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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)

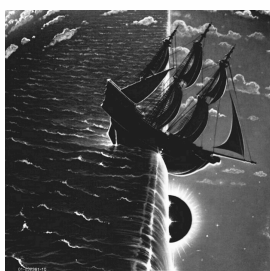
Knowing if reactions give energy off or
need energy to occur is important

**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

UNITS OF ENERGY

1 **calorie (cal)** = heat required to raise temperature of **1.00 g** of H_2O 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)**
(= $kg\ m^2 / s^2$)

1 cal = 4.184 joules

1 Cal = 1000 cal = 4184 J

also: **1000 J = 1 kJ**, etc.



James Joule
1818-1889

Memorize 4.184!

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Potential Energy

Two types of energy:
potential energy and
kinetic energy

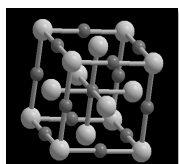
Potential energy - energy due to position or composition, "stored energy"

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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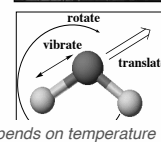
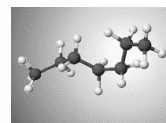
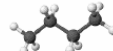
Kinetic Energy

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

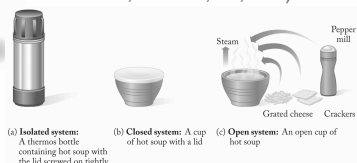
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System and Surroundings



Piston with H_2 and O_2

- 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

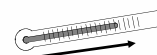
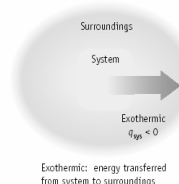
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Directionality of Heat Transfer

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

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

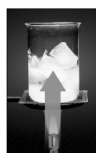
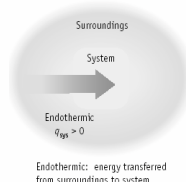


T(system) goes down
T(surr) goes up -
this is what we
usually measure

Directionality of Heat Transfer

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

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



$T(\text{system})$ goes up
 $T(\text{surr})$ 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

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

w is usually small, so $\Delta H \approx \Delta E$

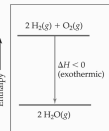


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Enthalpy of Reaction

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

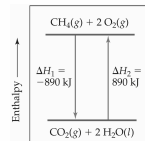


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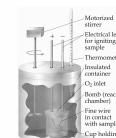
The Truth About Enthalpy

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.

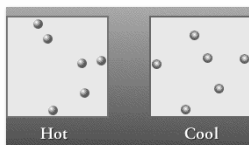


Bomb calorimeter

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Calorimetry

Calorimetry is the measure of heat (energy) transfer

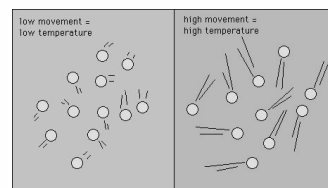


Heat energy is associated with molecular motions (Kinetic Molecular Theory)

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*

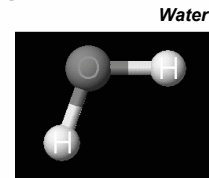
q is negative when heat flows out (hot surroundings) - *exothermic*

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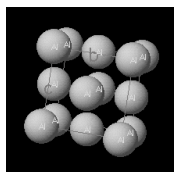
Specific Heat Capacity

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?



$$q = mC\Delta T$$

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

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

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

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

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

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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?

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

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

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

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

$$1060T_f = 22300$$

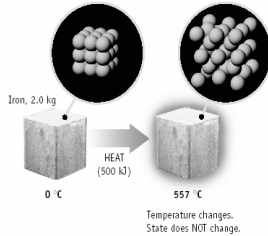
$$T_f = 21.0^\circ\text{C}$$

Efficient method to determine approximate final temperature of mixture

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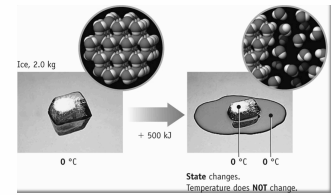
Heat Transfer No Change in State

