Ch. 6 –Enthalpy Changes

- Energy: "The capacity to do work."

  - In Physics, there are 2 main types of energy…
    - Kinetic (energy of motion) = ½ mv^2
    - Potential (energy of position due to gravity)= mgh

  - In Chemistry, we usually concern ourselves with the heat energy gained or lost during chemical reactions.

Systems and Surroundings

- For thermochemical reactions, we will need to define the following parts of the reaction…

  - System: part of the reaction we are interested in.

  - Surroundings: the rest of the universe.

    - Example: If we are interested in the reaction between hydrogen and oxygen in a cylinder, then the H_2 and O_2 in the cylinder form a system, and everything else is the surroundings.

Endothermic and Exothermic Processes

- An **endothermic** process is one that *absorbs* heat from the surroundings. (positive q)

An endothermic reaction feels cold.

Example--an "instant" ice pack

- An **exothermic** process is one that *transfers* heat to the surroundings. (negative q)

An exothermic reaction feels hot.

Example--burning paper

Surroundings	Surroundings
System	**System**
← Heat	Heat →
$\Delta H > 0$ Endothermic	$\Delta H < 0$ Exothermic
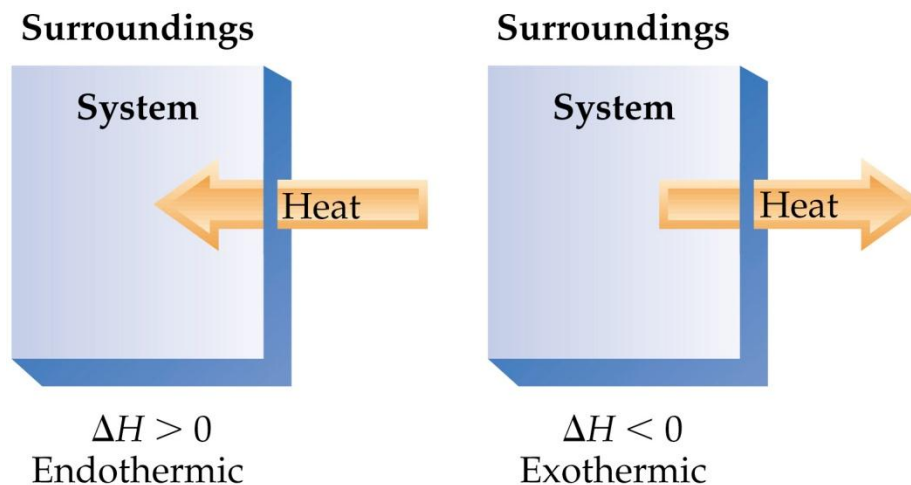
Transferring Energy

There are 2 ways to transfer energy in or out of a system…

   1) Work…applying a force to an object and moving it a distance (W=Fxd)

   2) Heat…the energy transferred from hotter objects to colder objects

• Energy is therefore capacity to do work OR transfer heat.

We will concern ourselves with the transfer of heat!

The 1st Law of Thermodynamics

- Energy cannot be created or destroyed.
  - The first law of thermodynamics is really just the law of conservation of energy.
  - The energy of (system + surroundings) is constant.
  - Thus any energy transferred from a system must be transferred to the surroundings (and vice versa).

