Thermochemistry and Thermodynamics

Name: _____

AP Chemistry Lecture Outline

Video 51903 (3:14)

Introduction to Energy

thermodynamics: the study of energy and its transformations

-- thermochemistry: the subdiscipline of thermodynamics involving

chemical reactions and energy changes

Energy is defined as the capacity to do work.

Units of energy are (among others) joules (J), kilojoules (kJ), calories (cal),

or nutritional calories (Cal or kcal).

-- conversions:

-- Energy moves whenever... (1)

...or (2)

Work (w) is done whenever a force moves through a distance.

If you push me, work is done ON _____ BY _____. Energy is transferred from _____ to _____.

Heat (q) is an amount of energy transferred from a hotter object to a colder one.

If you fall face-first into the snow, energy is transferred from _____ to _____.

Video 51906 (7:01)

kinetic energy:

-- All masses have KE. In chemistry, we are most interested in the kinetic energy of...
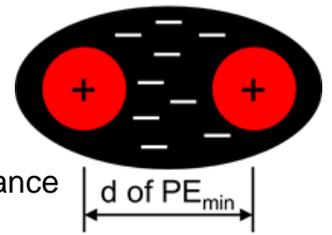
-- Thermal energy is due to the KE of tiny particles. We measure the

average KE of a collection of particles as...

EX.   Find the kinetic energy of a single dinitrogen monoxide molecule moving at 650 m/s.

potential energy:

    Chemical potential energy is due to...

    -- related to the specific arrangement of atoms and electrons in the substance

d of PE_{min}

Internal Energy and Its Changes

    system:

surroundings:

-- In chemistry, a system can exchange _____ but not _____ ^{w}/its surroundings.

internal energy (E) of a system: the sum of all the KE and PE of the components of a system

-- The change in the internal energy of a system would be found by:

    And for chemistry, this equation would become:

    ΔE is + if E_{final} $E_{initial}$ (i.e., system...   ) →

    ΔE is − if E_{final} $E_{initial}$ (i.e., system...   ) →

Short detour: Endergonic / Exergonic / Endothermic / Exothermic

    endergonic: energy goes IN...

    endothermic: energy goes IN...

Thus, all _____ processes are _____,
but NOT all _____ processes are _____.

    phase changes: e.g.,   photosynthesis:

    In 'end-', internal energy...

    exergonic: energy goes OUT...

    exothermic: energy goes OUT...

Thus, all _____ processes are _____,
but NOT all _____ processes are _____.

    phase changes: e.g.,   chemiluminescence:

    In 'ex-', internal energy...

The most efficient way to find the change in a system's internal
energy ΔE is by finding two rather-easily measured quantities:

    q:

    w:

If q is ( ), system RELEASED heat.

If q is ( ), system ABSORBED heat.

If w is ( ), system DID work.

If w is ( ), system had work done ON it.

Enthalphy (H)

-- Enthalpy (H) is defined as... $H = E + PV$ where   E = system's internal energy

P = pressure of the system

V = volume of the system

-- There is much that could be said about enthalpy, but what you need to know is:

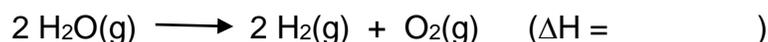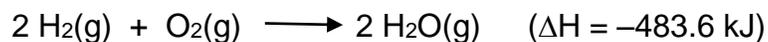If a process occurs at constant pressure...

i.e.,   P indicates constant pressure conditions.
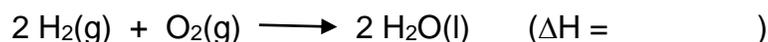
When ΔH is +, the system...

When ΔH is –, the system...

Enthalpy is an *extensive* property, meaning that…

ΔH for a reaction and its reverse are the opposites of each other.

$2\ H_2(g)\ +\ O_2(g)\ \longrightarrow\ 2\ H_2O(g)$ $(\Delta H = -483.6\ kJ)$

$2\ H_2O(g)\ \longrightarrow\ 2\ H_2(g)\ +\ O_2(g)$ $(\Delta H = \qquad\ )$

Enthalpy change depends on the states of reactants and products.

$2\ H_2(g)\ +\ O_2(g)\ \longrightarrow\ 2\ H_2O(g)$ $(\Delta H = -483.6\ kJ)$

$2\ H_2(g)\ +\ O_2(g)\ \longrightarrow\ 2\ H_2O(l)$ $(\Delta H = \qquad\ )$

An <u>enthalpy of formation</u> (ΔH_f) is the enthalpy change associated with the formation of a substance.

