CALORIMETRY

- the measurement of heat. How do we measure heat flow?

0.20 mol A

When we add the reactant to water, it decomposes - heating the water.

100 g water

A -> B + C

25 °C

100 g water

A -> B + C

38 °C
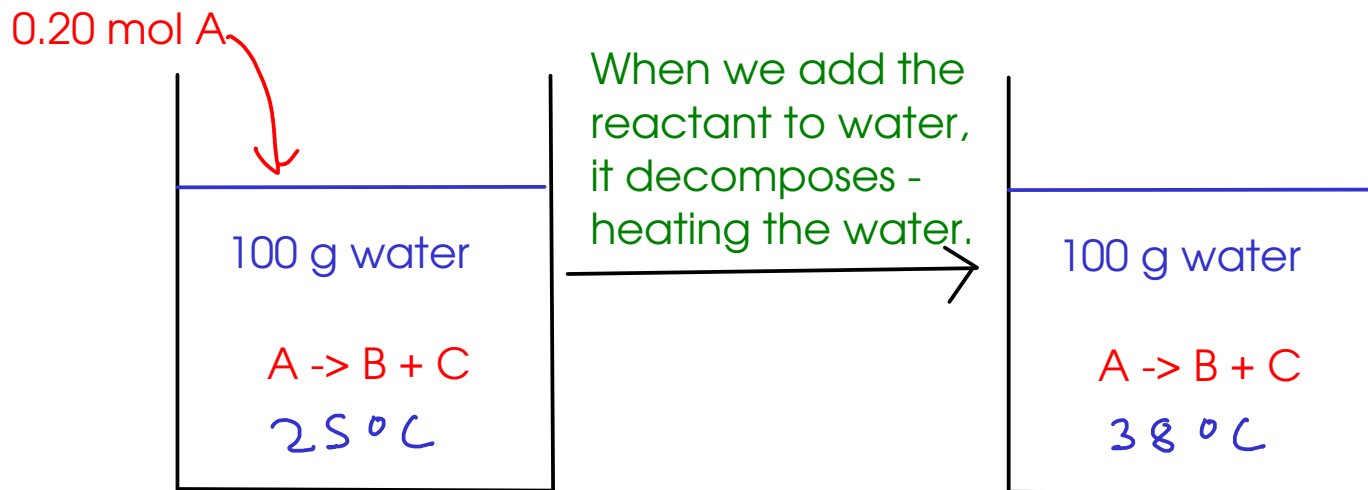
... what is Q for this reaction?

Assuming that no heat is lost from the water to the surrounding air,

$$Q_r + Q_w = 0$$

Conservation of energy. The terms add to zero because they have opposite signs.

reaction   water

... if we knew something about the WATER, we could use that to find the heat of the REACTION!

SPECIFIC HEAT

- a measured quantity. The amount of energy required to change the temperature of one gram of a particular substance by one degree Celsius.

- Specific heat information for common substances is readily available. For water,

$$4.184 \frac{J}{g\,°C} \quad = \quad 1.000 \frac{cal}{g\,°C}$$

$$Q = m \times S \times \Delta T$$

> m = mass
> s = specific heat
> ΔT = Tfinal - Tinitial

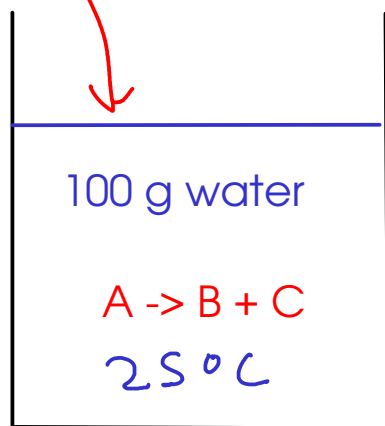This is ALWAYS final temp minus initial temp!

- For objects, like reaction vessels, you might know the HEAT CAPACITY, which is the amount of energy required to change the temperature of an object by one degree Celsius

$$\text{Units:} \quad \frac{J}{°C} \quad or \quad \frac{cal}{°C}$$

$$Q = C \times \Delta T$$

c = heat capacity

0.20 mol A

100 g water

A -> B + C

$25°C$

When we add the reactant to water, it decomposes - heating the water.

