

Chapter 18: Thermodynamics

1. What is a state function?

A state function is a mathematical function that depends only on the state of the system under observation. Our three main considerations in this chapter – enthalpy, entropy and Gibbs free-energy – are all independent of path and thus are state functions. For this reason, for a given chemical reaction, we can always perform the following calculations:

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

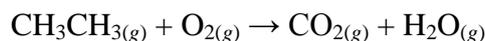
$$\Delta_r S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

2. Describe and discuss each of the following state functions.

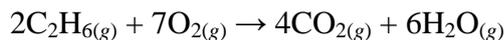
- a. Enthalpy – change in enthalpy, ΔH° , measures the change in heat of a reaction (it is usually measured in kJ mol^{-1} or in kJ). For this reason, change in enthalpy is a measure of the difference between bond energies of the reactants and products. For an exothermic reaction, more energy is released forming bonds in the products than is consumed breaking bonds in the reactants; thus, the products have more stable bonds than the reactants. For an endothermic reaction, less energy is released forming bonds in the products than is consumed breaking bonds in the reactants; thus, the products have less stable bonds than the reactants.
- b. Entropy – change in entropy, ΔS° , measures the change in disorder of a reaction (it is usually measured in $\text{J mol}^{-1} \text{K}^{-1}$ or in J K^{-1}). In general, more disorder is more stable. Due to the intrinsic freedom molecules enjoy, gases have greater entropy than liquids and liquids have greater entropy than solids.
- c. Gibbs free energy – change in Gibbs free-energy, ΔG° , measures the maximum amount of useful (i.e. non pressure-volume) work that may be extracted from a reaction. Change in Gibbs free-energy takes into account the energy terms from both enthalpy and entropy as demonstrated by this equation: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. At constant pressure, a spontaneous reaction has $\Delta G^\circ < 0$ (exergonic reaction; no external work is required for the reaction to be performed) whereas a non-spontaneous reaction has $\Delta G^\circ > 0$ (endergonic reaction; external work is required for the reaction to be performed)

3. This combustion of ethane is shown below.



	$\Delta_f H^\circ$ (kJ/mol)
$\text{CH}_3\text{CH}_3(g)$	-84.7
$\text{CO}_2(g)$	-393.5
$\text{H}_2\text{O}(g)$	-285.8

a. Balance the equation.



b. Using the table, calculate ΔH° for this reaction.

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = (4 \text{ mol})(-393.5 \text{ kJ mol}^{-1}) + (6 \text{ mol})(-285.8 \text{ kJ mol}^{-1}) - (2 \text{ mol})(-84.7 \text{ kJ mol}^{-1}) - 0$$

NOTE: because O_2 is in its natural state, $\Delta_f H^\circ(\text{O}_2) = 0 \text{ kJ mol}^{-1}$

$$\Delta_r H^\circ = -3119.4 \text{ kJ}$$

c. Predict the sign of ΔS° for this reaction.

We have in this reaction 9 mol gas becoming 10 mol gas and a complex molecule (ethane) breaking up into simpler molecules (carbon dioxide and water). Thus, we predict $\Delta S^\circ > 0$ because entropy (disorder) is increasing.