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Energy & Chemical Reactions: Thermochemistry or Thermodynamics

Chapter Five

Chemistry 221
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4/29/24

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Energy & Chemistry



Burning peanuts
supplies sufficient
energy to boil
water



Burning sugar (sugar
reacts with KClO_3 , a
strong oxidizing
agent)

Knowing if reactions give energy off or
need energy to occur is important

Thermochemistry or Thermodynamics: the
study of energy exchange

CHEMICAL REACTIVITY

What drives chemical
reactions? How do
they occur, and how
fast?

The first question is
answered by
THERMODYNAMICS,
and the second
question is answered
by **KINETICS**.



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CHEMICAL REACTIVITY

THERMODYNAMICS dictates if the reaction will
occur or not.



Sand will not
decompose into
silicon and oxygen

Paper will
combine with
oxygen to burn



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CHEMICAL REACTIVITY

KINETICS dictates how fast the reaction will
occur.

Example: diamond into graphite is
thermodynamically favored, but the kinetics
of the reaction is too slow to be of useful



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CHEMICAL REACTIVITY

We have already seen a number of "driving
forces" for reactions that are **PRODUCT-
FAVORED**.

- formation of a precipitate (*precipitation*)
- gas formation (*gas forming*)
- H_2O formation (*acid-base*)
- electron transfer (*redox*) i.e. in a battery



In general, reactions that
transfer energy to their
surroundings are **product-
favored**.



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All of thermodynamics depends on the law of **CONSERVATION OF ENERGY**:

- The total energy is unchanged in a chemical reaction.
- Energy expressed as **heat and/or work**. Chemists usually focus on heat (q) instead of work (w).
- First law of thermodynamics:

$$\Delta E = q + w = 0$$



Energy & Chemistry

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UNITS OF ENERGY

1 calorie (cal) = heat required to raise temperature of 1.00 g of H₂O by 1.0 °C.

1000 cal = 1 kilocalorie = 1 kcal

1 kcal = 1 Calorie (a "food calorie")

But in our science classes we will use the unit called the **JOULE (J)** (= kg m² / s²)

1 cal = 4.184 joules

1 Cal = 1000 cal = 4184 J

also: 1000 J = 1 kJ, etc.



James Joule
1818-1889

Memorize 4.184!

Potential Energy

Two types of energy: **potential energy** and **kinetic energy**

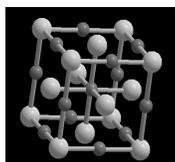
Potential energy - energy due to position or composition, "stored energy"

In chemistry, **positive and negative particles (ions) attract one another** - electrostatic energy.

Also: gravitational, nuclear



Bungee jumper



NaCl - composed of Na⁺ and Cl⁻ ions.

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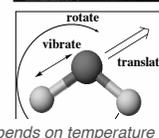
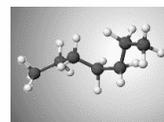
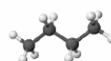
Kinetic Energy

Kinetic energy: energy of motion. Three forms of kinetic energy:

Translational - from physics, $KE = \frac{1}{2} mv^2 = 0.5(\text{mass})(\text{velocity})^2$

Vibrational

Rotational



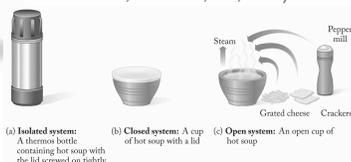
Kinetic energy depends on temperature

System and Surroundings



Piston with H₂ and O₂

- The **system** includes the molecules we want to study (here, the hydrogen and oxygen molecules).
- The **surroundings** are everything else (here, the cylinder and piston; could be water, solvent, air, etc.)



(a) Isolated system: A thermos bottle containing hot soup with the lid screwed on tightly
(b) Closed system: A cup of hot soup with a lid
(c) Open system: An open cup of hot soup

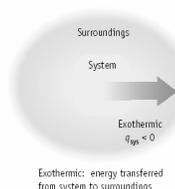
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Directionality of Heat Transfer

Heat always transfers from the hot object to the cooler object.

EXOthermic: heat transfers from **SYSTEM** to **SURROUNDINGS**.