100 g water

A -> B + C

$38°C$

Specific heat of water:

$4.184 \dfrac{J}{g°C}$

$Q_r + Q_w = 0$

$Q_w = m_w S_w \Delta T_w$

$= (100g)(4.184 \dfrac{J}{g°C})(38°C - 25°C)$

$= 5439.2 J$

$Q_r + 5439.2 J = 0 \quad ; \quad Q_r = -5439.2 J$

To report the energy change in this reactrion to others, we should express it in terms of heat transfer per mole of something. A different amount of reactant would have a diffferent Q

$Q_{rxn} = \dfrac{Q_r}{moles\ A} = \dfrac{-5439.2 J}{0.20\ mol\ A} = -27000 \dfrac{J}{mol\ A} = \boxed{-27 \dfrac{kJ}{mol\ A}}$

This number is called the "heat of reaction"

One problem ...

PATH. The amount of energy required for a process depends on how the process is carried out.

Example: Driving from Florence to Columbia. How much energy is required? (gas)

2000 Jeep Cherokee vs 2008 Toyota Prius. The Jeep will use much more fuel than the Prius even though they start and end from exactly the same place. So the fuel usage is what we call a PATH FUNCTION, while the location is a STATE FUNCTION.

- so the heat of reaction depends on how the reaction is done.

- we need (for reporting) some kind of standard condition. At constant pressure, we can define a state function called ENTHALPY (H)

$$H = U + PV$$

$$\Delta H = Q_{constant\ pressure}$$

... we record the "enthalpy change of reaction" in our data books.

$$\Delta H_r$$

SINCE the enthalpy change does NOT depend on path, this means that we can use standard values for enthalpy to predict the heat change in reactions that we have not tested in a calorimeter.

THERMOCHEMICAL EQUATIONS

- is like a regular chemical equation, except that phase labels are REQUIRED and the enthalpy for the reaction is given along with the equation.

$$CH_3COCH_3(l) + 4O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(l) \ ; \ \Delta H = -1800 \ kJ$$
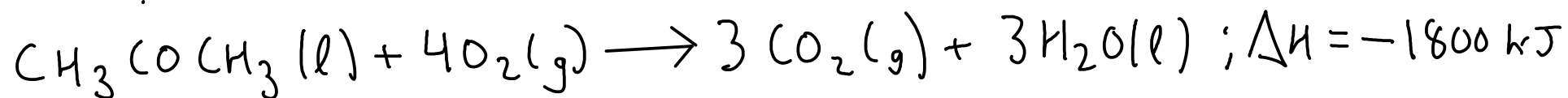
- Why are phase labels required? Because phase changes either absorb or release energy.

$\Delta H = -1800 \ kJ$ ... what does this mean?

$$1 \ mol \ CH_3COCH_3 = -1800 \ kJ$$

$$4 \ mol \ O_2 = -1800 \ kJ$$

$$3 \ mol \ CO_2 = -1800 \ kJ$$

$$3 \ mol \ H_2O = -1800 \ kJ$$

We treat the enthalpy change as if it's another product of the reaction!

$$CH_3COCH_3(\ell) + 4O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(\ell) \; ; \; \Delta H = -1800 \, kJ$$

What would be the enthapy change when 25 g of water are produced by the reaction?

1- Convert the ,mass of water to moles using the formula weight of water
2- Convert moles of water to enthalpy change using the thermochemical equation

$$18.02 \, g \; H_2O = 1 \, mol \; H_2O \qquad 3 \, mol \; H_2O = -1800 \, kJ$$

$$25 \, g \; H_2O \times \frac{1 \, mol \; H_2O}{18.02 \, g \; H_2O} \times \frac{-1800 \, kJ}{3 \, mol \; H_2O} = \boxed{-830 \, kJ = \Delta H}$$

This reaction is
EXOTHERMIC!
(energy released
to surroundings, warming
the surroundings)
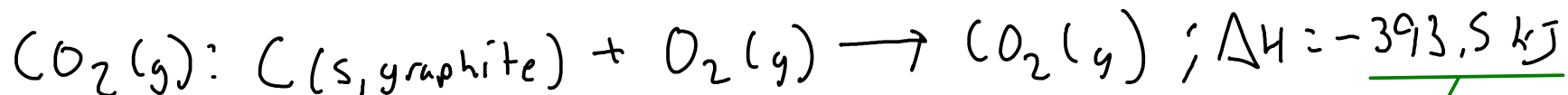
This is equal to
Q at contant pressure

A few more terms related to enthalpy:

- Enthalpy of vaporization / heat of vaporization: The enthalpy change on vaporizing one mole of a substance. (from liquid to vapor)

