

## Energy and Chemical Reactions

**Energy:** Critical for virtually all aspects of chemistry

Defined as:

We focus on **energy transfer**. We observe energy changes in:

- **Heat Transfer:** How much energy can a material absorb before a phase change or a reaction occurs?
- **Phase Change:** melting/freezing, boiling/condensing
- **Chemical Reactions:** Is energy absorbed or released in the reaction? Do we need to supply a little energy to get the reaction started (hexane combustion)?

**Thermodynamics:** Study of energy and energy conversions.

- The thermodynamics of a reaction determines whether or not a reaction will be *product-favored* or *reactant favored*
- Every thermodynamic value has a number and a sign.

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## Characterizing Energy:

**Potential Energy:**

- Chemically, potential energy results from:
  - Sharing of electrons in bonds
  - Electrostatic interactions

**Kinetic Energy:**

**Quantifying Energy:**

- **calorie (cal):**
- **kilocalories (kcal or Cal):**
- **joule (J):**            **1 cal = 4.184 joules**  
                                 **1 kcal = 4.184 kJ**
- **How big is a joule?**  
How high can I raise a 1 kg book using one joule of energy?

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## Thinking about Energy

### A Few Key Terms:

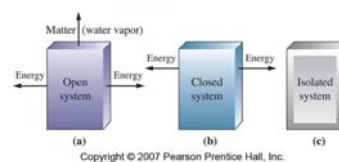
- **system:** specific part of the universe that we have our attention.
- **surroundings:** everything else (everything that is not the *system*)
- **universe** = system + surroundings.

*In general terms, energy is transferred between the system and the surroundings.*

*We take the perspective of the system*

*Energy in = positive*

*Energy out = negative*



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## Thinking about Energy

**Law of Conservation of Energy: VERY IMPORTANT, we rely on this!**

- At a given instant, a system has a fixed total energy:

$$U =$$

- We tend to focus on energy changes (Why?):
  - When working with energy changes, keep in mind that energy can be transferred in two ways: as heat, and as work

$$\Delta U =$$

- To simplify matters, we typically design experiments so that the work contribution is negligible (or at least understood)

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## Energy Transfer as Heat: Enthalpy Changes

**Enthalpy,  $\Delta H$ :** Heat transfer at constant pressure

- Exothermic process:  
Heat is transferred from \_\_\_\_\_ to \_\_\_\_\_  
q is \_\_\_\_\_
- Endothermic process:  
Heat is transferred from \_\_\_\_\_ to \_\_\_\_\_  
q is \_\_\_\_\_
- $\Delta H$  has the same sign as q
- $s \rightarrow l$ , or  $l \rightarrow g$  phase changes are endothermic, **positive  $\Delta H$**
- $l \rightarrow s$ , or  $g \rightarrow l$  phase changes are exothermic, **negative  $\Delta H$**

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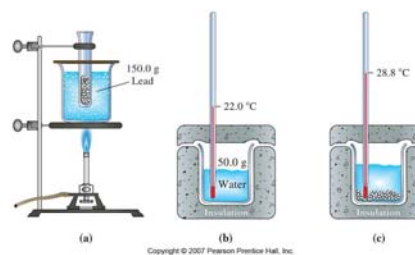
## Energy Transfer as Heat:

**Heat ALWAYS moves from a hotter to a cooler object!!!**

- Quantity of heat transferred depends on the **heat capacity** of the object being transferred to.

**Heat Capacity:**

Heat Capacity is an *extensive* property  
Because of its extensive character,  
we must specify heat capacity on a  
mass basis



**Specific Heat Capacity** (or specific heat):

- May be defined on a *per gram* or *per mole* basis

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## A couple of examples:

**Example:** If 24.1 kJ is used to warm a piece of aluminum with a mass of 250. g, what is the final temperature of the aluminum if its initial temperature is 5.0° C? The specific heat of aluminum is 0.902 J/gK.

A more experimentally common example: Heat transfer between materials.

**Example:** A piece of iron (400. g) is heated in a flame and dropped into a beaker containing 1000. g of water. The original temperature of the water was 20.0° C, but it is 32.8° C after the iron bar is dropped in and both have come to the same temperature. What was the original temperature of the hot iron bar? (Assume that no heat is lost to the beaker or the surrounding air.)

Specific heats: Fe = 0.451 J/gK; H<sub>2</sub>O(l) = 4.184 J/gK

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## Energy and Changes of State

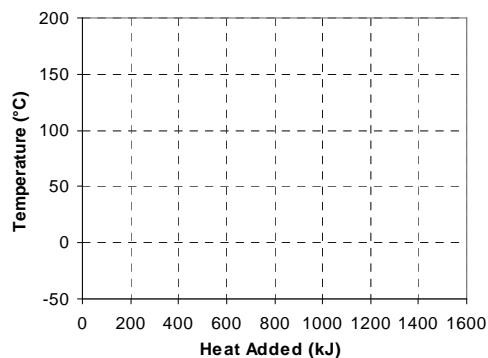
What energy changes are involved in converting ice at -20° C to steam at 200° C?

