Outline

- Nature of Energy

- First Law Calculations

- Enthalpy and Calorimetry

- Hess' Law

- Enthalpy of Formation

Nature of Energy

Thermodynamics is the study of energy and its interconversions

Energy is the capacity to do work or to transfer heat

Potential Energy is the energy of position…

Kinetic Energy is the energy of motion…

Internal Energy (E) is the kinetic and potential energies of particles in the system

The system is the part of the universe we want to focus on

The surroundings is the rest of the universe

Work is defined as force acting over a distance

   It is a process by which energy is transferred from one object to another

Heat is the transfer of energy between two objects due to a temperature difference

   Temperature is a measure of the random motion of the molecules in an object

First Law of Thermodynamics

   The energy of the universe is constant, and a system's internal energy can only change by work or heat transfer

$\Delta E = q + w$

ΔE change in internal energy
+q   heat transferred to a system
+w   work done on a system

Calculate ΔE for a system that gains 18.6 J of heat and does 1.36 J of work on the surroundings.

$\Delta E = q + w = 18.6\,J - 1.36\,J = 17.\underline{2}4\,J = \underline{17.2\,J}$

What if system lost 5.6 kJ of heat and did 467 J of work on the surroundings?

$\Delta E = q + w = -5.6\,kJ - 0.467\,kJ = -6.\underline{0}67\,kJ = \underline{-6.1\,kJ}$

The change in internal energy of a system is a <u>state function</u>

State Function

A property whose numerical value is independent of the pathway

ΔE the same no matter the pathway

Path Function

A property whose numerical value is dependent on the pathway

q   depends on the pathway

w   depends on the pathway

First Law Calculations

1. Calculating Work

   Reactions with gaseous products do work by expanding against an external pressure...

   work $=$ force x distance

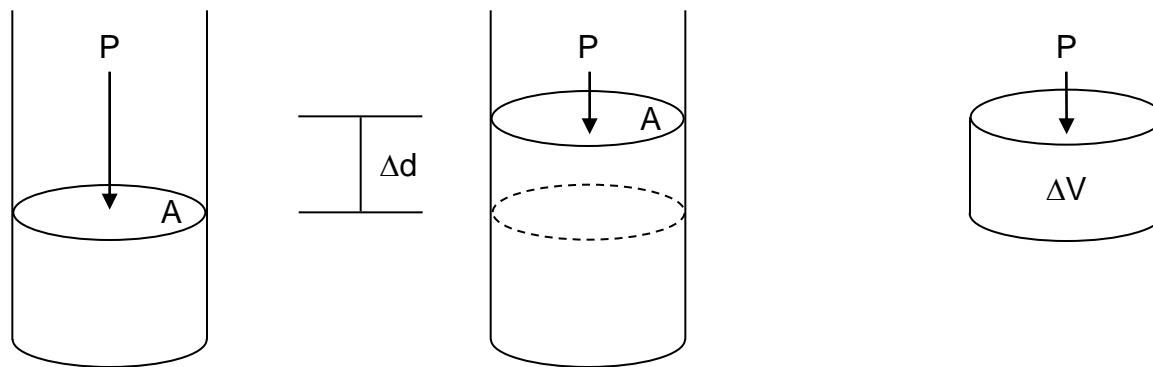 $$w = F \text{ x } \Delta d \qquad (\Delta d = d_f - d_i)$$

   pressure $=$ force $\div$ area

   $$P = F \div A \qquad \Rightarrow \qquad F = P \text{ x } A$$

   The work due to an expanding gas is...

   $$w = -P \text{ x } A \text{ x } \Delta d$$

   $$w = -P \text{ x } \Delta V \qquad (\Delta V = V_f - V_i)$$

When a gas expands from 42 L to 56 L against a pressure of 18 atm, how much work has it done?

$$w = -P\Delta V = -(18\,\text{atm})(14\,\text{L}) = -250\,\text{L atm}$$

$$w = -250\,\text{L atm} \times \frac{101.3\,\text{J}}{1\,\text{L atm}} = -2.5 \times 10^4\,\text{J}$$

A balloon is expanded from 3.00×10^6 L to 3.50×10^6 L against a pressure of 1.00 atm by adding 1.1×10^8 J through heat transfer. Calculate ΔE.