- Enthalpy of fusion / heat of fusion: The enthalpy change when a mole of liquid changes to the solid state.
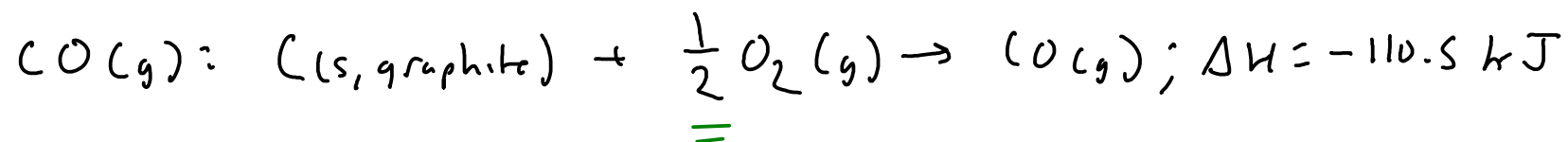
Phase changes require energy, too!

FORMATION REACTIONS

- A reaction that forms <u>exactly one mole</u> of the specified substance from its elements at their STANDARD STATE at 25C and 1 atm pressure.

$$CO_2(g): \quad C(s, graphite) + O_2(g) \longrightarrow CO_2(g) \; ; \; \Delta H = -393.5 \, kJ$$

heat of formation of carbon dioxide ΔH_f^0 or ΔH_f
"enthalpy of formation"

$$CO(g): \quad C(s, graphite) + \tfrac{1}{2} O_2(g) \longrightarrow CO(g) \; ; \; \Delta H = -110.5 \, kJ$$

you may see fractional coefficients in these formation reactions, because you MUST form exactly one mole of the product!
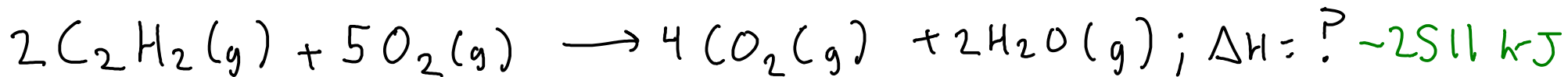
- The heat of formation for an element in its standard state at 25C and 1 atm is ZERO.

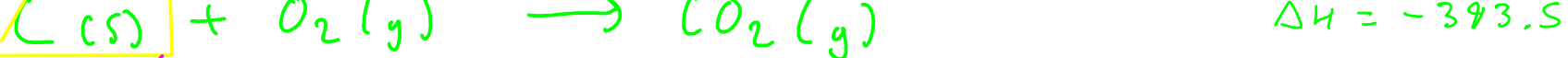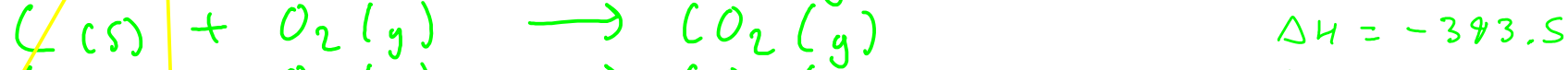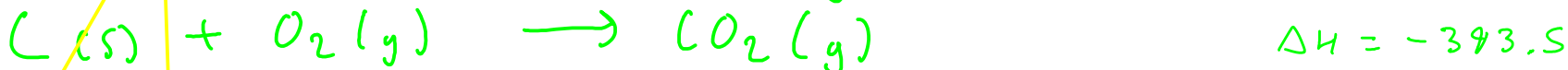$$\Delta H^0_{f, O_2(g)} = 0 \; kJ/mol$$

- What are formation reactions good for?

... finding enthalpies for more interesting reactions!

Let's say we would like to find the enthalpy of reaction for this equation:

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g) ; \Delta H = ? \sim 2511 \, kJ$$

Hess' Law: If you add two reactions to get a new reaction, their enthalpies also add.

