Thermochemistry

C020

ENERGY

When molecules react, there are energy changes, and energy can be released or consumed

Energy can appear and be measured as either:
Work: the ability to move a mass through a distance
or
Heat: increased molecular velocities, usually measured as temperature

The SI unit of energy is the joule, J

Note: 4.184 J = 1 calorie
Not to be confused with 1 Calorie = 1000 calories

Specific Heat
defined as the amount of heat required "to raise 1 gram of a substance 1 degree K; units: $Jg^{-1}K^{-1}$

Examples

Water	Specific Heat = 4.184 $Jg^{-1}K^{-1}$
Fe	Specific Heat = 0.451 $Jg^{-1}K^{-1}$
Glass	Specific Heat = 0.84 $Jg^{-1}K^{-1}$

∴ By knowing the specific heat of a substance one can calculate the amount of heat required to raise a substance from one temperature to a higher one

Related to specific heats is a substance's heat capacity, C where the amount of material;
that is the mass is not factored in. Units = JK^{-1}

∴ The heat capacity is the amount of energy required to raise the system by 1 K.

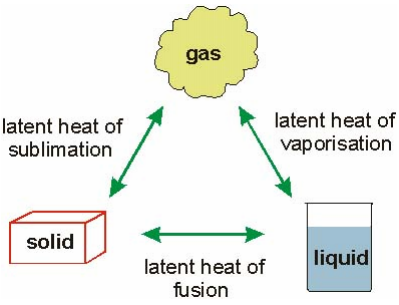
For example, $C(H_2O) = 4.184\ JK^{-1}$

Heat capacity C = mass x specific heat

Heat changes due to Phase Changes

Heat energy may be used not only to change the temperature of a system but also to cause phase changes at constant temperature

These are called **latent heats**



Energy is required for a phase change to occur

1 g ice at 0° C (melting point) → 1 g liquid water at 0° C
Latent heat of fusion (melting) q = +333 Jg^{-1}

1 g liquid water at 100° C (boiling point) → 1 g steam at 100° C
Latent heat of vaporization (evaporation) q = +2260 Jg-1

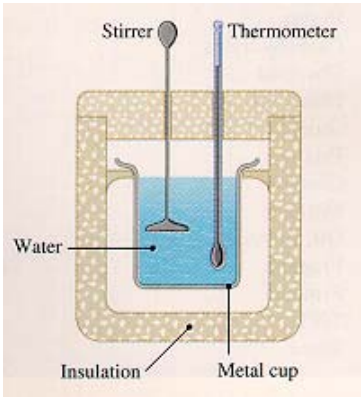
Example:
Suppose 750 g block of ice at -15°C is allowed to melt, and the resulting water warms up to 22°C. How much heat is absorbed in this process?

Useful data:
Specific heat of ice: 2.01 $J\ K^{-1}\ g^{-1}$
Heat of fusion of ice: 6.01 $kJ\ mol^{-1}$
Specific heat of water: 4.184 $J\ K^{-1}\ g^{-1}$

Calorimetry (measuring heat flow)

Experimental measurement of q is termed calorimetry.

The apparatus used is called a calorimeter: usually an enclosed metal vessel surrounded by water in an insulated container



For **exothermic** reactions, heat is released q = -ve

For **endothermic** reactions, heat is absorbed q = +ve

For an exothermic reaction carried out inside a calorimeter the heat evolved raises the temperature of the calorimeter and the water

$\therefore \quad -q_{reaction} = q_{calorimeter} + q_{water}$

For water: $q_{water} = C(water)m\Delta T$

For the calorimeter: $q_{calorimter} = C_C\Delta T$

ΔT is the temperature rise and C_C is the heat capacity of the calorimeter in J K^{-1}

Example:

1.148 g of benzoic acid ($C_7H_6O_2$) is burned in a calorimeter immersed in 1215 g H_2O.

The water temperature increases from 25.12 to 30.26° C.

What is the q evolved by the combustion reaction in kJ mol^{-1} for benzoic acid?