$\Delta E = q + w$

$q = +1.1 \times 10^8$ J

$w = -P\Delta V = -P(V_f - V_i)$

$= -(1.00 \text{ atm})(3.50 \times 10^6 \text{ L} - 3.00 \times 10^6 \text{ L}) = -5.00 \times 10^5 \text{ L atm}$

$= -5.00 \times 10^5 \text{ L atm} \times \dfrac{101.3 \text{ J}}{1 \text{ L atm}} = -5.07 \times 10^7 \text{ J}$

$\Delta E = +1.1 \times 10^8 \text{ J} - 5.07 \times 10^7 \text{ J} = +5.9 \times 10^7 \text{ J} = +6 \times 10^7 \text{ J}$

2. Calculating Heat

Exothermic processes are those where heat transfers out of the system… the surroundings heat up (q is –)

Endothermic processes are those where heat transfers into the system… the surroundings cool off (q is +)

Specific Heat Capacity
   The amount of heat needed to raise the temperature of 1 g of a substance 1 ^{o}C at constant pressure

   heat transferred = q = $mC\Delta T$

1.00 mole of gas is in a 2.50 L container at 20.0 °C. The temperature increases to 35.0 °C and the container expands to 3.75 L against a constant pressure of 1.00 atm. The molar heat capacity of the gas is 10 J/mol °C. Find q, w, and ΔE.

$$q_p = n\overline{C}\Delta T = (1.00\,\text{mol})(10.0\,\text{J/mol}\,^\circ\text{C})(15.0\,^\circ\text{C}) = \underline{150.\,\text{J}}$$

$$w = -P\Delta V = -(1.00\,\text{atm})(1.25\,\text{L})(101.3\,\text{J/L atm}) = \underline{-127\,\text{J}}$$

$$\Delta E = q + w = 150.\,\text{J} - 127\,\text{J} = \underline{23\,\text{J}}$$

Enthalpy

Consider first law at constant pressure,

$$\Delta E = q_p + w_p$$

$$\Delta E = q_p - P\Delta V$$

$$q_p = \Delta E + P\Delta V$$

$\Delta E + P\Delta V$ is a state function, renamed as ΔH, the <u>change in enthalpy</u>

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

For chemical reactions: $\Delta H_{rxn} = H_{products} - H_{reactants}$

Calorimetry

Heat flow from a chemical reaction is measured with a <u>calorimeter</u>

A calorimeter traps heat...

Heat from a chemical reaction can be transferred completely to a water solution if both are contained in the calorimeter

The heat absorbed by a water solution is

$$q_{soln} = m_{soln}C_{soln}\Delta T_{soln}$$

The heat absorbed by the water solution is equal in magnitude to the heat lost by the reaction, but opposite in sign

$$q_{rxn} = -q_{soln}$$

50.0 mL of 1.00 M HCl are mixed with 25.0 mL of 1.50 M NaOH at 25.0 ^{o}C in a calorimeter. After mixing, the solution was 31.6 ^{o}C, had a mass of 75.5 g, and (because it is mostly water) has a heat capacity of 4.184 J/g ^{o}C. Find the heat of the reaction.

$$q_{sol'n} = C_{sol'n}m_{sol'n}\Delta T_{sol'n}$$

$$= (4.184 \text{ J/g } ^{\circ}C)(75.5 \text{ g})(6.6 \text{ }^{\circ}C) = 2100 \text{ J}$$

$$q_{rxn} = - q_{sol'n}$$

$$= - (2100 \text{ J}) = \underline{- 2100 \text{ J}}$$

Reaction occurs under constant pressure, so $q_p = \Delta H$ and...

