



CHEM 1035 – Lecture 20

Enthalpy and Stoichiometry

The energy changes that accompany chemical reactions are an important part of chemistry. Much of the Chemistry field is devoted to using chemical reactions to efficiently extract energy.



Heat Capacity

The heat capacity is broadly defined as the ability of a substance to absorb heat.

$$q \propto \Delta T$$

$$\frac{q}{\Delta T} = \textit{Heat Capacity}$$

When an object absorbs heat, then the temperature rises. The temperature rise is proportional to the amount of heat absorbed, and the proportionality factor is the Heat Capacity.

Specific Heat Capacity (lower case c) is defined as the quantity of heat required to change the temperature of 1 gram of a substance by 1K.

Molar heat capacity (C) is defined as the quantity of heat required to change the temperature of 1 mole of a substance by 1K.

This is a proportionality factor that tells us the relationship between the amount of heat generated in a reaction and the Temperature change.

Work some example problems



Example

A 505g piece of copper ($c=0.387\text{J/gm}\cdot\text{K}$) is heated to 99.9°C and placed in an insulated vessel containing 59.8gm water at 24.8°C . Assuming no loss of water and a heat capacity for the vessel of 10.0J/K , what is the final temperature of the system?



Thermochemistry and Stoichiometry

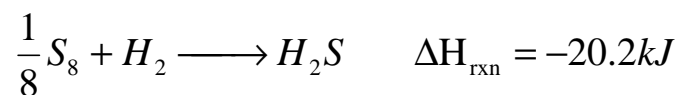
Have already indicated that we can think of “heat” as being a reactant (endothermic process) or a product (exothermic process) in a chemical reaction. This can be quantified by relating reaction stoichiometry to the “Heat of Reaction”

$$\Delta H_{\text{rxn}}$$

The heat of reaction (or the enthalpy of a balanced chemical reaction) provides a stoichiometric relationship between the moles of reactants/products and the Enthalpy change of the reaction.



Example



What is ΔH_{rxn} if 20.0gm S_8 reacts?

What does this reaction say? $1/8$ mole of S_8 reacts with 1 mole of H_2 to produce 1 mole of H_2S and produces 20.2kJ of heat. Is the reaction exothermic or endothermic? What is the enthalpy change if we change the stoichiometric coefficients to whole numbers?

What is the stoichiometric equivalence from this balanced Thermochemical reaction?

If we increase the amount of the reactants, what happens to the amount of heat generated? The heat released (or consumed) is directly proportional to the amount (number of moles) of the reactants/products.



Hess's Law of Heat Summation

Because Enthalpy:

- Is a State Function
- Is stoichiometrically related to the number of moles of reactant and product

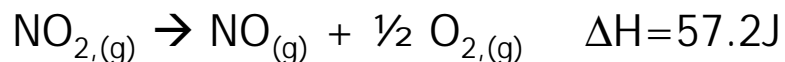
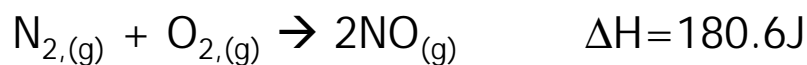
We can determine the Enthalpy of a reaction using combinations of other reactions.

This process is known as Hess's Law of Heat Summation – the Enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps.

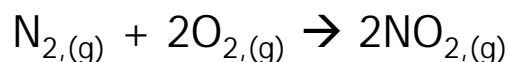


Example of Hess's Law

Given:



What is the ΔH for:



Because Enthalpy is a State function, how the reactants end up as the products doesn't matter. What matters is the starting state, and the ending state. Hess's law allows us to break overall chemical processes into smaller, sequential steps. If we can determine the $(\Delta)H$ for each of the sequential steps, then we can determine the overall $(\Delta)H$ by adding the individual steps together.

Rules:

1. Identify the target reaction equation
2. Manipulate the component equations so that they sum to the target chemical equation
 1. Change the sign of the component $(\Delta)H$ if you reverse the direction of the reaction
 2. Multiply the $(\Delta)H$ by the appropriate factor if you need to multiply the reaction equation by some factor
3. Add the manipulated component equations together to obtain the target equation, and add the $(\Delta)H$ values to get the $(\Delta)H$ of the desired reaction



Standard Heat of Reaction

$$\Delta H^{\circ}$$

The Enthalpy change of a reaction is dependent upon the conditions that the reaction is conducted with. Changing the temperature or pressure, for example, will influence the ΔH_{rxn} of a given reaction.

For this reason, we define Standard Conditions. Thermodynamic functions that are for Standard Conditions (or Standard State) are symbolized by a superscript o to the right of the Symbol for the thermodynamic function. This indicates that the Enthalpy has been determined with all reactants and products at their Standard State



Standard State

A set of specified conditions and concentrations, given by:

- For a gas – Standard State is an ideal gas at 1 atmosphere pressure
- For a solution – Standard State is 1 Molar concentration of the solute
- For a Pure Substance – the standard state is the most stable form of the substance at 1 atmosphere pressure and 25° C

Standard State for thermochemical functions should not be confused with STP (standard temperature and pressure for a gas). Especially note that the temperature for Standard State is different than Standard Temperature.



Standard Heat of Formation

Enthalpy change that accompanies the formation reaction of a compound from its constituent elements in their standard state.

One very important point that accompanies this definition: An element in its standard state is assigned a $(\Delta)H^\circ$ of formation of 0.



Putting it all together

Using Hess's law, and the ΔH_f° , we can calculate the $\Delta H_{\text{rxn}}^\circ$ for any reaction.

Concept – consider all reactions to proceed as follows.

1. All the reactants decompose into elements of pure substances in their standard state (this is effectively the reverse of the formation reaction)
2. All products are then formed from these elements in formation reactions.
3. The enthalpy of the reaction is then calculated using Hess's law of Heat summation (adding together the constituent reactions) to yield the desired net reaction