

CHEM 3410: Physical Chemistry I — Fall 2008

September 12, 2008

Lecture 5: Thermochemistry

References

1. Levine, *Physical Chemistry*, Sections 2.5–2.9, 5.1–5.6

Key Concepts

- Enthalpy is a useful thermodynamic function because is directly related to the heat transferred at constant pressure:

$$\Delta H = q_p$$

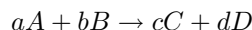
- We can always figure out the heat transferred into/out of a system through the heat capacity. At constant pressure (where we are for most of our lives):

$$\delta q_p = C_p dT \rightarrow q_p = \int C_p dT$$

This relationship is useful and we can:

1. determine how much heat is needed to change the temperature of a system. Said another way, what the enthalpy change of the system is when the temperature is changed.
 2. determine how the temperature changes when a given amount of heat is added or extracted from a system
 3. or we can measure the enthalpies of reactions through the use of calorimetry
- We can use enthalpy to understand the heat flow during reactions. This will allow us to understand the changes in energy for a particular reaction and gain insight into the nature of the chemical bonds.
 - There is no absolute energy scale, so a reference state needs to be defined so we can measure energy relative to that scale. In thermodynamics we define the standard state enthalpy as the change in enthalpy measured at 1 bar (about 1 atm) and 298 K.
 - Tabulated data is typically in the form of standard enthalpies of formation, ΔH_f° . It is defined as the enthalpy change in forming a compound from its constituent elements. Therefore, ΔH_f° for elements is equal to zero.
 - For a reaction occurring under standard conditions, we can use tabulated data to calculate the change in enthalpy for a particular chemical reaction. To do this, we employ the fact that enthalpy is a state function, and thus we can construct our desired chemical reaction as the sum of simple formation reactions for which data is available.

We can then take the enthalpy of formation of the products and subtract the enthalpy of formation of the reactants to get the overall change in enthalpy. Remember to multiply each term by the proper stoichiometric coefficient. For example, for the following reaction:



the change in enthalpy for the reaction under standard conditions would be:

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

- But we're not always interested in reactions occurring under standard conditions. Real systems are often at elevated or reduced temperatures. It would be useful to come up with a way to use all the data we have tabulated for the standard state and apply it to non-standard conditions.

- If we can construct a path from the reactants to the products that employ data we have (standard enthalpies of formation and heat capacities) then we are set since enthalpy is a state function (path independent). To do this we have to remember, that the heat flow into or out of a substance at constant pressure is equal to the enthalpy change in going from T_i to T_f and can be related to the heat capacity through the following relationship:

$$q_p = \Delta H = \int_{T_i}^{T_f} C_p dT$$

- If a substance changes phase (solid to liquid, liquid to vapor, solid to solid) there is an associated change of enthalpy. For example, in going from solid to liquid there is an enthalpy of melting or fusion, which is a quantity of heat that needs to be supplied at the melting temperature to produce the phase change.
- For example, if we wanted to calculate how much heat we needed to supply to a system of water to raise the temperature from 298 K to 500 K, we would need to consider the phase transformation of water that occurs at 373 K:

$$\Delta H_{total} = \int_{298}^{373} C_p^{liquid (H_2O)} dT + \Delta H_{vaporization}^\circ + \int_{373}^{500} C_p^{vapor (H_2O)} dT$$

Related Exercises in Levine

Exercises 5.10, 5.25