$$\Delta H_{rxn} = - 2100 \text{ J}$$

ΔH_{rxn}'s are usually given as J per mole of reactant or product
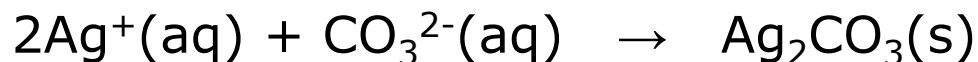
Calculate the ΔH_{rxn} in J/mol of NaCl

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
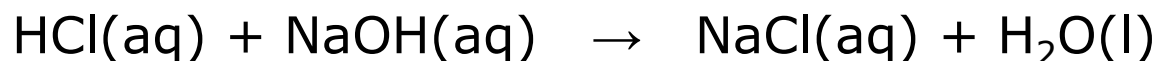
$$0.0250\,L \times \frac{1.50\,mol\,NaOH}{L} \times \frac{1\,mol\,NaCl}{1\,mol\,NaOH} = 0.0375\,mol\,NaCl$$

$$0.0500\,L \times \frac{1.00\,mol\,HCl}{L} \times \frac{1\,mol\,NaCl}{1\,mol\,HCl} = 0.0500\,mol\,NaCl$$

$$\frac{-2100\,J}{0.0375\,mol\,NaCl} = -56000\,J/mol\,NaCl \quad or \quad -56\,kJ/mol\,NaCl$$

The ΔH for the following reaction is -45.0 kJ/mol:

$$2Ag^+(aq) + CO_3^{2-}(aq) \rightarrow Ag_2CO_3(s)$$

A mixture of two solutions is prepared by combining 25.0 mL of 0.880 M Ag^+ and 25.0 mL of 0.525 M CO_3^{2-}, both at 22.0 °C. What is the final temperature of the mixture? (The mass of the solution is 50.7 g)

$$0.0250 \, L \times \frac{0.880 \, mol \, Ag^+}{L} \times \frac{1 \, mol \, Ag_2CO_3}{2 \, mol \, Ag^+} = 0.0110 \, mol \, Ag_2CO_3$$

$$0.0250 \, L \times \frac{0.525 \, mol \, CO_3^{2-}}{L} \times \frac{1 \, mol \, Ag_2CO_3}{1 \, mol \, CO_3^{2-}} = 0.0131 \, mol \, Ag_2CO_3$$

The ΔH_{rxn} for this calorimeter…

$$0.0110 \text{ mol Ag}_2\text{CO}_3 \times \frac{-45.0 \text{ kJ}}{1 \text{ mol Ag}_2\text{CO}_3} = -0.495 \text{ kJ} \quad (\text{or} - 495 \text{ J})$$

$$q_{sol'n} = -q_{rxn} = -(-495 \text{ J}) = 495 \text{ J}$$

$$q_{sol'n} = C_{sol'n}m_{sol'n}\Delta T_{sol'n}$$

$$\Delta T_{sol'n} = \frac{q_{sol'n}}{C_{sol'n}m_{sol'n}} = \frac{495 \text{ J}}{(4.184 \text{ J/g }^o\text{C})(50.7 \text{ g})} = 2.33 \text{ }^o\text{C}$$

$$\Delta T = T_f - T_i \quad \Rightarrow \quad T_f = \Delta T + T_i \quad \Rightarrow \quad T_f = 2.33 \text{ }^o\text{C} + 22.0 \text{ }^o\text{C} = \underline{24.3 \text{ }^o\text{C}}$$

