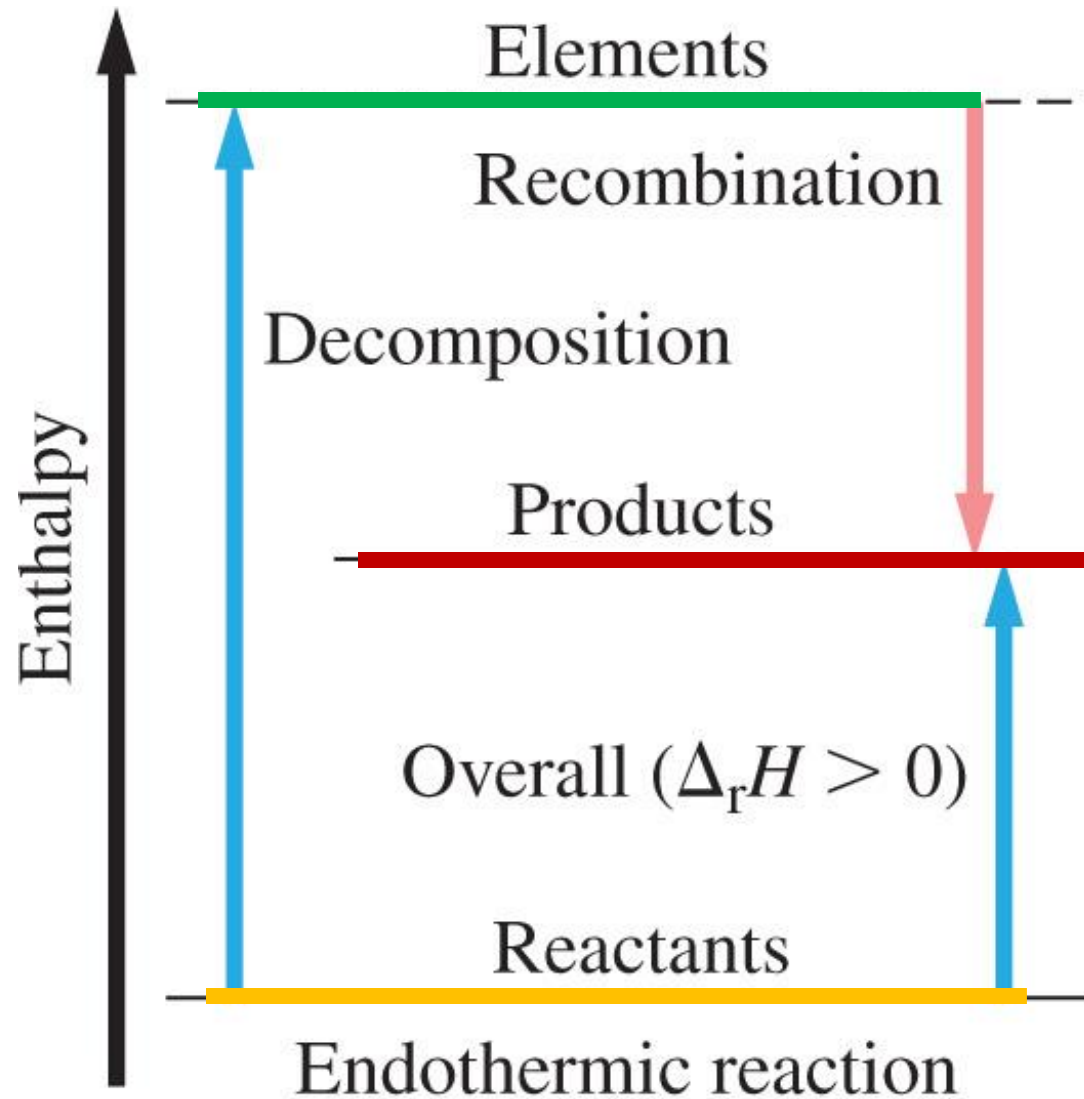
Application of Hess's Law

Hess's Law is simply a consequence of the state function property of enthalpy.