- multi-step process

**Heat of Fusion:**

**Heat of Vaporization:**

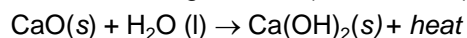
Let's look at this quantitatively:  
How much heat is required to convert 500. g of ice at -20° C to 500. g of steam at 200° C?



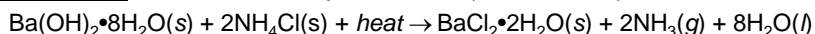
## Enthalpy and Chemical Reactions:

Heat may be released or absorbed during a chemical reaction.

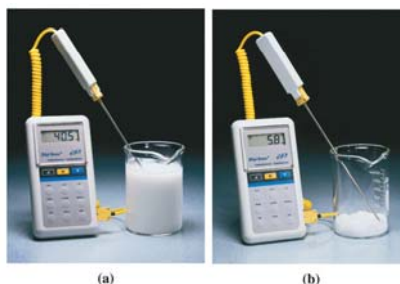
**Exothermic** Reactions have a negative  $\Delta H$  (release heat)



**Endothermic** Reactions have positive  $\Delta H$  (absorb heat)



What determines the quantity of heat transferred?



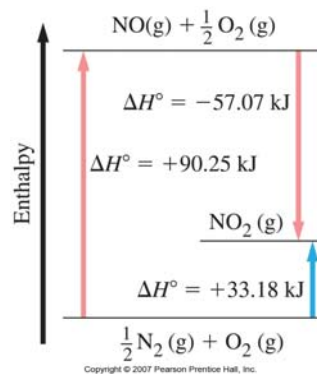
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## Enthalpy and Chemical Reactions:

There may be several pathways that allow reactants to get to products for a reaction

BUT: The energy change for the overall reaction must be the same.

- We can take advantage of this to make some predictions



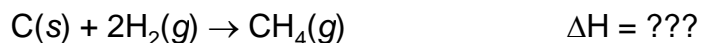
**Hess' Law:** if a reaction is the sum of two or more other reactions, the  $\Delta H$  for the overall process must be the sum of the  $\Delta H$  of the constituent reactions.

- Hess' law works because enthalpy ( $\Delta H$ ) is a *state function*. It only depends on the initial and final conditions and not on the path in between.

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## Hess' Law Example

**Example:** What is the enthalpy change for the formation of methane (CH<sub>4</sub>) from elemental carbon and hydrogen?



Lets look at 3 reactions:

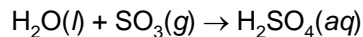
	Reaction	$\Delta H$ (kJ)
1	$\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$	-393.5
2	$\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$	-285.8
3	$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$	-890.3

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## State Functions are Handy!

Because enthalpy ( $\Delta H$ ) is a state function, we can usually take an multiple paths to its determination.

Consider the formation of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) from water and sulfur trioxide:



Let's propose 2 pathways for this reaction:

*NOTE: because  $\Delta H$  is a state function, it MUST be the same for both paths, as long as reactants and products are the same*

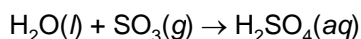
Reactants  
H<sub>2</sub>O(l) + SO<sub>3</sub>(g)

Products  
H<sub>2</sub>SO<sub>4</sub>(aq)

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## Enthalpies of Formation

The second, indirect pathway involves breaking the reagents down into their component elements and reassembling the elements into products:



Lets write the reactions:

	Reaction	$\Delta H_f^\circ$
1	$\text{H}_2(g) + 1/2\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$	-285.8 kJ/mol H <sub>2</sub> O
2	$\text{S}(s) + 3/2 \text{O}_2(g) \rightarrow \text{SO}_3(g)$	-395.7 kJ/ mol SO <sub>3</sub>
3	$\text{H}_2(g) + \text{S}(s) + 2\text{O}_2(g) \rightarrow \text{H}_2\text{SO}_4(aq)$	-909.3 kJ/mol H <sub>2</sub> SO <sub>4</sub>

The energy required to form 1 mol of a compound directly from its elements is the **standard molar enthalpy of formation ( $\Delta H_f^\circ$ )**.

"standard state" = 25°C, 1 bar (~0.986 atm)

We can "build" our reaction of interest by properly adding and/or subtracting reactions 1-3. Then we calculate  $\Delta H_{\text{rxn}}^\circ$  by doing the same thing to the  $\Delta H_f^\circ$  values.

