

**AP Chemistry**  
**Unit 4**



**THERMOCHEMISTRY**

# Thermochemistry



- **Thermochemistry** is the study of the relationships between chemical reactions and energy changes

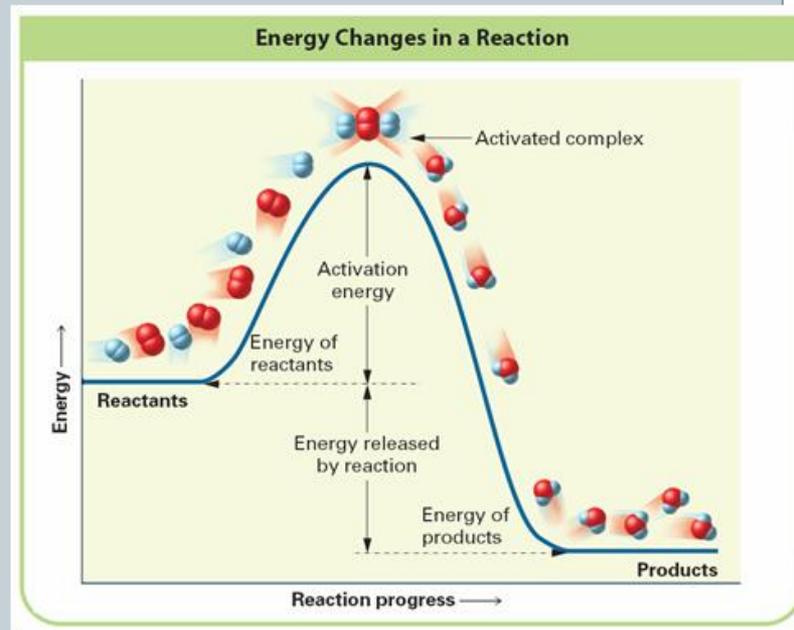
## **First Law of Thermodynamics**

- This is a restatement of the law of conservation of energy (energy cannot be created nor destroyed; it just switches forms)
- So, with chemical reactions - energy before and after reactions are the same. The reaction might give off energy or absorb energy

# Energy (E)



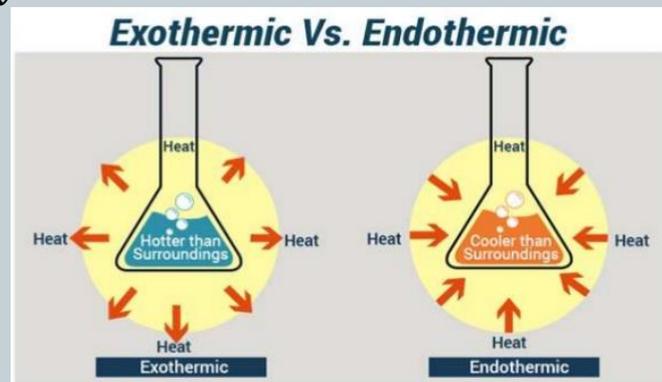
- **Energy** – the capacity to do work or to transfer heat.
  - Unit is Joules =  $\text{kg}\cdot\text{m}^2/\text{s}^2$
- **Kinetic Energy** - energy of motion;
  - $\text{KE} = \frac{1}{2} mv^2$
  - In chemistry proportional to K temperature