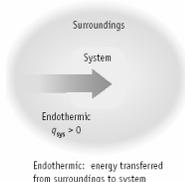


T(system) goes down
T(surr) goes up - **this is what we usually measure**

Directionality of Heat Transfer

Heat always transfers from the hot object to the cooler object.

ENDOthermic: heat transfers from **SURROUNDINGS** to the **SYSTEM**.



T(system) goes up
T(surr) goes down -
this is what we usually measure

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- ## Enthalpy (ΔH)
- Enthalpy (ΔH) is heat (q) transferred at constant pressure (i.e. $\Delta H = q_p$)
 - $\Delta H > 0$, **Endothermic**; $\Delta H < 0$, **Exothermic**
 - Add subscripts to indicate ΔH for specific process i.e., ΔH_{vap} , ΔH_{rxn} , ΔH_f

$$\Delta E = q + w \text{ and}$$

$$\Delta E = \Delta H + w \quad (P \text{ const})$$

w is usually small, so

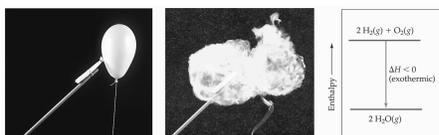
$$\Delta H \approx \Delta E$$



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Enthalpy of Reaction

The quantity, ΔH , is called the enthalpy of reaction (ΔH_{rxn}), or the heat of reaction and is usually measured in kJ/mol

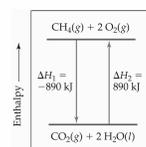


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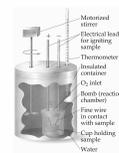
The Truth About Enthalpy

ΔH for a reaction in the forward direction is equal in size, but opposite in sign, to ΔH for the reverse reaction.

ΔH for a reaction depends on the state of the products and the state of the reactants.



We cannot know the exact enthalpy of the reactants and products, but we measure ΔH through **calorimetry**, the measurement of heat flow.

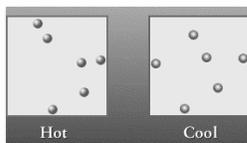


Bomb calorimeter

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Calorimetry

Calorimetry is the measure of heat (energy) transfer

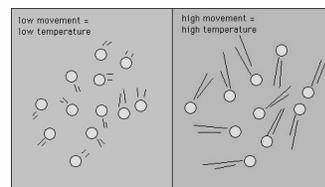


Heat energy is associated with molecular motions (Kinetic Molecular Theory)

Heat transfers until thermal equilibrium is established

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Heat & Matter - no change in state



When matter absorbs heat (q , in J), its temperature (ΔT) will rise depending on its mass (m , in g) and specific heat capacity (C):

$$q = mC\Delta T$$

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$$q = mC\Delta T$$

Heat transferred with no phase change

q = heat (or enthalpy) "lost" or "gained"

m = sample mass (usually grams)

C = specific heat capacity

ΔT = change in temperature, K or °C

ΔT = final T - initial T

q is positive when heat flows in (cold surroundings) - *endothermic*

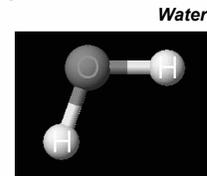
q is negative when heat flows out (hot surroundings) - *exothermic*

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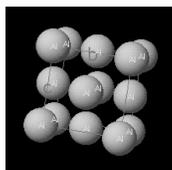
Specific Heat Capacity

The heat (J) required to raise 1 g of an object by 1 °C (or K)

Memorize 4.184 for water



Aluminum



| Substance | Spec. Heat (J/g·K) |
|---------------------|--------------------|
| H ₂ O(l) | 4.184 |
| Ethylene glycol(l) | 2.39 |
| Al(s) | 0.902 |
| glass(s) | 0.84 |

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Specific Heat Capacity

If 25.0 g of Al cool from 310. °C to 37 °C, how many joules of heat energy are lost by the Al?



$$q = mC\Delta T$$

$$C_{Al} = 0.902 \text{ J g}^{-1} \text{ K}^{-1}$$

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Specific Heat Capacity

If 25.0 g of Al cool from 310. °C to 37 °C, how many joules of heat energy are lost by the Al? $C_{Al} = 0.902 \text{ J g}^{-1} \text{ K}^{-1}$

$$\text{heat gain/lost} = q = (\text{mass})(\text{sp. ht.})(\Delta T)$$

where $\Delta T = T_{\text{final}} - T_{\text{initial}}$

$$q = (25.0 \text{ g})(0.902 \text{ J/g}\cdot\text{C})(37 - 310.)\text{C}$$

$$q = -6160 \text{ J}$$

Notice also that ΔT can be either K or °C - the difference in temperatures is the same!