Useful data: C_C = 817 JK^{-1}; $C(H_2O)$ = 4.184 J g^{-1} K^{-1}

Since $-q = C_C\Delta T + C(H_2O)m\Delta T$

$\Rightarrow \quad -q = (817\ JK^{-1})(5.14\ K) + (4.184\ Jg^{-1}K^{-1})(1215\ g)(5.14\ K)$

$= 30330\ J = 30.33\ kJ$ per 1.148 g benzoic acid

Molar mass $C_7H_6O_2$ = 122.0 $gmol^{-1}$

$\therefore$ Molar -q = 30.33 kJ/(1.148 g/122.0 g mol^{-1}) = 3223 kJ mol^{-1}

$q = -3323\ kJ\ mol^{-1}$

Enthalpy

If heat is added to a system, for example, a gas, the heat absorbed (q) must equal the increase in energy of the system, ΔE, plus the work done by the system (w)

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

or

$\Delta E = q - w$

This is the **first law of thermodynamics** says energy is conserved in all reactions

When chemical reactions are carried out at constant pressure (for example, at 1 atmosphere = 1 bar = 100 kPa), the heat term is called the enthalpy (q_P) and has the symbol ΔH.

For most chemical reactions $\Delta H \sim \Delta E$

ΔH, the enthalpy of a reaction is a measure of the energy difference between reagents and products, for reactions carried out at constant pressure

For **exothermic** reactions, heat is released ΔH = -ve

For **endothermic** reactions, heat is absorbed ΔH = +ve

ΔH values are customarily measured at 25^0C (298K) and P = 1 bar. They are labelled ΔH^0, the standard enthalpy of reaction

Example: For the combustion of heptane, C_7H_{16}

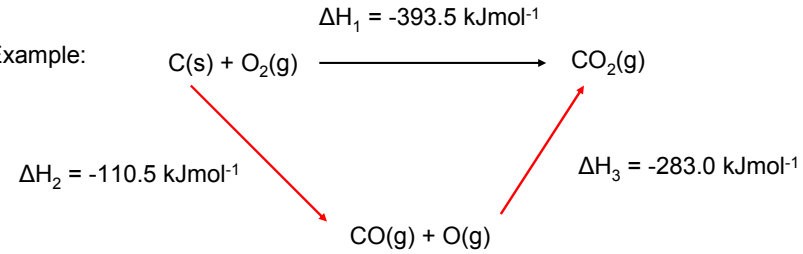
$$C_7H_{16}(\ell) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(\ell) \qquad \Delta H^0 = -4818 \text{ kJ}$$

This exothermic reaction releases 4.818×10^6 J energy / mole C_7H_{16}, a molar enthalpy of reaction

Hess's Law

For a given reaction, the enthalpy change is the same for a reaction performed in one step or in many steps

Example:



that is, by Hess's Law: $\Delta H_1 = \Delta H_2 + \Delta H_3$

⟶ $-393.5 = -110.5 + (-283.0)$ kJ mol^{-1}

Hess's Law **applies to all reactions**, and has two important consequences

i) ΔH for A →B; = $-\Delta H$ for B → A

ii) n(ΔH for A → B) = ΔH for nA → nB

Example: Calculate ΔH^0 for

$$C(gr) + 2S(s) \rightarrow CS_2(\ell)$$

Given that:

i) $C(gr) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_1^0 = -394$ kJ mol^{-1}

ii) $S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H_2^0 = -297$ kJmol^{-1}

iii) $CS_2(\ell) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$ $\Delta H^0_3 = -1077$ kJ mol^{-1}

To obtain the LHS of the desired reaction, we add i) + 2x ii) together.

iv) $C(gr) + O_2(g) + 2S(s) + 2O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$

= $C(gr) + 2S(s) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$

$\Delta H_4^0 = -394 + 2x(-297) = -988$ kJ mol^{-1}

To get the RHS of the desired reaction, take the reverse of iii)

v) $CO_2(g) + 2SO_2(g) \rightarrow CS_2(\ell) + 3O_2(g)$ $\Delta H_5^0 = +1077$ kJ mol^{-1}

