

# Entropy & Gibbs Free Energy

Define entropy:

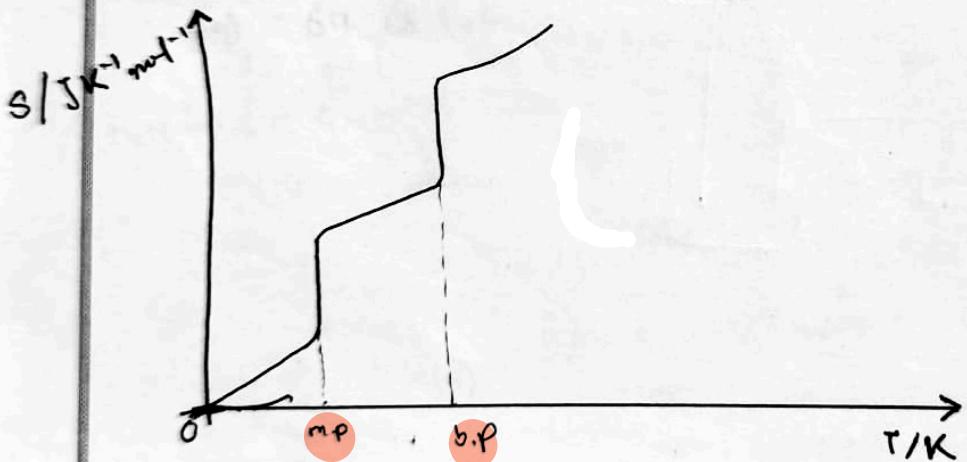
It is the measurement of dispersal of energy or disorderliness in a system.

Define standard molar entropy:

It is the measurement of the entropy of 1 mol of a substance. (under standard condition)  
symbol of entropy =  $S^\circ$  → Its unit is  $\text{JK}^{-1}\text{mol}^{-1}$

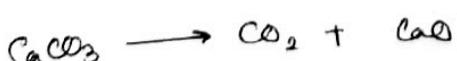
# At a specific temperature solid substance have lower  $S^\circ$  than liquid which has lower  $S$  than gas.

for a substance with increase in temperature its  $S$  will increase



PREDICTING ENTROPY CHANGE OF A REACTION ( $\Delta S$ ):

For a reaction to be spontaneous, its  $\Delta S^\circ$  value has to highly positive and vice versa. # NOT ALWAYS TRUE



This reac<sup>n</sup> is spontaneous. As gaseous molecules are produced. Thus, there is an increase in disorderness causing entropy to change. ( $\Delta S > 0$ )



This reac<sup>n</sup> is spontaneous. As no. of gaseous molecule increases. Thus, disorderness increases causing  $\Delta S > 0$ .

Reactant → Product

$$\Delta S^\circ_{\text{reaction}}$$

or

$$\Delta S^\circ_{\text{system}}$$

$$= \sum S^\circ_{\text{product}} - \sum S^\circ_{\text{reactant}}$$

Q



Given that  $S^\circ$  of methane

$$S^\circ [\text{CH}_4] = 186.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\circ [\text{O}_2] = 205.0 \text{ "}$$

$$S^\circ [\text{CO}_2] = 213.6 \text{ "}$$

$$S^\circ [\text{H}_2\text{O}] = 188.7 \text{ "}$$

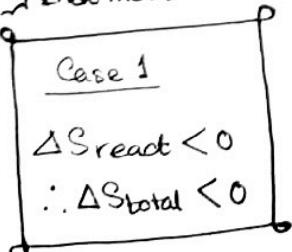
$$\begin{aligned}\Delta S^\circ &= \sum S^\circ_{\text{product}} - \sum S^\circ_{\text{reactant}} \\ &= [213.6 + 2(188.7)] - [186.2 + 2(205.0)] \\ &= -5.2 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\Delta S^\circ_{\text{surrounding}} = \frac{-\Delta H}{T}$$

most constant from 6.3 to 3

$$\begin{aligned}\Delta S^\circ_{\text{total}} &= \Delta S^\circ_{\text{reaction}} + \Delta S^\circ_{\text{surrounding}} \\ &= -5.2 + 2990 \\ &= 2984.8 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Endothermic Reaction



$$\Delta S^\circ = -\frac{\Delta H}{T}$$

$\Delta S$

$$\Delta S_{\text{total}} = \Delta S_{\text{reaction}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{reaction}} = \sum S_{\text{product}} - \sum S_{\text{reactant}}$$

Define Gibbs Free Energy:

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

It is the useful work done in a chemical reaction to convert reactants into products. The energy required to drive a chemical reaction is called Gibbs free energy.