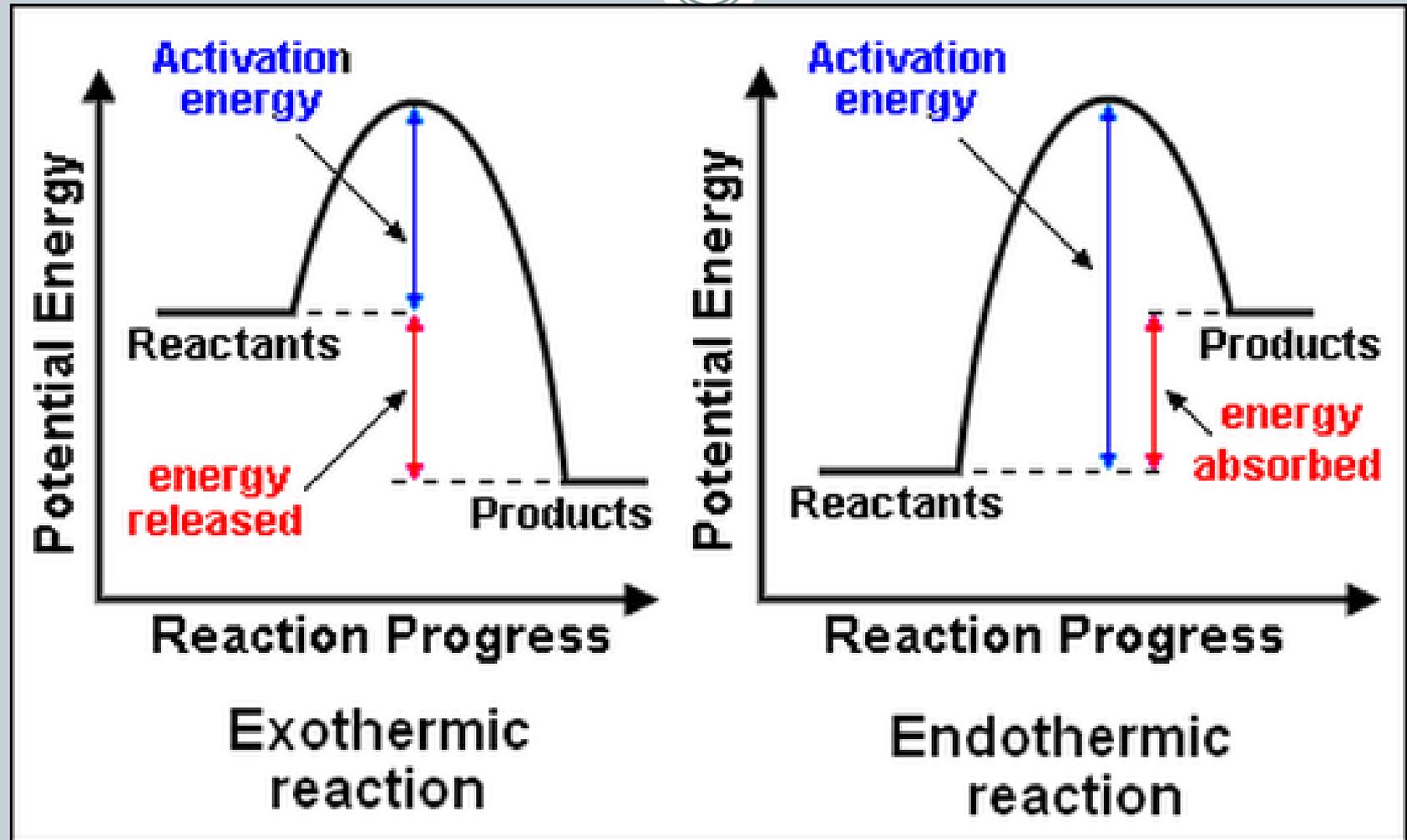
# Energy (E)



- **Potential Energy** – Energy stored in bonds
  - When bonds separated – PE  $\uparrow$ 
    - Because Energy must be added to overcome coulombic attraction
    - **Endothermic**: Reactants + Energy  $\rightarrow$  Products
    - Energy flows IN
  - When atoms bond- PE  $\downarrow$ 
    - Because energy is released
    - **Exothermic**: Reactants  $\rightarrow$  Products + Energy
    - Energy flows OUT



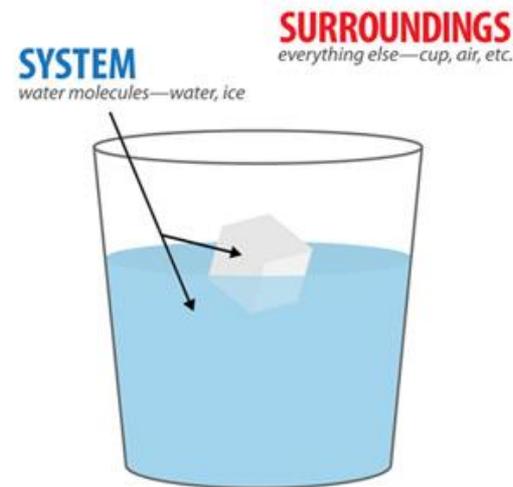
# Potential Energy or Energy Diagram



# System and Surroundings



- **System** - what we are studying
  - It can be a beaker or large parts of a factory.
    - ✦ Defined in problem
  - Allows you to simply study and measure matter and energy.

