

REAL GASES

- The empirical gas laws (including the ideal gas equation) do not always apply.
 - The gas laws don't apply in situations where the assumptions made by kinetic theory are not valid.
 - When would it be FALSE that the space between gas molecules is much larger than the molecules themselves?
 - at high pressure, molecules would be much closer together!
 - When would it be FALSE that attractive and repulsive forces would be negligible?
 - at high pressure, attractions and repulsions should be stronger!
 - at low temperature, attractions and repulsions have a more significant affect on the paths of molecules



- The gas laws are highly inaccurate near the point where a gas changes to liquid!
- In general, the lower the pressure and the higher the temperature, the more IDEAL a gas behaves.

van der Waals equation

- an attempt to modify $PV = nRT$ to account for several facts.
 - gas molecules actually have SIZE (they take up space)
 - attractive and repulsive forces

$$PV = nRT \quad] \text{ Ideal gas equation}$$

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \quad] \text{ van der Waals equation}$$

attempts to account for molecular size

attempts to account for attractive / repulsive forces

* "a" and "b" are experimentally determined parameters that are different for each gas. p 208

He: $a = 0,0346$, $b = 0,0238$ tiny, no special attractive forces

H₂O: $a = 5,537$, $b = 0,03049$ small, but strong attractions between molecules

CH₃CH₂OH: $a = 12,56$ $b = 0,08710$ larger, and strong attractions between molecules

- 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"

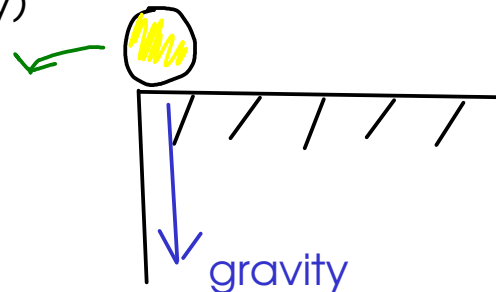
↑
motion of matter

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.

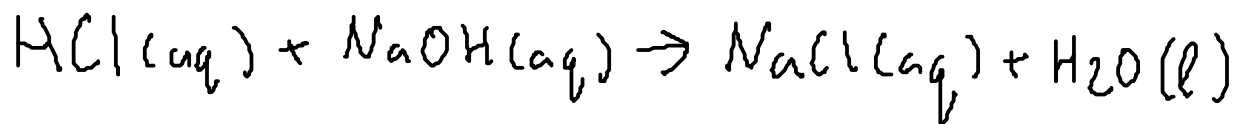
- We measure energy transfer ... which is called HEAT. (HEAT is the flow of energy from an area of higher temperature to an area of lower temperature)

Q: heat

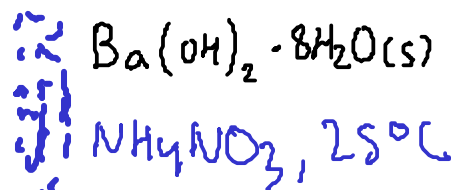
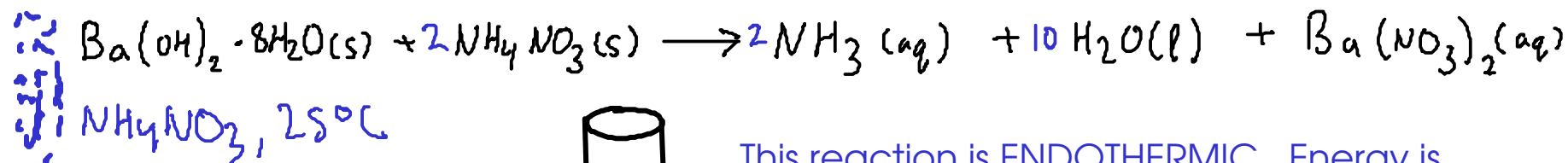
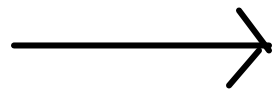
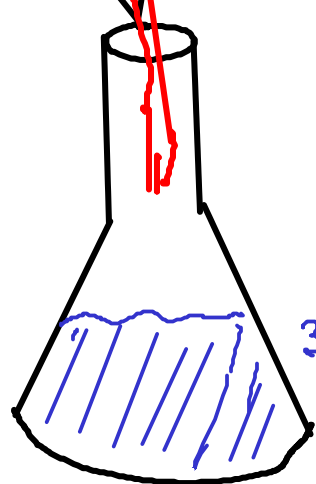
SYSTEM: the object or material under study

SURROUNDINGS: everything else

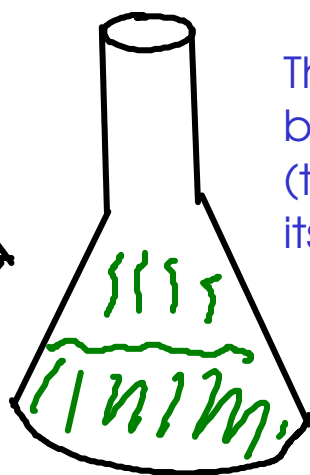
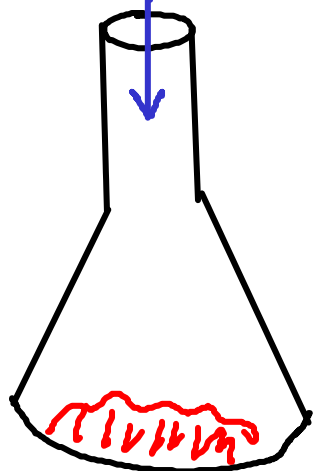
Type of process	Energy is ...	Sign of Q	Temp of SURROUNDINGS ...
ENDOTHERMIC	transferred from SURROUNDINGS to SYSTEM	+	decreases
EXOTHERMIC	transferred from SYSTEM to SURROUNDINGS	-	increases



