

- thermodynamics: the study of energy transfer

Conservation of energy: Energy may change form, but the overall amount of energy remains constant. "first law of thermodynamics"

- ... but what IS energy?

- energy is the ability to do "work"

↑
motion of matter

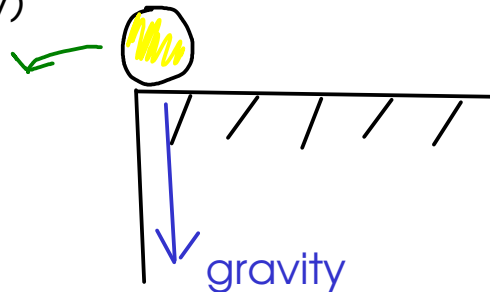
Kinds of energy?

- Kinetic energy: energy of matter in motion $E_K = \frac{1}{2} m v^2$

mass

↑
velocity

- Potential energy: energy of matter that is being acted on by a field of force (like gravity)



When the ball falls, its potential energy is converted to kinetic!

- What sort of energy concerns chemists? Energy that is absorbed or released during chemical reactions.

- Energy can be stored in chemicals ... molecules and atoms.

INTERNAL ENERGY: "U"



related to the kinetic and potential energy of atoms, molecules, and their component parts.

- We measure energy transfer ... which is called HEAT. (HEAT is the flow of energy from an area of higher temperature to an area of lower temperature)

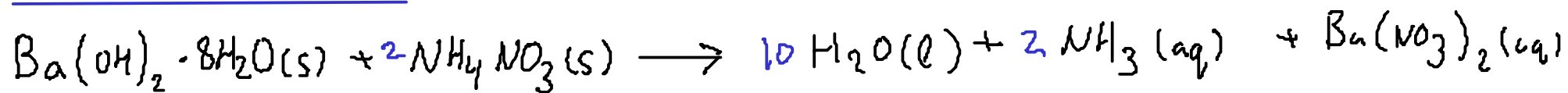
Q: heat

SYSTEM: the object or material under study

SURROUNDINGS: everything else

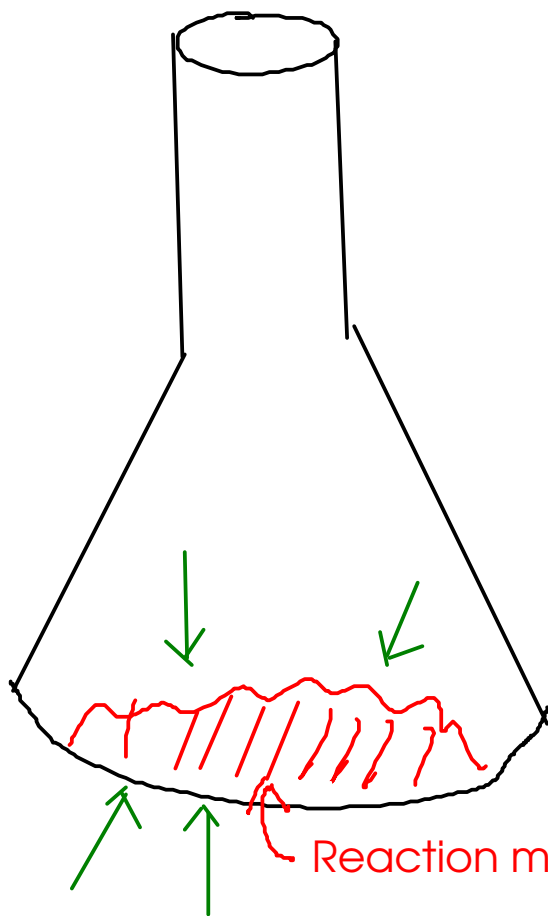
Type of process	Energy is ...	Sign of Q	Temp of SURROUNDINGS ...
ENDOTHERMIC	transferred from SURROUNDINGS to SYSTEM	+	decreases
EXOTHERMIC	transferred from SYSTEM to SURROUNDINGS	-	increases

Reaction demonstration:



Observation:

- * Formation of liquid (water?)
- * Smell of ammonia
- * Temperature change; flask is COLD