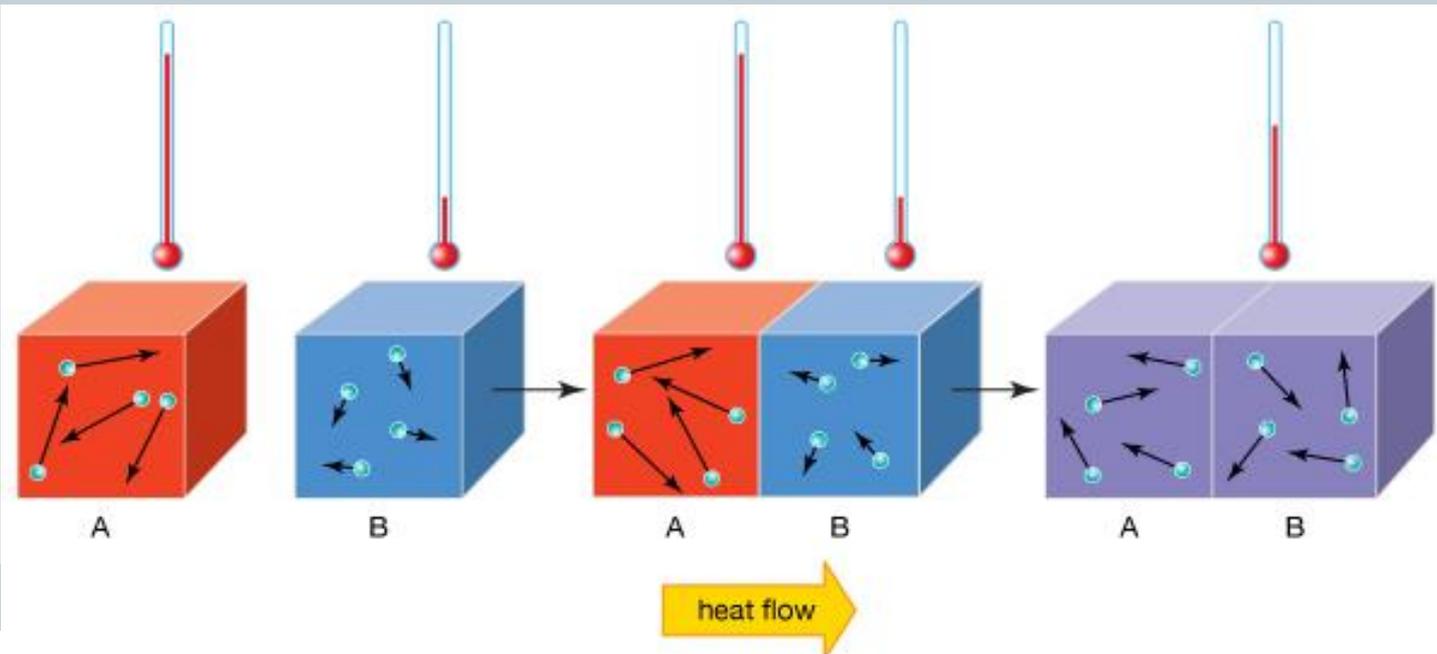


- **Surroundings** - Quite literally everything else.
- So if your reaction “loses” matter or energy - it’s not lost It just got transferred to the surroundings - and now you can’t measure it
- Without defining ‘**system**’ and ‘**surroundings**,’ it would be impossible to quantitatively measure the exchange of energy that occurs in all of the processes in the universe

# Heat ( $q$ ), Temperature ( $T$ ), Kinetic Energy



- These three things are related but not 100% similar.
- **Temperature** ( $T$ ) - this is the **AVERAGE kinetic energy** in a sample of molecules. It is also a measure of heat.
- **Heat** ( $q$ ) is a form of energy that can be transferred from one object to another – or from a system to the surroundings. Units - Joules



# Heat vs. Temperature



Basis for comparison	Heat	Temperature
Meaning	Heat is the amount of energy in a body	Temperature is the measure of the intensity of heat
Measures	Total kinetic and potential energy contained by the molecules in the object	Average kinetic energy of molecules in a substance
Property	Flows from hotter object to cooler object	Rises when heated and falls when cooled
Working Ability	Yes	No
Unit of Measurement	Joules	Kelvin
Device	Calorimeter	Thermometer
Labeled as	q	T

