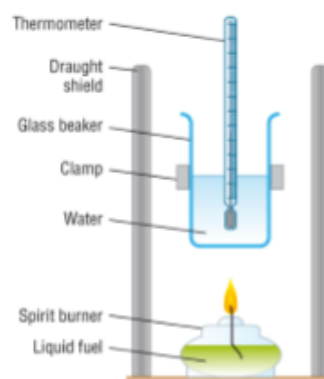


Physical Chemistry

CHEMICAL ENERGETICS



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Gibbs Free Energy (G^θ)

1. What is Gibbs free energy & why it is important?

The total entropy which includes the system & surrounding was used previously to predict the feasibility of a reaction. In chemical thermodynamics it's often preferred to focus on the system than the surroundings. Free energy enables us to do this for changes that occur at constant temperature and pressure. (Not necessary at standard conditions).

Gibbs free energy refers to the amount of energy of the system available to do work. This energy is referred to as the "FREE" energy as it is the remaining energy of the system after it had used some of its energy for entropy. Since this was discovered by J. Willard Gibbs it is called as Gibbs Free Energy. Symbolized by ΔG .

Gibbs free energy is important to predict the feasibility of a reaction where feasibility cannot be predicted when enthalpy & entropy is considered together. Eg: Reaction which is feasible with respect to enthalpy but not entropy (exothermic reaction with negative entropy) or Feasible with respect to entropy but not enthalpy. (Endothermic reaction with positive entropy)

2. Define Standard Gibbs free energy change, ΔG^θ

Gibbs free energy / Gibbs function is the combination of entropy and enthalpy. The change in the Gibbs free energy of the system that occurs during a reaction is therefore equal to the change in the enthalpy of the system minus the change in the product of the temperature times the entropy of the system. And can be defined by the following equation:

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

Where, ΔH^θ is the standard enthalpy change of the reaction. (298K, 1atm)

T is the temperature in Kelvin

ΔS^θ is the standard entropy change of the system.

ΔG^θ is the standard Gibbs free energy. Remember that the superscript θ on ΔG^θ indicates that the numerical value of Gibbs free energy is based on the reaction at standard conditions and it refers to 1M concentrated solution & 1 atm pressure. Temperature is NOT a part of standard conditions for ΔG^θ .

3. Derive the Gibbs free energy equation from total entropy equation. Gibbs free energy change is given by the equation $\Delta G = -T\Delta S_{\text{total}}$

4. Define the term Standard molar Gibbs free energy of formation.

Standard molar Gibbs free energy of formation is the free energy change which accompanies the formation of one mole of a compound from its elements in their standard state.

Symbolized by ΔG^θ_f and units are kJ mol^{-1}

5. Explain how ΔG determines the direction & extent of a chemical change hence spontaneity.

$\Delta G < 0$ reaction can spontaneously proceed to the right: $A \rightarrow B$

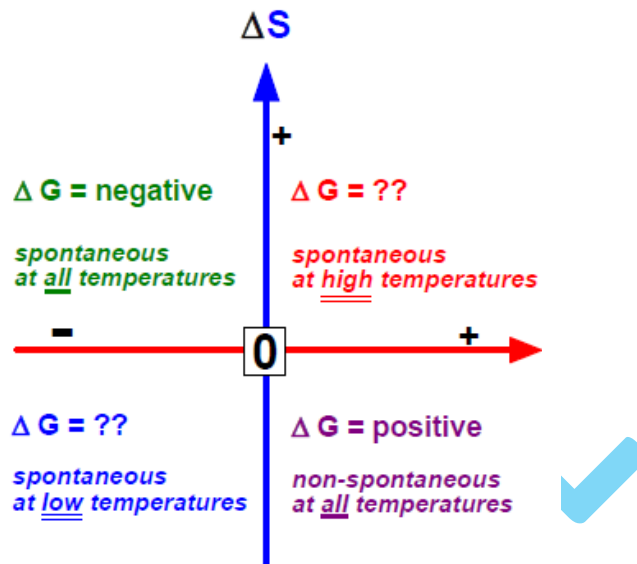
$\Delta G > 0$ reaction can spontaneously proceed to the left: $A \leftarrow B$

$\Delta G = 0$ the reaction is at *equilibrium*; the quantities of A and B will not change

Thus negative ΔG indicates that the reaction is spontaneous, a positive ΔG indicates a non-spontaneous reaction and if ΔG is zero the reaction is at equilibrium. ΔG^θ_f is a measure of the stability of the compound. Greater the negative value greater the stability thus difficult to decompose and vice versa.

- The ΔG^θ_f of an element under standard condition is zero.
(Eg: $\text{H}_2, \text{O}_2, \text{Br}_2, \text{C}, \text{Mg}, \text{Na}$)

6. Discuss the effect of temperature on spontaneity of a reaction



As $\Delta G = \Delta H - T\Delta S$, ΔG changes with temperature.

