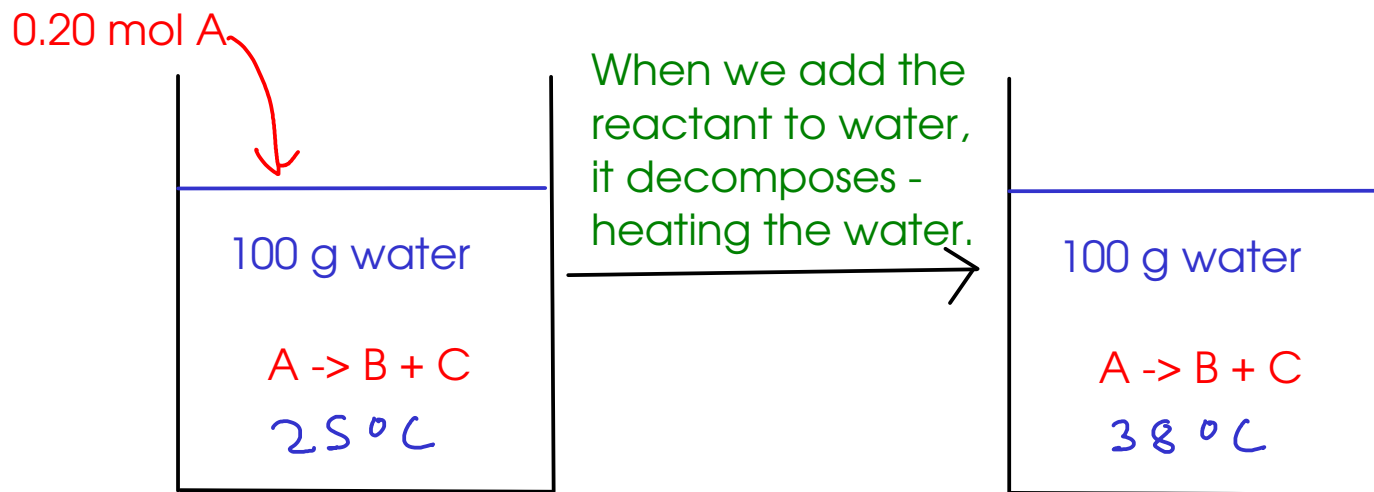


## CALORIMETRY

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



... what is  $Q$  for this reaction?

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

$$\underbrace{Q_r}_{\text{reaction}} + \underbrace{Q_w}_{\text{water}} = 0$$

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

... 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,

$$4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \quad \underline{\underline{=}} \quad 1.000 \frac{\text{cal}}{\text{g}^\circ\text{C}}$$

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

$m$  = mass  
 $s$  = specific heat  
 $\Delta T$  =  $T_{\text{final}} - T_{\text{initial}}$

This is ALWAYS final temp minus initial temp!

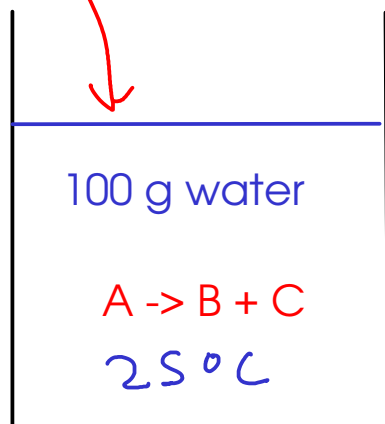
- For objects, like reaction vessels, you might know the HEAT CAPACITY, which is the amount of energy required to change the temperature of an object by one degree Celsius

$$\text{units: } \text{J}/^\circ\text{C} \quad \text{or} \quad \text{cal}/^\circ\text{C}$$

