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University Chemistry I
Chemistry 120, Section A
Chapter 6 — Thermochemistry

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Energy

- The capacity to do *work* or to produce *heat*.

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First Law of Thermodynamics

AKA Law of Conservation of Energy
Energy can neither be created nor destroyed,
but can be converted from one form to another.
In other words, E_{universe} is constant

Examples

Electrical energy can provide heat
oil can be burned to provide light
many others

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The Two Types of Energy

Potential: result of position, stored, chemical
bonds; can be converted to work

Kinetic: result of motion of an object

$$KE = \frac{1}{2} mv^2$$

where (m = mass, v = velocity)

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Temperature vs. Heat

Temperature reflects random motions of
particles, therefore related to kinetic energy of the
system.

Heat involves a transfer of energy between two
objects due to a temperature difference.

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State Function

Fig. 6.4 Chang, 9th Ed.

Depends only on the present state of the system - not
how it arrived there.

It is independent of pathway.

For example, the potential energy of someone standing on
the roof does not depend on whether (s)he took the stairs
or the elevator.



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System and Surroundings

System: That on which we focus attention

Surroundings: Everything else in the universe

Universe = System + Surroundings

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Exothermic and Endothermic

Heat exchange accompanies chemical reactions.

Exothermic: Heat flows out of the system (to the surroundings). This is energy released from bonds.

Endothermic: Heat flows into the system (from the surroundings).

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First Law of Thermodynamics

First Law of Thermodynamics: The energy of the universe is constant.

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First Law

$$\Delta E = q + w$$

where

ΔE = change in system's internal energy

q = heat

w = work

If $\Delta E = <0$, system does work on surroundings,

If $\Delta E = >0$, surroundings do work on system

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Work

work = force \times distance

and since pressure = force / area,

work = pressure \times volume

or,

$$w_{\text{system}} = -P\Delta V$$

NB: P is *external* pressure: it causes compression or resists expansion.

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Enthalpy

Enthalpy = $H = E + PV$

where E is internal energy

$$\Delta E = \Delta H - P\Delta V$$

$$\Delta H = \Delta E + P\Delta V$$

At constant pressure,

$$q_P = \Delta E + P\Delta V,$$

where $q_P = \Delta H$ at constant pressure

ΔH = energy flow as heat (at constant pressure)

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The Really Important Thing About Enthalpy

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

If ΔH is negative, exothermic reaction

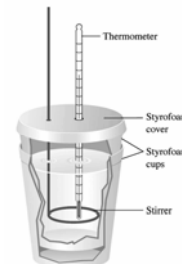
If ΔH is positive, endothermic reaction

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Calorimetry

Fig. 6.9 Chang, 9th Ed.

- It is easy to measure heat released or absorbed when a rxn occurs, e.g.
- ?: What takes longer to get hot, 100 mL water or 250 mL water?
- **Extensive property**- depends on amount of matter
- ?: What has the higher density, 100 mL water or 250 mL water?
- Density is an *intensive property*
- **Intensive property**- property that does *not* depend on amount of matter

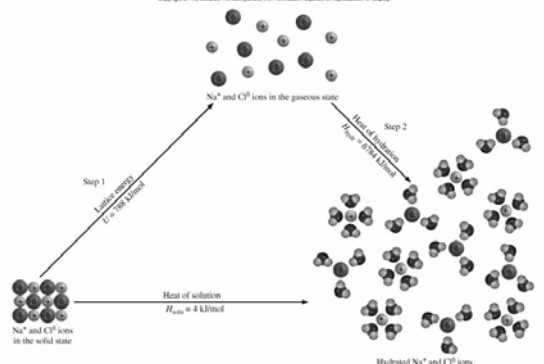


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Heat of Solution

Fig. 6.11 Chang, 9th Ed.

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Heat of Solution

Fig. 6.11 Chang, 9th Ed.

Heat of solution, ΔH_{soln} - the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.

Lattice energy- the energy required to completely separate one mole of a solid ionic compound into gaseous ions

Heat of hydration- energy involved in surrounding a gaseous ion with water

These concepts require thinking about forces of attraction.

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Sample Problems

Calculate ΔE for $q = -47 \text{ kJ}$, $w = +88 \text{ kJ}$. Do the surroundings work on the system, or does the system work on the surroundings?

