

TERMS AND DEFINITIONS IN THERMOCHEMISTRY

(v.2.0 16/3/90 8hrs.)

(v.2.1 12/4/90 2hrs.)

1) ENTHALPY CHANGE (ΔH)

This is the same as the heat change involved in a process (provided the initial and final states are at the same pressure). It is positive for an endothermic process (where heat energy is changed into chemical energy) and negative for an exothermic process (where chemical energy is changed into heat).

If the process occurs at constant volume (*ie* in a sealed vessel) the heat change is **not** the same as the enthalpy change, though the enthalpy change may be calculated.

The value of an enthalpy change depends on the temperature, the physical states (s, l, g, aq) of the reactants and products, the pressures of gaseous reactants and products, and the concentrations of solutions. Enthalpy changes are therefore stated for standard conditions.

2) STANDARD CONDITIONS

The standard conditions are a pressure of 1 atmosphere and a concentration of 1 M for solutions. Solids and liquids are taken to be pure and in their standard states unless otherwise specified. The standard enthalpy change is denoted by ΔH^\ominus_T , meaning the standard enthalpy change at temperature T, which should be specified (*eg* ΔH^\ominus_{298}). If no temperature is stated it is normally taken to be 298 K (25°C).

3) STANDARD STATE

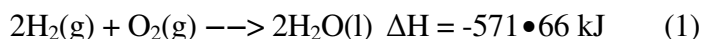
In the case of an element or compound the standard state is the most stable state of the substance at 1 atmosphere pressure and a specified temperature (usually 298 K). Thus the standard state of hydrogen at 298 K is the gaseous state, and for water it is the liquid state, whilst for carbon it is graphite, not diamond. Diamond is only apparently stable (metastable). The standard state for solutions is considered to be 1M.

4) ENTHALPY OF REACTION (ΔH)

This is the enthalpy change involved in the reaction between substances in the quantities and states indicated by the chemical equation.

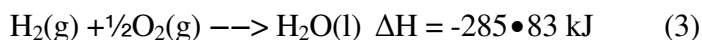
It can be calculated as the total enthalpy of the products minus the total enthalpy of the reactants. It is usually expressed in kJ. Often it is necessary to convert the result to Joules for further calculations. Just put 10^3 in place of the prefix "k". *ie* $-285 \cdot 83 \text{ kJ} = -285 \cdot 83 \times 10^3 \text{ J}$.

The enthalpy change for a given reaction will vary depending on the *states* of the reactants and products. *eg*



For this reason it is *extremely* important when writing thermochemical equations to put in the correct states. Note that the difference between the two values above is just twice the molar latent heat of vaporization of water, *ie* the heat required to convert 2 moles of water from liquid to gas.

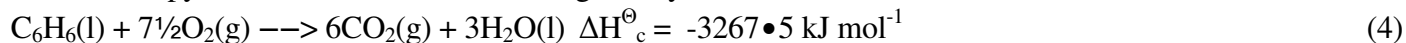
The enthalpy change will also vary according to the *quantities* of substances involved in the reaction. For example:



Thus, unless *standard* enthalpies are quoted, a ΔH value must always be referred to a particular equation which you have written down.

5) STANDARD ENTHALPY OF COMBUSTION (ΔH_c^\ominus)

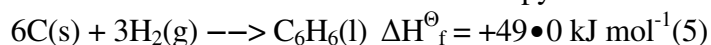
This is the enthalpy change involved in the complete combustion of 1 mole of a substance in excess oxygen under standard conditions. It is usually negative since heat is given out in such reactions. Thus the standard molar enthalpy of combustion for benzene is given by:



Note that the ΔH value given in (3) above is the standard molar enthalpy of combustion for hydrogen, whilst those in (1) and (2) above are not.

6) STANDARD ENTHALPY OF FORMATION (ΔH_f^\ominus)

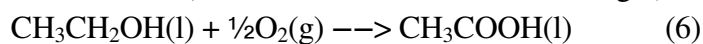
This is the enthalpy change involved in the formation of one mole of a compound from its elements in their standard states. Thus the standard enthalpy of formation of benzene is given by:



(Since the enthalpy of formation of benzene is positive it is known as an endothermic compound.)