Add iv) + v)

$C(gr) + 3O_2(g) + 2S(s) + CO_2(g) + 2SO_2(g) \rightarrow CS_2(\ell) + 3O_2(g) + CO_2(g) + 2SO_2(g)$

= desire equation $\Delta H^0 = \Delta H_4^0 + \Delta H_5^0$

$= -988 + 1077 = 89$ kJ mol^{-1}

Enthalpies of Formation

Most wisely used enthalpy values are standard enthalpies of formation, ΔH_f^0 which are defined as:

"the **enthalpy change** for the formation of 1 mole of a substance at 1 bar from its **constituent elements** In their standard state at 25^0 C (298 K)

The standard state of an element is its most stable physical form at 25^0 C and 1 atmosphere (in Si units 1 bar)

For all elements in their standard states $\Delta H_f^0 = 0$

For example: C(gr) : 0 but C(s, diamond) : 1.895 kJ mol^{-1}
and C(g, atom) : 716.7 kJ mol^{-1}

Similarly, $O_2(g)$: 0.0 but $O_3(g)$: 142.7 kJ mol^{-1} and O(g, atom) : 249.2 kJ mol^{-1}

Note: ΔH_f^0 of $Cl_2(g)$, $Br_2(\ell)$ and $I_2(s)$ = 0.0 but for $Br_2(g)$: 30.91 kJ mol^{-1}

Thus energy is required to convert any element from its standard state to a different allotropic form

See M&H Appendix 1, p. 608-609 for tables of ΔH_f^0 or a very limited list in Table 8.3 p. 210

Heats of formation for compounds are also given

For example: ΔH_f^0 for $CH_4(g)$ =-74.8 kJ mol^{-1}

This represents the ΔH for the reaction of formation:

$$C(gr) + 2H_2(g) \rightarrow CH_4(g)$$

Make sure you can write formation equations

The ΔH^0 for any reaction can be calculated if the ΔH_f^0 of all reactants and products are known

Example:
Calculate ΔH^0 for the production of ethane (C_2H_6) from acetylene (C_2H_2) and hydrogen (H_2)

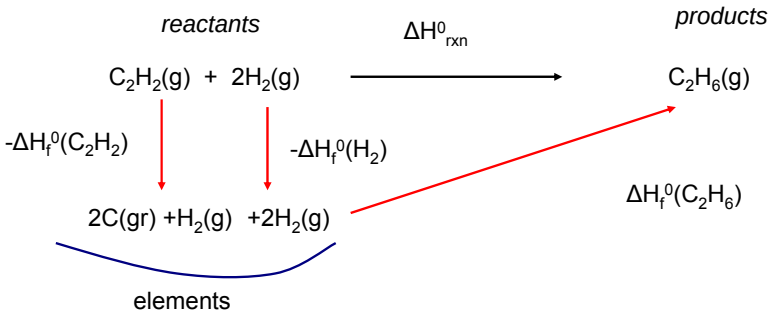
Begin with the balanced equation:

$$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$$

Look up the appropriate ΔH_f^0's:

$C_2H_2(g)$; that is, $2C(gr) + H_2(g) \rightarrow C_2H_2(g)$	ΔH_f^0 = 226.7 kJ mol^{-1}
$H_2(g)$	ΔH_f^0 = 0
$C_2H_6(g)$; that is, $2C(gr) + 3H_2(g) \rightarrow C_2H_6(g)$	ΔH_f^0 = -84.7 kJ mol^{-1}

The formation of products can be viewed as proceeding through the sequence:



By Hess's Law:

$\Delta H^0_{rxn} = -\Delta H_f^0(C_2H_2) - 2\Delta H_f^0(H_2) + \Delta H_f^0(C_2H_6)$