Calculate the kinetic energy of a $1.0 \times 10^{-5} \text{ g}$ object with a velocity of $2.0 \times 10^5 \text{ cm/s}$.

A calorimeter containing 50.0 mL 1.0 M HCl is determined to have a temperature of 23.2 °C. A second calorimeter which contains 50.0 mL 1.0 M NaOH is found to have a temperature of 23.4 °C. When the NaOH is poured into the HCl, the temperature increases to 37.1 °C. Is this an exothermic or an endothermic reaction? Calculate the heat gained by the system, assuming no loss to the surroundings. The specific heat of 0.5 M NaCl is 3.93 J/g °C and the density is 1.04 g/mL.

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Heat Capacity

$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}} = \frac{\text{J}}{^{\circ}\text{C}} \text{ or } \frac{\text{J}}{\text{K}}$$

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Some Heat Exchange Terms

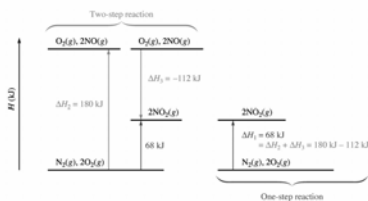
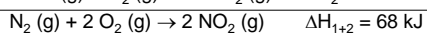
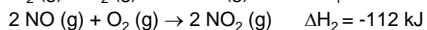
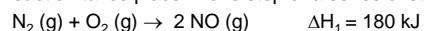
- specific heat capacity- the amount of energy required to raise one gram of matter by one degree Celcius (from 14.5 to 15.5 °C for water)
 - heat capacity per gram = J/g °C or J/K g
- molar heat capacity
 - heat capacity per mole = J/mol °C or J/mol·K
- Intensive property- what is being measured does not depend on how much of it there is.

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Hess's Law

See Fig. 6.10 Chang, 9th Ed.

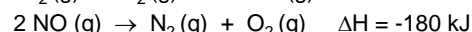
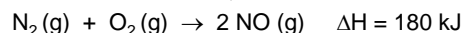
Hess's Law- The change in enthalpy is the same whether the reaction takes place in one step or a series of steps.



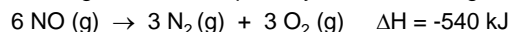
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Calculations via Hess's Law

1. If a reaction is reversed, ΔH is also reversed.



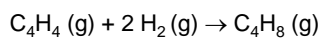
2. If the coefficients of a reaction are multiplied by an integer, ΔH is multiplied by that same integer.



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Sample Problem

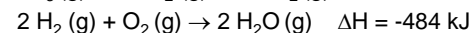
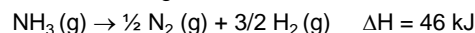
Combustion reactions involve reacting a substance with oxygen. When compounds containing carbon and hydrogen are combusted, carbon dioxide and water are the products. Using the enthalpies of combustion for C_4H_4 (-2341 kJ/mol), C_4H_8 (-2755 kJ/mol), and H_2 (-286 kJ/mol), calculate ΔH for the reaction



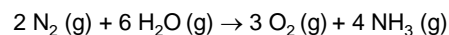
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STQ

Given the following data



calculate the ΔH for the reaction



On the basis of the enthalpy change, is this a useful reaction for the synthesis of ammonia?

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Standard Enthalpy of Formation

A way of calculating enthalpies when reactions don't cooperate.

Standard Enthalpy of Formation (ΔH_f°)- the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their *standard states*.

The " f " indicates formation

The " ° " indicates standard state used

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Standard States

Compound

For a gas, pressure is exactly 1 atmosphere.

For a solution, concentration is exactly 1 molar.

For a pure substance (liquid or solid), it is the pure liquid or solid.

Element

The form in which it exists at 1 atm and 25 °C.

For examples:

N_2 (g)

Hg (l)

K (s)

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STQ

Write the reaction for which the enthalpy change will be the ΔH_f° for solid aluminum oxide.

What is the ΔH_f° for the above reaction (table 6.4 Chang)?

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Change in Enthalpy

- Can be calculated from enthalpies of formation of reactants and products.

$$\Delta H_{rxn}^\circ = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})$$

products-reactants

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STQ

Use the values of ΔH_f° in Appendix 3 to calculate the ΔH° for the following reaction