From the definition the enthalpies of formation of elements in their standard states must be zero.

Standard enthalpies of formation can be found in published tables. They are very convenient for the calculation of other enthalpy changes. The enthalpy change for a reaction is the total enthalpy of formation of the products, less the total enthalpy of formation of the reactants. Thus the enthalpy change for the oxidation of ethanol to ethanoic acid (as occurs when wine turns to vinegar) may be calculated:



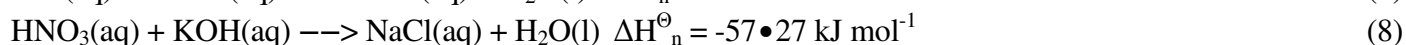
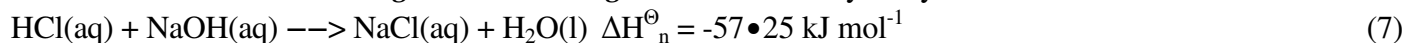
$$(-276 \cdot 98 + 0) \quad +(-484 \cdot 13)$$

$$\text{gives } \Delta H^\ominus = -207 \cdot 15 \text{ kJ mol}^{-1}$$

(This result is not entirely accurate for vinegar since this is an aqueous solution and the above equation relates to the pure reactants and product.)

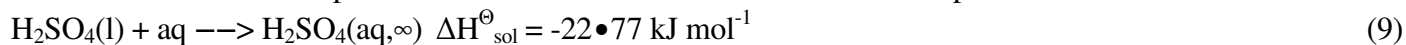
7) STANDARD ENTHALPY OF NEUTRALIZATION (ΔH_n^\ominus)

This is the enthalpy change involved in the neutralization of an acid by a base to form 1 mole of water under standard conditions. For **strong** acids and **strong** bases this is always very close to $-57.24 \text{ kJ mol}^{-1}$.



8) STANDARD ENTHALPY OF (DIS)SOLUTION ($\Delta H_{\text{sol}}^\ominus$)

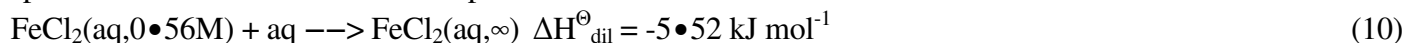
This is the enthalpy change involved in the dissolution of 1 mole of a substance in a specified amount of solvent. If no volume is specified infinite dilution is assumed. Thus for sulphuric acid we have:



The symbol aq standing alone is used to represent an indefinite amount of water. The ∞ symbol is used to indicate that an infinitely dilute solution is formed.

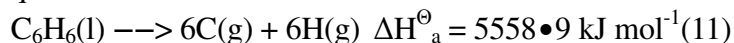
9) ENTHALPY OF DILUTION (ΔH_{dil})

This is the enthalpy change involved in the dilution of a solution containing 1 mole of the substance, from one specified concentration to a second specified concentration.

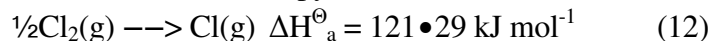


10) STANDARD ENTHALPY OF ATOMIZATION (ΔH_a^\ominus)

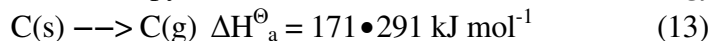
This is the enthalpy change involved in the conversion of an element or compound to free atoms in the gaseous state. Sometimes it is quoted for the formation of 1 mol of atoms, and sometimes for the atomization of 1 mol of an element or compound. Thus it is always necessary to specify exactly what you mean when you use this term. Quoting the equation involved will do this. Thus the molar enthalpy of atomization of benzene may be quoted as:



whilst the molar enthalpy of atomization of chlorine is usually quoted as:



This enthalpy value is also the **bond dissociation energy** of chlorine. For carbon we have:



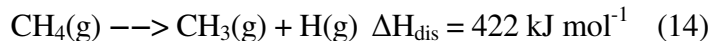
This is also called the **enthalpy of sublimation** of carbon.