$\Delta G$  = Gibbs Free energy change

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

$$= -T(\Delta S_{\text{surr}} + \Delta S_{\text{reac}})$$

$$= -T\left(-\frac{\Delta H}{T} + \Delta S_{\text{reac}}\right)$$

$$\boxed{\Delta G = \Delta H - T\Delta S_{\text{reac}}}$$

$$\boxed{\Delta H = \Delta G + T\Delta S_{\text{reac}}}$$

useful  
energy

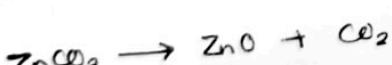
$$\underbrace{\Delta G}_{(KJ/mol)} = \Delta H - T\Delta S_{\text{reac}}$$

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

For a reaction to be spontaneous,  
 $\Delta G < 0$ .

For a reaction to be non-spontaneous  
 $\Delta G > 0$

\* Calculate the Gibbs Free energy change for the decomposition of  $ZnCO_3$  at i)  $298 K \leq ii) 1200 K$



$$\Delta H_r = +71.0 \text{ kJ mol}^{-1}$$

$$\begin{aligned} S^\circ(CO_2) &= +213.6 & \rightarrow J K^{-1} mol^{-1} \\ S^\circ(ZnCO_3) &= +82.4 \\ S^\circ(ZnO) &= +43.6 \end{aligned}$$

$$\begin{aligned} \Delta S_{\text{reaction}} &= (43.6 + 213.6) - (82.4) \\ &= +174.8 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} i) \Delta G &= \Delta H - T\Delta S_{\text{reac}} \\ &= 71 - 298 \left( \frac{174.8}{1000} \right) \\ &= +18.9 \text{ kJ mol}^{-1} \\ \Delta G &> 0 \end{aligned}$$

Reaction is non-spontaneous

-ve sign



$$\Delta G^\circ = -nE^\circ_{\text{cell}} F$$

$n$  = no. of mol's of  $e^-$

$\Delta G^\circ$  = Standard Gibbs free energy change of a reaction

$E^\circ_{\text{cell}}$  = standard cell potential

$F$  = Faraday constant = 96500 C mol<sup>-1</sup>

Find enthalpy for the react<sup>n</sup> & for the following react<sup>n</sup>



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

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{red}} - E^\circ_{\text{oxid}} \\ &= (+0.77) - (+0.84) \\ &= +0.43 \text{ V} \end{aligned}$$

$$\begin{aligned} \Delta G &= -(2)(0.43)(96500) \\ &= -82900 \text{ J/mol} \\ &= -83.0 \text{ kJ mol}^{-1} \end{aligned}$$

- $\Delta S_{\text{total}} = \Delta S_{\text{reaction}} + \Delta S_{\text{surrounding}}$

$$-\frac{\Delta H}{T}$$

- $\Delta S_{\text{reaction}} = \sum S_{\text{product}} - \sum S_{\text{reactant}}$

- $\Delta S_{\text{surrounding}} = -\frac{\Delta H}{T}$

\* Temperature must be in Kelvin

Exothermic reac<sup>n</sup> → For any exothermic reac<sup>n</sup>,  $\Delta S_{\text{surr}}$  will always be greater than 0

Case 1

$$\Delta S_{\text{reac}} > 0$$

$$\therefore \Delta S_{\text{total}} > 0$$

Case 2

$$\Delta S_{\text{reac}} < 0$$

$$\Delta S_{\text{surr}} > \Delta S_{\text{reac}}$$

$$\therefore \Delta S_{\text{total}} > 0$$

Case 3

$$\Delta S_{\text{reac}} < 0$$

$$\Delta S_{\text{reac}} > \Delta S_{\text{surr}}$$

$$\therefore \Delta S_{\text{total}} < 0$$

Cases 1 & 2 are spontaneous,  
Case 3 reaction is non-spontaneous

Endothermic reac<sup>n</sup> → For any endothermic reac<sup>n</sup>,  $\Delta S_{\text{surr}}$  will always be less than 0

Case 1

$$\Delta S_{\text{sys}} < 0$$

$$\Delta S_{\text{surr}} < 0$$

$$\therefore \Delta S_{\text{total}} < 0$$

Case 2

$$\Delta S_{\text{sys}} > 0$$

$$\Delta S_{\text{sys}} < \Delta S_{\text{surr}}$$

$$\therefore \Delta S_{\text{total}} < 0$$

Case 3

$$\Delta S_{\text{sys}} > 0$$

$$\Delta S_{\text{sys}} > \Delta S_{\text{surr}}$$

$$\therefore \Delta S_{\text{total}} > 0$$

Cases 1 & 2 are non-spontaneous,  
Case 3 reaction is spontaneous.