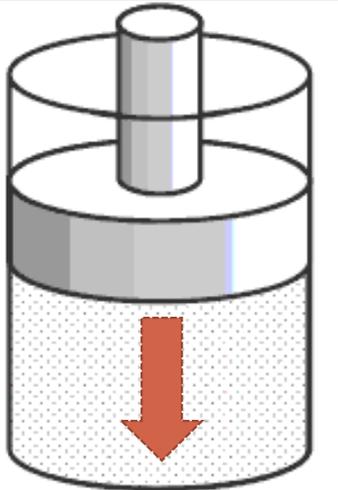
# Energy (E), Work (W), Heat (q)



- Thermodynamic quantities have 2 parts
  - Number: magnitude
  - Sign : + or - direction of flow
    - ✦ **The sign reflects the SYSTEM'S point of view**

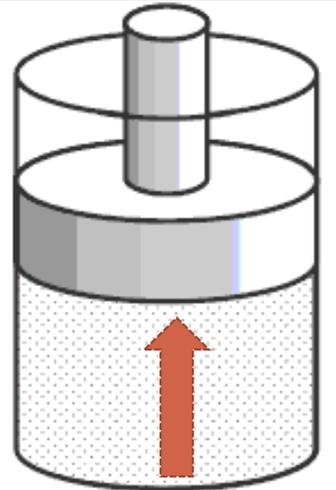
**Work (W)** = Force acting over a distance  
 $W = -P\Delta V$  with gases

## Work done on System



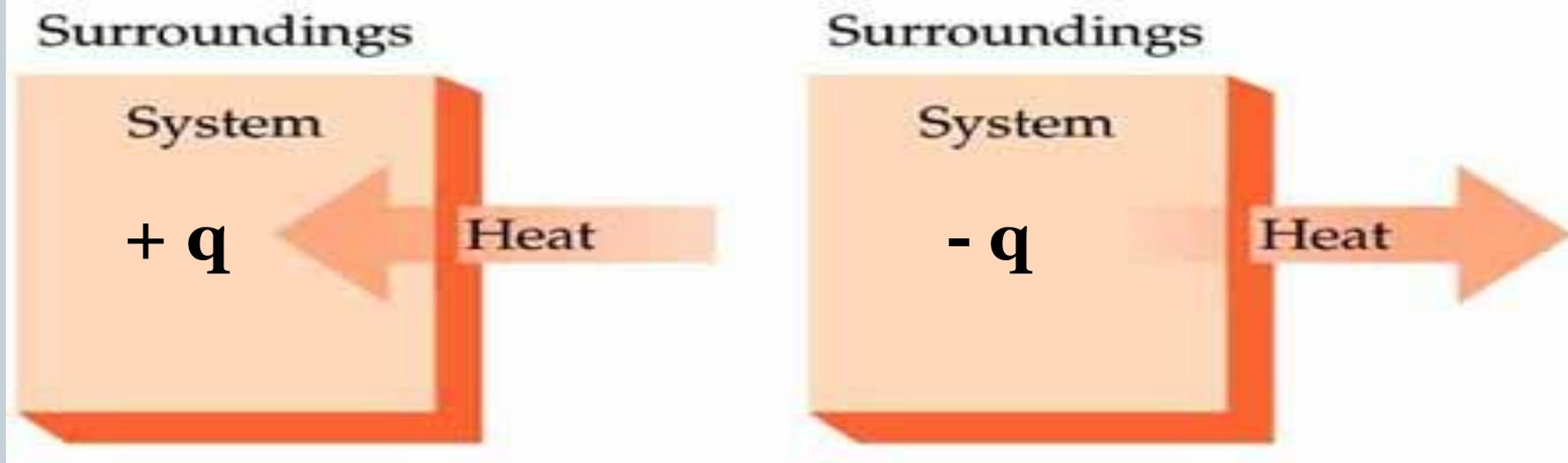
Compression  
+ work  
 $-\Delta V$

## Work done by System



Expansion  
- work  
 $+\Delta V$

# Energy (E), Work (W), Heat (q)



**+q heat absorbed  
(Reactant side)  
Endothermic**

**-q heat released  
(Product side)  
Exothermic**

# Energy (E), Work (W), Heat (q)



The total energy contained in a system is defined by

Energy, work, & heat  
(E) (w) (q)

the ability to do work (w) or  
produce heat (q)

$$\Delta E = w + q$$

+ w = work is done ON the system  
(compression)  
- w = work is done BY the system  
(expansion)