  - We are going to be concerned with the energy
  - Exchange between a chemical reaction and its
  - Surroundings at constant pressure.
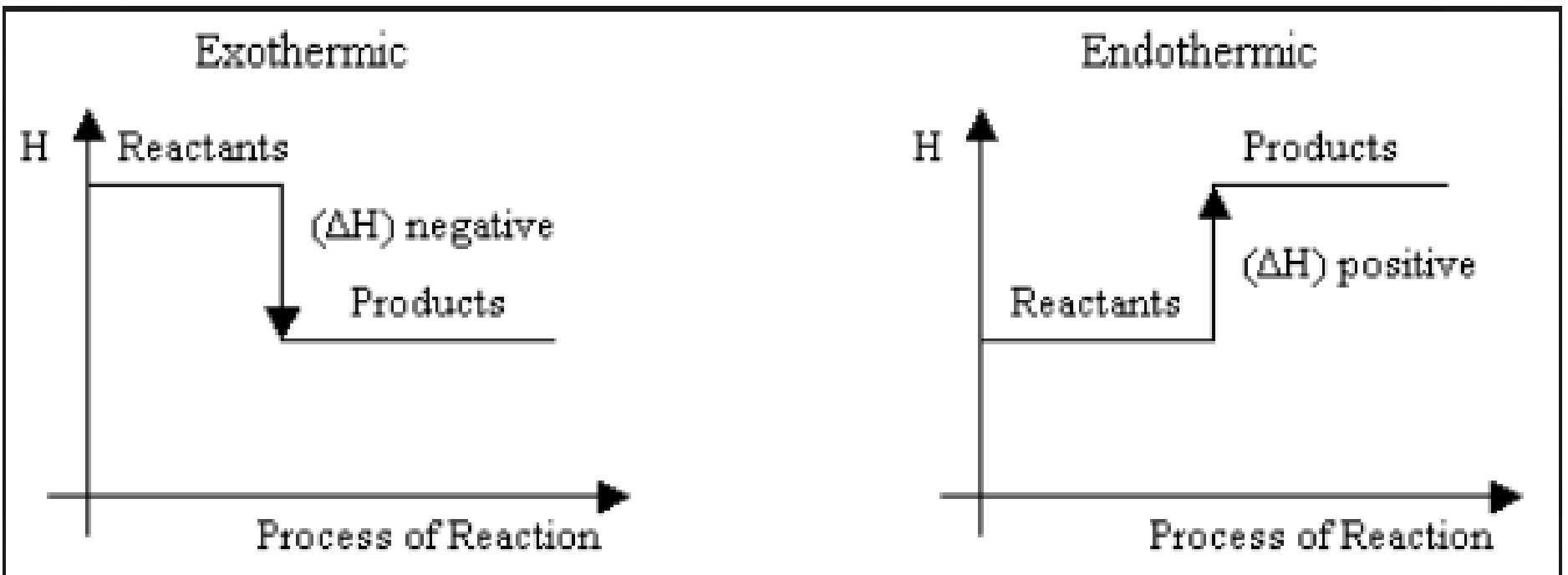
Enthalpy

•Enthalpy, *H*:

-Enthalpy is heat transferred between the system and surroundings carried out under constant pressure 100kPa or 1000000Pa and temperature of 298K

-            ΔH is (+) for endothermic reactions

ΔH is ($-$) for exothermic reactions

The units of enthalpy change are kJ / mol

Enthalpy profile diagrams

Enthalpies of Reactions

•We can only measure the change in enthalpy, ΔH.

$$\Delta H = H_{final} - H_{initial}$$

•For a reaction…

$$\Delta H_{rxn} = H_{(products)} - H_{(reactants)}$$

•The enthalpy change that accompanies a reaction is called the *enthalpy of reaction* or *heat of reaction* (ΔH_{rxn}).

•Consider the equation for the production of water:

$$2H_{2(g)} + O_{2(g)} \text{-----}> 2H_2O_{(g)} \quad \Delta H_{rxn} = -483.6 \text{ kJ}$$
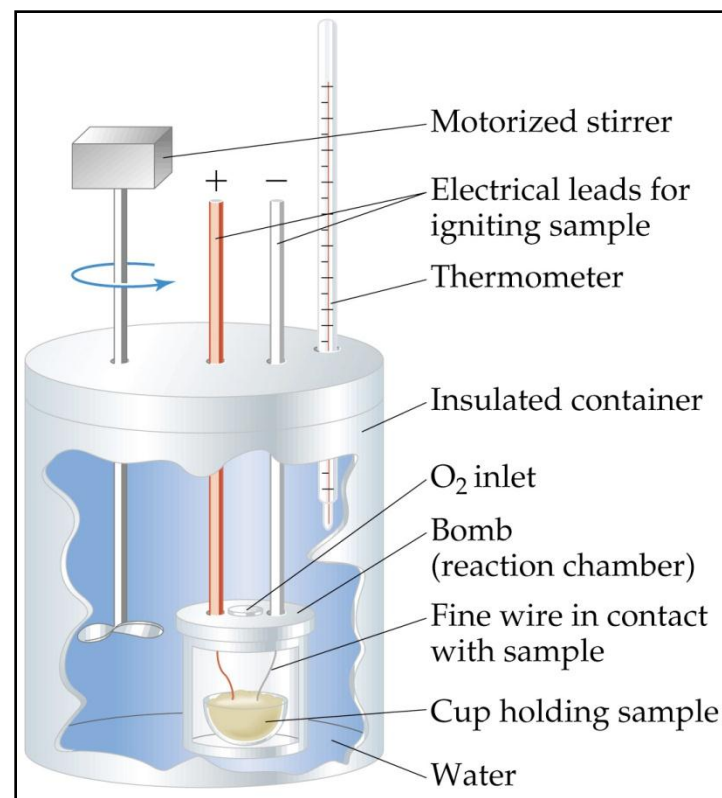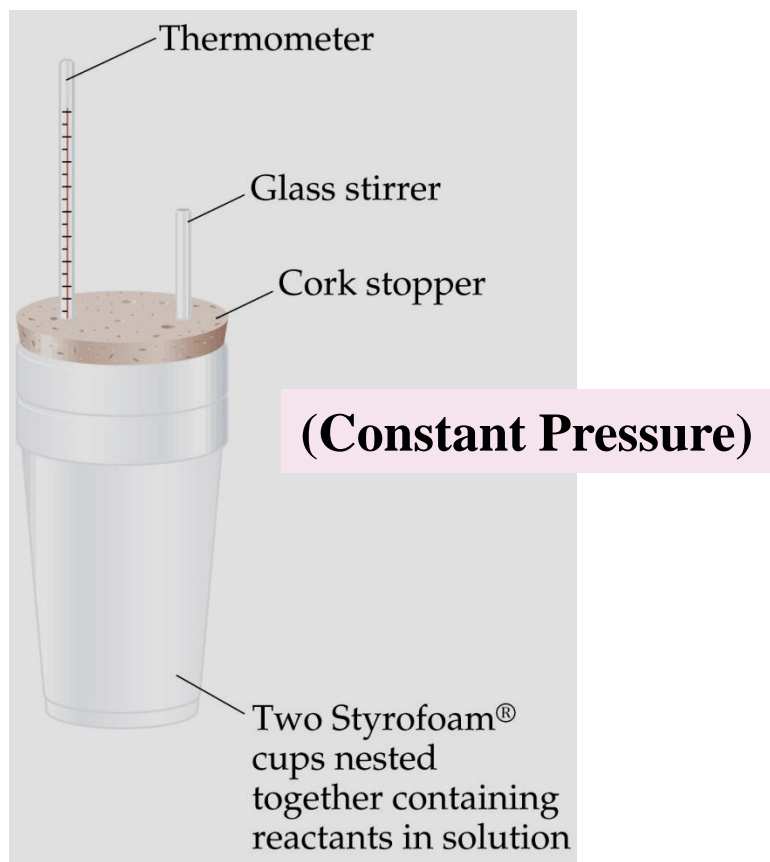
-The equation tells us that 483.6 kJ of energy are released to the surroundings when water is formed & the reaction would feel hot.

-These equations are called *thermochemical equations*.

Calorimeters

•Calorimeters measure heat flow. It measures changes in water temperature after a reaction is performed.