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## Enthalpies of Formation

**TABLE 7.2** Some Standard Molar Enthalpies of Formation at 298.15 K,  $\Delta H_f^\circ$

Substance	kJ/mol <sup>a</sup>	Substance	kJ/mol <sup>a</sup>
CO(g)	-110.5	HBr(g)	-36.40
CO <sub>2</sub> (g)	-393.5	HI(g)	26.48
CH <sub>4</sub> (g)	-74.81	H <sub>2</sub> O(g)	-241.8
C <sub>2</sub> H <sub>2</sub> (g)	226.7	H <sub>2</sub> O(l)	-285.8
C <sub>2</sub> H <sub>4</sub> (g)	52.26	H <sub>2</sub> S(g)	-20.63
C <sub>2</sub> H <sub>6</sub> (g)	-84.68	NH <sub>3</sub> (g)	-46.11
C <sub>3</sub> H <sub>8</sub> (g)	-103.8	NO(g)	90.25
C <sub>4</sub> H <sub>10</sub> (g)	-125.6	N <sub>2</sub> O(g)	82.05
CH <sub>3</sub> OH(l)	-238.7	NO <sub>2</sub> (g)	33.18
C <sub>2</sub> H <sub>5</sub> OH(l)	-277.7	N <sub>2</sub> O <sub>4</sub> (g)	9.16
HF(g)	-271.1	SO <sub>2</sub> (g)	-296.8
HCl(g)	-92.31	SO <sub>3</sub> (g)	-395.7

<sup>a</sup>Values are for reactions in which one mole of substance is formed. Most of the data have been rounded off to four significant figures.

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## Enthalpies of Formation

In general, we can calculate the enthalpy change for any reaction by:

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma[n\Delta H_{\text{f}}^{\circ}(\text{products})] - \Sigma[n\Delta H_{\text{f}}^{\circ}(\text{reactants})]$$

where n is the stoichiometric coefficient for each reactant and product from the balanced reaction.

So, for  $\text{H}_2\text{O}(l) + \text{SO}_3(g) \rightarrow \text{H}_2\text{SO}_4(aq)$ , calculate  $\Delta H_{\text{rxn}}^{\circ}$  by:

$$\Delta H_{\text{rxn}}^{\circ} = [1\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{SO}_4(aq))] - [1\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}(l)) + 1\Delta H_{\text{f}}^{\circ}(\text{SO}_3(g))]$$

$$\Delta H_{\text{rxn}}^{\circ} = (-909.3 \text{ kJ}) - [(-285.8 \text{ kJ}) + (-395.7 \text{ kJ})] \text{ ***}$$

\*\*\*why no "mol" units??

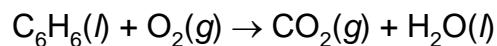
$$\Delta H_{\text{rxn}}^{\circ} = -909.3 \text{ kJ} - (-681.5 \text{ kJ}) = \mathbf{-227.8 \text{ kJ}}$$

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## Enthalpies of Formation

**Example:** Benzene ( $\text{C}_6\text{H}_6$ ) is an important hydrocarbon. Calculate its enthalpy of combustion (in kJ/mol  $\text{C}_6\text{H}_6$ ) from the following reaction:

$$\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}(l)) = -285.8 \text{ kJ/mol}, \quad \Delta H_{\text{f}}^{\circ}(\text{C}_6\text{H}_6(l)) = +40.9 \text{ kJ/mol}, \\ \Delta H_{\text{f}}^{\circ}(\text{CO}_2(g)) = -393.5 \text{ kJ/mol}.$$



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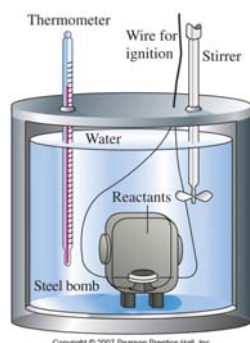


## Calorimetry

Experimental determinations of  $\Delta H^\circ_{\text{rxn}}$ : Calorimetry

- Based on 1<sup>st</sup> Law of Thermodynamics

$$q_{\text{system}} = -q_{\text{surroundings}}$$



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## Calorimetry

**Example:** In a coffee-cup calorimeter, 1.60 g of ammonium nitrate is mixed with 75.0 g of water at an initial temperature of 25.00°C. After dissolution of the salt, the final temperature of the calorimeter contents is 23.34°C. Assuming that the heat capacity of the calorimeter is 4.18 J/gK (close to that of water), and assuming no heat is lost outside the calorimeter, calculate the enthalpy change for the dissolution ( $\Delta H_{\text{soln}}$ ) of ammonium nitrate in kJ/mol.

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## Aside: Energy, Heat and Work

Remember:  $\Delta U = q + w$

- When does work play a (significant) role?

Work occurs when a material expands to a new volume or contracts to a smaller volume.

$$w = -P\Delta V$$

$P$  = external pressure (typically constant)

- When might this become important?
- How would we deal with this?