Standard Enthalpy of Formation and Reaction

The standard enthalpy of formation → Is the heat changes that result when 1 mole of the compound is formed from its elements at pressure of 1 atm.

standard state → doesn't specify a temperature ,but we use $\Delta H^{o}F$ values measured at 25°C why?!

Because most of thermodynamic are collected at this temperature.

What is the importance of $\Delta H^{o}f$?!

we can calculate $\Delta H^{o}rxn$

Note that we can determine the enthalpy change by measuring the heat absorbed or released at constant pressure.

The standard enthalpy of formation of any element in its most stable form is zero.

Example 1

O_2 is more stable than the other allotropic form of oxygen , ozone (O_3) at 1 atm and 25°C thus

we can write (a) $\Delta H^{o}F\ (O_2) = 0$

(b) $\Delta H^{o}F\ (O_3) = 142.2KJ/mol$

Example 2

$\Delta H^{o}F$ (C , graphite) = 0

$\Delta H^{o}F$ (C , diamond) =1.90KJ/mol

Standard Enthalpies of Formation of Some Inorganic Substances at 25° C

Substance	ΔH_f°(kJ/mol)	Substance	ΔH_f°(kJ/mol)
$Ag(s)$	0	$H_2O_2(l)$	−187.6
$AgCl(s)$	−127.0	$Hg(l)$	0
$Al(s)$	0	$I_2(s)$	0
$Al_2O_3(s)$	−1669.8	$HI(g)$	25.9
$Br_2(l)$	0	$Mg(s)$	0
$HBr(g)$	−36.2	$MgO(s)$	−601.8
C(graphite)	0	$MgCO_3(s)$	−1112.9
C(diamond)	1.90	$N_2(g)$	0
$CO(g)$	−110.5	$NH_3(g)$	−46.3
$CO_2(g)$	−393.5	$NO(g)$	90.4
$Ca(s)$	0	$NO_2(g)$	33.85
$CaO(s)$	−635.6	$N_2O(g)$	81.56
$CaCO_3(s)$	−1206.9	$N_2O_4(g)$	9.66
$Cl_2(g)$	0	$O(g)$	249.4
$HCl(g)$	−92.3	$O_2(g)$	0
$Cu(s)$	0	$O_3(g)$	142.2
$CuO(s)$	−155.2	S(rhombic)	0
$F_2(g)$	0	S(monoclinic)	0.30
$HF(g)$	−271.6	$SO_2(g)$	−296.1

Ex: consider the hypothetical reaction

$$aA + bB \rightarrow cC + dD$$

where a ,b ,c ,d (stoichiometric coefficients)

for this reaction ΔHºrxn is given by

$$\Delta H^{\circ}rxn = [C\Delta H^{\circ}F(C) + d\Delta H^{\circ}F(D)] - [a\Delta H^{\circ}F(A) + b\Delta H^{\circ}F(B)]$$

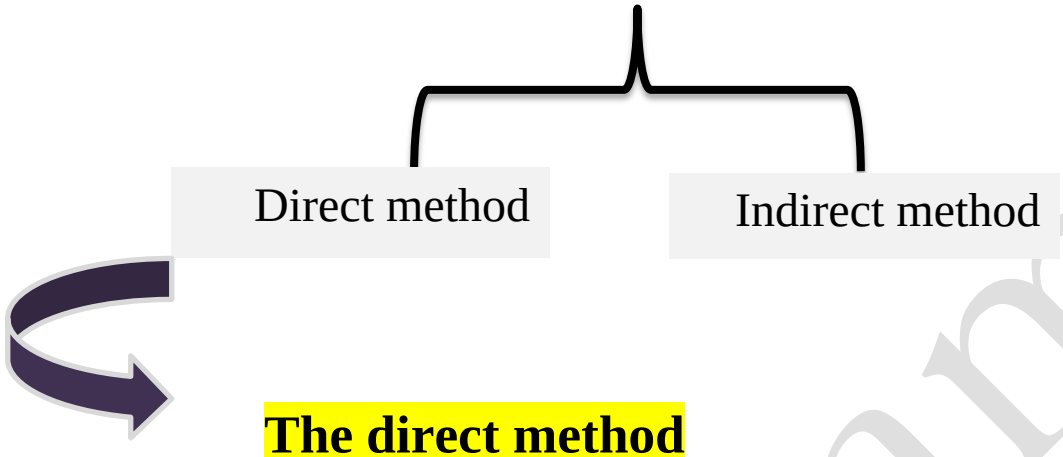
general equation is:

$$\Delta H^{\circ}rxn = \sum_n \Delta H^{\circ}F(product) - \sum_m \Delta H^{\circ}F(reactants)$$

: $\sum_{\rightarrow} means\ the\ sum\ of\ n, m$

n,m Stoichiometric coefficients.

To calculate $\Delta H^{o}rxn$, we must know the $\Delta H°F$ values in the reactions by



The direct method

Where measuring $\Delta H^{o}F$ synthesized from their elements.

Ex: we want know $\Delta H^{o}F$ of CO_2

we must measure enthalpy of reaction when C " graphite" and molecular oxygen in their standard state are converted to CO_2.

C (graphite) + $O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H^{o}rxn = -393.5KJ/mol$.

from equation

$\Delta H^{o}rxn = \Delta H^{o}F(CO_2)g - [\Delta H°F(C\ graphite) + \Delta H°F(O2)g]$

= product – reactant

$\Delta H^{o}rxn = \Delta H^{o}F(CO_2)g = -393KJ/mol$

where O_2 , C are stable $\therefore \Delta H°F = zero$

☒ In thermochemistry we are interested only in enthalpy change because they can be determined experimentally whereas absolute enthalpy value cannot.

☒ Other compounds that can be studied by the direct method are SF_6 , P_4O_{10} and CS_2 The equation representing are:

$$S\ (\text{rhombic}) + 3F_2(g) \rightarrow SF_6(g)$$

$$P_4\ (\text{white}) + 5O_2\ (g) \rightarrow P_4O_{10}(s)$$

$$C(\text{graphite}) + 2S(\text{rhombic}) \rightarrow CS_2$$

where S,P,C more stable $\therefore \Delta H°\text{F} = zero.$ at 1atm and 25°C

The indirect method

In these cases , $\Delta H°F$ can be determined by Hess's law of heat summation , where reactions are converted to products , the change in enthalpy is the same reaction takes place in one step or in a series of steps.

☒ If we break down the reaction into series of reactions for which $\Delta H°rxn$, we can calculate $\Delta H°rxn$ for over all reaction , where Hess's law is depend on initial and final state.

Ex: $\Delta H°F$ of CO . we might represent the reaction as

$$C(graphite) + \frac{1}{2}O2 \rightarrow CO_{(g)}$$

we use indirect method because C graphite also produces some CO_2 , so we can't measure the enthalpy change force directly.

a) C (graphite) + $O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H°rxn$ = -393.5KJ/mol.

b) $CO_{(g)} + \frac{1}{2} O_2 \rightarrow CO_{2(g)}$ $\Delta H°rxn$ = -283.5KJ/mol.

first , we reverse equation (b) to get

c) $CO_{2\ (g)} \rightarrow CO_{(g)} + \frac{1}{2} O_2$ $\Delta H°rxn$ = 283.5KJ/mol.

we carry out the operation (a) + (c) and obtain

a) C (graphite) + $O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H°rxn$ = -393.5KJ/mol.

c) $CO_{2\ (g)} \rightarrow CO_{(g)} + \frac{1}{2} O_2$ $\Delta H°rxn$ = 283.5KJ/mol.

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d) C (graphite) + $\frac{1}{2} O_2 \rightarrow CO_{(g)}$ $\Delta H°rxn$ = -110.5KJ/mol.