+ q = heat is absorbed  
- q = heat is released

$$w = -P\Delta V$$

**Compression:**  $-\Delta V$  decreases, +w Work done on system

**Expansion :**  $+\Delta V$  increases, - w Work done by system

# Work = $-P\Delta V$ Example



We can do work on the air in the bike pump by compressing it. Initially, the gas has a volume of 3.00 L. We apply a constant external pressure of 1.10 atm, to push down the handle of the bike pump until the gas is compressed to a volume of 2.50 L. How much work did we do on the gas?

## Given:

$$P = 1.10 \text{ atm}$$

$$V_{\text{final}} = 2.50 \text{ L}$$

$$V_{\text{initial}} = 3.00 \text{ L}$$

## Soln:

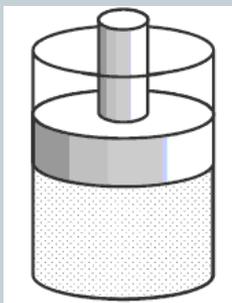
$$W = -P\Delta V$$

$$= -P(V_{\text{final}} - V_{\text{initial}})$$

$$= -(1.10 \text{ atm})(2.50 \text{ L} - 3.00 \text{ L})$$

$$W = 0.55 \text{ L}\cdot\text{atm}$$

Sign make sense? Yes compression, work done on system, so work should be positive



+w done on system  
-  $\Delta V$  compression

# Enthalpy (H)

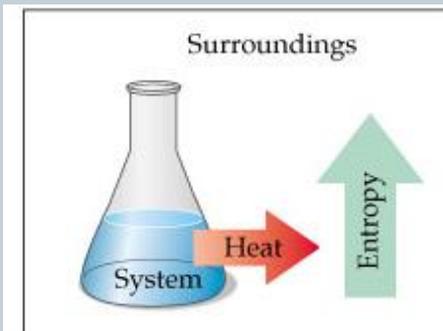
- **Enthalpy (H)** - The heat content of a chemical reaction
  - The enthalpy change ( $\Delta H$ ) is amount of heat energy released or absorbed when a chemical rxn occurs at constant pressure

$$\Delta H = \sum H_{\text{Products}} - \sum H_{\text{reactants}}$$

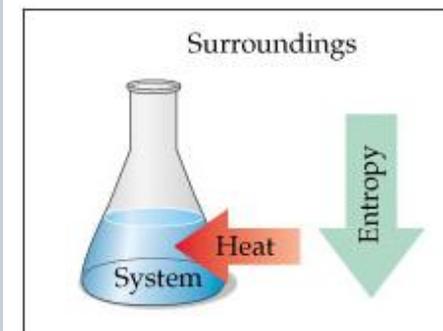
✦ Units are  $\text{KJ/mol}_{\text{rxn}}$

**Standard enthalpy change ( $\Delta H^\circ$ )** – energy changes for any rxn which are measured under standard conditions of temp and pressure

**25°C**, 1 atm, 1 Molarity



(a)