     -- also called...

If we say "standard" something, it means (for one thing) that the temperature is _____. Also, we write the *something* with...

     e.g., <u>standard enthalpy of formation</u> is...

-- ΔH_f^o for the most stable form of an element is ZERO, e.g.,

Enthalpy Changes in Solution Formation

Consider the dissolution of a chunk of the generic ionic compound MN_2 in water:

There are three enthalpy components that together make up the ΔH of the solution process:

1. The solvent m'cules pull the ions out of the lattice.
2. The solvent m'cules separate to make space so there is room
    for a 'surrounded ion' to fit in.
3. IMFs btwn solvent m'cules and ions cause ions to 'nestle in,'
 ^{w}/solvent m'cules all around.

Common Heats of Solution	
substance	kJ/mol
NH_4NO_3	25.69
NaOH	−44.51
KOH	−57.61
HNO_3	−33.28
HCl	−74.84
NH_4Cl	14.78

The relative magnitude of these three enthalpy components determines the overall ΔH of the solution process...
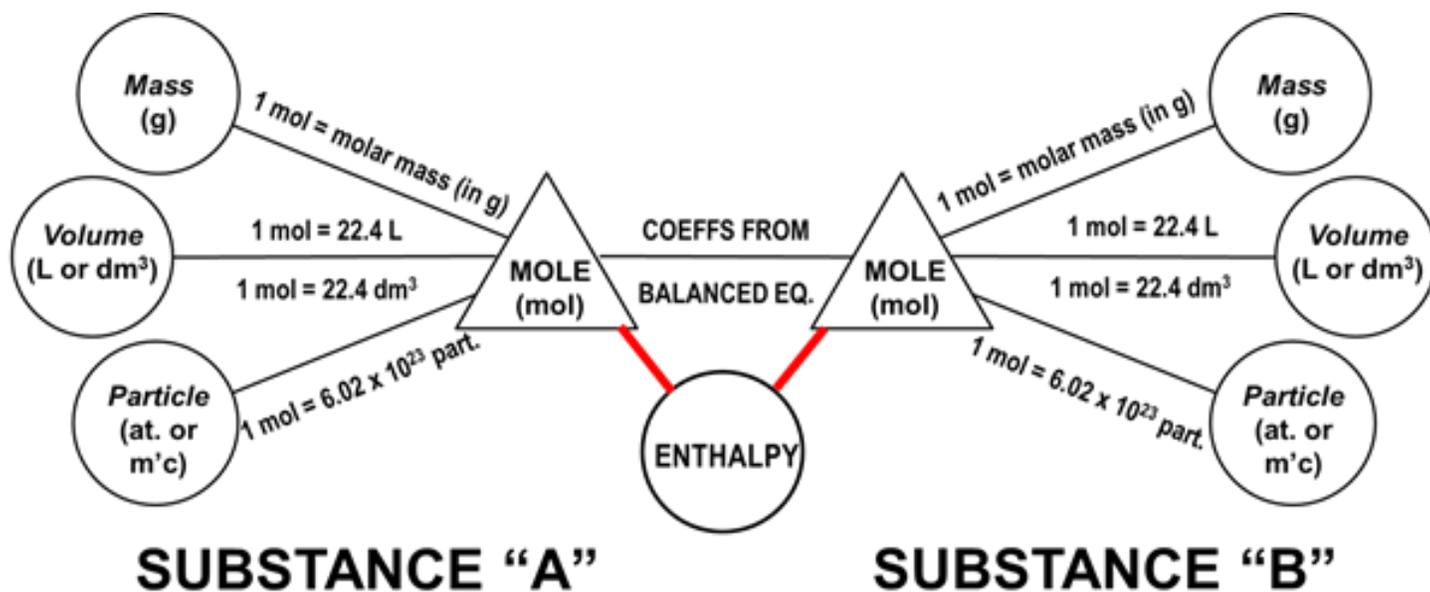
Heats of solution for many solids in aqueous have been tabulated and are easily accessed.

For a reaction, the change in enthalpy ΔH – sometimes called _____ or _____ – is for the number of moles of reactants and products shown by the coefficients in the equation.

    $2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(g)$ ($\Delta H = -483.6$ kJ)
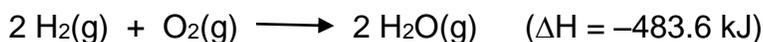
The proportions shown in the equation are used in...