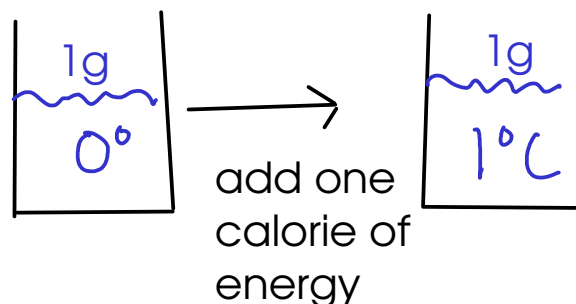


Energy flows from the SURROUNDINGS (the flask, your hands, etc.) into the SYSTEM. This is an ENDOTHERMIC process:

$$Q > 0$$

ENERGY UNITS

- calorie (cal): the amount of energy required to change the temperature of one gram of water by one degree Celsius (or Kelvin)



$1g \approx 1mL$ for water

- Calories in food? The "Calorie" that is given on American food labels is actually the kilocalorie (kcal)

- Joule (J): SI unit for energy. It's defined based on the equation for kinetic energy.

$$1 \text{ J} = 1 \frac{\text{Kg m}^2}{\text{s}^2}, \text{ from}$$

$$E_K = \frac{1}{2} m v^2$$

kinetic
energy

mass

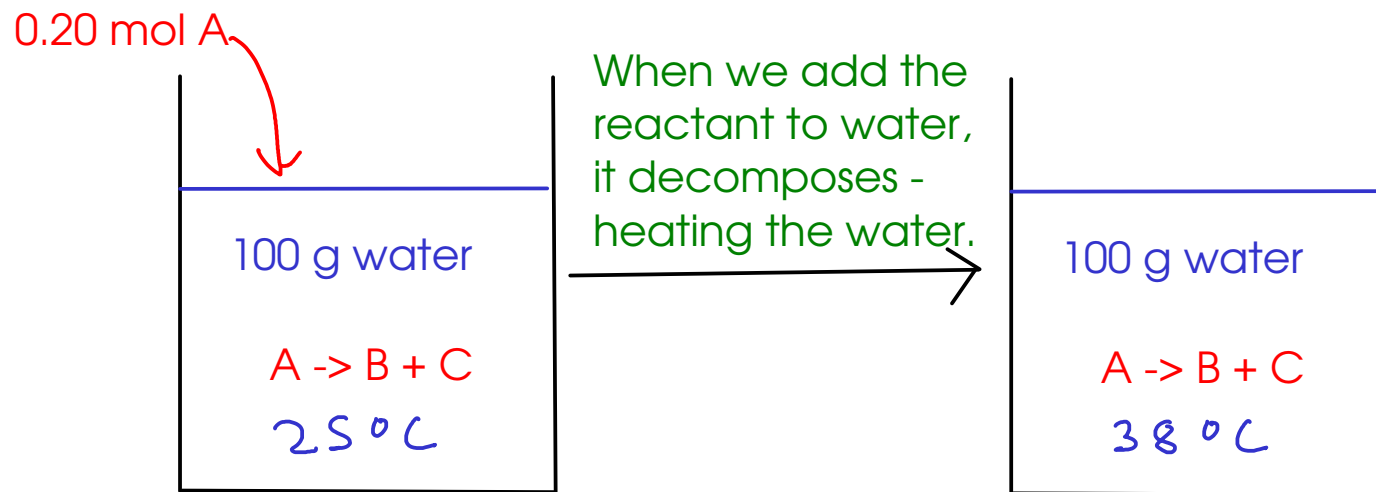
velocity

$$4.184 \text{ J} = 1 \text{ cal}$$

- the Joule is a small unit. For most reactions at lab scale, we'll use kilojoules (kJ).

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,

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

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

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

This is ALWAYS final temp minus initial temp!

