

## FlexiPrep

### Spontaneity of Chemical Reaction: Gibbs Energy and Spontaneity (For CBSE, ICSE, IAS, NET, NRA 2022)

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#### Gibbs Energy and Spontaneity

We use this equation

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

At constant temperature and pressure if  $q_p$  is the heat given out by the system to the surroundings,  $-q_p$  is the heat gained by the surroundings we can write

$$\Delta S_{\text{surroundings}} = \frac{-q_p}{T} = \frac{-H_{\text{system}}}{T}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

$$T\Delta S_{\text{total}} = T\Delta S_{\text{system}} - H_{\text{system}}$$

$$-T\Delta S_{\text{total}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

It is defined as Gibbs energy and given by the equation

$$G = H - TS$$

For a change in Gibbs energy, we write

$$\Delta G = \Delta H - \Delta(TS)$$

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

At constant temperature

$$\Delta T = 0$$

Therefore,

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

H, T and S are state functions, so G is also a state function.

$$\Delta G = -T\Delta S_{\text{total}}$$

The Gibbs energy can be useful in defining that a process is spontaneous or non-spontaneous.

If a process occurring at constant temperature and pressure, then

- $G < 0$  (negative), the process is spontaneous
- $G > 0$  (positive), the process is non-spontaneous.
- $G = 0$  (zero), the process is at equilibrium

**The Spontaneity of chemical reaction is depend upon two factor:**

- The energy factor ( $\Delta H$ )
- The entropy factor ( $\Delta S$ )

**Based on the signs of ( $\Delta H$ ) and ( $\Delta S$ ), there are four possibilities:**

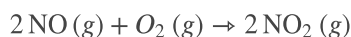
These possibilities are outlined in table

S.No	$H$	$S$	$G$	Result
1	–	+	–	Spontaneous at all temperatures.
2.	–	–	–	Spontaneous at low temperatures. Non-spontaneous at high temperatures.
3.	+	+	+	Non-spontaneous at low temperatures. Spontaneous at high temperatures.
4.	+	–	+	Non-spontaneous at all temperatures.

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### Example:

For the reaction



Calculate  $\Delta_r G$  at 700K when enthalpy and entropy changes ( $\Delta_r H$  and  $\Delta_r S$ ) are respectively  $-113.0 \text{ KJ mol}^{-1}$  and  $-145 \text{ JK}^{-1} \text{ mol}^{-1}$

### Solution:

Given

$$\Delta_r H = -113.0 \text{ KJ mol}^{-1}$$

$$\Delta_r S = -145 \text{ JK}^{-1} \text{ mol}^{-1} = -145 \times 10^{-3} \text{ KJ K}^{-1} \text{ mol}^{-1}$$

$$T = 700\text{K}$$

Substituting the values in

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

$$= (-113.0 \text{ KJ mol}^{-1}) - (700\text{K})(-145 \times 10^{-3} \text{ KJ K}^{-1} \text{ mol}^{-1})$$

$$= (-113.0 \text{ KJmol}^{-1}) + (101.5 \text{ KJmol}^{-1})$$

$$-11.5 \text{ KJ mol}^{-1}$$

### Standard Gibbs Energy Change ( $G^O$ ) and Equilibrium Constant (K)

The standard Gibbs energy change is defined as the change in Gibbs energy for the process in which the reactants in their standard states are converted into the products in their standard states.

It is denoted by the symbol  $\Delta_r G^\circ$ .

The value of  $\Delta_r G^\circ$  can be found from the standard Gibbs energy of formation of substance.

The standard Gibbs energy of formation of a compound is defined as the change in Gibbs energy when 1 mole of the compound is formed from its constituent elements in their standard states.

The standard Gibbs energy of formation of an element in its standard state is taken as zero. Thus, for the reaction  $aA + bB + \dots \rightarrow pP + qQ + \dots$

$$\Delta_r G^\circ = [p \Delta_f G^\circ P + q \Delta_f G^\circ Q + \dots] - [a \Delta_f G^\circ A + b \Delta_f G^\circ B + \dots]$$

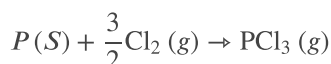
$$\Delta_r G^\circ = \sum v_r \Delta_f G^\circ (\text{products}) - \sum v_r \Delta_f G^\circ (\text{reactants})$$

The standard Gibbs energy change ( $rG^\circ$ ) is related to the equilibrium constant ( $K$ ) of the reaction by the expression

$$\Delta_r G^\circ = -RT \ln K = -2.303 RT \log K$$

### Example:

The equilibrium constant of the reaction



is  $2.00 \times 10^{24}$  at  $500K$ . Calculate the value of  $\Delta_r G^\circ$ .

### Solution:

Given

$$K = 2.00 \times 10^{24}$$

$$T = 500K$$

$$\Delta_r G^\circ = -2.303 RT \log K$$

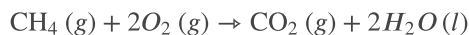
$$= -2.303 \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (500K) \log 2.0 \times 10^{24}$$

$$= -2.303 \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (500K) 24.30$$

$$= -232.6 \text{ KJ mol}^{-1}$$

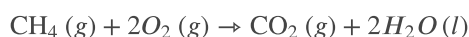
### Example:

Calculate the standard Gibbs energy change for the reaction



at  $298K$ . The standard Gibbs energies of formation of  $CH_4$ ,  $CO_2$  and  $H_2O$  at  $298K$  are  $-50.8 \text{ KJ mol}^{-1}$ ,  $-394.4 \text{ KJ mol}^{-1}$ , and  $-237.2 \text{ KJ mol}^{-1}$  respectively.

### Solution:



$$\Delta_r G^\circ = \Delta_f G^\circ (CO_2) + 2 \Delta_f G^\circ (H_2O) - \Delta_f G^\circ (CH_4) - 2 \Delta_f G^\circ (O_2)$$

$$= -394.4 + 2 \times (-237.2) - (-50.8) - 2 \times 0$$

$$= -394.4 - 474.4 + 50.8$$

$$= -818 \text{ KJ mol}^{-1}$$