ΔH_{rxn}'s (heats of reactions) are experimentally determined with calorimeters
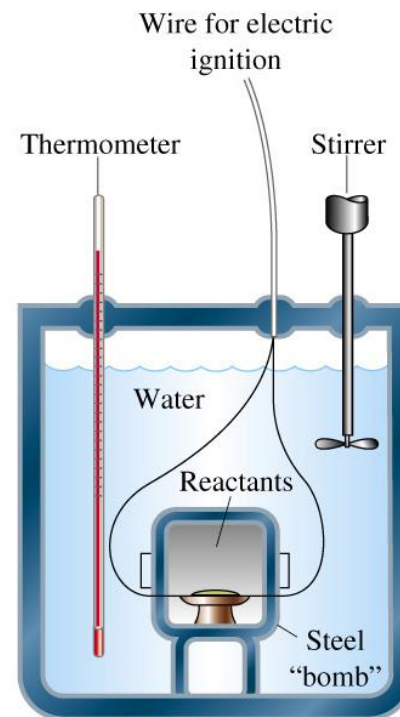
When q is measured in a constant volume calorimeter, it equals the state function ΔE

$\Delta E = q + w$

$\Delta E = q - P\Delta V$

$\Delta E = q_v$

A constant volume calorimeter is called a
bomb calorimeter

Wire for electric
ignition

Thermometer

Stirrer

Water

Reactants

Steel
"bomb"

To measure the energy of combustion of C_8H_{18}, 0.5269 g C_8H_{18} are burned in a bomb calorimeter that has a heat capacity of 11.3 kJ/ºC. If the calorimeter's temperature increases 2.25 ºC, find q_{comb} in kJ/mol C_8H_{18}

$$q_{calor} = C_{calor}\Delta T_{calor} = (11.3\,kJ/°C)(2.25\,°C) = 25.4\,kJ$$

$$q_{comb} = -q_{calor} = -(25.4\,kJ) = -25.4\,kJ$$

$$0.5269\,g\,C_8H_{18} \times \frac{1\,mol\,C_8H_{18}}{114.26\,g\,C_8H_{18}} = 0.004611\,mol\,C_8H_{18}$$

$$\frac{-25.4\,kJ}{0.004611\,mol\,C_8H_{18}} = -5510\,kJ/mol\,C_8H_{18}$$

The energy of combustion of benzene is -41.8 kJ/g. If a 0.3143 g sample of benzene is burned in a bomb calorimeter with a heat capacity of 10.7 kJ/^{o}C and an original temperature of 21.42 ^{o}C, find the final temperature of the bomb calorimeter.

$$q_{comb} = 0.3143 \text{ g C}_6\text{H}_6 \times \frac{-41.8 \text{ kJ}}{\text{g C}_6\text{H}_6} = -13.1 \text{ kJ}$$

$$q_{calor} = -q_{comb} = -(-13.1 \text{ kJ}) = 13.1 \text{ kJ}$$

$$q_{calor} = C_{calor}\Delta T_{calor} \quad \Rightarrow \quad \Delta T_{calor} = \frac{q_{calor}}{C_{calor}} = \frac{13.1 \text{ kJ}}{10.7 \text{ kJ}/^{\circ}\text{C}} = 1.22 \,^{\circ}\text{C}$$

$$\Delta T = T_f - T_i \quad \Rightarrow \quad T_f = \Delta T + T_i = 1.22 \,^{\circ}\text{C} + 21.42 \,^{\circ}\text{C} = \underline{22.64 \,^{\circ}\text{C}}$$

Extensive Properties depend on the amount of material...

Enthalpy (ΔH) is an extensive property

    burn 1 gallon of gasoline: ΔH_{rxn} = −115 MJ

    burn 2 gallons of gasoline: ΔH_{rxn} = −230 MJ

For... $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ ΔH_{rxn} = −92 kJ
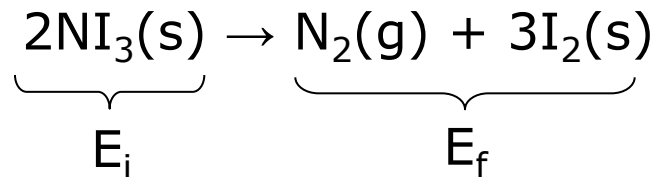
The ΔH value means −92 kJ per 1 mole N_2 reacted...