Specific Heat Capacity

A piece of iron (88.5 g) at 77.8 °C is placed in 244 g of water at 18.8 °C. What is the final temperature of the mixture?

By the law of conservation of energy:

$$q_{\text{hot}} + q_{\text{cold}} = 0, \text{ or}$$

$$m_{\text{Fe}}C_{\text{Fe}}\Delta T_{\text{Fe}} + m_{\text{water}}C_{\text{water}}\Delta T_{\text{water}} = 0$$

$$C_{\text{Fe}} = 0.449 \text{ J g}^{-1} \text{ K}^{-1}$$

$$C_{\text{water}} = 4.184 \text{ J g}^{-1} \text{ K}^{-1} \text{ Memorize}$$

Final Temperature (warm) same for Fe & H₂O

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Specific Heat Capacity

Fe (88.5 g, 0.449 J/g·K, 77.8 °C) and water (244 g, 4.184 J/g·K, 18.8 °C); final temperature?

$$q_{\text{hot}} + q_{\text{cold}} = 0$$

$$m_{\text{Fe}}C_{\text{Fe}}\Delta T_{\text{Fe}} + m_{\text{water}}C_{\text{water}}\Delta T_{\text{water}} = 0$$

$$88.5 * 0.449 * (T_f - 77.8) + 244 * 4.184 * (T_f - 18.8) = 0$$

$$39.7T_f - 3090 + 1020T_f - 19200 = 0$$

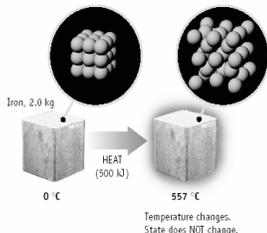
$$1060T_f = 22300$$

$$T_f = 21.0 \text{ °C}$$

Efficient method to determine approximate final temperature of mixture

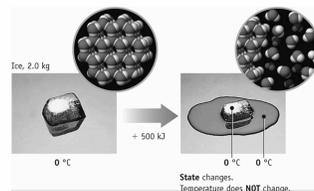
Heat Transfer No Change in State

$$q \text{ transferred} = (\text{mass})(\text{sp. ht.})(\Delta T)$$



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Heat & Changes of State

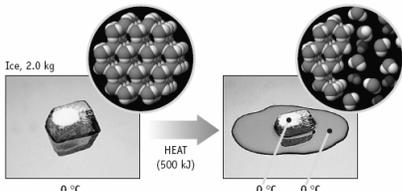


When matter absorbs heat, its temperature will rise until it undergoes a *Phase Change* (solid to liquid, liquid to gas, solid to gas)

The matter will continue to absorb energy, however during the phase change its temperature remains constant (no ΔT): Phase changes are "isothermal" processes.

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Heat Transfer with Change of State



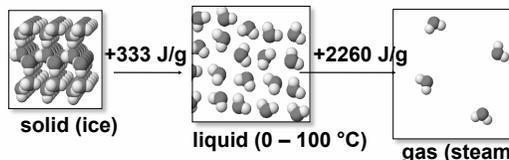
Changes of state involve energy (at constant T)
Ice + 333 J/g (heat of fusion) -----> Liquid water
 $q = (\text{heat of "something"})(\text{"mass"})$

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Heat & Changes of State

What quantity of heat is required to melt 500. g of ice at 0.0 °C and heat the water to steam at 100.0 °C?

Heat of fusion (ΔH_{fus}) for ice = 333 J/g
Specific heat of water = 4.184 J/g·K
Heat of vaporization (ΔH_{vap}) = 2260 J/g



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What quantity of heat is required to melt 500. g of ice at 0.0 °C and heat the water to steam at 100.0 °C?