$= -226.7 - 2x(0.0) + (-84.7)$ kJ mol^{-1} $= -311.4$ kJ mol^{-1}

For this example, note that $-\Delta H_f^0(C_2H_2) - 2\Delta H_f^0(H_2) + \Delta H_f^0(C_2H_6)$
$= -\Delta H_f^0(C_2H_2 + 2H_2) + \Delta H_f^0(C_2H_6)$
$= -\Delta H_f^0$(reactants) $+ \Delta H_f^0$(products

In general for any reaction:

$$\Delta H^0_{rxn} = \sum \Delta H_f^0(\text{products}) - \sum \Delta H_f^0(\text{reactants})$$

Thus, the **enthalpy of any reaction** can be calculated if the ΔH_f^0 of **all products and reactants** are known

Example:
Calculate ΔH^o for the combustion of heptane, $C_7H_{16}(\ell)$

Start by writing a balanced equation with all substances in their standard state; that is, 25^o C, 1 bar pressure

$C_7H_{16}(\ell) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(\ell)$

Look up required ΔH_f^o / kJ mol^{-1}

$C_7H_{16}(\ell)$: -224.0 $CO_2(g)$: -393.5
$O_2(g)$: 0.0 $H_2O(\ell)$: -285.8

$\therefore$ $\sum\Delta H_f^o$(products) - $\sum\Delta H_f^o$(reactants)

= 7x(-383.5) + 8x(-285.8) -1x(-224.0)-11x(0.0)

= -4816.9 kJ mol^{-1}

Bond Enthalpy

M&H Chpt. 8.6 p. 210

The bond enthalpy of a bond A-B can be measured by determining the enthalpy required to break "one mole of gaseous AB(g) to its two gaseous atoms"

$\Rightarrow$ $AB(g) \rightarrow A(at,g) + B(at, g)$ ΔH is +ve

This is always an endothermic reaction with a +ve ΔH

The measured value is termed the bond dissociation (enthalpy) energy or bond energy (enthalpy)

Symbol = D; unit = kJ mol^{-1}

If you calculate the D for all the C-H bonds in a number of molecules, you can obtain an average bond enthalpy for C-H. This can be done for any bond.

Examples:

Bond	ΔH kJ mol^{-1}
C-H	414
C-C	347
C=C	612
C≡C	820

Note that average bond enthalpies correlate with the bond order (multiple bonds are stronger than single bonds).

In addition, bond enthalpies correlate with bond lengths: stronger bonds have shorter bond lengths

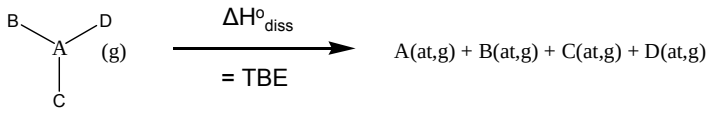
Single Bond Energies (kJ mol^{-1}) at 25°C

	H	C	N	O	S	F	Cl	Br	I
H	436	414	389	464	339	565	431	368	297
C		347	293	351	259	485	331	276	238
N			159	222	--	272	201	243	--
O				138	--	184	205	201	201
S					226	285	255	213	--
F						153	255	255	--
Cl							243	218	209
Br								193	180
I									151

If a molecule has several bonds, then the enthalpy of dissociation yields the total bonding energy (TBE)

TBE = "the enthalpy required to dissociate 1 mole of gaseous compound into its free gaseous atoms"

For example:



One can use tables of ΔH_f^o to calculate TBE for a molecule and exact bond energies

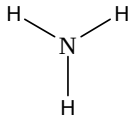
Example:
Calculate the bond energy of a N-H bond in NH_3 given ΔH_f^o of $NH_3(g)$, N(at,g) and H(at,g) are -46.1, 472.7 and 218.0 kJ mol^{-1}, respectively.