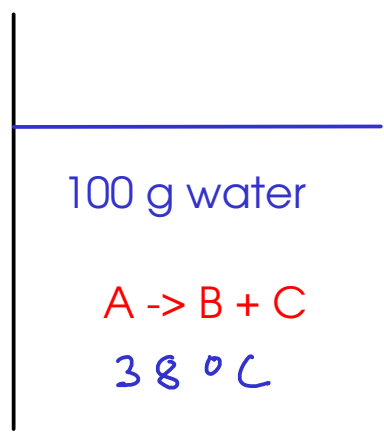
$$Q = C \times \Delta T$$

$c$  = heat capacity

0.20 mol A



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



Specific heat of water:

$$4.184 \frac{\text{J}}{\text{g}^\circ\text{C}}$$

$$Q_r + Q_w = 0 \quad / \quad Q_w = (m_w) (s_w) (\Delta T_w) = (100 \text{ g}) (4.184 \text{ J/g}^\circ\text{C}) (38^\circ\text{C} - 25^\circ\text{C}) = 5439.2 \text{ J}$$

$$Q_r + 5439.2 \text{ J} = 0 ; \quad Q_r = -5439.2 \text{ J}$$

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

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

This number is usually 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)

$$H = U + PV$$

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

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

$$\Delta H_r$$

<sup>158</sup> 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.

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## 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.



- Why are phase labels required? Because phase changes either absorb or release energy.

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

$$1 \text{ mol CH}_3\text{COCH}_3 = -1800 \text{ kJ}$$

$$4 \text{ mol O}_2 = -1800 \text{ kJ}$$

$$3 \text{ mol CO}_2 = -1800 \text{ kJ}$$

$$3 \text{ mol H}_2\text{O} = -1800 \text{ kJ}$$

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



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

- 1 - Convert 25 grams water to moles using formula weight.
- 2 - Convert moles water to enthalpy change using THERMOCHEMICAL EQUATION

$$18.016 \text{ g H}_2\text{O} = 1 \text{ mol H}_2\text{O} \quad \Bigg| \quad 3 \text{ mol H}_2\text{O} = -1800 \text{ kJ}$$

$$25.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.016 \text{ g H}_2\text{O}} \times \frac{-1800 \text{ kJ}}{3 \text{ mol H}_2\text{O}} = \boxed{-830 \text{ kJ}}$$

↑ This also equals Q, assuming the pressure is constant!

This reaction is EXOTHERMIC. Energy is released from the reaction mixture to the surroundings!

(True for all combustion reactions!)

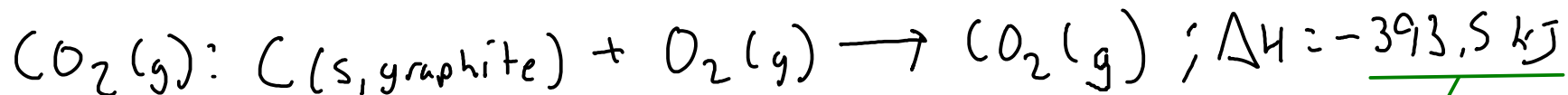
A few more terms related to enthalpy:

- 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.

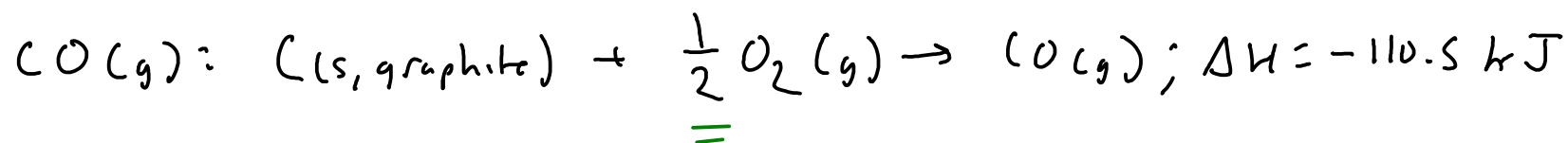
↑  
Phase changes require energy, too!

## 160 FORMATION REACTIONS

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



heat of formation of carbon dioxide  $\Delta H_f^\circ$  or  $\Delta H_f$   
"enthalpy of formation"



you may see fractional coefficients in these formation reactions, because you MUST form exactly one mole of the product!

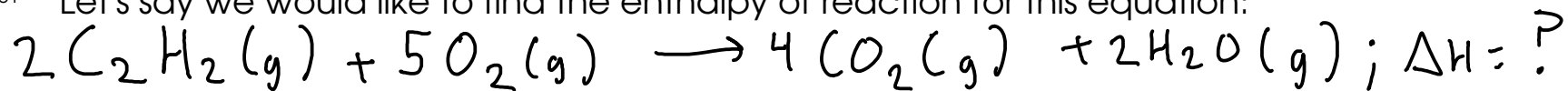
- The heat of formation for an element in its standard state at 25C and 1 atm is ZERO.

$$\Delta H_f^\circ, \text{O}_2(\text{g}) = 0 \text{ kJ/mol}$$

- What are formation reactions good for?