Questions

1. Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements: $2C\ (graphite) + H_2\ (g) \rightarrow C_2H_2\ (g)$

The equations for each step and the corresponding enthalpy changes are

a) $C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H°rxn = -393.5\ kJ/mol$

b) $H_2(g) + 1/2\ O_{2(g)} \rightarrow H_2O(l)$ $\Delta H°rxn = -285.8\ kJ/mol$

c) $2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l)$ $\Delta H°rxn = -2598.8\ kJ/mol$.

Solution

a) $2C\ (graphite) + 2O_2(g) \rightarrow 2CO_2(g)$

$\Delta H°rxn = 2(-393.5\ kJ/mol) = -787.0\ kJ/mol$

b) $H_2(g) + 1/2\ O_{2(g)} \rightarrow H_2O(l)$

$\Delta H°rxn = -285.8\ kJ/mol$

-c) $2CO_2(g) + H_2O(l) \rightarrow C_2H_2(g) + 5/2O_2(g)$

$\Delta H°\ rxn = 1299.4\ kJ/mol$

$2C(graphite) + H_2(g) \rightarrow C_2H_2(g)$ $\Delta H°\ rxn = 226.6\ kJ/mol$

Therefore,

$\Delta H°f = \Delta H°\ rxn = 226.6\ kJ/mol.$

The $\Delta H°f$ value means that when 1 mole of C_2H_2 is synthesized from 2 moles of C(graphite) and 1 mole of H_2 , 226.6 kJ of heat are absorbed by the reacting system from the surroundings. Thus, this is an endothermic process.

Choose

1) To which one of these reactions occurring at 25◦C does the symbol
2) $\Delta H°f\ [H_2SO_{4\ (l)}]$ refer?

A) $2H_{(g)} + S_{(g)} + 4O_{(g)} \rightarrow H_2SO_{4(l)}$

B) $H_2(g) + S(g) + 2O_2(g) \rightarrow H_2SO_4(l)$

C) $H_2SO_{4(l)} \rightarrow H_{2(g)} + S_{(s)} + 2O_{2(g)}$

D) $H_2(g) + S(s) + 2O_2(g) \rightarrow H_2SO_4(l)$

2) To which one of these reactions occurring at 25°C does the symbol $\Delta H°f\ [HNO_3\ (l)]$ refer?

A) $H(g) + N(g) + O_3(g) \rightarrow HNO_3(l)$

B) $(1/2)H_2(g) + (1/2)N_2(g) + (3/2)O_2(g) \rightarrow HNO_3(l)$

C) $HNO_3(l) \rightarrow H(g) + N(g) + 3O(g)$

D) $H_2(g) + N_2(g) + O_3(g) \rightarrow HNO_3(l)$

3) When 0.560 g of Na(s) reacts with excess $F_2(g)$ to form NaF(s), 13.8 kJ of heat is evolved at standard-state conditions. What is the standard enthalpy of formation (ΔH°f) of NaF(s)?

A) 24.8 kJ/mol

B) 570 kJ/mol

C) -24.8 kJ/mol

D) -570 kJ/mol

4) Ethanol undergoes combustion in oxygen to produce carbon dioxide gas and liquid water. The standard heat of combustion of ethanol, C_2H_5OH (l), is -1366.8 kJ/mol. Given that $\Delta H°f [CO_2(g)]$ = -393.5 kJ/mol and $[H_2O(l)]$ = -285.8 kJ/mol, what is the standard enthalpy of formation of ethanol?

A) 3,010 kJ/mol
C) -277.6 kJ/mol
B) -687.6 kJ/mol
D) 687.6 kJ/mol

5) Find the standard enthalpy of formation of ethylene, C_2H_4 (g), given the following data: heat of combustion of C_2H_4 (g) = -1411 kJ/mol; $\Delta H°f [CO_2 (g)]$ = -393.5 kJ/mol; $\Delta H°f [H_2O (l)]$ = -285.8 kJ/mol.

A) 52 kJ/mol
C) 731 kJ/mol
B) 87 kJ/mol
D) 1.41×10^3 kJ/mol