SUBSTANCE "A"   **SUBSTANCE "B"**

EX. $CH_4(g) + 2 O_2(g) \longrightarrow CO_2(g) + 2 H_2O(g)$ $\Delta H = -891$ kJ

What is the change in enthalpy when 54 g methane are burned?

EX.   What mass of water is made if 10,540 kJ are released?

| Video 51924 (7:51) | Earlier, we used the equation: $CH_4(g) + 2 O_2(g) \longrightarrow CO_2(g) + 2 H_2O(g)$ $\Delta H = -891$ kJ |

Where did THIS

come from?

-- But...we can roughly estimate any heat of reaction using the ΔH_f° of all Rs and Ps in the reaction:

where n and m are the coefficients in the balanced equation.   In short:

EX.   Approximate the enthalpy change for the combustion of one mole of methane.

$$CH_4(g) \quad + \quad 2 O_2(g) \longrightarrow CO_2(g) \quad + \quad 2 H_2O(g)$$

EX.   Predict the equilibrium shifts and the changes in K with temperature for...

$$2 \text{ POCl}_3(g) \rightleftharpoons 2 \text{ PCl}_3(g) + \text{O}_2(g)$$

Strategy:

Calorimetry: the measurement of heat flow

-- device used is

called a...

heat capacity of an object: amount of heat needed to raise object's temp. 1 K

molar heat capacity: amt. of heat needed to raise temp. of 1 _____ of a substance 1 K

specific heat (capacity): amt. of heat needed to raise temp. of 1 _____ of a substance 1 K

For H_2O: i.e.,

We calculate the heat a substance   where   q = heat
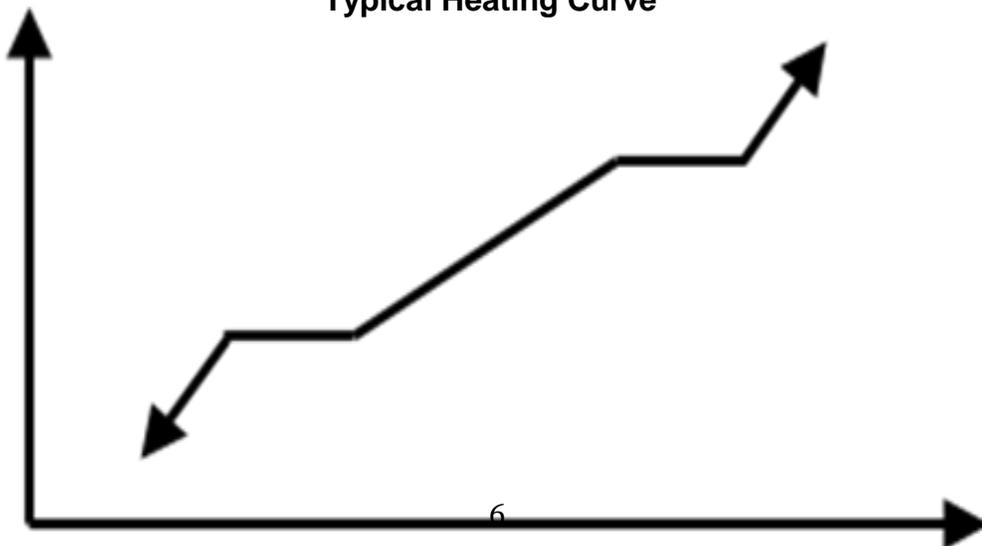
loses or gains using: m = amount of substance

cP = heat capacity

ΔT = temperature change

cf or v = heat of fusion (s/l) or

heat of vaporization (l/g)

Typical Heating Curve

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How do magnitudes of c_v c_f compare?

e.g., For H_2O...

Phase Change Constants for Water

$c_{P,ice} = 2.077$ J/g-K
$c_f = 333$ J/g
$c_{P,water} = 4.18$ J/g-K
$c_v = 2256$ J/g
$c_{P,wv} = 2.042$ J/g-K

EX.   Find the enthalpy change when 82.4 g of ice at –13.5°C turns to water at 72.8°C.

EX.   Using the constants given, find the enthalpy change when 679 g of water at 27.4°C are converted into water vapor at 121.2°C.