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



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Heat & Changes of State

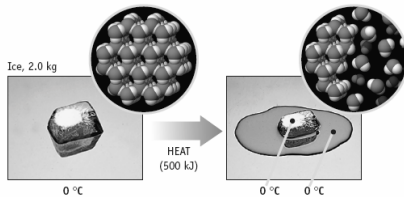


When matter absorbs heat, its temperature will rise until it undergoes a *Phase Change* (solid to liquid, liquid to gas, solid to gas)

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



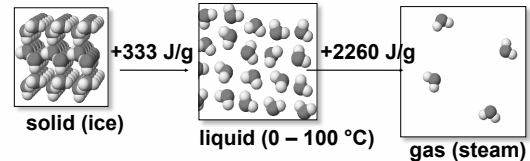
Changes of state involve energy (at constant T)
Ice + 333 J/g (heat of fusion) \rightarrow Liquid water
 $q = (\text{heat of "something"}) (\text{"mass"})$

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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



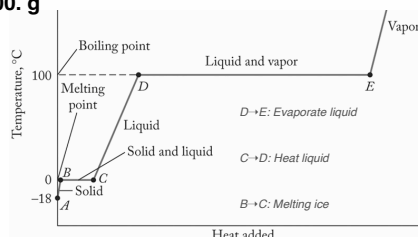
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What quantity of heat is required to melt 500. g of ice at 0.0 °C and heat the water to steam at 100.0 °C?

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



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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?

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

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Heat Transfer covered more in Chapter 10 of CH 222

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 $^\circ\text{C}$

with all species in **standard states**

i.e., C = graphite and O_2 = gas

ΔH_x°

Δ = change in

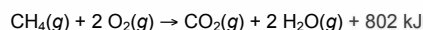
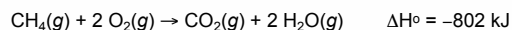
H = heat energy

$^\circ$ = standard conditions

x = type of change

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Thermochemical equations are regular chemical equations with an energy term.



Energy is a **product** just like CO_2 or H_2O ! (*Exothermic*)

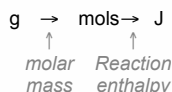
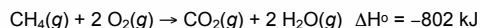
This provides new conversion factors!

From the equation:

$$\frac{+802 \text{ kJ of Energy Released}}{1 \text{ mol CH}_4(\text{g}) \text{ consumed}} \quad \frac{+802 \text{ kJ of Energy Released}}{2 \text{ mol H}_2\text{O}(\text{g}) \text{ produced}}$$

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Example: How many kJ of energy are released when 128.5 g of methane, $\text{CH}_4(\text{g})$, are combusted?

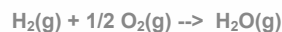


$$128.5 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g}} \times \frac{1 \text{ mol rxn}}{1 \text{ mol CH}_4} \times \frac{-802 \text{ kJ}}{1 \text{ mol rxn}} = -6.43 \times 10^3 \text{ kJ}$$

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Enthalpy Values

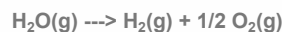
ΔH values depend on how the reaction is written and on phases of reactants and products



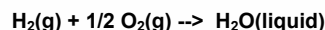
$$\Delta H^\circ_1 = -242 \text{ kJ}$$



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



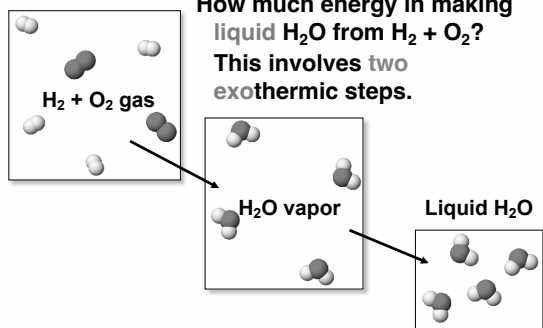
$$\Delta H^\circ_3 = +242 \text{ kJ} = -(\Delta H^\circ_1)$$



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

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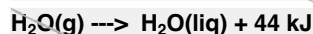
USING ENTHALPY



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USING ENTHALPY

Making H_2O from H_2 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.