Strategy: break this problem into **three calculations**:

- Melt ice (phase change, ice - liquid, ΔH_{fus})
- Heat liquid (0 °C to 100 °C)
- Evaporate liquid (Phase change, liquid - steam, ΔH_{vap})
- Mass is constant at 500. g

Heat & Changes of State

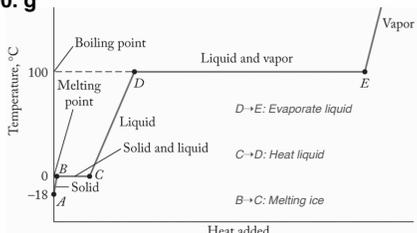
What quantity of heat is required to melt 500. g of ice at 0.0 °C and heat the water to steam at 100.0 °C?

- To **melt ice** at 0.0 °C (use ΔH_{fus})
 $q = (500. \text{ g})(333 \text{ J/g}) = 1.67 \times 10^5 \text{ J}$
- To **heat water** from 0.0 °C to 100.0 °C
 $q = (500. \text{ g})(4.184 \text{ J/g}\cdot\text{K})(100. - 0.)\text{K} = 2.09 \times 10^5 \text{ J}$
- To **evaporate water** at 100. °C (use ΔH_{vap})
 $q = (500. \text{ g})(2260 \text{ J/g}) = 1.13 \times 10^6 \text{ J}$
- Total heat energy = $1.51 \times 10^6 \text{ J} = 1510 \text{ kJ}$

Heat Transfer covered more in Chapter 10 of CH 222

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Heat & Changes of State



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Standard Enthalpy Values

Most ΔH values are labeled ΔH°

Measured ($^\circ$) under standard conditions

P = 1 bar (approx. 1 atm)

Concentration = 1 mol/L

T = usually 25 °C

with all species in *standard states*

i.e., C = graphite and O₂ = gas

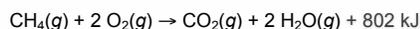
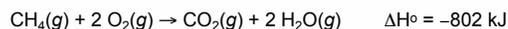
$$\Delta H_x^\circ$$

Δ = change in
H = heat energy
 θ = standard conditions
x = type of change

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Thermochemical Equations

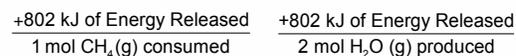
Thermochemical equations are regular chemical equations with an energy term.



Energy is a **product** just like CO₂ or H₂O! (*Exothermic*)

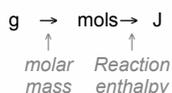
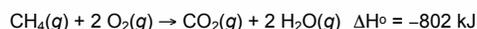
This provides new conversion factors!

From the equation:



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Example: How many kJ of energy are released when 128.5 g of methane, CH₄(g), are combusted?



$$128.5 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g}} \times \frac{1 \text{ mol rxn}}{1 \text{ mol CH}_4} \times \frac{-802 \text{ kJ}}{1 \text{ mol rxn}} = -6.43 \times 10^3 \text{ kJ}$$

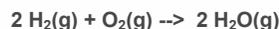
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Enthalpy Values

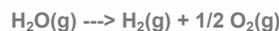
ΔH values depend on how the reaction is written and on phases of reactants and products



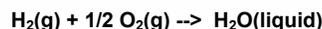
$$\Delta H^\circ_1 = -242 \text{ kJ}$$



$$\Delta H^\circ_2 = -484 \text{ kJ} = 2 * \Delta H^\circ_1$$



$$\Delta H^\circ_3 = +242 \text{ kJ} = -(\Delta H^\circ_1)$$

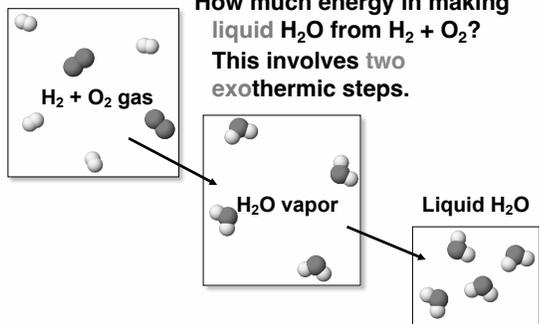


$$\Delta H^\circ_4 = -286 \text{ kJ} \neq \Delta H^\circ_1$$

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USING ENTHALPY

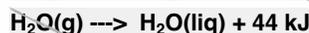
How much energy in making liquid H₂O from H₂ + O₂? This involves two exothermic steps.