$c_f = 333$ J/g
$c_v = 40.61$ kJ/mol
$c_{P,L} = 4.18$ J/g-K
$c_{P,S} = 2.077$ J/g-K
$c_{P,G} = 36.76$ J/mol-K

With a <u>coffee-cup calorimeter</u>, a reaction is carried out under constant pressure conditions.

-- Why is the pressure constant?

If we assume that no heat is exchanged between the system and the surroundings, then the heat 'something-in-the-system' loses must equal the heat 'something-else-in-the-system' gains.

i.e.,

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EX.   76.2 g of tungsten at 413°C are added to 177 g of 22.0°C water.
If the specific heat of tungsten is 0.134 J/g-K, find the system's
final temp. (As you recall, water's specific heat is 4.18 J/g-K.)

EX.   25.2 g of ice at –8.0°C are dropped into 215 g of
93.5°C vegetable oil. The oil's specific heat is
1.67 J/g-K; the constants for H_2O are shown at
right. Find the system's final temp.

c_f = 333 J/g
c_v = 40.61 kJ/mol
$c_{P,L}$ = 4.18 J/g-K
$c_{P,S}$ = 2.077 J/g-K
$c_{P,G}$ = 36.76 J/mol-K

EX.   When 50.0 mL of 0.100 M $AgNO_3$ and 50.0 mL of 0.100 M HCl are mixed in
a coffee-cup calorimeter, the mixture's temperature increases from 22.30°C
to 23.11°C. Calculate the enthalpy change for the rxn, per mole of $AgNO_3$.

Combustion reactions are studied using constant-volume calorimetry.

This technique requires a <u>bomb calorimeter</u>.

-- The _____ of the bomb calorimeter (C_{cal}) must be known.

-- As with constant-pressure calorimetry, we assume that no energy escapes into the surroundings. So the magnitudes of heat absorbed by the calorimeter and the heat given off by the reaction are...
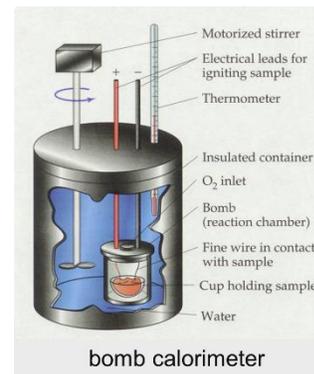
bomb calorimeter

EX. A 0.343-g sample of propane, C_3H_8, is burned in a bomb calorimeter with a heat capacity of 3.75 kJ/°C. The temperature of the material in the calorimeter increases from 23.22°C to 27.83°C. Calculate the molar heat of combustion of propane.

<u>Chemical Thermodynamics</u>

Thermodynamics involves enthalpy changes AND changes in order/disorder.

<u>spontaneous processes</u>:

Spont. processes **tend** to be EXO / ENDO (i.e., have ___ enthalpy changes) and **tend** to result in INCREASED / DECREASED order.

<u>reversible process</u>: "undo exactly what you did and you've got what you started with"

-- both system and surroundings go back to original states

-- e.g.,

irreversible process: getting back what you started with requires more than just an "undo"

    -- we can restore the original system, but the surroundings will have changed

    -- e.g.,

Points of note:

    1. Whenever a system is in equilibrium, we can go reversibly between reactants and products.

    2. In any spontaneous process, the path between reactants and products is irreversible.

    3. Thermodynamics refers to the direction of a reaction, not its speed.

<table>
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51951
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Entropy (S)

-- Processes in which the system's **disorder** increases tend to occur spontaneously.

$$\Delta S = S_f - S_i$$

$+ \Delta S \rightarrow$ P are more _____ than R

$- \Delta S \rightarrow$ P are more _____ than R

Entropy at the Particle Level

There are three types of motion, each having kinetic energy (KE).

    --

    -- The more KE we have, the _____ entropy we have.

In general…   As T ↑ / ↓ , S /   and… S_{solid} S_{liquid} S_{gas}

Process	freezing	melting	condensing	boiling
Sign of ΔS				

Entropy increases when: 1. the number of gas particles increases

    2. liquids or solutions are formed from solids

    3. gases are formed from liquids or solids

EX.   Which has the   1 mol O_2(g) @ 300 K   or   1 mol O_2(g) @ 500 K   (same volume)
       greater entropy?

