

Thermochemistry

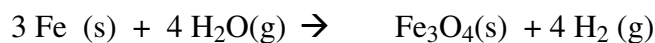
Thermodynamic is the study of the energy effects which accompany chemical and physical changes. It is concerned with the relationships between work, heat, and other forms of energy that are involved in all types of changes.

First law of thermodynamics: Energy cannot be created or destroyed.

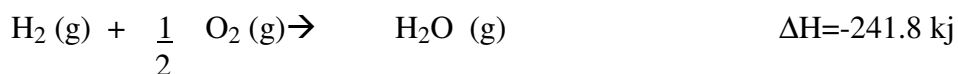
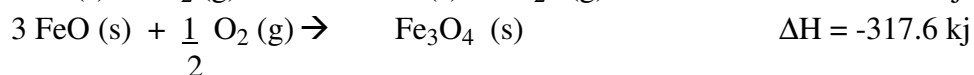
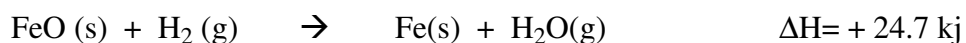
Hess law of constant heat summation: The change in enthalpy, that is, the change in heat at constant pressure for any chemical reaction is constant regardless if the chemical reaction occurs in one step or several steps.

1) Calculating heat of reaction using other reactions:

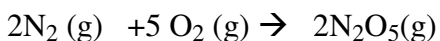
1) Calculate the value of ΔH_{rxn} for the reaction:



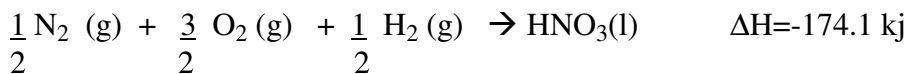
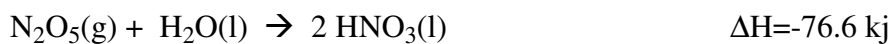
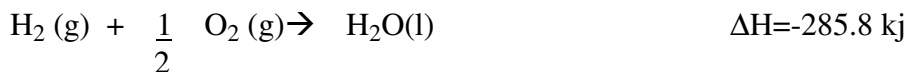
Given:



2) Calculate the value of ΔH_{rxn} for the reaction:



Given the following data:



2) Calculating heat of reaction using standard heat of formation, ΔH_f° :

The standard heat of formation of a compound, ΔH_f° , is the change in enthalpy for the reaction in which one mole of the compound in its standard state is formed from its elements in their standard states.

For example, $C(s) + H_2(g) \rightarrow CH_4(g)$ $\Delta H_f^\circ = -74.9$ kJ/mole

The above elements are in their standard states.

ΔH_f° are important since they can be used to calculate heats of reaction that are not conveniently measured directly

Example 1: For the reaction: $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$, the value of ΔH_{rxn} is -23.5 kJ.

The standard heat of formation of: CO(g) is -110.5 kJ/mole

CO₂(g) is -393.5 kJ/mole

Calculate the standard heat of formation of Fe₂O₃(s).

Example 2: Given the following data for the reaction:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ ΔH_{rxn} is -890.4 kJ.

ΔH_f° for CH₄(g) = -74.9 kJ/mole

ΔH_f° for H₂O(l) = -285.9 kJ/mole

Calculate ΔH_f° for CO₂(g).

Recall, the standard heat of formation of an element is zero.

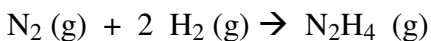
3)Calculating heat of reaction using bond energies:

Example1 :Use the average bond energy table to calculate the heat of reaction for the following reaction in the vapor state.



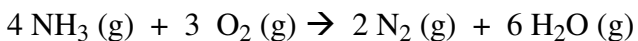
bond	Bond energy	Bond	Bond energy
C-H	414 kj/mole	C-Cl	326 kj/mole
Cl-Cl	243 kj/mole	H-Cl	431 kj/mole

Example2: Use the average bond energy table provided to calculate the heat of reaction for the following:



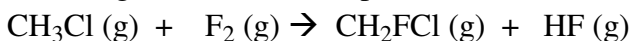
Bond	Bond energy	Bond	Bond energy
N-N triple bond	941 kj/mole	N-H	389 kj/mole
H-H	435 kj/mole	N-N single bond	159 kj/mole

Example 3 : Use the average bond energy table to calculate the heat of reaction for the following reaction in the vapor state.



Bond	Bond energy	Bond	Bond energy
N-H	389 kJ/mole	N-N triple bond	941 kJ/mole
O-O double bond	494 kJ/mole	O-H	464 kJ/mole

Example 4 : Use the average bond energy table to calculate the heat of reaction for the following reaction in the vapor state.