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USING ENTHALPY

Making H₂O from H₂ involves two steps.



Example of HESS'S LAW-

If a rxn. is the sum of 2 or more others, the net ΔH is the sum of the ΔH 's of the other rxns.



Mr. Hess

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Hess's Law Problem

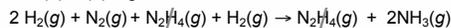
Example: Determine the ΔH° for the reaction:



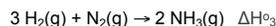
Given the following:

- (1) $2 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow \text{N}_2\text{H}_4(\text{g}) \quad \Delta H^\circ_1 = +95.4 \text{ kJ}$
 (2) $\text{N}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}) \quad \Delta H^\circ_2 = -187.6 \text{ kJ}$

Desired equation has no N_2H_4 , so try to remove by adding equations (1) & (2) together:



Combine like terms, reduce to:



And get:

$$\Delta H^\circ_3 = \Delta H^\circ_1 + \Delta H^\circ_2 = +95.4 \text{ kJ} + (-187.6 \text{ kJ}) = -92.2 \text{ kJ}$$

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Standard Enthalpy Values

| Compound | ΔH_f° (kJ/mol) | Compound | ΔH_f° (kJ/mol) |
|----------|-----------------------------|---|-----------------------------|
| AgBr(s) | -99.5 | $\text{C}_2\text{H}_2(\text{g})$ | +226.7 |
| | | $\text{C}_2\text{H}_4(\text{g})$ | +52.3 |
| | | $\text{C}_2\text{H}_6(\text{g})$ | -84.7 |
| | | $\text{C}_3\text{H}_8(\text{g})$ | -103.8 |
| | | n-C ₄ H ₁₀ (g) | -124.7 |
| | | $\text{C}_4\text{H}_{10}(\text{l})$ | -173.1 |
| | | $\text{C}_2\text{H}_5\text{OH}(\text{l})$ | -277.6 |

NIST (Nat'l Institute for Standards and Technology) gives values of

ΔH_f° standard molar enthalpy of formation

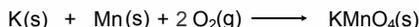
- the enthalpy change when 1 mol of compound is formed from elements under standard conditions.

These values are available in your text

All elements in standard states have $\Delta H_f^\circ = 0$ (graphite but not diamond, $\text{O}_2(\text{g})$ but not O_3 or $\text{O}_2(\text{l})$, etc.)

Question: What is the standard molar enthalpy of formation equation for potassium permanganate?

elements compound



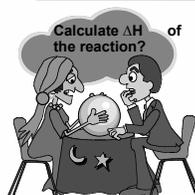
- salts, metals: solids at *standard state conditions*. oxygen is a gas
- balance for one mole of the product; reactants elements in their standard states



KMnO₄(aq) and KMnO₄(s)

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Using Standard Enthalpy Values



In general, when ALL enthalpies of formation are known:

$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H_f^\circ (\text{products}) - \sum n \Delta H_f^\circ (\text{reactants})$$

Σ = summation sign, or "add up all of the"
 n = stoichiometric coefficients
 "Energy gained" - "Energy spent"

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Using Standard Enthalpy Values

Example: Find $\Delta H^\circ_{\text{rxn}}$ for



using:

$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H_f^\circ (\text{prod}) - \sum n \Delta H_f^\circ (\text{react})$$

Answer:

$$\Delta H^\circ_{\text{rxn}} = \{\Delta H_f^\circ (\text{CaO}) + \Delta H_f^\circ (\text{CO}_2)\} - \{\Delta H_f^\circ (\text{CaCO}_3)\}$$

$$\Delta H^\circ_{\text{rxn}} = \{-635.1 + -393.5\} - \{-1206.2\}$$

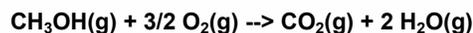
$$\Delta H^\circ_{\text{rxn}} = +177.6 \text{ kJ}$$

