

## Thermochemistry

## State Functions

- Depend only on the initial and final states
- Do not depend on the path taken
- Denoted by upper case letters
  - e.g. T, E, H, S, G, P, V (or the height of Mt Everest)
- Path functions depend on how change took place (discharging a battery, or path taken while climbing mt Everest for example)
  - e.g. q, w

## Internal Energy E

- Sum of all the KE and PE of all particles in the system

## Systems and Surroundings

- To keep track of energy changes we have to define a system (the part we are studying)
- And the surroundings (everything else)
- There may be a boundary (or it may be imaginary)

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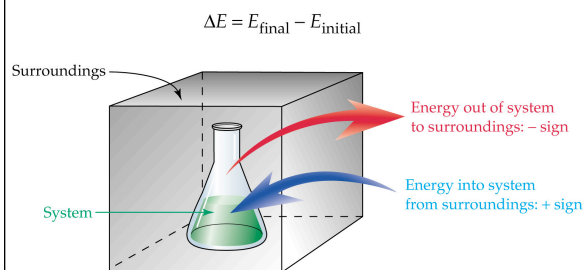
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System and Surroundings must be defined



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## Open, Closed and Isolated systems

- Open – can transfer matter and energy
- Closed – transfer energy but not matter
- Isolated – no transfer of matter or energy
  - (hard to do!)

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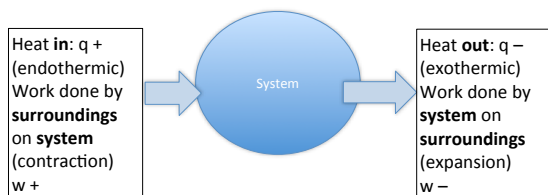
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## First Law of Thermodynamics

- Energy can not be created or destroyed (can be transferred or transformed)
- $\Delta E = q + w$ 
  - $q$  is the thermal energy (heat) change (J)
  - $w$  is the work done (J)
- In chemistry most systems we study (except gases) do not expand or contract much
  - $\Delta E = q$

Surroundings



## State and Path functions

- $q$  and  $w$  are path functions– it matters **how** the change occurs - (eg discharging a battery in different ways)
- BUT at **constant pressure**  $q$  (the thermal energy change) is a **state function**, **Enthalpy**  $q = \Delta H$

## Enthalpy

- Heat absorbed or emitted during a reaction under **constant pressure** (which is almost everything we are interested in)
- Endothermic  $\Delta H$  is + (heat goes **into** the reaction and the surroundings get **cold**)
- Exothermic  $\Delta H$  is – (heat goes **out of** the reaction and the surroundings get **hot**)

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## Exothermic or Endothermic?

- Sweat evaporating
- Water freezing
  - (for system – water and the surroundings - everything else?)
- Wood burning
- Chemical handwarmer

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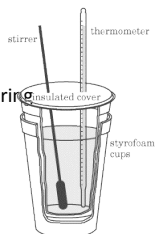
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## Calorimetry at constant P

- To find thermal energy change ( $q$ ) during a given process
- Do reaction in insulated container
- Measure T change
- $q = m \times c \times \Delta T$ 
  - Mass x specific heat x temperature change
- Specific heat = heat to raise 1g by 1°C
- Heat capacity C = heat to raise whole thing 1°C
- Molar heat capacity  $C_m$  = heat to raise 1mol by 1°C
- Enthalpy change  $\Delta H$  can be calculated by



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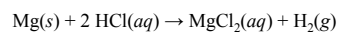
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## Calorimetry

- What are you measuring the T of? (system or surroundings)
- What is the sign of q?
- How will you change q to  $\Delta H$ ?

What is  $\Delta H_{\text{rxn/mol Mg}}$  for the reaction



if 0.158 g Mg reacts in  
100.0 mL of solution changes the temperature from  
25.6°C to 32.8°C?

(assumptions: specific heat of solution = 4.18 J/g°C

Density of solution = 1 g/mL)

Example – What is  $\Delta H_{\text{rxn/mol Mg}}$  for the reaction

$\text{Mg}(s) + 2 \text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2(g)$  if 0.158 g Mg reacts in  
100.0 mL of solution to change the temperature from 25.6°C to 32.8°C?

Use  $C_s = 4.18 \text{ J/g}^\circ\text{C}$ ,  $d_{\text{soln}} = 1.00 \text{ g/mL}$

$$q_{\text{soln}} = m \times C_s \times \Delta T$$

$$= 1.00 \times 10^2 \text{ g} \times 4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} \times 7.2^\circ\text{C} = 3.0 \times 10^3 \text{ J}$$

$$q_{\text{rxn}} = -q_{\text{soln}} = -3.0 \times 10^3 \text{ J}$$

$$0.158 \text{ g Mg} \times \frac{1 \text{ mol}}{24.31 \text{ g}} = 6.4994 \times 10^{-3} \text{ mol}$$

$$\Delta H = \frac{q_{\text{rxn}}}{\text{mol Mg}} = \frac{-3.0 \times 10^3 \text{ J}}{6.4994 \times 10^{-3} \text{ mol}}$$

$$= -4.6 \times 10^5 \text{ J/mol}$$

## The Second Law

- For any change in a system the total Entropy of the Universe must increase.
- (you cant get as much energy back when a change occurs as you put in – some is always lost – spread out as thermal energy – unusable)
- $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

## Entropy

- Entropy is a measure of the number of possible arrangements
- The more possible arrangements – the higher the probability of that state.
- $S = k \ln W$  (where  $W$  = number of arrangements)

## Which has more entropy

- A deck of cards in order or a shuffled deck?
- Separated dye and water or mixed up?
- $\text{H}_2\text{O}_{(s)}$  or  $\text{H}_2\text{O}_{(l)}$
- $\text{CaCO}_3(s)$  or  $\text{CaO}(s) + \text{CO}_2(g)$

Can you think of examples where the

- what effect does a more ordered system have on the surroundings?
- Why don't living systems violate the second law?

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