C_2H_2: $2C(s) + H_2(g) \longrightarrow C_2H_2(g)$ $\Delta H = 226.7$

CO_2: $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5$

H_2O: $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$ $\Delta H = -241.8$

$C_2H_2(g) \longrightarrow 2C(s) + H_2(g)$ $\Delta H = 226.7$

$C_2H_2(g) \longrightarrow 2C(s) + H_2(g)$ $\Delta H = 226.7$

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

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$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$ $\Delta H = -241.8$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$ $\Delta H = -241.8$

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(\ell)$$

$$\Delta H = 2(-226.7) + 4(-393.5) + 2(-241.8) = \boxed{-2511 \, kJ}$$

Hess' Law using enthalpy of formation:

$$\Delta H = \sum \Delta H_{f, products} - \sum \Delta H_{f, reactants}$$

$$\Delta H = \left(\overset{CO_2}{4(-393.5)} + \overset{H_2O}{2(-241.8)} \right) - \left(\overset{C_2H_2}{2(226.7)} + \overset{O_2}{5(0)} \right)$$

$$= \boxed{-2511 \; kJ}$$

See Appendix C in the textbook for enthalpy of formation data: p A-8 to A-11

* Remember:

- Multiply each enthalpy by its stoichiometric coefficient from the reaction

- Enthalpy of formation of an element at its standard state is zero

- Watch phase labels. You will usually find SEVERAL enthalpies of formation for a given substance in different phases!

- For ionic substances in solution, remember that they exist as free ions, so look up the aqueous IONS!
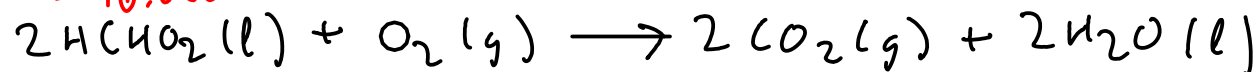
Example problems:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \; ; \; \Delta H = -484 \text{ kJ}$$

(handwritten above H_2: 2.016)
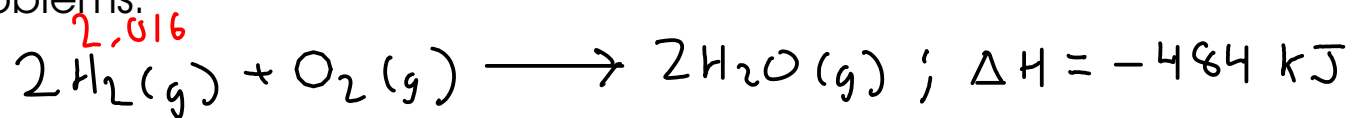
Calculate the enthalpy change for the combustion of 1.00 kg of hydrogen gas.

1 - Convert mass hydrogen to moles using formula weight (and definition of "kilo-")
2 - Convert moles hydrogen to energy using thermochemical equation

$$2.016 \text{ g } H_2 = \text{mol } H_2 \quad | \quad kg = 10^3 \text{ g} \quad | \quad 2 \text{ mol } H_2 = -484 \text{ kJ}$$

$$1.00 \text{ kg } H_2 \times \frac{10^3 \text{ g}}{kg} \times \frac{\text{mol } H_2}{2.016 \text{ g } H_2} \times \frac{-484 \text{ kJ}}{2 \text{ mol } H_2} = \boxed{-120000 \text{ kJ}} \text{ per kg}$$

① ②

FW: 46.026

$$2 HCHO_2 (l) + O_2 (g) \longrightarrow 2 CO_2 (g) + 2 H_2O (l)$$

If 50.3 kJ of heat was <u>released</u> when <u>5.48 g</u> of formic acid are burned at constant pressure, then what is the enthalpy change of this reaction per mole of formic acid?
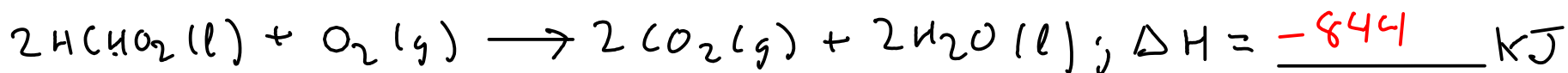
$$\Delta H = \frac{Q_{constant\ P}}{moles\ HCHO_2} = ?$$

$$Q = -50.3\ kJ$$

$$5.48_g\ HCHO_2 \times \frac{mol\ HCHO_2}{46.026_g\ HCHO_2} = 0.119063\ mol\ HCHO_2$$

$$\Delta H = \frac{Q_{constant\ P}}{moles\ HCHO_2} = \frac{-50.3\ kJ}{0.119063\ mol\ HCHO_2} = \boxed{-422\ \frac{kJ}{mol}}$$

Based on the calculation above, can we complete this thermochemical equation?

$$2 HCHO_2 (l) + O_2 (g) \longrightarrow 2 CO_2 (g) + 2 H_2O (l); \Delta H = \underline{-844}\ kJ$$

We'd calculated the heat per ONE MOLE of formic acid reacting, and this equation is written on the basis of TWO MOLES formic acid reacting.