All stoichiometries (n) are one in this example

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Using Standard Enthalpy Values

Calculate the heat of combustion of methanol, i.e., $\Delta H^\circ_{\text{rxn}}$ for



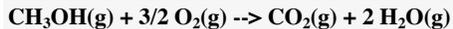
$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H_f^\circ (\text{prod}) - \sum n \Delta H_f^\circ (\text{react})$$

As before, look up ΔH_f° values for reactants and products in your text

Elements in standard states have $\Delta H_f^\circ = 0$

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Using Standard Enthalpy Values



$$\Delta H^\circ_{\text{rxn}} = \sum \Delta H_f^\circ(\text{prod}) - \sum \Delta H_f^\circ(\text{react})$$

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= \{\Delta H_f^\circ(\text{CO}_2) + 2 \Delta H_f^\circ(\text{H}_2\text{O})\} \\ &\quad - \{3/2 \Delta H_f^\circ(\text{O}_2) + \Delta H_f^\circ(\text{CH}_3\text{OH})\} \\ &= \{(-393.5 \text{ kJ}) + 2(-241.8 \text{ kJ})\} \\ &\quad - \{0 + (-201.5 \text{ kJ})\} \end{aligned}$$

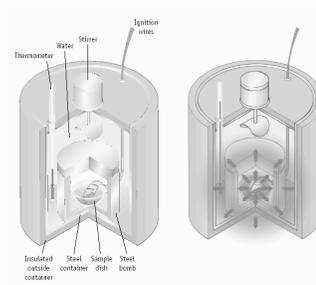
$$\Delta H^\circ_{\text{rxn}} = -675.6 \text{ kJ per mol of methanol}$$



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CALORIMETRY

Measuring Heats of Reaction

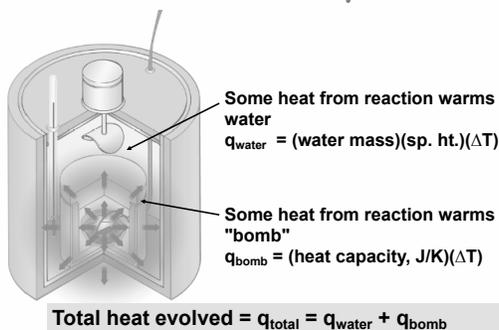
Constant Volume
"Bomb"
Calorimeter

- Burn combustible sample.
- Measure heat evolved in a reaction.
- Derive ΔE for reaction.



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Calorimetry

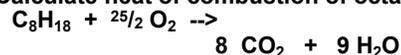


$$\text{Total heat evolved} = q_{\text{total}} = q_{\text{water}} + q_{\text{bomb}}$$

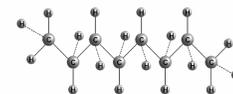
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Measuring Heats of Reaction: CALORIMETRY

Calculate heat of combustion of octane:



- Burn 1.00 g of octane
- Temp rises from 25.00 to 33.20 °C
- Calorimeter contains 1200. g water
- Heat capacity of bomb = 837 J/K



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Measuring Heats of Reaction: CALORIMETRY

Step 1: Calculate heat transferred from reaction to water.

$$q = (1200. \text{ g})(4.184 \text{ J/g}\cdot\text{K})(8.20 \text{ K}) = 41,200 \text{ J}$$

Step 2: Calculate heat transferred from reaction to bomb

$$\begin{aligned} q &= (\text{bomb heat capacity})(\Delta T) \\ &= (837 \text{ J/K})(8.20 \text{ K}) = 6860 \text{ J} \end{aligned}$$

Step 3: Calculate total heat **absorbed**

$$41,200 \text{ J} + 6860 \text{ J} = 48,100 \text{ J} * \text{kJ}/10^3 \text{ J} = 48.1 \text{ kJ}$$

Step 4: Total heat **evolved** = -(Total heat **absorbed**) = - 48.1 kJ

$$\begin{aligned} \text{Heat of combustion for 1.00 g of octane} &= (-48.1 \text{ kJ} / 1.00 \text{ g}) * \\ & (114.23 \text{ g} / \text{mol C}_8\text{H}_{18}) = -5.49 * 10^3 \text{ kJ/mol} \end{aligned}$$