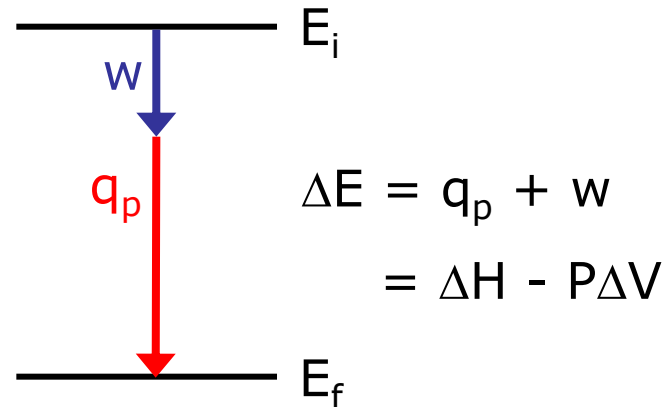   or −92 kJ per 3 moles H_2 reacted...
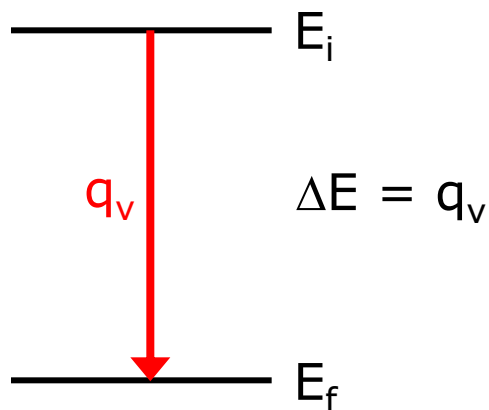
       or −92 kJ per 2 moles of NH_3 produced!

ΔH versus ΔE

Reactants and products in chemical reaction (system) can be thought of as initial and final states

$$2NI_3(s) \rightarrow N_2(g) + 3I_2(s)$$

$E_i \qquad E_f$

Two different paths can lead to the same internal energy change in system

$q_v \qquad \Delta E = q_v$

$q_p \qquad w \qquad \Delta E = q_p + w$

$$= \Delta H - P\Delta V$$

$E_i \qquad E_f$

Calculate the difference in kJ between ΔE and ΔH for the decomposition of one mole of ammonium chloride at 25°C.

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

$$\Delta E = \Delta H - P\Delta V$$

$$\Delta E - \Delta H = -P\Delta V = -\Delta nRT = -(n_f - n_i)RT$$

$$= -(2-0)(8.314\ J/mol\,K)(298\,K)$$

$$= \underline{-4.95\,kJ}$$

$\Delta H = +176.0$ kJ

$\Delta E = +176.0$ kJ $-$ 4.95 kJ $=$ 171.0 kJ ($<$ 3% difference!)

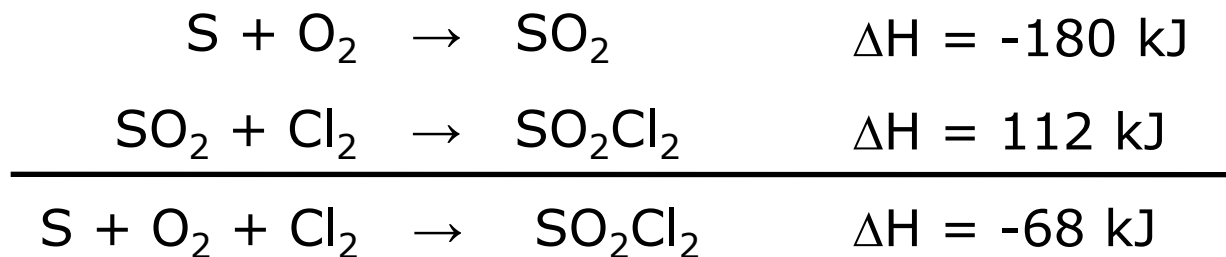Pressure-volume work is usually insignificant, therefore $\Delta H \sim \Delta E$!