(Constant Pressure)

Thermometer

Glass stirrer

Cork stopper

Two Styrofoam® cups nested together containing reactants in solution

Motorized stirrer

Electrical leads for igniting sample

Thermometer

Insulated container

O_2 inlet

Bomb (reaction chamber)

Fine wire in contact with sample

Cup holding sample

Water

Bomb Calorimeter
Usually studies combustion (Constant Volume)

Measuring Heat, q

• **Specific Heat Capacity** is the amount of energy required to raise the temperature of an 1 g of a liquid by 1 ℃.

$$q = mc\Delta T$$

q = (grams of substance) x (specific heat) x ΔT.

q = energy transferred , in J

m = mass of water, in g

c $_{(water)}$ = 4.184 J/g ℃ or 1.0 cal/g ℃

T = temperature change in ℃

Measuring Heat

•<u>Practice Problems:</u> How many joules of heat will raise the temperature of exactly 50 g of water at 25 ℃ to 75 ℃

$$q = mc\Delta T$$

$q = (50 \text{ g}) \times (4.18 \text{J/g ℃}) \times (50 \text{ ℃}) = 10450 \text{ J}$

*Note: $q_{(solution)} = - q_{(rxn)}$

•What is the molar heat capacity for water?

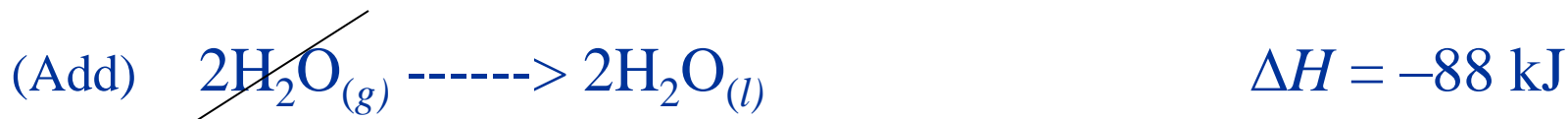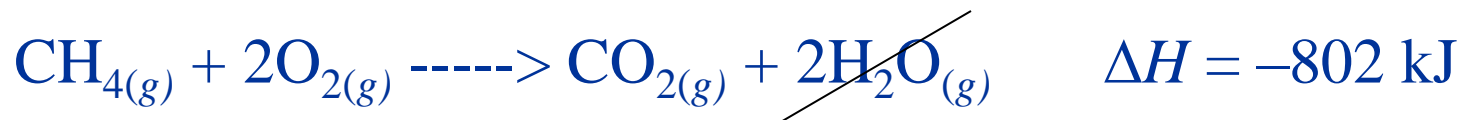$C = (4.18 \text{ J/g ℃}) \times (18.0 \text{ g/mole}) = 75.2 \text{ J/mol ℃}$

So…

$$C = c \times M$$

Hess's Law

• If a reaction is carried out in a series of steps, ΔH for the reaction is the sum of ΔH for each of the steps.

• The total change in enthalpy is independent of the number of steps.

• Total ΔH is also independent of the nature of the path.

$$CH_{4(g)} + 2O_{2(g)} \text{-----> } CO_{2(g)} + 2H_2O_{(g)} \qquad \Delta H = -802 \text{ kJ}$$

(Add) $\quad 2H_2O_{(g)} \text{------> } 2H_2O_{(l)} \qquad\qquad\qquad \Delta H = -88 \text{ kJ}$

(Total) $\quad CH_{4(g)} + 2O_{2(g)} \text{------> } CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = -890 \text{ kJ}$

• Hess's Law provides a useful means of calculating energy changes that are difficult to measure…(in this case it's getting liquid water to form instead of water vapor.)

Enthalpies of Formation

•If a compound is formed from its constituent elements, then the enthalpy change for the reaction is called the **enthalpy of formation**, ΔH_f.

Example: $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_f = -393.5$ kJ
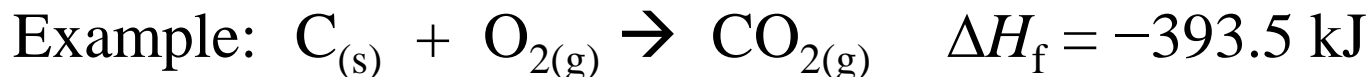
Standard state (standard conditions) refer to the substance at:

1 atm and 25ºC (298 K)

(We will assume that reactants and products are both at 25 ºC unless otherwise stated.)

•**Standard enthalpy**, ΔH^o, is the enthalpy measured when everything is in its standard state.