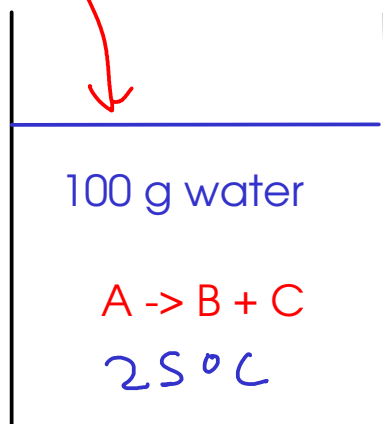
- For objects, like reaction vessels, you might know the HEAT CAPACITY, which is the amount of energy required to change the temperature of an object by one degree Celsius

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

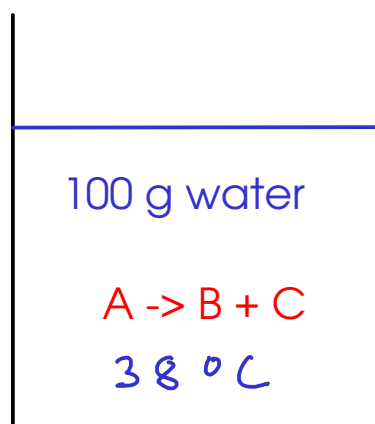
$$Q = C \times \Delta T$$

c = heat capacity

0.20 mol A



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



Specific heat of water:

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

$$Q_r + Q_w = 0$$

$$\begin{aligned} Q_w &= m_w \times s_w \times \Delta T_w \\ &= (100\text{g})(4.184 \text{ J/g}^\circ\text{C})(38^\circ\text{C} - 25^\circ\text{C}) \\ &= 5439.2 \text{ J} \end{aligned}$$

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

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

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

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)

$$H = U + PV$$

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

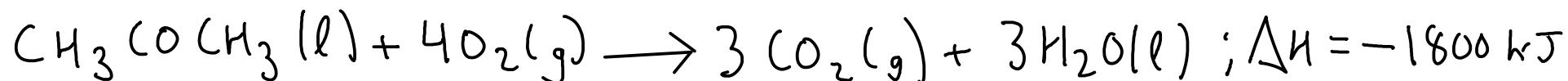
... we record the "enthalpy change of reaction" in our data books.

$$\Delta H_r$$

¹⁵⁸ 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.



- 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 of water to moles.

2 - Convert moles of water to enthalpy change using THERMOCHEMICAL EQUATION

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

$$25 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.016 \text{ g H}_2\text{O}} \times \frac{-1800 \text{ kJ}}{3 \text{ mol H}_2\text{O}} = \boxed{-830 \text{ kJ}}$$

↻ This also equals Q, provided pressure is constant.

This reaction is EXOTHERMIC. Energy is released from the reaction mixture to the surroundings. (True for all combustions.)

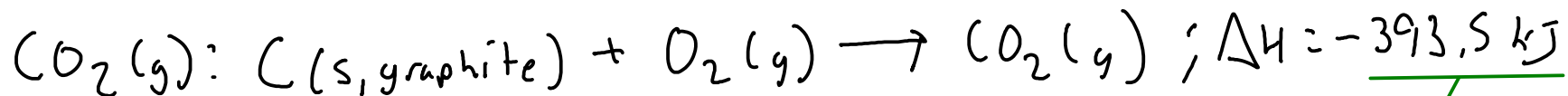
A few more terms related to enthalpy:

- 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.

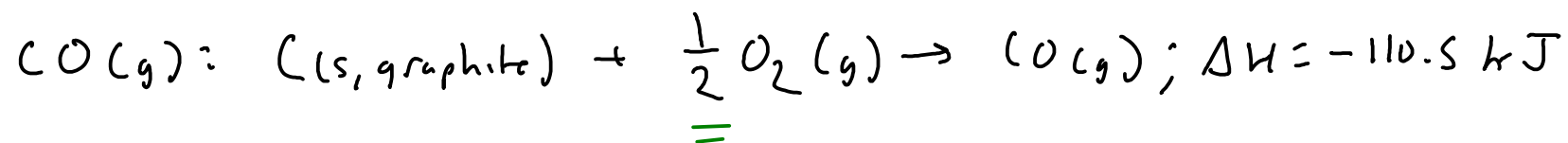
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Phase changes require energy, too!

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 ΔH_f° or ΔH_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.

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

- What are formation reactions good for?

... finding enthalpies for more interesting reactions!