Bond	Bond energy	Bond	Bond energy
C-H	414 kJ/mole	C-F	485 kJ/mole
F-F	155 kJ/mole	H-F	565 kJ/mole

Predicting the Spontaneity of Reactions

a) Mechanical systems tend to move spontaneously to the state of minimum potential energy
Spontaneous Processes:

- Water flows downhill without help
- An apple falls spontaneously to the ground

In all of the above spontaneous processes the SYSTEM (the collection of matter under study) loses energy and goes to a lower energy state. Therefore a chemical reaction should be spontaneous if the chemical potential energy of its products is less than the chemical potential energy of the reactants. According to the minimum potential energy principle, exothermic reactions should be spontaneous and endothermic reactions should be nonspontaneous.

Are these predictions correct?

Experimental results show that at (or near) normal temperature (25 °C and 1 atm) most exothermic reactions are spontaneous and most endothermic reactions are nonspontaneous.

$\Delta H = + \text{value} , \Delta H > 0 , \text{endothermic, nonspontaneous}$
$\Delta H = - \text{value} , \Delta H < 0 , \text{exothermic, spontaneous}$

b) The Second Law of Thermodynamics : *Any SYSTEM and its SURROUNDINGS as a whole tend spontaneously toward increasing disorder or randomness.*

There are many exceptions to the minimum potential energy rule.

a) Ice + heat \rightarrow Liquid water Endothermic , yet spontaneous

b) KCl(s) + H₂O (l) + heat \rightarrow KCl (aq) Endothermic, yet spontaneous

All of the above systems exhibit an increase in the disorder (randomness). These suggest that a SYSTEM tends spontaneously toward increasing disorder.

Exceptions to the increase in disorder (entropy) rule:

a) 4 Fe(s) + 3 O₂ (g) \rightarrow 2 Fe₂O₃ (s) Spontaneous, yet there is decrease in entropy

b) Ag⁺(aq) + Cl⁻(aq) \rightarrow AgCl(s) Spontaneous, yet there is decrease in entropy

To predict the spontaneity we must look at the changes in disorder (entropy) of the SYSTEM and the SURROUNDING, not just the SYSTEM. We need to consider the disorder that is created in the environment. Any input of heat to the environment represents an increase in entropy. There is always a **net** increase in entropy with any spontaneous change. The original hypothesis must be modified to include the SURROUNDINGS.

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

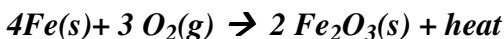
ΔS_{total} is + value; spontaneous

ΔS_{total} is - value; nonspontaneous

The combined effect of enthalpy change, ΔH , and change in entropy, ΔS , decides whether the reaction is spontaneous or not.

A process is highly spontaneous if it is exothermic and there is increase in entropy.

Sometimes the enthalpy and entropy changes work in opposite directions:



In the previous example, there is a decrease in entropy, and exothermic. It seems that the exothermic factor over rides the unfavorable entropy change.

We need a new function that combines ΔH and ΔS , by which we can tell if the process is spontaneous or nonspontaneous.

Gibb's Free Energy, ΔG :

$$\Delta G = \Delta H - T \Delta S$$

At room temperature $T\Delta S$ is too small, such that all exothermic reactions are spontaneous.

The reaction is spontaneous when ΔG is a negative value, and nonspontaneous when ΔG is positive.

$$\begin{array}{l} \Delta G < 0 \text{ spontaneous} \\ \Delta G > 0, \text{ nonspontaneous} \end{array}$$

The Third Law of Thermodynamics

The entropy of a perfect crystalline substance at absolute zero is equal to zero.

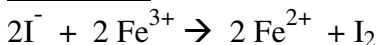
The Relationship between ΔG° and the standard cell potential, E°_{cell}

$$\Delta G^\circ = -nF E^\circ_{\text{cell}}$$

The Relationship between ΔG° and the equilibrium constant, K_p :

$$\Delta G^\circ = -2.303 RT \log K_p$$

Exercise 1: Calculate E° for a cell utilizing the following reaction



where $\Delta G^\circ = -45.4 \text{ kJ}$

$F = 96500 \text{ coulomb}$, Joules = volts \times coulomb

The standard free energy, ΔG°_f , is a measure of how far a mixture of reactants and products at their standard states will shift in the direction of either more reactants or more products.

If ΔG° is negative, the equilibrium lies towards more products (reaction is spontaneous)

If ΔG° is positive, the equilibrium lies towards more reactants (reaction is nonspontaneous)

Exercise 2: Calculate K_p at 25 °C for the reaction;

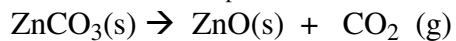


Given: G°_f for $\text{PCl}_5(\text{g}) = -325 \text{ kJ/mole}$

G°_f for $\text{PCl}_3(\text{g}) = -286 \text{ kJ/mole}$

$R = 8.314 \text{ J/K.mole}$

Exercise 3: Calculate K_p at 25 °C for the reaction:



Given G°_f for $\text{ZnCO}_3(\text{s}) = -731.36 \text{ kJ/mole}$

G°_f for $\text{ZnO}(\text{s}) = -318.19 \text{ kJ/mole}$

G°_f for $\text{CO}_2(\text{g}) = -394.38 \text{ kJ/mole}$

$R = 8.314 \text{ J/K.mole}$