•**Standard enthalpy of formation** of a compound, ΔH^o_f, is the enthalpy change for the formation of *1 mole* of compound with all substances in their standard states.
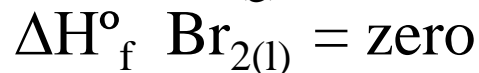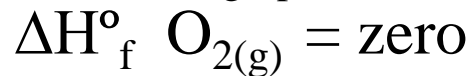
Enthalpies of Formation

- If there is more than one state for a substance under standard conditions, the more stable one is used.

  - Example: When dealing with carbon we use graphite because graphite is more stable than diamond or C_{60}.

- By definition, the standard enthalpy of formation of the most stable form of an element is zero. Why?

  - Because there is no formation reaction needed when the element is already in its standard state.

$$\Delta H°_f \ \ C_{(graphite)} = zero$$
$$\Delta H°_f \ \ O_{2(g)} = zero$$
$$\Delta H°_f \ \ Br_{2(l)} = zero$$

Using ΔH^o_f to calculate ΔH^o_{rxn}

• In general:

$$\Delta H^o_{rxn} = \Sigma \, n\Delta H^o_{f \, (products)} - \Sigma \, m\Delta H^o_{f \, (reactants)}$$

Where *n* and *m* are the coefficients from the balanced chemical equation.

Let's do one for practice!!!

Using ΔH^o_f to calculate ΔH^o_{rxn}

- Example: Use Hess's Law to calculate ΔH^o_{rxn} for…

$$C_3H_{8(g)} + 5O_{2(g)} \text{ -------> } 3CO_{2(g)} + 4H_2O_{(l)}$$
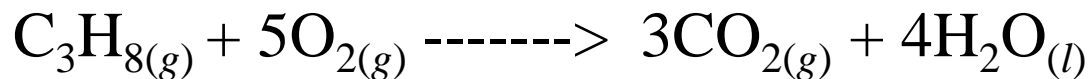
- *Step 1*, the products…Form $3CO_2$ and $4H_2O$ from their elements:

$3C_{(s)} + 3O_{2(g)} \text{ ------>} 3CO_{2(g)}$ $\quad \Delta H_1 = 3\Delta H^of[CO_{2(g)}]$…tripled it!

$4H_{2(g)} + 2O_{2(g)} \text{ ------>} 4H_2O_{(l)}$ $\quad \Delta H_2 = 4\Delta H^o_f[H_2O_{(l)}]$…quadrupled it!