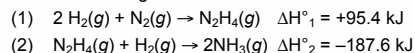
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Hess's Law Problem

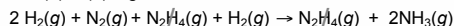
Example: Determine the ΔH° for the reaction:



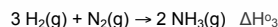
Given the following:



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

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

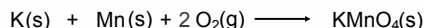
All elements in standard states have $\Delta H^\circ_f = 0$ (graphite but not diamond, $\text{O}_2(\text{g})$ but not O_3 or $\text{O}_2(\text{l})$, etc.)

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 $_4\text{H}_{10}(\text{g})$	-124.7
		$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.6

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

elements compound



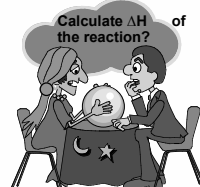
- salts, metals: solids at *standard state conditions*. oxygen is a gas
- balance for one mole of the product; reactants elements in their standard states



$\text{KMnO}_4(\text{aq})$ and $\text{KMnO}_4(\text{s})$

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Using Standard Enthalpy Values



In general, when **ALL** enthalpies of formation are known:

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

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:

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

Answer:

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

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

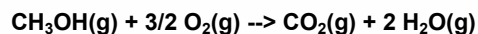
$$\Delta H^\circ_{\text{rxn}} = +177.6 \text{ kJ}$$

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



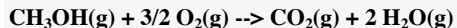
$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_f (\text{prod}) - \sum n \Delta H^\circ_f (\text{react})$$

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

Elements in standard states have $\Delta H^\circ_f = 0$

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Using Standard Enthalpy Values



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

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

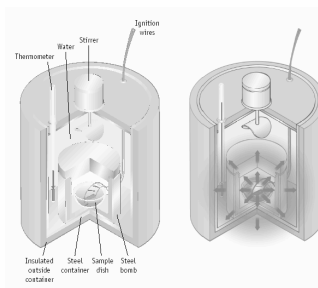
$$\Delta H^\circ_{\text{rxn}} = -675.6 \text{ kJ per mol of methanol}$$



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CALORIMETRY

Measuring Heats of Reaction



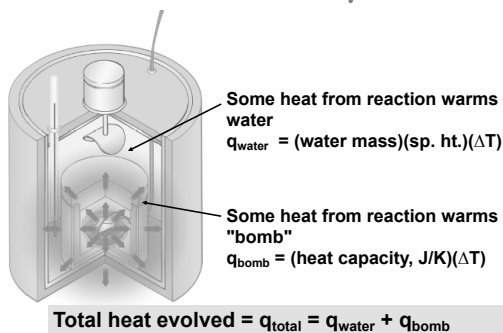
Constant Volume "Bomb" Calorimeter

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



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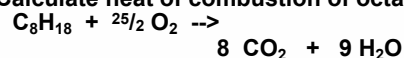
Calorimetry



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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**

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

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

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

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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

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

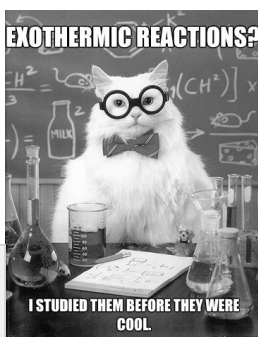
understand how to use:

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

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

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

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

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

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

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

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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? $C_{\text{Fe}} = 0.449 \text{ J/g K}$
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:
 $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \quad \Delta H^{\circ} = -802.4 \text{ kJ}$
 $\text{CH}_3\text{OH}(\text{g}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \quad \Delta H^{\circ} = -676 \text{ kJ}$
 Use these values and Hess's law to determine the enthalpy change for the reaction: $\text{CH}_4(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g})$
5. Write a balanced chemical equation for the formation of $\text{Li}_2\text{CO}_3(\text{s})$ from the elements in their standard states. Find the value of ΔH°_f for $\text{Li}_2\text{CO}_3(\text{s})$ in a table of values.
6. $\text{Ca}(\text{OH})_2$ reacts slowly with CO_2 to give CaCO_3 : $\text{Ca}(\text{OH})_2(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{g})$ 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. $2 \text{Li}(\text{s}) + \text{C}(\text{s}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{Li}_2\text{CO}_3(\text{s}) \quad \Delta H^{\circ} = -1216.04 \text{ kJ}$
6. $\Delta H^{\circ}_{\text{rxn}} = -83.1 \text{ kJ}$

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