Notice that all these values are positive since energy must be put in to break bonds.

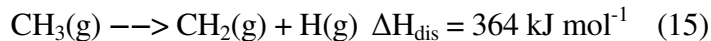
11) BOND DISSOCIATION ENTHALPY (BOND DISSOCIATION ENERGY) (ΔH_{dis})

This is the enthalpy change involved in the breaking of 1 mole of a SPECIFIED bond, **all reactants and products being in the gas phase**.

Thus the bond dissociation energy for the first C–H bond in methane is given by:



whilst the bond dissociation energy for the breaking of the second C–H bond in methane (*ie* once the first C–H bond has been broken) is given by:



Note that bond dissociation energies are always large and positive. Some useful bond dissociation energies are:

BOND ENERGY/kJ mol⁻¹

H–H 436

O=O 498

Cl-Cl 242

12) MEAN BOND ENERGY (BOND ENTHALPY TERM, or AVERAGE STANDARD BOND ENTHALPY)

This is the average molar enthalpy change involved when several similar bonds in a variety of substances are broken.

Thus the average strength of the C–H bond may be estimated from the enthalpy of atomization of methane:



Clearly the average energy for one C–H bond will be a quarter of this:

$$\frac{1}{4} \times 1662 = 416 \text{ kJ mol}^{-1}$$

This is the mean bond energy for the C-H bonds in methane. Similar bonds in many compounds have roughly the same mean bond energy. Different bonds have different energies. These values may be found in tables:

BOND ENERGY TERM/kJ mol⁻¹

C–C 348

C=C 682

C≡C 962

C–O 360

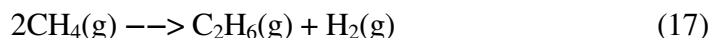
C=O 743

O–H 463

C–H 416

Note that the value for the C=C double bond is nearly twice that for the single C–C bond, and the value for the C≡C bond nearly three times as much. This is what one would expect.

Using these mean bond energies it is possible to estimate the enthalpy change for a reaction which cannot be studied in the laboratory. For example one might wish to calculate the enthalpy change of the following reaction:



In this reaction two C–H bonds are broken, one C–C bond and one H–H bond are formed. You can see this better if you draw out full structural formulae for the compounds:

The enthalpy change may be calculated as follows:

$$\text{Enthalpy change for bond broken (2 C-H bonds)} = 2 \times 416 = 832 \text{ kJ}$$

$$\text{Enthalpy change for bonds formed (1 C–C bond + 1 H–H bond)}$$

$$= (-348) + (-436) = -784 \text{ kJ mol}^{-1}$$

$$\text{Total enthalpy change} = 832 + (-784) = 48 \text{ kJ mol}^{-1}$$

13) IONIZATION ENERGY (ENTHALPY OF IONIZATION) (ΔH_I)

This is the minimum amount of energy required to remove 1 mole of electrons from 1 mole of atoms or ions (as appropriate), both reactants and products being in the gaseous state. For example



1st ionization energy of sodium



2nd ionization energy of sodium

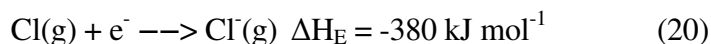
Successive ionization energies increase very rapidly for a given element, especially once the valence electrons

have been removed.

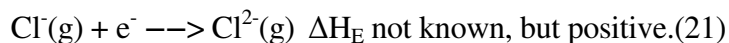
14) ELECTRON AFFINITY (ΔH_E)

This is the enthalpy change involved when 1 mole of atoms or ions (as appropriate) gains one mole of electrons, all reactants and products being in the gaseous state.

For example



1st electron affinity of chlorine



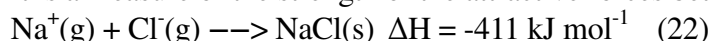
2nd electron affinity of chlorine

Most first electron affinities are negative, showing that the ions formed are stable (as isolated ions in the gaseous state). All second electron affinities are positive.