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO(g) + \frac{1}{2}O_2(g) \qquad \Delta_rH^o = +90.25 \text{ kJ mol}^{-1}$$

$$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g) \qquad \Delta_rH^o = -57.07 \text{ kJ mol}^{-1}$$

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta_rH^o = +33.18 \text{ kJ mol}^{-1}$$
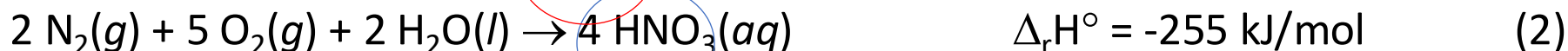
If a process occurs in stages or steps (even hypothetically), the enthalpy change for the overall process is the sum of the enthalpy changes for the individual steps.

Compute $\Delta_r H$ using Hess's Law

Example 2: Application of Hess's Law
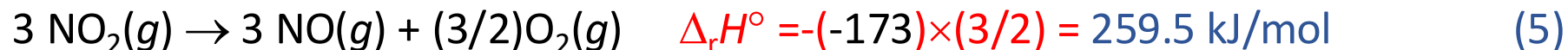
Given the following information:

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g) \qquad \Delta_r H° = -173\ \text{kJ/mol} \qquad (1)$$

$$2\ N_2(g) + 5\ O_2(g) + 2\ H_2O(l) \rightarrow 4\ HNO_3(aq) \qquad \Delta_r H° = -255\ \text{kJ/mol} \qquad (2)$$

$$N_2(g) + O_2(g) \rightarrow 2\ NO(g) \qquad \Delta_r H° = +181\ \text{kJ/mol} \qquad (3)$$

Calculate the $\Delta_r H°$ for the following reaction:

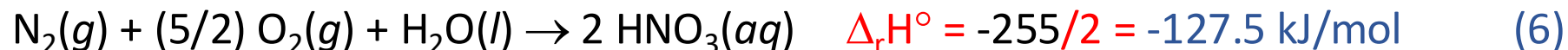$$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g) \qquad \Delta_r H° = ? \qquad (4)$$

Solution: Identify in your final reaction a reactant and a product that appear only once in the provided reactions. They are $NO_2(g)$ and HNO_3 in this case.
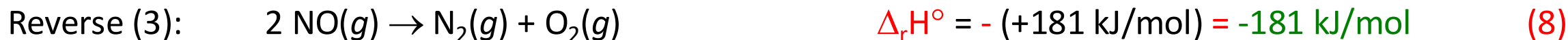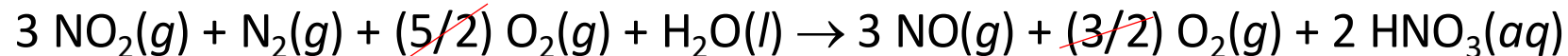
This means that you must reverse (1) and then multiply it by 3/2.

$$3\ NO_2(g) \rightarrow 3\ NO(g) + (3/2)O_2(g) \qquad \Delta_r H° = -(-173)\times(3/2) = 259.5\ \text{kJ/mol} \qquad (5)$$

Multiplying (2) by 1/2 gives:

$$N_2(g) + (5/2)\ O_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) \qquad \Delta_r H° = -255/2 = -127.5\ \text{kJ/mol} \qquad (6)$$

Adding (5) and (6) results in

$$3\ NO_2(g) + N_2(g) + (5/2)\ O_2(g) + H_2O(l) \rightarrow 3\ NO(g) + (3/2)\ O_2(g) + 2\ HNO_3(aq)$$

$$3\ NO_2(g) + N_2(g) + O_2(g) + H_2O(l) \rightarrow 3\ NO(g) + 2\ HNO_3(aq) \qquad \Delta_r H° = 259.5 + (-127.5) = 132\ \text{kJ/mol} \qquad (7)$$

Reverse (3): $\qquad 2\ NO(g) \rightarrow N_2(g) + O_2(g) \qquad \Delta_r H° = - (+181\ \text{kJ/mol}) = -181\ \text{kJ/mol} \qquad (8)$

Adding (7) and (8) gives the final targeted (4): $3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$,

$$\Delta_r H° = 132 + (-181) = -49\ \text{kJ/mol}$$