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g); \quad \Delta H = -906 \text{ kJ}$$
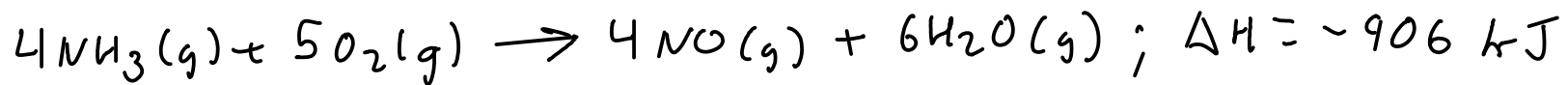
What is the enthalpy change when 150. L of nitrogen monoxide are formed by this reaction at 25.0 C and 1.50 atm pressure?

1 - Convert volume of NO gas to moles using ideal gas law
2 - Convert moles NO to enthalpy using thermochemical equation

---

$$PV = nRT \qquad P = 1.50 \text{ atm} \qquad\qquad R = 0.08206 \frac{L \cdot atm}{mol \cdot K}$$

$$\frac{PV}{RT} = n \qquad V = 150. \text{ L}$$

$$\qquad\qquad\qquad\qquad n = ???$$

$$T = 25.0°C = 298.2 K$$

$$① \; n_{NO} = \frac{(1.50 \text{ atm})(150. \text{ L})}{\left(0.08206 \frac{L \cdot atm}{mol \cdot K}\right)(298.2 K)} = 9.19482 \text{ mol NO}$$

$$4 \text{ mol NO} = -906 \text{ kJ}$$

$$9.19482 \text{ mol NO} \times \frac{-906 \text{ kJ}}{4 \text{ mol NO}} = \boxed{-2080 \text{ kJ}}$$

$$②$$

Heat of formation / enthalpy of formation!

$$\overset{-20.50}{2\,H_2S\,(g)} + \overset{0}{3\,O_2\,(g)} \longrightarrow \overset{-285.8}{2\,H_2O\,(\ell)} + \overset{-296.8}{2\,SO_2\,(g)} \Big]\,\Delta H_f^0,\ kJ/mol$$
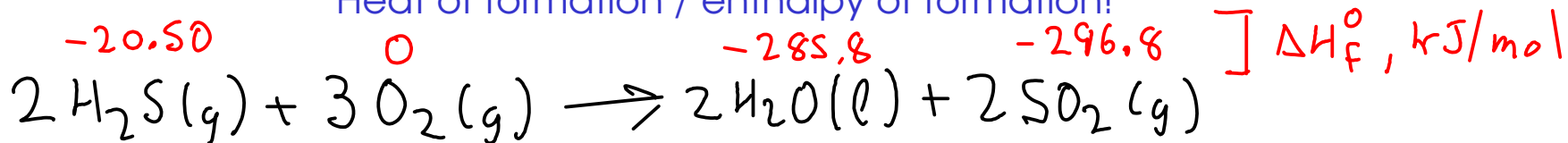
What is the enthalpy change at standard conditions when 25.0 grams of hydrogen sulfide gas is reacted?

1 - Find the enthalpy of the reaction using Hess's Law and enthalpy of formation
2 - Convert 25.0 g of hydrogen sulfide to moles using formula weight
3 - Convert moles hydrogen sulfide to enthalpy using the therochemical equation we created in our first step.

① $\Delta H = \sum \Delta H_f^0 \text{ products} - \sum \Delta H_f^0 \text{ reactants}$

$= \Big[\,2(-285.8) + 2(-296.8)\,\Big] - \Big[\,2(-20.50) + 3\,(0)\,\Big]$

$\Delta H = -1124.2\ kJ$

The complete thermochemical equation for this reaction:

$2\,H_2S\,(g) + 3\,O_2\,(g) \longrightarrow 2\,H_2O\,(\ell) + 2\,SO_2\,(g)\,;\ \Delta H = -1124.2\ kJ$

$34.086g\ H_2S = mol\ H_2S \quad\big|\quad 2\,mol\ H_2S = -1124.2\ kJ$

$25.0g\ H_2S \times \dfrac{mol\ H_2S}{34.086g\ H_2S} \times \dfrac{-1124.2\ kJ}{2\,mol\ H_2S} = \boxed{-412\ kJ}$

② ③