TBE(NH_3) found from reaction: $NH_3(g) \rightarrow N(at,g) + 3H(at,g)$

$\therefore$ TBE = $\sum\Delta H_f^o$(products) - $\sum\Delta H_f^o$(reactants)

= 1x(472.7) + 3x(218.0)- 1x(-46,1) kJ mol^{-1}

= 1172.8 kJ mol^{-1}

Since NH_3 = 

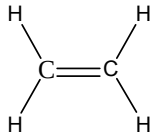
$\therefore$ D(N-H) = 1172.8/3 = 390.9 kJ mol^{-1}

Compare with M&H Table 8.4 D(N-H) = 389 kJ mol^{-1}

Estimates of TBE

TBEs can be estimated by summing the average bond enthalpies for all bonds in a molecule.

This is useful when ΔH_f^os are not available

Example TBE of 

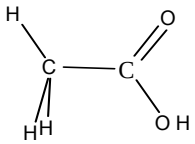
~ 4xD(C-H)+ 1xD(C=C)

= 4x(414) +1x(611) = 2267 kJ mol^{-1}

Note: this is an estimate only because average bond enthalpies are used

One can also use this estimate to calculate ΔH_f^o of a molecule

Example:
Estimate ΔH_f^o of acetic acid, CH_3COOH
given D(C-H) = 414, D(C-C) = 347, D(C=O) = 745, D(C-O) = 351, and D(O-H) = 464, all in kJ mol^{-1}.
Similarly, ΔH_f^os of C(at, g), H(at, g) and O(at, g) are 716.7, 218.0 and 249.2 kJ mol^{-1}, respectively

Structure of CH_3COOH: 

$\therefore$ TBE ~ 3D(C-H) + D(C-C) + D(C=O) + D(C-O) + D(O-H)

~ 3x(414) + 1x(347) + 1x(745) + 1x(351) +1x(464) = 3149 kJ mol^{-1}

Remember, this is an estimate

The equation for TBE is:

$CH_3COOH(g) \rightarrow 2C(at,g) + 4H(at,g) + 2O(at,g)$

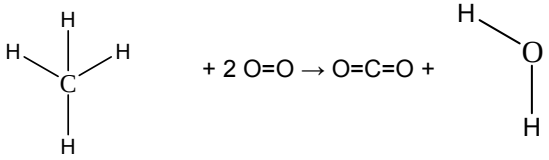
$\therefore$ TBE ~ 3149 kJ mol^{-1} = $\sum\Delta H_f^o$(products) - $\sum\Delta H_f^o$(reactants)

$\Rightarrow$ 3149 = 2x(716.7) +4x(218.0) + 2(249.2)-$\Delta H_f^o(CH_3COOH)$

$\therefore$ $\Delta H_f^o(CH_3COOH)$ = -345.2 kJ mol^{-1}

Example:
Estimate the heat of combustion for $CH_4(g)$
use average bond enthalpies (in kJ mol^{-1}): D(C-H) = 414, D(C=O) = 803, D(O-H) = 464 and ΔH_f^o(O,at,g) = 249.2 kJ mol^{-1}

The combustion reaction is:



1.) energy required to break reagent bonds

= 4xD(C-H) + 2xD(O=O) = 4x(414) + 2x D(O=O)

Since bond enthalpy for O=O is not given we have to calculate it using ΔH_f^o(O(at,g))

$$O_2(g) \xrightarrow{TBE} 2O(at,g)$$

TBE = $2\Delta H_f^o(O(at,g) - \Delta H_f^o(O_2(g)) = 2x(249.2) -0 = 498.4$ kJ mol^{-1}

$\therefore$ ΔH^o to break reagent bonds = 4x(414)+2x(498.4) = +2652.8 kJ mol^{-1}

2.) energy released by formation of product bonds:

= 2xD(C=O) + +4xD(O-H)

= 2x(803) + 4x(464)= 3463 kJ mol^{-1}

3.) The ΔH^o of the reaction will be the energy absorbed – energy released

= 2652.8 – 3462.0 = -809.2 kJ mol^{-1}

The method used to solve this problem can be generalized to:

ΔH^o_{rxn} ~ TBE(reactants) – TBE(products)

Note: this method of using average bond energies to calculate ΔH^o_{rxn} gives only **approximate** values.
Exact values are obtained if ΔH_f^o values for products and reactants are used – this is the better method if all the necessary data is available.