This reaction is EXOTHERMIC. Energy is transferred from the reactants and products (the SYSTEM) to the water in the flask, the flask, etc. (the SURROUNDINGS)

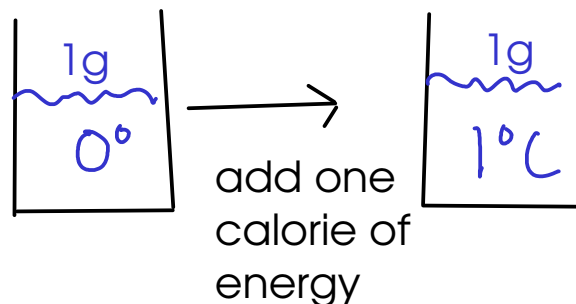


This reaction is ENDOTHERMIC. Energy is being transferred from the room/flask/etc. (the SURROUNDINGS) to the reaction itself (the SYSTEM).



ENERGY UNITS

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



$1\text{g} \approx 1\text{mL}$ 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

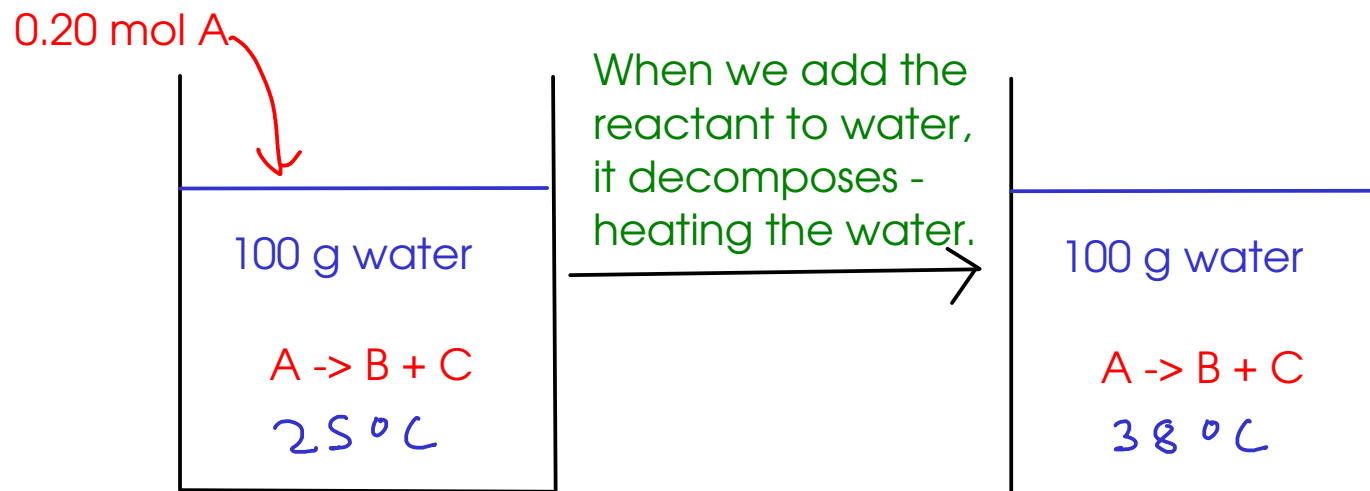
velocity

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

- 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,

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

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

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

This is ALWAYS final temp minus initial temp!

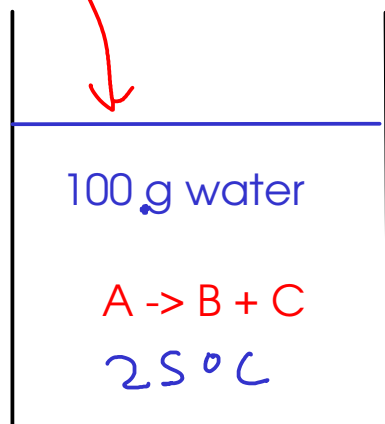
- For objects, like reaction vessels, you might know the HEAT CAPACITY, which is the amount of energy required to change the temperature of an object by one degree Celsius

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

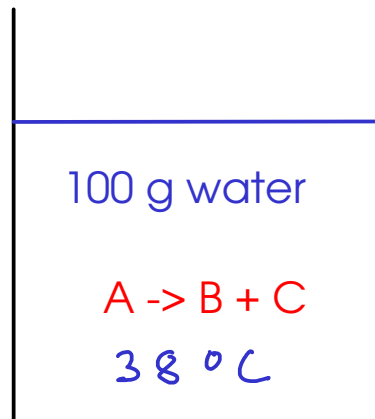
$$Q = C \times \Delta T$$

c = heat capacity

0.20 mol A



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



Specific heat of water:

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

$$Q_r + Q_w = 0$$

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

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

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 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.

$$\Delta H_r$$