15) STANDARD LATTICE ENERGY (ΔH_L^\ominus)

This is the enthalpy change involved when one mole of a crystalline ionic substance is created from the free ions in the gaseous state.

It is a measure of the strength of the attractive forces between the ions. For example



lattice energy of sodium chloride

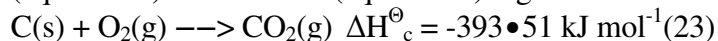
16) HESS'S LAW

This is the law on which the whole of thermochemistry is based. It states that the enthalpy change for a process does not depend on the nature of any intermediate steps involved in bringing the process about. That is, the enthalpy change does not depend on the path chosen to accomplish the process, but only on the initial and final states involved. It is another statement of the law of conservation of energy.

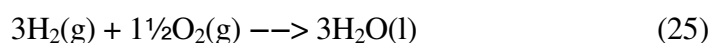
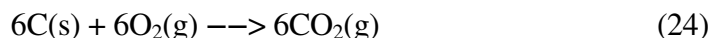
For example copper can be converted directly to copper(II) oxide by heating in oxygen. Copper(II) oxide may also be produced indirectly if the copper is first dissolved in nitric acid to form copper(II) nitrate, and this is then heated to form the copper(II) oxide. In either case the total enthalpy change is the same.

Hess's law allows the calculation of enthalpy changes which are difficult or impossible to measure directly (for example, enthalpies of formation) from those which are easy to measure (such as enthalpies of combustion).

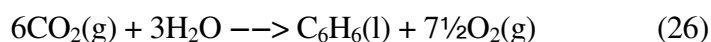
Thus the enthalpy of formation of benzene (equation 5) is calculated from the heats of combustion of hydrogen (equation 3) and benzene (equation 4) together with the heat of combustion of carbon:



The idea is that (in principle) we can bring about the formation of 1 mole of benzene from its elements indirectly. We start with 6 moles of carbon, three moles of hydrogen, and a total of $7\frac{1}{2}$ moles of oxygen and convert them first into carbon dioxide and water:



Next we turn these into 1 mole of benzene and $7\frac{1}{2}$ moles of oxygen:



The enthalpy change for equation (24) is just 6 times that for the combustion of carbon (equation 23), whilst that for equation (25) is 3 times that for the combustion of hydrogen (equation 3). The enthalpy changes involved in equations (24) and (25) is therefore:

$$(24): 6 \times (-393 \cdot 51) = -2361 \cdot 06 \text{ kJ mol}^{-1}$$

$$(25): 3 \times (-285 \cdot 83) = -857 \cdot 49 \text{ kJ mol}^{-1}$$

Although equation (26) cannot actually be carried out in the laboratory, it is the reverse of the combustion of benzene (equation 4) which can, and so the enthalpy change is just the same but with the sign changed: $+3267 \cdot 5 \text{ kJ mol}^{-1}$

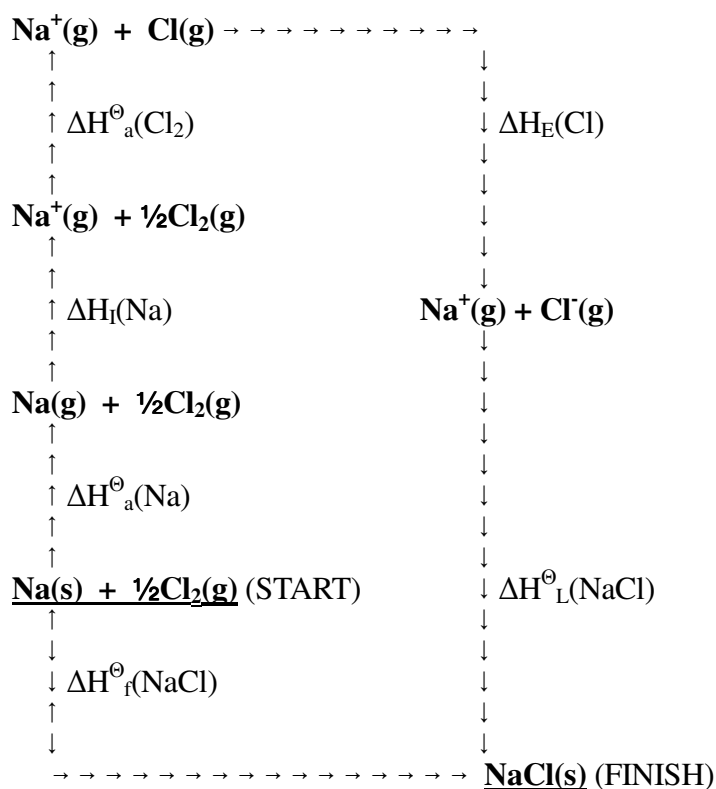
Hess's law tells us that the overall enthalpy change is just the sum of the changes for the individual steps involved, so that the standard enthalpy of formation of benzene is given by the sum of the enthalpy changes for equations (24), (25) and (26):

