3.6: Thermochemistry

The standard enthalpy of formation is defined as the change in enthalpy when one mole of a substance in the standard state (1 atm of pressure and 298.15 K) is formed from its pure elements under the same conditions.

Introduction

The standard enthalpy of formation is a measure of the energy released or consumed when one mole of a substance is created under standard conditions from its pure elements. The symbol of the standard enthalpy of formation is ΔH_f.

- Δ = A change in enthalpy
- ^{o} = A degree signifies that it's a standard enthalpy change.
- f = The f indicates that the substance is formed from its elements

The equation for the standard enthalpy *change* of formation (originating from Enthalpy's being a State Function), shown below, is commonly used:

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This equation essentially states that the standard enthalpy *change* of formation is equal to the **sum of the standard enthalpies of formation of the *products*** minus the **sum of the standard enthalpies of formation of the *reactants***.

Example *[Math Processing Error]*

Given a simple chemical equation with the variables A, B and C representing different compounds:

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and the standard enthalpy of formation values:

- $\Delta H_f^o[A]$ = 433 KJ/mol
- $\Delta H_f^o[B]$ = -256 KJ/mol
- $\Delta H_f^o[C]$ = 523 KJ/mol

the equation for the standard enthalpy change of formation is as follows:

$$\Delta H_{reaction}^o = \Delta H_f^o[C] - (\Delta H_f^o[A] + \Delta H_f^o[B])$$

$$\Delta H_{reaction}^o = (1\ \cancel{mol})(523\ kJ/\cancel{mol}) - ((1\ \cancel{mol})(433\ kJ/\cancel{mol}) + (1\ \cancel{mol})(-256\ kJ/\cancel{mol})\backslash)$$

Because there is one mole each of A, B and C, the standard enthalpy of formation of each reactant and product is multiplied by 1 mole, which eliminates the mol denominator:

$$\Delta H_{reaction}^o = \mathbf{346\ kJ}$$

The result is 346 kJ, which is the standard enthalpy change of formation for the creation of variable "C".

> The standard enthalpy of formation of a pure element is in its reference form its standard enthalpy formation is **zero**.

Carbon naturally exists as graphite and diamond. The enthalpy difference between graphite and diamond is too large for both to have a standard enthalpy of formation of zero. To determine which form is zero, the more stable form of carbon is chosen. This is also the form with the lowest enthalpy, so graphite has a standard enthalpy of formation equal to zero. Table 1 provides sample values of standard enthalpies of formation of various compounds.

Table 1: Sample Table of Standard Enthalpy of Formation Values. Table T1 is a more comprehensive table.

Compound	ΔH_f^o
$O_2(g)$	0 kJ/mol
C(graphite)	0 kJ/mol
CO(g)	-110.5 kJ/mol

Compound	ΔH_f^o
$CO_2(g)$	-393.5 kJ/mol
$H_2(g)$	0 kJ/mol
$H_2O(g)$	-241.8 kJ/mol
HF(g)	-271.1 kJ/mol
NO(g)	90.25 kJ/mol
$NO_2(g)$	33.18 kJ/mol
$N_2O_4(g)$	9.16 kJ/mol
$SO_2(g)$	-296.8 kJ/mol
$SO_3(g)$	-395.7 kJ/mol

All values have units of kJ/mol and physical conditions of 298.15 K and 1 atm, referred to as the "standard state." These are the conditions under which values of standard enthalpies of formation are typically given. Note that while the majority of the values of standard enthalpies of formation are exothermic, or negative, there are a few compounds such as NO(g) and $N_2O_4(g)$ that actually require energy from its surroundings during its formation; these endothermic compounds are generally unstable.

Example [Math Processing Error]

Between $Br_2(l)$ and $Br_2(g)$ at 298.15 K, which substance has a nonzero standard enthalpy of formation?

Solution

$Br_2(l)$ is the more stable form, which means it has the lower enthalpy; thus, $Br_2(l)$ has $\Delta H_f = 0$. Consequently, **$Br_2(g)$ has a nonzero standard enthalpy of formation.**

Note: that the element phosphorus is a unique case. The reference form in phosphorus is not the most stable form, red phosphorus, but the less stable form, white phosphorus.

Recall that standard enthalpies of formation can be either positive or negative.

Example [Math Processing Error]

The enthalpy of formation of carbon dioxide at 298.15K is ΔH_f = -393.5 kJ/mol $CO_2(g)$. Write the chemical equation for the formation of CO_2.

Solution

This equation must be written for one mole of $CO_2(g)$. In this case, the reference forms of the constituent elements are $O_2(g)$ and graphite for carbon.

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The general equation for the standard enthalpy change of formation is given below:

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Plugging in the equation for the formation of CO_2 gives the following:

$$\Delta H_{reaction}^o = \Delta H_f^o[CO_2(g)] - (\Delta H_f^o[O_2(g)] + \Delta H_f^o[C(graphite)]$$

Because $O_2(g)$ and C(graphite) are in their most elementally stable forms, they each have a standard enthalpy of formation equal to 0:

$$\Delta H_{reaction}^o = -393.5\ kJ = \Delta H_f^o[CO_2(g)] - ((1\ mol)(0\ kJ/mol) + (1\ mol)(0\ kJ/mol))$$

$$\Delta H_f^o[CO_2(g)] = -393.5\ kJ$$

Example [Math Processing Error]

Using the values in the above table of standard enthalpies of formation, calculate the $\Delta H_{reaction}^o$ for the formation of $NO_2(g)$.

Solution

[Math Processing Error] is formed from the combination of [Math Processing Error] and [Math Processing Error] in the following reaction:

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To find the $\Delta H_{reaction}^o$, use the formula for the standard enthalpy change of formation:

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The relevant standard enthalpy of formation values from Table 1 are:

- $O_2(g)$: 0 kJ/mol
- $NO(g)$: 90.25 kJ/mol
- $NO_2(g)$: 33.18 kJ/mol

Plugging these values into the formula above gives the following:

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Kirchhoff's Law describes the enthalpy of a reaction's variation with temperature changes. In general, enthalpy of any substance increases with temperature, which means both the products and the reactants' enthalpies increase. The overall enthalpy of the reaction will change if the increase in the enthalpy of products and reactants is different.

Kirchoff's Law - Enthalpy is Temperature Dependent

At constant pressure, the heat capacity is equal to change in enthalpy divided by the change in temperature.

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Therefore, if the heat capacities do not vary with temperature then the change in enthalpy is a function of the difference in temperature and heat capacities. The amount that the enthalpy changes by is proportional to the product of temperature change and change in heat capacities of products and reactants. A weighted sum is used to calculate the change in heat capacity to incorporate the ratio of the molecules involved since all molecules have different heat capacities at different states.

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If the heat capacity is temperature independent over the temperature range, then Equation [Math Processing Error] can be approximated as

[Math Processing Error]

with

- [Math Processing Error] is the (assumed constant) heat capacity and
- [Math Processing Error] and [Math Processing Error] are the enthalpy at the respective temperatures.

Equation [Math Processing Error] can only be applied to small temperature changes, (<100 K) because over a larger temperature change, the heat capacity is not constant. There are many biochemical applications because it allows us to predict enthalpy changes at other temperatures by using standard enthalpy data.

Contributors and Attributions

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