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octane is C₈H₁₈, 114.23 g/mol

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Quick & Dirty Thermochemistry!

memorize 4.184 J/g°C heat capacity liquid water

$$q = m\Delta T \text{ heat transfer no change in phase}$$

$$q = \text{"heat"x"mass"} \text{ heat transfer with change in phase}$$

be able to use Hess's Law

understand Heat of Formation, ΔH_f° (1 mol product, reactants are elements in standard states)

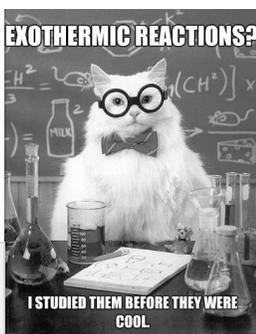
understand how to use:

$$\Delta H^\circ_{\text{rxn}} = \sum n\Delta H_f^\circ(\text{prod}) - \sum n\Delta H_f^\circ(\text{react})$$

End of Chapter Five

See also:

- [Chapter Five Study Guide](#)
- [Chapter Five Concept Guide](#)
- [Important Equations \(following this slide\)](#)
- [End of Chapter Problems \(following this slide\)](#)



Important Equations, Constants, and Handouts from this Chapter:

Thermodynamics:

- endothermic & exothermic
- product & reactant favored
- Law of Conservation of Energy
- units of energy (J, kJ, cal, etc.)
- system & surroundings
- heat & work
- enthalpy
- calorimetry
- heat of reaction and heat of formation
- standard enthalpy conditions
- Hess's Law

$$\Delta E = q + w = 0$$

$$q = m\Delta T \text{ (no phase change)}$$

$$q = (\text{heat of "something"}) \text{ ("mass")} \text{ (phase change)}$$

$$\text{memorize } C_{\text{water(liquid)}} = 4.184 \text{ J g}^{-1} \text{ K}^{-1}$$

$$\Delta H^{\circ}_{\text{rxn}} = \sum n\Delta H_f^{\circ} \text{ (products)} - \sum n\Delta H_f^{\circ} \text{ (reactants)}$$

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End of Chapter Problems: Test Yourself

1. The initial temperature of a 344 g sample of iron is 18.2 °C. If the sample absorbs 2.25 kJ of heat, what is its final temperature? $C_{Fe} = 0.449 \text{ J/g K}$
2. One beaker contains 156 g of water at 22 °C and a second beaker contains 85.2 g of water at 95 °C. The water in the two beakers is mixed. What is the final water temperature?
3. What quantity of heat is required to vaporize 125 g of benzene, C_6H_6 , at its boiling point, 80.1 °C? The heat of vaporization of benzene is 30.8 kJ/mol.
4. The enthalpy changes for the following reactions can be measured:

$$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(g) \quad \Delta H^{\circ} = -802.4 \text{ kJ}$$

$$CH_3OH(g) + 3/2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(g) \quad \Delta H^{\circ} = -676 \text{ kJ}$$
 Use these values and Hess's law to determine the enthalpy change for the reaction: $CH_4(g) + 1/2 O_2(g) \rightarrow CH_3OH(g)$
5. Write a balanced chemical equation for the formation of $Li_2CO_3(s)$ from the elements in their standard states. Find the value of ΔH_f° for $Li_2CO_3(s)$ in a table of values.
6. $Ca(OH)_2$ reacts slowly with CO_2 to give $CaCO_3$: $Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(g)$ Calculate the standard enthalpy change for this reaction.

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End of Chapter Problems: Answers

1. 306.0 K (32.8 °C)
2. 321 K (48 °C)
3. 49.3 kJ
4. -126 kJ
5. $2 Li(s) + C(s) + 3/2 O_2(g) \rightarrow Li_2CO_3(s) \quad \Delta H^{\circ} = -1216.04 \text{ kJ}$
6. $\Delta H^{\circ}_{\text{rxn}} = -83.1 \text{ kJ}$

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