                            1 mol KCl(s) @ 300 K   or   1 mol HCl(g) @ 300 K

                            2 mol HCl(g) @ 300 K   or   4 mol HCl(g) @ 300 K   (same volume)

                            1 mol HCl(g) @ 300 K   or   1 mol Ar(g) @ 300 K   (same volume)

                            2 mol HCl(g) @ 300 K   or   2 mol HCl(g) @ 300 K
                              (in a 10-L vessel)   (in a 5-L vessel)

Video 51954 (6:23)

<u>zeroth law of thermodynamics</u>: If Object A is in thermal equilibrium with Object B and
                    Object B is in thermal equilibrium with Object C, then...

<u>first law of thermodynamics</u>:

Energy morphs between its various forms,   Often expressed as:
  but the total amount remains the same.

<u>second law of thermodynamics</u>:

   In the rare instance that a system is isolated and is the site of a reversible process...

   Otherwise...   THIS is definitely the case for all _____
                                  (i.e., _____) processes.
       Entropy is NOT conserved;

   <u>third law of thermodynamics</u>: The entropy of a pure, crystalline
                         substance at absolute zero is...
            --

Video 51957 (8:52)

Calculating Entropy Changes

For a system in which heat is transferred at constant temperature...
    --
    -- common unit for entropy

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EX.   Find the change in entropy when 87.3 g of
        water vapor condense, given that water's
        heat of vaporization is 5.99 kJ/mol.

    standard molar entropies, S°: molar entropy values of substances in their standard states

        S° values typically…   --

                                    --

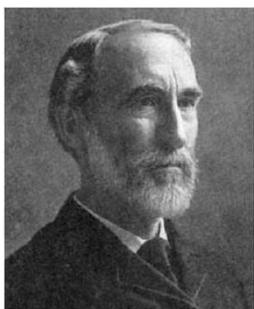   --

        For a chemical reaction…

EX.   Calculate the standard molar
        entropy change for… $P_4(s,white) + 10\ Cl_2(g) \rightarrow 4\ PCl_5(g)$

Change in Gibbs Free Energy

Enthalpy changes (ΔH) and entropy changes (ΔS) both have a "say" in whether or not
a process is spontaneous, i.e.,

Josiah Willard Gibbs
1839–1903

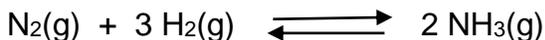We know that
processes having...   ...tend to be...   But the "final word" on
            $+\Delta H$ t.f./spontaneity is spoken
            $-\Delta H$ by the Gibbs free energy
            $+\Delta S$ equation:
            $-\Delta S$

    ΔG (–) means…
    ΔG (+) means…
     ΔG = means…

$$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$$

|	Say we start with only...	
	...N_2 and H_2:	...NH_3:
We know: Thus...		

More often, we calculate ΔG first. THIS tells us...

standard free energies of formation, ΔG_f^o

     -- have been tabulated for pure solids, pure liquids,

       gases at ~1 atm pressure, and 1 M solutions

     -- For elements in their standard states…

     -- For a reaction, the standard free-energy change is found by…

EX.   Calculate the standard free-energy change for… $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$
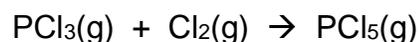
Gibbs Free Energy and Solubility

In general, for SOLIDS dissolving in liquids,

as temp. increases, solubility...

and for GASES dissolving in liquids,

as temp. increases, solubility...
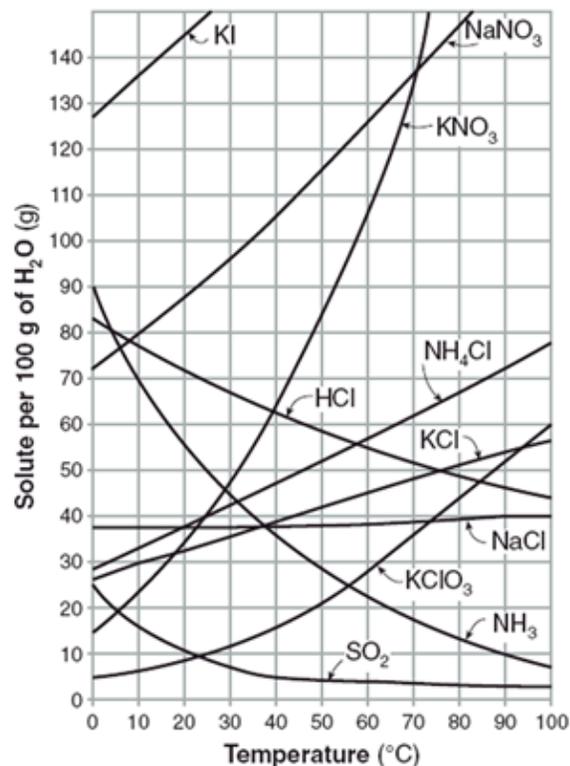
The change in Gibbs free energy equation...