- *Step 2*, the reactants…(Note: O_2 has no enthalpy of formation since it is in the elemental state, so we concern ourselves with C_3H_8.)
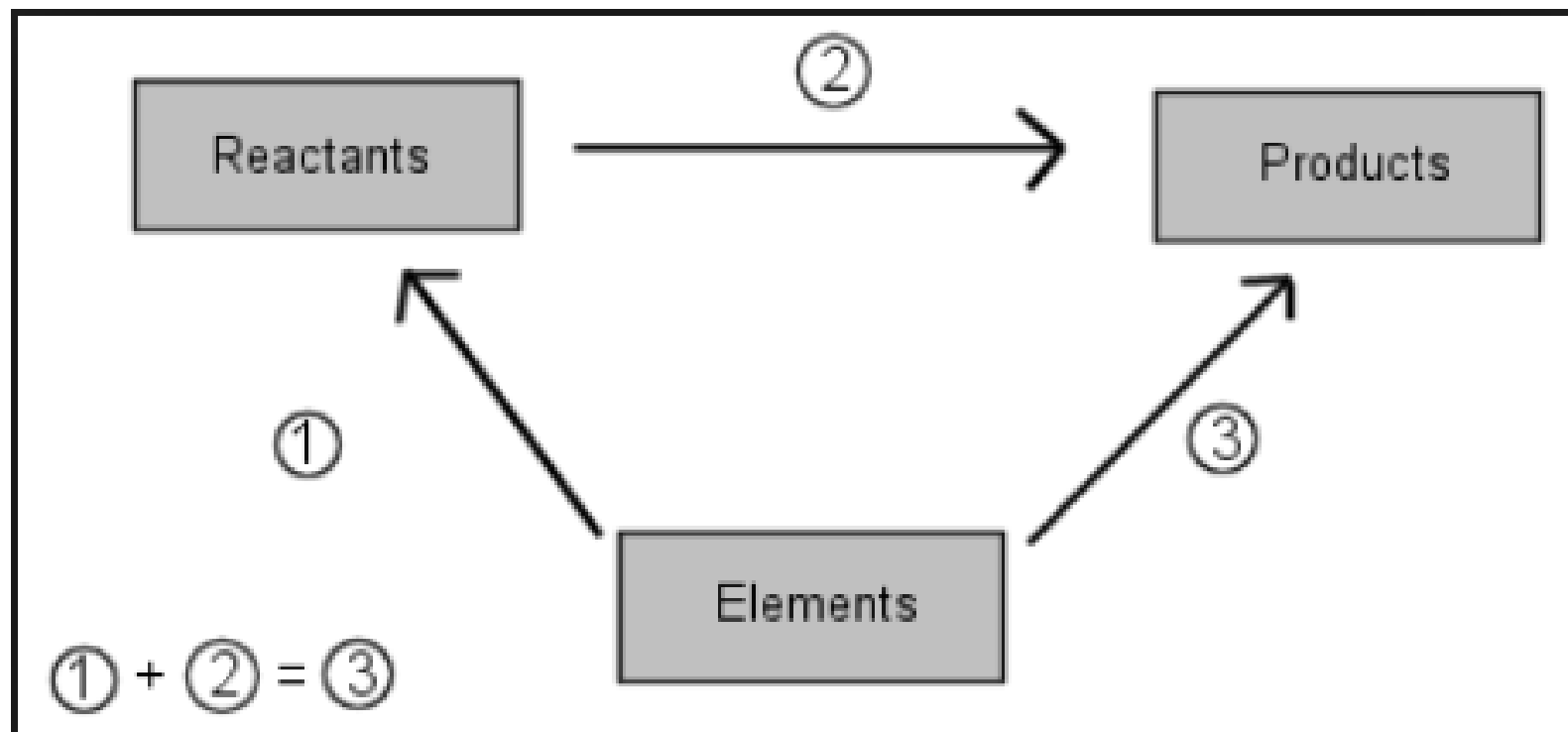
$3C_{(s)} + 4H_{2(g)} \text{ ------>} C_3H_{8(g)}$ $\quad \Delta H_3 = \Delta H^o_f[C_3H_{8(g)}]$
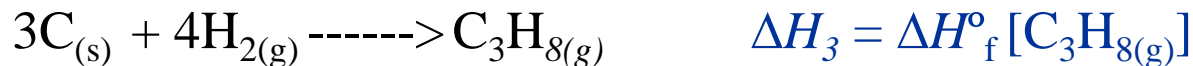
- *Step 3*, Now look up the values on p.177 and do the math!

$$\Delta H^o_{rxn} = \Delta H^o_{f \text{ (products)}} - \Delta H^o_{f \text{ (reactants)}}$$

$$\Delta H^o_{rxn} = [3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ})] - [(-103.85 \text{ kJ})]$$