$$-3218 \cdot 5 + 3267 \cdot 5 = +49 \cdot 0 \text{ kJ mol}^{-1}$$

Note that the oxygen is reformed in the original amount ($7\frac{1}{2}$ moles) at the end of the process, so that it does not affect the calculation of the overall enthalpy change.

17) BORN HABER CYCLE

This is one particular example of the application of Hess's Law.



In the diagram above the following terms are used

$\Delta H_f^\ominus(\text{NaCl})$ - the standard enthalpy of formation of sodium chloride.

$\Delta H_a^\ominus(\text{Na})$ - the standard enthalpy of atomization of sodium.

$\Delta H_i(\text{Na})$ - the first ionization energy of sodium.

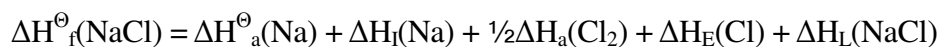
$\Delta H_a^\ominus(\text{Cl}_2)$ - the standard enthalpy of atomization of chlorine (per mole of chlorine atoms produced).

$\Delta H_E(\text{Cl})$ - the first electron affinity of chlorine.

$\Delta H_L^\ominus(\text{NaCl})$ - the standard lattice energy of sodium chloride.

Upward arrows represent endothermic changes, and downward arrows represent exothermic changes.

Since, according to Hess's law, going from START to FINISH one way round the cycle is the same thing as going from START to FINISH the other way round the cycle, the enthalpy terms are related by:



This allows the calculation of the lattice energy, which otherwise could not be found.

18) HEAT CAPACITY (C)

This is the amount of heat required to raise the temperature of a body by 1 K (or equally 1°C). Units: J kg⁻¹K⁻¹

Thus for a calorimeter of heat capacity C J K⁻¹ and a temperature rise of ΔT K, the heat given up to the calorimeter is given by

$$q = C \times \Delta T \text{ Joules}$$

19) SPECIFIC HEAT CAPACITY

This is the amount of heat required to raise the temperature of 1 kg of a substance by 1 K. Units: J mol⁻¹K⁻¹

20) MOLAR HEAT CAPACITY (C_M)

This is the amount of heat required to raise the temperature of 1 mole of a substance by 1 K. Units: J mol⁻¹K⁻¹

21) MOLAR ENTHALPY OF FUSION (ΔH_{fus})

This is the amount of heat required to convert 1 mole of a solid into the liquid state at the same temperature. Units: J mol⁻¹K⁻¹

22) MOLAR ENTHALPY OF EVAPORATION (ΔH_{vap})

This is the amount of heat required to convert 1 mole of a liquid into the gaseous state at the same temperature.

23) MOLAR ENTHALPY OF SUBLIMATION (ΔH_{sub})

This is the amount of heat required to convert 1 mole of a solid into the gaseous state.

For elements which do not consist of discrete molecules it is often essentially the same as the molar enthalpy of atomization.

24) ENDOTHERMIC COMPOUND

See *ENTHALPY OF FORMATION*