         ...can give us some insight as to WHY.

When SOLIDS dissolve in liquids, e.g.,

the change in entropy ΔS is...

   --

   --

     $\Delta G = \Delta H - T\Delta S$

So as T increases, ΔG becomes more...

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When GASES dissolve in liquids, e.g.,

the change in entropy ΔS is...

--

$$\Delta G = \Delta H - T\Delta S$$

So as T increases, ΔG becomes more...

Free Energy and Temperature

From $\Delta G = \Delta H - T\Delta S$, we see that ΔG varies with temperature.

--

-- ΔH and ΔS change little with temperature.

EX.   (a)   Calculate ΔH^o, ΔG^o, and ΔS^o for... $2\ NO(g)\ +\ O_2(g)\ \rightarrow\ 2\ NO_2(g)$

(b)   Estimate ΔG at 400 K.

EX.   Estimate the normal boiling pt. of ethanol, CH_3CH_2OH.

Strategy:

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Taking a closer look, we found...

   We estimated the NBP of ethanol to be ____ $^{\circ}$C; the actual is ____ $^{\circ}$C.

At ____ $^{\circ}$C, $\Delta G =$ $\Delta G = \Delta H - T\Delta S$

As T increases, ΔG becomes...   As T increases, ΔG becomes...

   --   --

Free Energy Changes under Non-standard Conditions

For a reaction, ΔG° is the standard free-energy change if all substances in the reaction are at standard conditions. If we DON'T have standard conditions, the free-energy change ΔG is found using...

EX.   Calculate ΔG at 198 K, given the following: $N_2(g)$ + $3 H_2(g)$ ⇌ $2 NH_3(g)$
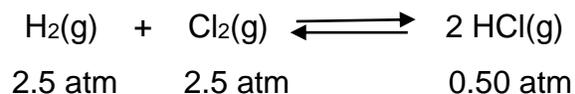
   1.0 atm   3.0 atm   0.50 atm

Free Energy and the Equilibrium Constant

Imagine a system that is at equilibrium, at some temperature T.
By definition, when a system is AT equilibrium...

$\Delta G = \Delta G^{\circ} + RT \ln Q$

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EX. Calculate K and ΔG at 135ºC for… $H_2(g)$ + $Cl_2(g)$ $\rightleftharpoons$ $2\ HCl(g)$

                                                        2.5 atm   2.5 atm   0.50 atm
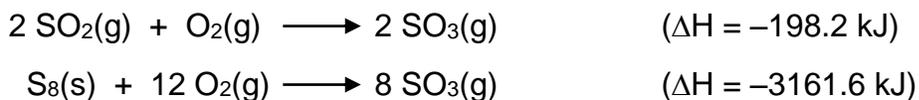

Video 51981 (10:11)

Hess's Law

Thermodynamic quantities have been measured and tabulated – not only for substances – but also for many simple 'building-block' reactions. Hess's law allows us to manipulate several 'building-block' rxns such that we can find thermodynamic values for a more-complicated reaction. We do this by taking multiples of the building-block rxns and manipulating their forward-backward nature...

EX. Calculate the heat of reaction for the combustion of sulfur to form sulfur dioxide.

$2\ SO_2(g)\ +\ O_2(g)\ \longrightarrow\ 2\ SO_3(g)$ ($\Delta H = -198.2$ kJ)

$S_8(s)\ +\ 12\ O_2(g)\ \longrightarrow\ 8\ SO_3(g)$ ($\Delta H = -3161.6$ kJ)

EX. Calculate ΔH for the reaction… $5\ C\ +\ 6\ H_2\ \longrightarrow\ C_5H_{12}$

$C_5H_{12}\ +\ 8\ O_2\ \longrightarrow\ 5\ CO_2\ +\ 6\ H_2O$ ($\Delta H = -3535.6$ kJ)

$C\ +\ O_2\ \longrightarrow\ CO_2$ ($\Delta H = -393.5$ kJ)

$H_2\ +\ \frac{1}{2}\ O_2\ \longrightarrow\ H_2O$ ($\Delta H = -285.8$ kJ)