Define Gibbs Free Energy:

It is the useful work done in a chemical reac<sup>n</sup> to convert reactants into products at constant temperature & pressure  
 $\rightarrow$  symbol G → unit kJ/mol

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

$$\begin{aligned}\Delta G &= -T\Delta S_{\text{total}} \\ &= -T(\Delta S_{\text{reac}} + \Delta S_{\text{surr}}) \\ &= -T\left(-\frac{\Delta H}{T} + \Delta S_{\text{reac}}\right)\end{aligned}$$

$$\therefore \Delta G = \Delta H - T\Delta S_{\text{reac}}$$

for a reac<sup>n</sup> to be spontaneous,  $\Delta G < 0$   
since when reac<sup>n</sup> is spontaneous

$$\begin{aligned}\Delta S_{\text{total}} &\text{ has to be +ve :} \\ &= -(+\text{ve } S_{\text{total}} \text{ value}) \\ &= -\text{ve } \Delta G \text{ value}\end{aligned}$$

for a reac<sup>n</sup> to be non-spontaneous,  
 $\Delta G > 0$  since when reac<sup>n</sup> is  
spontaneous  $\Delta S_{\text{total}}$  has to be -ve:  
 $= -(-\text{ve } S_{\text{total}} \text{ value})$   
 $= +\text{ve } \Delta G \text{ value}$

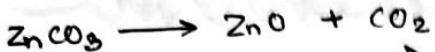
$$\Delta H = [\Delta G] + T\Delta S_{\text{reac}}$$

useful energy

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

Q

Calculate the Gibbs free energy change for the decomposition of Zinc Carbonate at i) 298 K ii) 1200 K



$$\Delta S_{\text{reac}} = (43.6 + 213.6) - (82.4) \\ = +174.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{i) } \Delta G = 71 - 298 \left( \frac{174.8}{1000} \right) \\ \text{KJ mol}^{-1} \\ = +18.9 \text{ kJ mol}^{-1}$$

$\Delta G > 0$ , reac<sup>n</sup> is non-spontaneous

$$\text{ii) } \Delta G = 71 - 1200 \left( \frac{174.8}{1000} \right) \\ \text{KJ mol}^{-1} \\ = -139 \text{ kJ mol}^{-1}$$

$\Delta G < 0$ , reac<sup>n</sup> is spontaneous

$$\Delta H_r = +71.0 \text{ KJ mol}^{-1}$$

$$S^\ominus(\text{CO}_2) = +213.6 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$S^\ominus(\text{ZnCO}_3) = +82.4 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$S^\ominus(\text{ZnO}) = +43.6 \text{ JK}^{-1} \text{ mol}^{-1}$$

\* find the minimum temperature for the reac<sup>n</sup> to be spontaneous for the reac<sup>n</sup> to be spontaneous :  $\Delta G < 0$

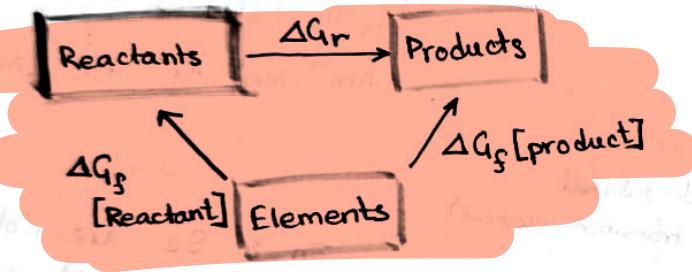
$$\Rightarrow 71 - T \left( \frac{174.8}{1000} \right) < 0$$

$$\Rightarrow T \left( \frac{174.8}{1000} \right) < +71$$

$$\Rightarrow T > \frac{(71)(1000)}{174.8}$$

$$\therefore T > 406 \text{ K}$$

X



$$\Delta G_f[\text{reactant}] + \Delta G_r = \Delta G_f[\text{product}]$$

$$\therefore \Delta G_r = \Delta G_f[\text{product}] - \Delta G_f[\text{reactants}]$$

$$\Delta G_s[\text{element}] = 0$$

$$\Delta G^\ominus = -n E^\ominus_{\text{cell}} F$$

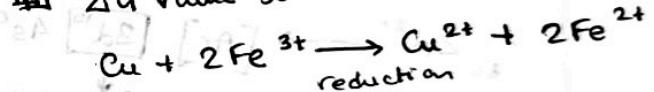
$E^\ominus$  = standard cell potential

F = Faraday constant

n = no. of mol of e<sup>-</sup>

$\Delta G^\ominus$  = standard Gibbs free energy change of a reac<sup>n</sup>.

\*  $\Delta G$  value for the reac<sup>n</sup>



$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{reduction}} - E^\ominus_{\text{oxidation}} \\ &= (+0.77) - (+0.34) \\ &= +0.43 \text{ V} \end{aligned}$$

$$\Delta G = -n E^\ominus_{\text{cell}} F$$

$$\begin{aligned} &= -(2)(0.43)(96500) \\ &= -82900 \text{ J mol}^{-1} \end{aligned}$$

$$\therefore \Delta G = -83.0 \text{ kJ mol}^{-1} (\text{3 s.f.})$$