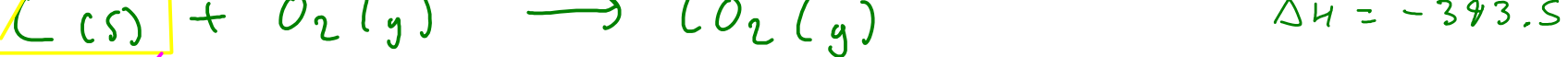
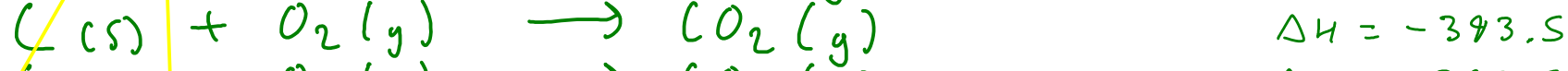
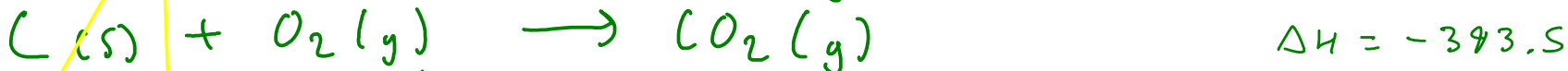
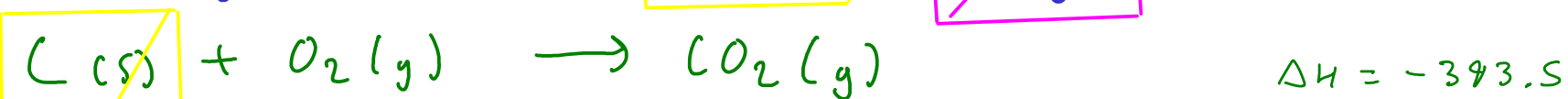
... finding enthalpies for more interesting reactions!

<sup>161</sup> Let's say we would like to find the enthalpy of reaction for this equation:



From  
A-8,  
text  
↓

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



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



Hess' Law using enthalpy of formation:

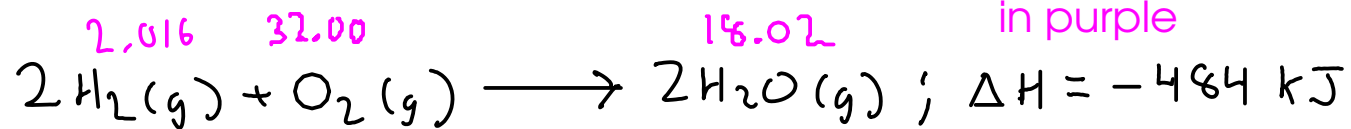
$$\Delta H = \sum \Delta H_{f, \text{products}} - \sum \Delta H_{f, \text{reactants}}$$

$$\Delta H = (4(-393.5) + 2(-241.8)) - (2(226.7) + 5(0))$$
$$= \boxed{-2511 \text{ kJ}}$$

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!



Calculate the enthalpy change for the combustion of 1.00 kg of hydrogen gas.

1 - Convert 1.00 kg hydrogen gas to moles using formula weight.

2 - Convert moles hydrogen gas to enthalpy change using THERMOCHEMICAL EQUATION

$$2.016 \text{ g H}_2 = \text{mol H}_2 \quad | \quad 2 \text{ mol H}_2 = -484 \text{ kJ} \quad | \quad \text{kg} = 10^3 \text{ g}$$

$$1.00 \text{ kg H}_2 \times \frac{10^3 \text{ g}}{\text{kg}} \times \frac{\text{mol H}_2}{2.016 \text{ g H}_2} \times \frac{-484 \text{ kJ}}{2 \text{ mol H}_2} = -120000 \text{ kJ per kg H}_2$$