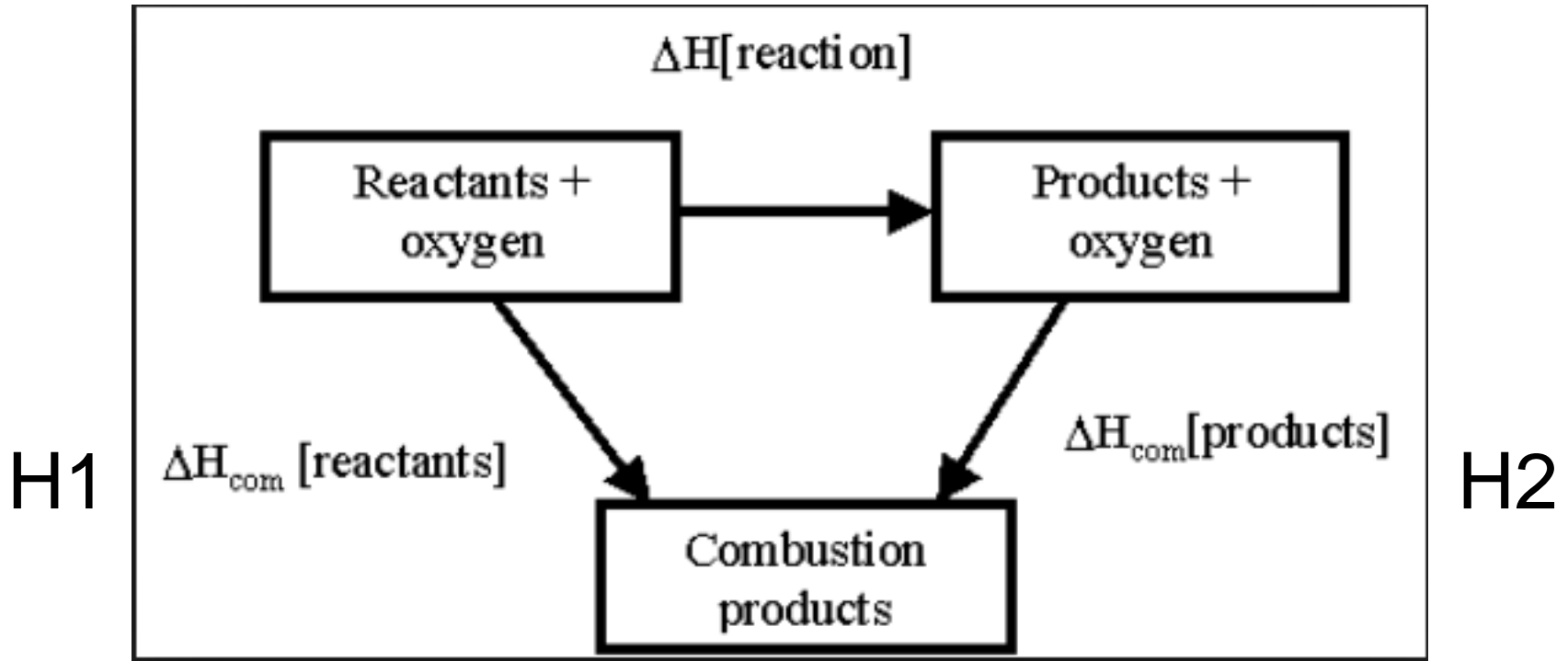$$\Delta H^o_{rxn} = -1180.5 - 1143.2 + 103.85 = -2220 \text{ kJ}$$
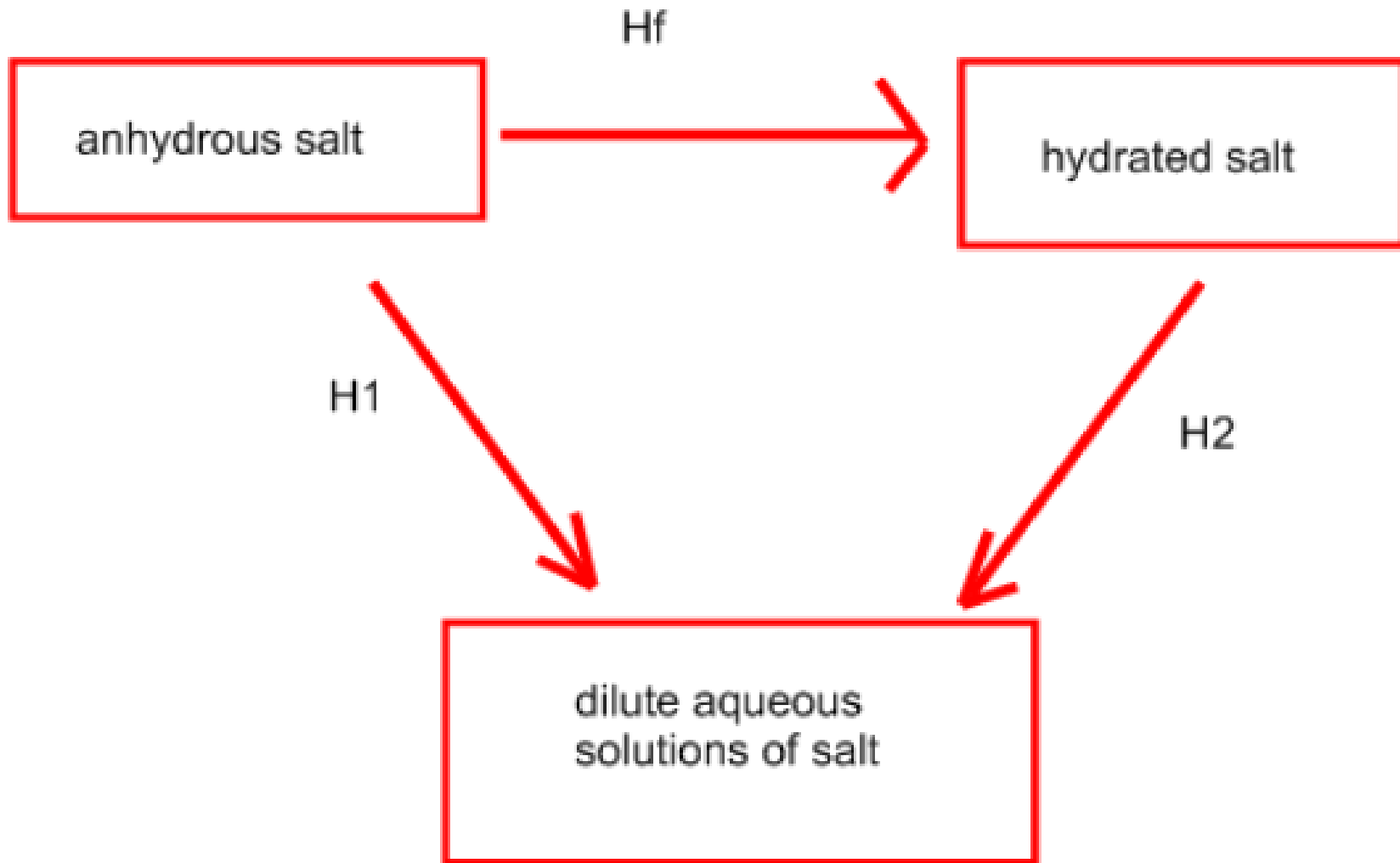
Enthalpy cycle diagram