Hess' Law

Because enthalpy is a state function, the change in enthalpy (ΔH) is the same whether the reaction takes place in one step or a series of steps
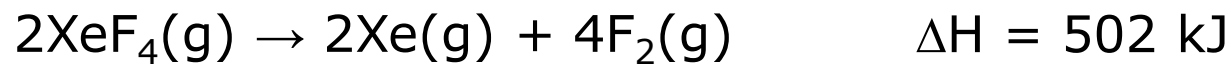
If...   reaction = reaction(1) + reaction(2) + ...

Then... $\Delta H = \Delta H_1 + \Delta H_2 + ...$

$$S + O_2 \rightarrow SO_2 \qquad \Delta H = -180 \text{ kJ}$$

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2 \qquad \Delta H = 112 \text{ kJ}$$

$$S + O_2 + Cl_2 \rightarrow SO_2Cl_2 \qquad \Delta H = -68 \text{ kJ}$$

To use Hess' Law:

1. If a reaction is reversed, the sign of ΔH is changed

2. If the coefficients in a balanced equation are multiplied by an integer, the value of ΔH is multiplied by that integer

$$Xe(g) + 2F_2(g) \rightarrow XeF_4(g) \qquad \Delta H = -251 \text{ kJ}$$

$$XeF_4(g) \rightarrow Xe(g) + 2F_2(g) \qquad \Delta H = 251 \text{ kJ}$$

$$2XeF_4(g) \rightarrow 2Xe(g) + 4F_2(g) \qquad \Delta H = 502 \text{ kJ}$$

From the reactions:

$$2O_3 \rightarrow 3O_2 \qquad \Delta H = -428 \text{ kJ}$$

$$O_2 \rightarrow 2O \qquad \Delta H = 496 \text{ kJ}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \Delta H = -199 \text{ kJ}$$

find ΔH for: $NO + O \rightarrow NO_2$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \Delta H = -199 \text{ kJ}$$

$$O \rightarrow {}^1/_2 O_2 \qquad \Delta H = -248 \text{ kJ}$$

$$^3/_2 O_2 \rightarrow O_3 \qquad \Delta H = 214 \text{ kJ}$$

$$NO + O \rightarrow NO_2 \qquad \Delta H = -233 \text{ kJ}$$
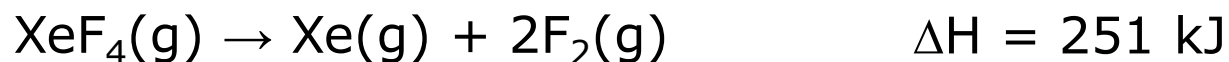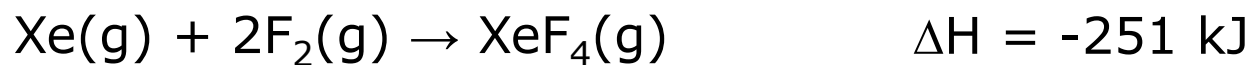
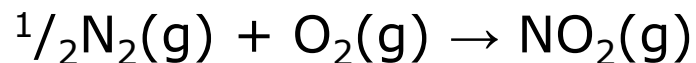# Enthalpy of Formation

Formation Reaction

A reaction that forms 1 mole of a substance from the elements composing it

The formation reaction of $NO_2(g)$:

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$$

Heat of Formation (ΔH_f)