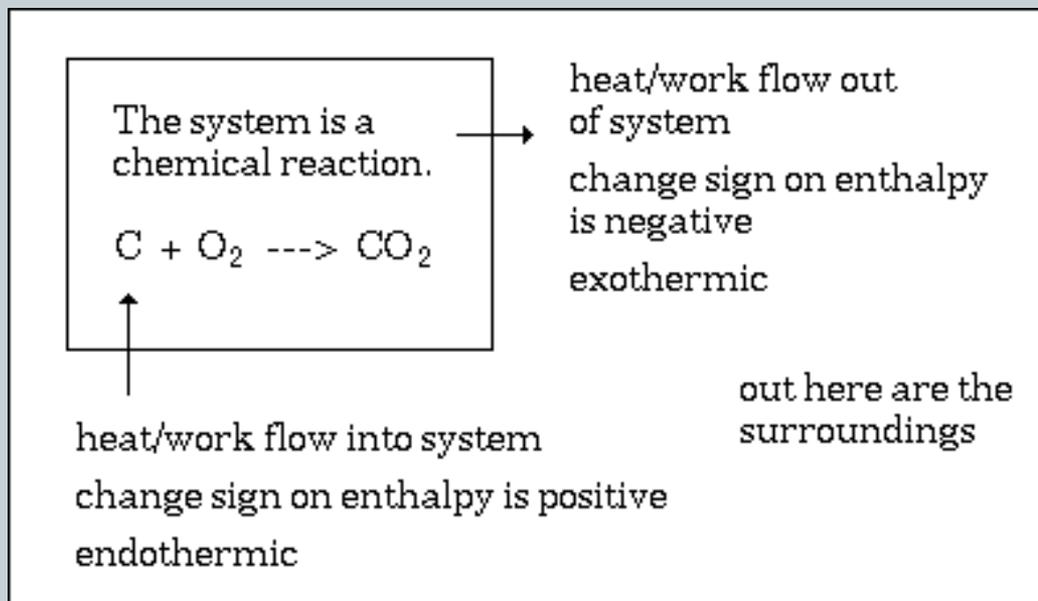


(b)

# Enthalpy (H)



- Thermodynamic quantities have 2 parts
  - Number – magnitude
  - Sign + or - direction of flow
    - ✦ **The sign reflects the SYSTEM'S point of view**



+q  
+ΔH

- q  
- ΔH

# Enthalpy of formation ( $\Delta H_f$ )



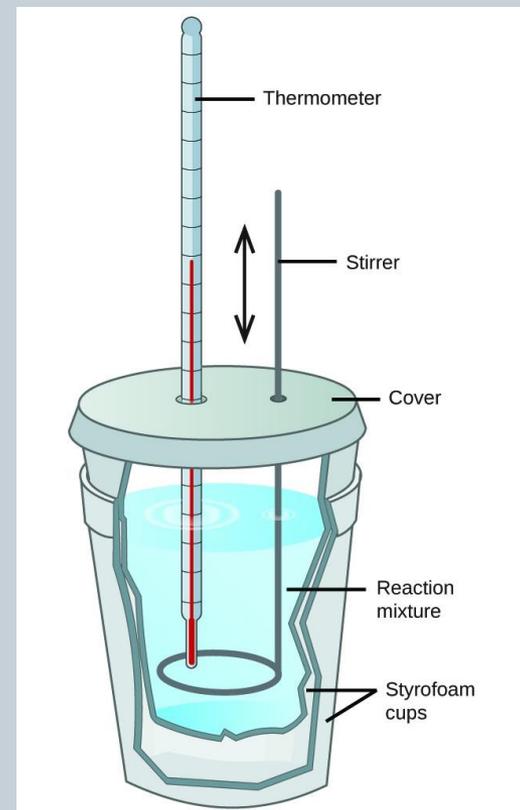
- **Enthalpy** is a STATE FUNCTION – Describes the equilibrium state of a system.
  - Distance is dependent on the path.
  - Displacement only looks at where you start and where you end.
- **Enthalpy** is the 2nd one - In order to determine the change in enthalpy - you just look at where you start and where you end (the measurement does NOT depend on the route you take to get there).
- $\Delta H_f$  = Energy change to produce **one mole of a compound** from ELEMENTS in their standard state. This assumes an enthalpy of ZERO for elements in their standard state.
- Standard state: 298K, 1 atm, 1 molar (slightly different than STP for gases)
- You only need to know the enthalpies of your products and reactants - remember, enthalpy is INDEPENDENT of the path you take. We care about where we started and where we end up.

# Calorimeter



- **Calorimetry**

- The amount of heat absorbed or released during a physical or chemical change can be measured usually by the change in temp of a known quantity of water in a **calorimeter**



# Hess Law



- $\Delta H$  is not dependent on Rxn Pathway
  - $\Delta H$  is the same whether Rxn takes place in 1 step or several

## Hess Rules

1. When a reaction is reversed, the sign of  $\Delta H$  must also be reversed
2. If all the coefficients of an eqn are multiplied or divided by a common factor, the  $\Delta H$  must be changed likewise
3. When canceling compounds the state of the compounds is important