ΔH could be negative (an exothermic reaction) or positive (an endothermic reaction). Similarly ΔS could be either positive or negative. Thus there are four possible combinations of the signs of ΔH and ΔS

a. ΔH is negative and ΔS is positive:

As both ΔH and $-T\Delta S$ terms are negative irrespective of the temperature, ΔG is also will to be negative. **The reaction will be spontaneous at all temperatures.**

b. ΔH is positive and ΔS is negative :

As both ΔH and $-T\Delta S$ terms are positive irrespective of the temperature, ΔG is also will be positive. **The reaction will not be spontaneous at any temperature.**

c. ΔH is positive and ΔS is positive :

ΔH is positive. $-T\Delta S$ is negative.

Increasing the temperature will result $-T\Delta S$ will become more negative, and will eventually outweigh ΔH thus the reaction will be spontaneous.

But at low temperatures, ΔG becomes positive thus the reaction will be non spontaneous. Eg : Decomposition of CaCO_3

d. ΔH is negative and ΔS is negative :

ΔH is negative. $-T\Delta S$ is positive.

As temperature increases, $-T\Delta S$ will become more positive, and will eventually outweigh the effect of ΔH thus reaction will be non spontaneous. But at low temperatures ΔG will be negative thus be spontaneous.

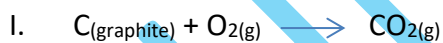
7. State the factors which is to be considered when Calculating ΔG° hence explain how ΔG of a reaction is calculated.

ΔG° and ΔH° are both measured in kJmol^{-1} whereas the entropy change is calculated in $\text{JK}^{-1}\text{mol}^{-1}$, Thus one must change the entropy change value into kJ before when calculating ΔG° .

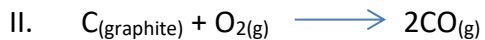
Similar to enthalpies and entropies the standard Gibbs free energy of a reaction can be calculated as to the below equation:

$$\Delta G^\circ = \sum n \Delta G^\circ_{(\text{products})} - \sum n \Delta G^\circ_{(\text{reactants})} \quad n = \text{no. of moles}$$

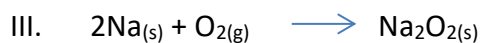
8. Calculate the ΔG° in below examples hence comment on the feasibility of the reaction.



Calculate ΔG° for CO_2 at 298 K. $\Delta H^\circ(\text{CO}_2) = -393 \text{ kJ/mol}$, $S^\circ(\text{O}_2) = 205 \text{ J/mol.K}$, $S^\circ(\text{C}) = 6 \text{ J/mol.K}$, $S^\circ(\text{CO}_2) = 213 \text{ J/mol.K}$



Calculate ΔG° for CO at 298 K. ΔH_f° (CO) = -110 KJ/mol, $S^\circ(O_2)$ = 205 J/mol.K, $S^\circ(C)$ = 6 J/mol.K, $S^\circ(CO)$ = 198 J/mol.K



Calculate ΔG° for the reaction at 298 K. $\Delta H = -510$ KJ/mol, $S^\circ(Na)$ = 51.2 J/mol.K, $S^\circ(Na_2O_2)$ = 95.0 J/mol.K, $S^\circ(O_2)$ = 205.0 J/mol.K

9. Calculate ΔG° for the following Reactions, Given that;

$$\Delta G_f^\circ (SO_{2, g}) = -300 \text{ kJ/mol}$$

$$\Delta G_f^\circ (H_2SO_{4, l}) = -690 \text{ kJ/mol}$$

$$\Delta G_f^\circ (H_2O, l) = -237 \text{ kJ/mol}$$

$$\Delta G_f^\circ (SO_{3, g}) = -371 \text{ kJ/mol}$$

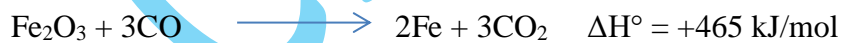
$$\Delta G_f^\circ (H_2SO_{4, aq}) = -742 \text{ kJ/mol}$$

$$\Delta G_f^\circ (H_2S, g) = -34 \text{ kJ/mol}$$





10. Calculate the temperature above at which the following non spontaneous reaction becomes spontaneous. (Assume that ΔH° and ΔS° does not change much with temperature)



$\Delta S^\circ = +552 \text{ J/molK}$

$\Delta G^\circ = +301 \text{ kJ/mol (at 298 K)}$

11. With the help of a Gibbs free energy cycle calculate ΔG^{θ}_f for the below decomposition, hence comment on the feasibility.



The relevant ΔG^{θ}_f values are :

$$\begin{array}{llll} \Delta G^{\theta}_f[\text{NaHCO}_{3(s)}] & = -850 \text{ kJmol}^{-1} & \Delta G^{\theta}_f[\text{H}_2\text{O}_{(l)}] & = -235. \text{ kJmol}^{-1} \\ \Delta G^{\theta}_f[\text{CO}_{2(g)}] & = -390 \text{ kJmol}^{-1}, & \Delta G^{\theta}_f[\text{Na}_2\text{CO}_{3(s)}] & = -1045 \text{ kJmol}^{-1} \end{array}$$