The enthalpy for a formation reaction

Heat of Formation is usually given as <u>Standard Heat of Formation</u>, ΔH_f^o

"o" means reactants and products are in the <u>standard states</u>
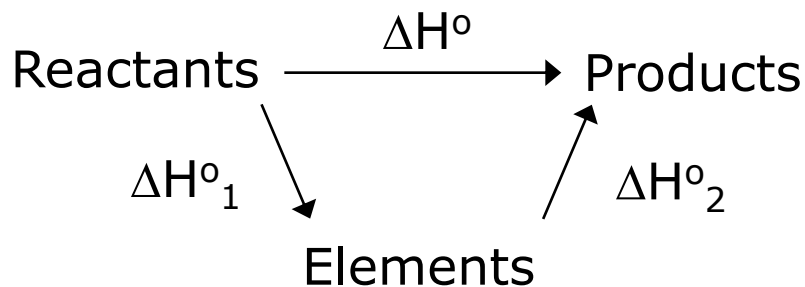
Standard State:

1. For a gas, pressure is 1 atm

2. For a substance in solution, molarity is 1 M

3. For an element...

   how it exists at room temperature and pressure!

ΔH_f^o of elements in their standard state equals zero!

ΔH_f^o's and Hess' Law can be used to calculate the ΔH^o for any reaction

$$\text{Reactants} \xrightarrow{\ \Delta H^o\ } \text{Products}$$

$\Delta H^o_1 \searrow \qquad \nearrow \Delta H^o_2$

Elements

$$\Delta H^o = \Delta H^o_1 + \Delta H^o_2$$

$$\Delta H^o_{rxn} = -\Delta H^o_{react} + \Delta H^o_{prod}$$

$$\boxed{\Delta H^o_{rxn} = \Delta H^o_{prod} - \Delta H^o_{react}}$$

ΔH^o_{rxn} equals ΔH_f^o of products, minus ΔH_f^o of reactants, each multiplied by their coefficient in the balanced equation

Find the standard enthalpy change for
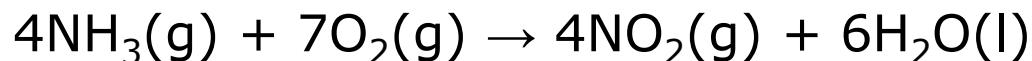
$$4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(l)$$

$\Delta H^o_{NH_3} = -46 \text{ kJ/mol} \quad \Delta H^o_{O_2} = 0 \text{ kJ/mol}$

$\Delta H^o_{NO_2} = 34 \text{ kJ/mol} \quad \Delta H^o_{H_2O} = -286 \text{ kJ/mol}$

$\Delta H^o_{rxn} = \Delta H^o_{Products} - \Delta H^o_{Reactants}$

$\Delta H^o_{rxn} = \left[(4 \text{ mol} \times 34 \text{ kJ/mol}) + (6 \text{ mol} \times -286 \text{ kJ/mol})\right]$

$\quad\quad - \left[(4 \text{ mol} \times -46 \text{ kJ/mol}) + (7 \text{ mol} \times 0 \text{ kJ/mol})\right]$

$\Delta H^o_{rxn} = \underline{-1396 \text{ kJ}}$

Find the standard enthalpy change for
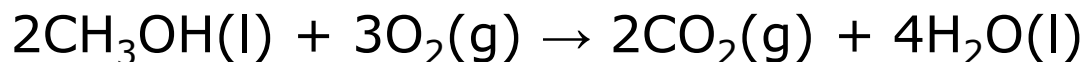
$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$$

$\Delta H^o_{CH_3OH} = -239 \text{ kJ/mol}$ $\Delta H^o_{CO_2} = -394 \text{ kJ/mol}$

$\Delta H^o_{H_2O} = -286 \text{ kJ/mol}$

$\Delta H^o_{rxn} = \Delta H^o_{Products} - \Delta H^o_{Reactants}$

$\Delta H^o_{rxn} = \left[(2 \text{ mol} \times -394 \text{ kJ/mol}) + (4 \text{ mol} \times -286 \text{ kJ/mol})\right]$

$\qquad - \left[(2 \text{ mol} \times -239 \text{ kJ/mol}) + (3 \text{ mol} \times 0 \text{ kJ/mol})\right]$

$\Delta H^o_{rxn} = \underline{-1454 \text{ kJ}}$