- 1) write balanced equation up top
- 2) put elements at the bottom
- 3) draw arrows
- 4) make sure you account for # of moles

Enthalpy of Combustion

- Hr

H1   H2

Enthalpy of salt w/o water

Heat of Fusion & Heat of Vaporization

• Molar heat of fusion (ΔH_{fus}) : the amount of energy required to take 1 mole of a solid to the liquid state.

Example: $H_2O_{(s)} \rightarrow H_2O_{(l)}$ $\Delta H_{fus} = 6.01$ kJ

-Heat of fusion is usually greater for ionic solids than molecular solids since ionic solids are more strongly held together.

For ice to water … $\Delta H_{fus} = 6.01$ kJ/mol

• Molar heat of vaporization (ΔH_{vap}): the amount of energy required to take 1 mole of a liquid to the gaseous state.

Example: $H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\Delta H_{vap} = 40.67$ kJ
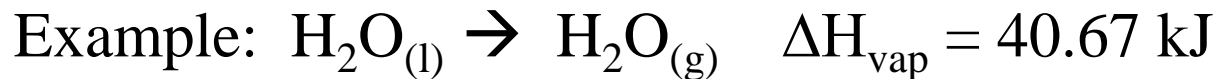
For water to steam … $\Delta H_{vap} = 40.67$ kJ/mol

These values are mainly used as conversion factors!